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FOR THE METAL, CERAMIC AND CARBIDE INJECTION MOULDING INDUSTRIES

powder injection moulding INTERNATIONAL

in this issue

Ti-PIM: Managing properties

CIM zirconia for luxury products

PM2010 World Congress review

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POWDER INJECTION MOULDING INTERNATIONAL

For the metal, ceramic and carbide injection moulding industries

Ti-PIM: Ready for business!

Titanium powder injection moulding (Ti-PIM) remains an area of great promise for the PIM industry. In this issue of *PIM International* we return to the topic with our specially commissioned review of the impact of the various PIM processing steps on the mechanical and chemical properties of Ti-PIM components (page 22). Ranging from initial powder analysis through to post sintering operations, the review clearly demonstrates that, with the correct checks and systems in place, Ti-PIM is more than capable of matching, if not exceeding, the expectations of the all important aerospace and medical sectors.

At the 2010 Powder Metallurgy World Congress held in Florence in October, there was a mood of quiet optimism about the prospects for the PIM industry. Rumours of major orders for PIM equipment suppliers lifted confidence, and several MIM powder suppliers indicated that they are moving to increase capacity, enabling them to retain market position in MIM and other fine powder consuming industries. We review some highlights from the conference sessions and satellite meetings, many of which reflected the positive mood (pages 43 & 48) .

Also in this issue, we look at how CIM zirconia products are fast becoming a core part of the luxury goods market (page 33). White, black and coloured injection moulded ceramic parts can now frequently be spotted in the numerous luxury watches that are advertised in high-end glossy magazines.

In our profile of China's AT&M, we report how China's MIM producers are manufacturing an ever more advanced range of products for both the global and domestic markets (page 39).

Last but not least, don't miss our three technical papers that deal with the processing of high performance PIM materials, titanium and superalloys.

Nick Williams
Managing Director and Editor

Cover image
PIM knee implant parts made by Ti6Al4V-PIM (Courtesy of Maetta Sciences Inc., Canada)

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To submit news for inclusion in *Powder Injection Moulding International* please contact Nick Williams nick@inovar-communications.com

Legal battle over gas-assisted injection moulding resolved

A 16 year legal battle to resolve the ownership of the patent rights to gas-assisted injection moulding technology has been brought to a conclusion with Cinpres Gas Injection having been declared the undisputed owner of all appropriate patents on gas-assisted moulding technologies. Cinpres's Managing Director, Jon Butler, confirmed that he is acquiring all the remaining Melea patents, part of a complex web of intellectual property divided between the two companies. Mr Butler said now that the patents, and the trading names, were being acquired by Cinpres, the risk of a continuing dispute with another buyer would be removed. The resolution of the legal case is expected to allow significant expansion of the gas-assist process worldwide including gas-assisted PIM which has been investigated by a number of organisations over the past 10 years.

Gas-assisted injection moulding is defined as a process which uses nitrogen or another inert gas to create hollow channels within moulded parts. The channels can be designed into the part, reducing the weight of thick parts, improving strength and surface finish, and speeding up cycle times in moulding thereby reducing costs. Flow channels may also eliminate the need for hot runners. Cinpres Gas Injection states that gas-assisted injection moulding allows tubular sections to be designed into the product, and can eliminate the need for expensive undercuts and lifters in the moulding tool.

Cinpres also reports that it has signed a deal with a German partner, Maximator, that will lead to a revitalised global offering for gas-assisted injection moulding. Under the deal Maximator, the market leader in high pressure technology and Germany's leading supplier of high pressure industrial gas systems and Cinpres will merge their global product offering. In terms of merged technology, Cinpres will concentrate on gas controllers, generators, electric compressors and liquid cool systems; Maximator will concentrate on compressor stations, air-driven gas boosters, hydraulic-driven compressors, water assist systems, proportioning and dosing systems, nozzles and injectors.

www.cinpres.com

French language PIM group promotes technology

The "Groupement Francophone de Moulage par Injection de Poudres" (GFPIM) is a French language group that is looking to promote awareness and the use of PIM technology in French-speaking areas, including France, Belgium, Switzerland and Quebec, Canada.

Bringing scientists and commercial businesses together, the mission of this group is stated as introducing PIM technology to major industries, structuring and coordinating R&D projects, and developing a long-term plan for PIM technology.

A training course was recently organised in France, drawing much attention from French speaking potential end-users to PIM technology. The seminar dealt with a number of topics including the advantages of PIM technology, designing for PIM, modelling and simulation. The group now has 14 members. Commenting to *PIM International*, Pierre-Yves Filippi of Eurotungstene Metal Powders, said, "We are confident that this group will make a major contribution to the spread of PIM technology, and interest is growing continually."

Members at the time of publication are: Aimé Griffond, Alliance, CEA, CRITT, CNRC, ECAM, ENSMM, Eurotungstene, Jr Gnaegi, Magetex, PEP, Plastipolis, Pôle De Microtechniques and Sirris.

www.gf-pim.fr

SIMTech launches 'Nanotechnology in Manufacturing Initiative'

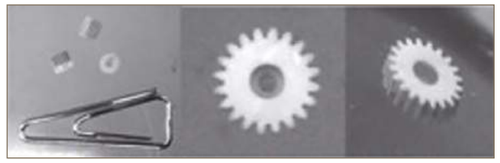
The Singapore Institute of Manufacturing Technology (SIMTech), supported by International Enterprise (IE) Singapore, Singapore Economic Development Board (EDB) and SPRING Singapore, has launched the 'Nanotechnology in Manufacturing Initiative (NiMI)'. This initiative will explore nano-materials for industry applications and addresses challenges in the adoption of nanotechnology for manufacturing.

Dr Lim Ser Yong, Executive Director of SIMTech, said that manufacturing enterprises in Singapore will be able to tap into the research institute's existing know-how and infrastructure resources. "This initiative enables industry to partner with SIMTech in innovative R&D to develop value-added nano-materials and manufacturing processes and to cope with nanotechnology in manufacturing of optimised high performance products with enhanced functionalities" stated Dr Yong.

In its first phase, NiMI will focus on the application of nanotechnology in the processes of forming, joining and coating. Specifically, these translate into the development of high performance complex composites for automotive applications; large area carbon nanotube growth; development of lead-free solders with nano-fillers for use in the electronics industry; nano-adhesives for improved performance; nanocomposite physical vapour deposition coatings and modular-based profilometer, to name a few.

SIMTech has already integrated nanotechnology in its research activities including laser fabrication and nanobump arrays, lead-free nanofillers solder composite, powder injection moulding with nano-particle feedstock, and super-hard nanocomposite. For example, the Powder Processing Group has been studying the powder injection moulding of nano-sized zirconia, alumina, and their mixtures with small amounts of additives to form micro-PIM components for MEMS, micromechanical devices, watch components, etc. SIMTech states that using nano-sized Y-TZP zirconia powders for PIM feedstock, components could be produced with micron sized features which could not be produced using micron sized powders. Using nano-size powders results in fine grain microstructures with average grain size of about 300 nm.

www.SIMTech.a-star.edu.sg



MicroMIM zirconia gears produced by SIMTech

Expert Group launches new booklet on MIM

Germany's MIM-Expertenkreis (MIM Expert Group) has launched a new booklet promoting MIM technology. Available as a free download, this English language guide provides a basic introduction to MIM's advantages, it's processing steps along with information on production volumes, tolerances, design considerations as well as mechanical properties of 38 commonly processed materials.

The MIM expert group consists of industrial companies and research institutes. MIM parts producers co-operate closely with powder and feedstock suppliers, as well as with injection moulding machine or furnace distributors and research facilities. The group currently has more than 35 members. Meetings are scheduled twice a year, and conducted in German.

The new 8 page MIM booklet can be downloaded from: www.mim-experten.de

MIM2011 conference programme now available

The conference programme has now been published for the MIM2011 International Conference on the Injection Molding of Metals, Ceramics & Carbides, March 14-16 2011.

MIM2011 will be held at the Hilton Hotel in Disney, Orlando, USA and the focus of the technical program is "Manufacturing Best Practices". The event is to be co-chaired by Animesh Bose, Materials Processing, Inc., and Bruce Dionne, Megamet Solid Metals Inc.

The conference is sponsored by the Metal Injection Molding Association (MIMA), a trade association of the MPIF and its affiliate APMI International. The objective of the event is to explore the latest advances in MIM, assist in the transfer of technology, and investigate new developments in the field of injection moulding of metal, ceramics, and carbides.

The conference is targeted at product designers, engineers, consumers, manufacturers, researchers, teachers and students. All individuals with an interest in this fascinating technology and application of its parts are encouraged to attend.

Immediately prior to the conference, on Monday, March 14, a one day PIM tutorial will be conducted by Prof. Randall M. German, San Diego State University. This intensive course will provide a basis for determining options, uses, properties, applications, and opportunities for cost-effective PIM manufacturing. Individuals who will benefit from the tutorial include engineers, business managers, procurement managers, component designers and technicians.

"This course is a must for consumers of PIM components and organisations that are exploring the opportunities associated with developing their own PIM manufacturing facilities", state the organisers. Full programme information is available from the MPIF website.

www.mpif.org

The Hilton Hotel in Disney, Orlando, is the venue for the MIM2011 conference

Submitting News

To submit news to *Powder Injection Moulding International* please contact Nick Williams: nick@inovar-communications.com

Near spherical electrolytic iron powder for MIM applications

Industrial Metal Powders Pvt Ltd has been producing high purity (>99.5%) electrolytic iron powders at its state of the art production facility near Pune, India, since 1974.

The ISO 9001 and ISO 14001 accredited company told *PIM International* at the recent PM2010 World PM Congress in Florence that it has developed a near spherical grade of electrolytic iron powder which it claims is a suitable alternative to carbonyl iron powders for metal injection moulding, and can also replace carbonyl iron powder in various other applications.

The ultra-fine iron powders are said to have particle sizes of D_{10} = 3.1µm; D_{50} = 6.2µm and D_{90} = 13.07µm.

For further information: www.imp-india.com

Parmatech-Proform's Rhode Island MIM facility opens

The grand opening of Parmatech-Proform Corporation's (Proform's) new manufacturing facility in East Providence, Rhode Island, took place on October 21st. The event featured presentations by ATW executives, a tour of the factory and visits from community leaders. The new manufacturing facility will serve as Proform's headquarters.

Proform is a wholly owned subsidiary of ATW Companies, acquired by ATW in 2009 specifically to augment and complement Parmatech's California-based MIM operation.

According to Peter C. Frost, president of ATW Companies, "We are very excited to be opening Proform's new East Providence facility, where we will showcase our technical MIM expertise. MIM has established itself as a mainstream metal fabrication technique, and the existence of two separate facilities offers significantly enhanced logistical, security, and redundancy benefits. It also places us closer to customers and markets."

ATW Companies is the parent company of A. T. Wall Company (Warwick, RI), Judson A. Smith Company (Boyertown, PA), Parmatech Corporation (Petaluma, CA), and now Proform (East Providence, RI).

www.parmatech.com

The opening of Parmatech-Proform's Rhode Island plant

MIM used to create premium manicure sets

Two long established manufacturers of knives, kitchen utensils, scissors, and beauty instruments have turned to metal injection moulding to create uniquely styled, high quality manicure sets.

KITA's grooming kit designed by Toshiyuki Kita

Zwilling j.a. Henckels of Solingen, Germany, uses the MIM production process to manufacture a set of five satin-finished stainless steel pieces in its TWIN 1731 manicure set. TWIN 1731 comprises nail scissors, cuticle nippers, tweezer, nail file and nail scraper/cleaner. The company states that its long heritage of top class craftsmanship was successfully transferred to MIM to achieve a combination of unmistakable design, outstanding functionality and exceptional precision.

Kai Corporation began as a pocket knife manufacturer in Seki, Japan, just over 100 years ago, and is today a leading producer of high quality knives, utensils, surgical instruments, etc. The company celebrated its 100th anniversary with a number of new, unique products including the KITA manicure set designed by Toshiyuki Kita. The KITA manicure set is made by metal injection moulding, and the designer stated that MIM enabled him to convert his ideas into precise forms and shapes combined with high quality.

www.kai-group.com | www.zwilling.com

JPMA award for Fine Sinter MIM diesel turbo part

Fine Sinter Co., Ltd., Japan, received a 2010 JPMA award for a MIM variable nozzle vane for diesel turbochargers. The part meets strict dimensional tolerance requirements as close as ±0.015mm on the wing profile, which was achieved with machining. It is produced using a special tool that has a unique sliding function when opening, reducing deformation during ejection. MIM production offered a 20% cost saving

Fine Sinter Co., Ltd's award winning MIM turbocharger vane

CERAM to focus on new materials development

CERAM, UK, an independent global organisation specialising in materials testing, analysis and consultancy has put innovation at the forefront of its agenda by committing to develop a portfolio of new materials and technologies relevant to its markets. To support the drive of the innovation-side of its business, the company has recently recruited a team of seven highly qualified scientists, with a breadth of expertise, as Technical Consultants.

After starting out as a research association which supported the ceramics and associated industries, CERAM has, over the past 20 years, diversified into other markets and other materials, bringing its expertise to provide solutions for numerous products and processes. One of the largest markets that CERAM now provides testing and consultancy services to is the medical material sector, in which turnover topped £1million in 2009 and continues to grow.

As Technical Consultants, the new team will work with CERAM's already renowned materials scientists on projects that include controlled release glasses, bio-ceramics and new drug delivery materials, novel methodologies to reduce water used in product/manufacture and sustainability in the built environment, and on radical technologies for the reduction of energy consumption in the manufacture of ceramics, bricks, tiles, etc.

Tony Kinsella, Chief Executive, stated, "This is an exciting time for us. We are leading the way in materials innovation and, to increase the speed at which we can do this, we've invested heavily in new people and new equipment. We've recruited the best science graduates from the UK and abroad to allow us to develop services and capabilities to help those industries, such as healthcare and construction, that will face significant materials challenges moving forward."

www.ceram.com

Feedstock producer AMP relaunches website

Advanced Metalworking Practices, LLC (AMP) of Carmel, Indiana has recently re-launched its website, www.advancedmetalworking.com. The redesigned site now features updated information on the company's ADVAMET® feedstock for metal injection moulding including Material Safety Data Sheets for several varieties of its feedstock.

AMP, an ISO 9001:2008 certified feedstock producer, has been supplying the MIM industry since 1988. "Our company was started in 1984 by Dr. Kishor Kulkarni and has maintained a constant focus on quality, service, and product reproducibility", stated William R. Mossner, PMT, Director of Technology.

In 2007, AMP was purchased by Purity Zinc Metals (PZM) of Clarksville, Tennessee. PZM is a custom fabricator of zinc dust, anodes, alloys and other zinc products for the global market.

www.advancedmetalworking.com

New method of sinter bonding PIM compacts to solid substrates developed

A new method of sinter bonding powder injection moulded (PIM) compacts to solid substrates has been developed at the Clemson University International Center for Automotive Research (CU-ICAR) in Greenville, SC, USA.

The traditional PIM process has part size and shape limitations. Besides the cost of the feedstock, these limitations are mainly imposed by the debinding and sintering operations. Thick cross sections are difficult to debind or would take too much time to debind and make this process step too cost intensive. Unsupported parts of the compacts can sag during sintering.

These limitations could be overcome by joining the PIM parts with solid parts and create composite parts that could be made of one or multiple materials to satisfy multifunctional design requirements. Advantages of composite parts are that; 1) the amount of powder used can be reduced while maintaining a merit of the PIM process, that is, parts of complex shape can be made easily, 2) parts that are only difficult to make by PIM (for example limited by mould design, cost or size) can be fabricated, for example, by combining a MIM part with a long, thick or thin solid metal, and 3) high mechanical strength or other properties can be acquired only at a necessary portion by using different materials, for example, an alloy steel feedstock and comparatively cheap steel, or other properties such as magnetic and non-magnetic in one part. Each of the above mentioned advantages will also lead to cost reduction.

Sinter bonding a PIM compact to a solid substrate has been considered impossible or very difficult in the past due to the large sinter shrinkage of the powder compact relative to a solid material. This shrinkage would typically lead to cracking in the compact, breaking of the bonded interface, deformation of the compact and, depending on part thickness, deformation of the substrate.

The new method employs a structure of micro features on the surface of the powder component. These features are moulded with the compacts in the injection mould. The powder compact is then placed on the solid substrate and both are joined during sintering.

The micro features allow for post bonding shrinkage through deformation, until the compact reaches its final density, thus avoiding cracks or warping of the bulk of the powder compact.

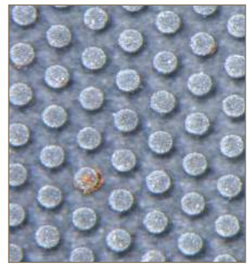


Fig. 1 Micro features on powder compact

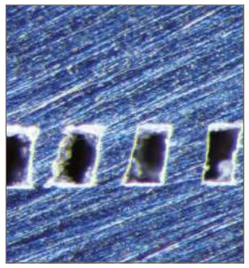


Fig. 2 Composite part

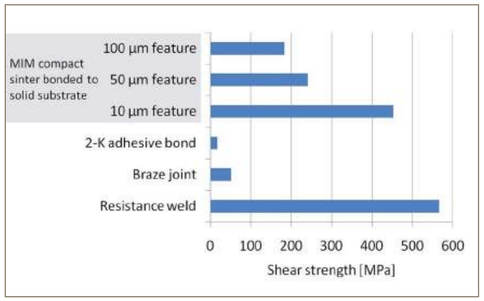


Fig. 3 Shear strength results

Fig. 1 shows the micro features on the surface of an injection moulded powder compact. These features can vary in shape and size; in this case they have a circular shape with a diameter of 100µm. Fig. 2 shows a crosscut of a composite part after sinter bonding, with the powder compact on top and the solid part below, joined with the structure seen in Fig. 1.

Tests with 17-4PH powder compacts joined to 17-4PH solid substrates have shown shear strengths of the sinter bonded joints of up to 80% of that of welded joints, as illustrated in Fig. 3. The strength of the joints depend on the size and shape of the micro features.

Email: mears@clemson.edu

MIM Moly caps find success in microwave ovens

Molybdenum (Mo) is widely used as an alloying element in steels and high alloy steels. Its outstanding electrical and heat conducting capabilities also sees the use of PM Mo and Mo alloys for a range of applications in the electrical and electronic sectors, and for resistance elements in electric furnaces capable of operating at temperatures up to 2200°C.

Most of the Mo components are produced by machining of wrought PM semi-products. Xiamen Honglu Tungsten Molybdenum Industry Ltd in Xiamen, China, has now successfully adopted the metal injection moulding process to produce a complex shaped Mo cap. Jiupeng Song in a presentation at PM2010 in Florence, reported that the Mo cap is used together with a Mo supporting rod as the core component of a magnetron tube in microwave ovens. The rod and cap support the magnetron coil which operates at temperatures up to 2000°C, and prevent microwaves from dispersing axially.

Jiupeng Song outlined the Mo powder production process used for the successful application of the MIM caps. He stated that the conventional chemical reduction of MoO_3 to produce fine Mo powder was not suitable for the MIM process because of the particle shape and resulting poor flowability of the powder.

The company therefore developed a special chemical reduction process which, when combined with a jet milling step, produced a very fine, rounded shape and deagglomerated Mo powders of high purity and relatively uniform particle size (D_{50} = 2.7µm) with a tap density of 4.35 g/cm^3. This was the highest tap density of the Mo powders evaluated which included imported grades EM FM1 from Climax, USA, and MMP II from H.C. Starck, Germany (Table 1). The company used a wax-polymer binder containing 51 wt.% paraffin wax, 30 wt.% polypropylene, 16 wt.% polyethylene, and 3 wt.% stearic acid for the MIM feedstock using the jet milled Mo powders, said Jiupeng Song.

Jiupeng Song reported successful injection moulding with a critical solid loading of 62-64 vol% in the feedstock. Injection moulding was done in an 8-cavity mould using an Arburg Allrounder 360S moulding machine. The moulded Mo parts were debound first by solvent debinding in heptane at 37°C followed by thermal debinding at up to 900°C in nitrogen, and then sintering in hydrogen at 1700°C. Sintered density of the MIM Mo caps was said to be 98% with a low carbon and oxygen content of 8ppm and 10ppm respectively. Nearly all the grains of the high purity (>99.95% Mo) sintered MIM parts were found to be less than 10µm.

www.tungsten-china.com ■

Fig. 1 MIM molybdenum caps are used with supporting Mo rods in the magnetron tube of microwave ovens. (Courtesy Xiamen Honglu Tungsten Industry Co Ltd)

	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	Tap density (g/cm3)
Chemical reduced	2.081	5.390	20.727	2.22
Rod milled	1.600	4.043	11.095	4.26
Jet milled	1.619	2.704	4.479	4.35
EM FM1	1.958	4.550	9.542	3.81
MMP II	1.862	3.493	6.428	3.75

Table 1 Characteristics of the various Mo powders evaluated for use in the MIM caps (from paper by Jiupeng Song etal., published in Proceedings of PM2010 World Congress, Florence, 10-14 October)

Copper micro-structures made by NIL/micro-SPiMIM

Researchers at Kinki University, Osaka Prefectural College of Technology, and Taisei-Kogyo Co Ltd, reported at PM2010 on a process called NIL/µ-SPiMIM to produce micro-structures having a 5µm to 10µm fine line and space pattern for use as optical fibre connectors, micro-impellers, micro-reactors, etc. As with the technology used to produce micro-heat sinks from Cu-diamond composites also developed at Osaka Prefectural College of Technology and reported in the June 2010 issue of *PIM International*, the researchers adopted their sacrificial plastic mould (SP-mould technology) into which are inserted polymethylmethacrylate (PMMA) films made by thermal nanoimprint lithography (NIL) techniques. The PMMA films produced by NIL can have line and space (L/S) pattern structures with dimensional accuracy of the order of nanometers, and micro-structures of just a few microns.

The researchers stated that their thermal NIL process consists of three steps; 1) Heating the PMMA film to above the glass transition temperature, 2) pressing and cooling to transcribe the Si-mould shape to the PMMA film, and 3) de-moulding the film from the Si-mould. The subsequent µ-SPiMIM process involves three further steps; injection moulding of MIM feedstock into the SP-mould; ejecting the green compacts and SP-mould as one component, removing the SP-mould; and solvent debinding the polymeric binders followed by sintering at 973K in Ar+20%H_2 gas to achieve the desired sintered density.

The materials used for producing the injection moulding feedstock for the micro-structured MIM parts are pure copper powder and polyacetyl based binder. The nano-sized copper powder is manufactured commercially by a wet-reduction method (Fukuda Metal Foil & Powder Co. Ltd.) and has a mean diameter: D_{50}=0.7µm, tap density: ρ_a = 3.17 g/cm^3, specific surface area: S_v = 1.69 m^2/g).

Fig. 1 shows the SEM images of green and sintered parts processed at 573K and 973K. In the green compacts with both L/S = 5µm and 10µm, the researchers found that the feedstock has seemingly filled the micro-channels completely, but the polymer binder builds up at the upper corners of microscopic structures. The sintered parts processed at 573K have many sub-micron pores, because both debinding and oxidising have not been completed at this lower temperature. However, it was found that the sintered parts processed at 973K keep the edge sharpness under optimised debinding and sintering conditions. ■

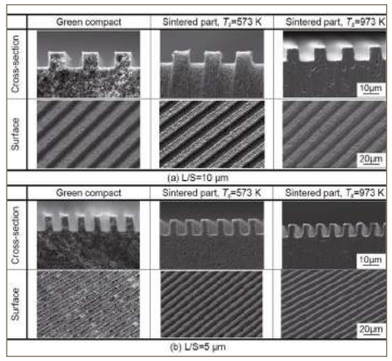


Fig. 1 SEM images of green and sintered micro-patterned parts produced from nano Cu powder. From paper by K. Nishiyabu etal, published in Proceedings of PM2010 World Congress, Florence, 10-14 October

OBE wins EPMA award for 0.028g eyewear component

OBE Ohnmacht & Baumgaertner GmbH (OBE), Germany, won a 2010 EPMA Award for Innovation in the "Component" category for what is described as a revolutionary locking device for spring hinges in spectacles (Fig. 1). The award was presented at the PM2010 World Congress, Florence, October 10-14.

This extremely small MIM 316L part weighs just 0.028g, however despite its small size, production volumes are high, with more than 4 million parts being produced each year. The part is manufactured in a 32 cavity mould.

The locking device is the most sensitive component of a sprung spectacle frame hinge. The high levels of abrasion during the function of the spring hinge make it necessary to use a hard, corrosion resistant material. A high level of accuracy was needed to enable a connection with a spring of 0.56 mm diameter. www.obe.de

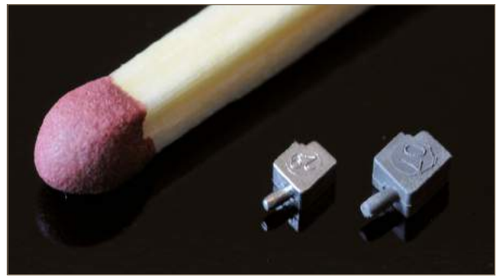


Fig. 1 OBE's MIM locking device in the sintered and green state. The cavity markings make it easy to trace any damage in the tooling

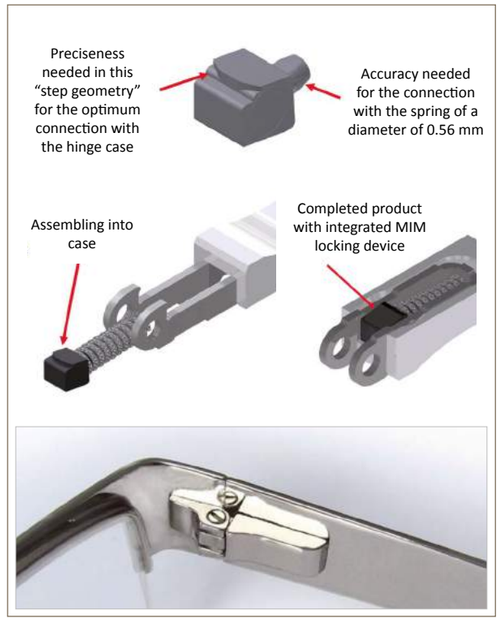


Fig. 2 An illustration of the function of the MIM locking device

EPMA award entries highlight the diversity of Europe's MIM industry

Entries submitted to the EPMA's 2010 awards competition by Europe's MIM producers demonstrate well the technology's acceptance by a wide range of end-user sectors.

Schunk Sintermetalltechnik GmbH, Germany, submitted a sensor housing (A) for distance sensors in automotive bumpers. This unusual shaped part required a flawless visual surface in the collar area. Made from carbonyl iron, this part weighs 10g and is 26mm long.

Mimest Spa, Italy, submitted a large 260g MIM photographic tripod component (B). Manufactured from 316L for corrosion resistance, this part is resized after sintering and machined to remove supports and create the thread. Finished height is 65mm

Parmaco Metal Injection Molding AG, Switzerland, submitted five MIM components to the awards competition.

Three of these are for a "Jet Protector" law enforcement device. The latch (C, 60mm length), counter plate (D, width 35mm) and striker (E, length 35mm) are all manufactured from 7%NiFe. Parmaco also submitted a neck link part for a diagnostic device (F, height 22mm) manufactured from 316L and weighing 15.91g, and a small 316L lock component (G) weighing just 0.265g.

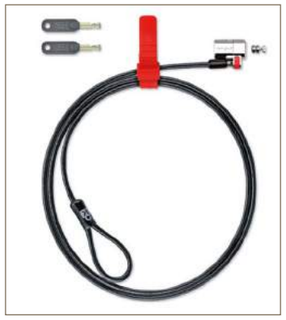
MIM laptop hinge producer operating at capacity

According to the Taiwan based Digitimes, laptop hinge producer Shin Zu Shing (SZS) has seen its metal injection moulding production facilities operating at full capacity in September, with around 50% of the capacity allocated for smartphone hinge products.

Digitimes stated that SZS recently received smartphone hinge orders from High Tech Computer (HTC), however volumes are still relatively small compared to the company's other product lines. It was estimated that of the current global handset market, about 40% of shipments are smartphones, but only 10% of smartphone shipments adopt hinges.

MIM lock part gives laptops physical security

Kensington Computer Products Group of Redwood Shores, CA, USA, is the globally recognised creator of the 'Kensington Security Slot', now said to be built into 99% of all laptop computers, plus award winning MicroSaver® and ComboSaver® computer security locks.



The Kensington ClickSafe™ laptop lock features a MIM locking mechanism

The company has now introduced a new locking device called ClickSafe™ which is a keyed lock inserted into a laptop, where the complex shaped lock part is made by the metal injection moulding (MIM) of stainless steel powder. Kensington states that the ClickSafe™ lock protects computers in just one single, simple step by easily attaching the MIM antitheft engagement mechanism to a laptop with one motion to be fully secured. The mechanism pairs with a cable made from superior carbon strengthened materials. Kensington states that it has rigorously tested this security product for real-world conditions to resist lock-picking, corrosion, tampering and extreme environments.

"ClickSafe™ makes locking down a laptop as easy as buckling a seat-belt, so users never have to worry about getting their laptop stolen," said Rob Humphrey, Director, Security Products, Global Business at Kensington. "It's so quick to use, there's no reason for business users to leave their laptop unprotected ever again."

The estimated cost of replacing content along with a stolen corporate laptop itself is said to be an astronomical $49,246, according to the Ponemon Institute, which conducted a 2009 study on lost laptops and the value of the sensitive business data within them.

www.kensington.com

New W-Cu powders offer opportunities for MIM in electronic applications

The properties of tungsten-copper (W-Cu) alloys with a Cu content of 20% meet the requirements of designers in electronic applications such as heat sinks, high power diodes, etc. which must provide a combination of low coefficient of thermal expansion (CTE) and good thermal conductivity.

W-Cu parts are usually made by Cu infiltration of a pre-sintered W skeleton. The only competitive alternative to Cu-infiltration appears to be pressing and sintering or MIM, if a fine and uniform distribution of a copper phase can be achieved in the sintered material so as to reach the required CTE values.

Herve Senillou of Eurotungstene Metal Powders, Grenoble, France, reported at PM2010 on the development of a new pseudo-alloyed W-Cu powder which has shown itself capable of meeting the requirement of microstructure homogeneity, fine dispersion of Cu in the W network, and controlled impurity levels, whilst attaining high sintered density and high thermal conductivity. The W-20%Cu pseudo-alloy (WCu8020) has been specially developed for both the press and sinter and MIM processes, stated Senillou.

The micron size W powder used in the pseudo-alloy powder is of high purity, and was found to give a good compromise between the high sinterability of submicron W and the good compounding and pressing ability of the micron W powders. The WCu8020 powder is said to be free of agglomerates, and has a very tight grain size distribution with a high level of homogeneity of the copper phase. The elementary powders used for the blended W-20%Cu reference powder includes a micron size and highly de-agglomerated industrial tungsten powder (AW7110) and an ultra-fine copper powder (MT120). Table 1 gives the chemical and physical characteristics of the powders used in the study.

Senillou reported that sintered density in the press and sintered samples is higher for the WCu8020 prealloyed powder than the reference blended material. Sintering was done at 1345°C in pure hydrogen to reduce the high 2.52% oxygen level in the starting WCu8020 powder. A reasonably low oxygen and transition metal contents (220ppm) was reported in the sintered parts which reached 98% density after starting from a relatively low green density (54%). The thermal conductivities were calculated at 165W/mK and 162W/mK for WCu8020 and W+20%Cu materials respectively. However, these values are said to be lower than the conductivity values reportedly reached through the Cu-infiltration process.

Eurotungstene also investigated the metal injection moulding of the WCu8020 powder using a polyethylene-wax binder system to prepare a feedstock with a 50vol% solids loading. A sintered density of 98% was achieved after debinding, presintering at 750°C and final sintering at 1350°C with oxygen content put at 0.029%. A linear shrinkage of 25.9-26.1% was observed in the sintered parts. Further work is said to be in progress to evaluate the thermal properties of the WCu8020 MIM materials.

www.eurotungstene.com

	AW7110	CuMT120	W + 20%Cu blended powders	WCu8020
D_{10} (µm)	1.04	1.09	1.22	2.15
D_{50} (µm)	1.78	1.91	2.11	4.59
D_{90} (µm)	2.90	3.54	3.57	9.62
Tap density	6.45	4.0	5.0	4.54
Apparent Scott density	3.74	2.52	2.41	2.43
BET (m^2/g)	0.83	1.1	0.88	0.74
Fe (%)	0.005	<0.001	0.008	0.011
Ni (%)	0.0007	<0.001	0.005	0.005
Co (%)	0.0006	<0.001	0.005	0.003
Cr (%)	0.0012	/	/	0.003
O (%)	0.26	0.25	0.33	2.52
C (%)	-	0,10	0.0277	0.0172

Table 1 Chemical and physical characteristics of the powders used

PIM successfully used to produce hard ferrite magnets

Hard ferrites, or 'hexaferrites' are ceramic magnets based on Fe_2O_3 and metal oxides MO (M = Pb, Ba, Sr) with $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ most frequently used. Their main magnetic properties are not as high as those of metallic (e.g. rare earth) magnets such as NdFeB and Sm-Co magnets, but their advantages include a high Curie temperature (450°C), high operating temperature (250°C), water resistance, chemical stability, large coercivity and high electrical resistance. They are also inexpensive and easy to produce as relatively simple shapes using powder pressing and sintering.

A research consortium entitled 'MagnetoPIM' with partners from Austria and Serbia and with funding from the Austrian Federal Funding Agency, has recently concluded a study of the use of the powder injection moulding process to produce complex shaped hard ferrite magnets and their work was presented at PM2010 in Florence.

The researchers stated that it is desirable to perform injection moulding in a magnetic field in order to achieve maximum magnetic properties of the final product. Applying a high intensity magnetic field in the injection phase results in a saturated orientation of single domain hexaferrite particles in parallel to the z-axis. Once oriented during injection, the particles remain oriented during debinding and sintering. The hexaferrite powder for the feedstock was prepared by dry-mixing of hematite (Fe_2O_3) and strontium carbonate $SrCO_3$ followed by calcination at 1100°C for two hours in air and then slow ball milling for a further 24 hours. The average resulting particle size was 1.25 µm measured by a Fisher Subsieve Sizer. The resulting $SrFe_{12}O_{19}$ powder was mixed with a 'solvent debinding system' containing mainly wax, thermoplastics and additives.

The green samples were demagnetised in a magnetising box before debinding which was carried out in a gently agitated acetone bath at 45°C for about 18 hours followed by thermal debinding together with sintering in air. Isothermal sintering was performed at 1180, 1200, 1220, 1240 and 1260°C, with a holding time of 120 min. The researchers report that the sintering temperature of 1200°C gives the highest maximal energy product for both types of anisotropic samples (Table 1). The values obtained for axial aligning are slightly higher which is due to the differences in design of the magnetic field source. ■

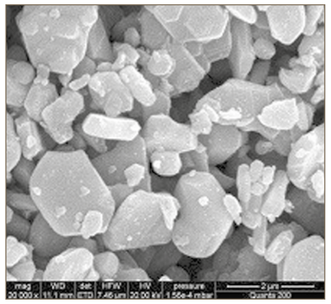


Fig. 1 SEM of the starting $SrFe_{12}O_{19}$ powder (from paper by B.S. Zlatov etal, published in proceedings of PM2010 World Congress, Florence, 10-14 October)

Sintering parameters	Magnetisation modes	Remanent induction Br [T]	Coercive force H_{cb} [kA/m]	Max energy product $(BxH)_{max}$ [kJ/m³]	Saturation Coer. Force Hs [kA/m]	Saturation induction Js=Bs [T]
1180°C/2h	isotropic	0.183	110.12	6.20	490.9	0.241
	anisotropic axial	0.325	180.15	18.02	495.8	0.331
	anisotropic diametral	0.335	160.28	16.52	487.1	0.351
1200°C/2h	isotropic	0.1932	129.35	7.69	521.46	0.255
	anisotropic axial	0.354	230.63	25.12	572.75	0.361
	anisotropic diametral	0.343	210.20	22.18	510.19	0.353
1220°C/2h	isotropic	0.2064	134.05	8.51	545.55	0.281
	anisotropic axial	0.3912	182.50	21.97	592.96	0.399
	anisotropic diametral	0.3618	170.63	18.99	515.63	0.371
1240°C/2h	isotropic	0.21	134.40	8.68	542.83	0.285
	anisotropic axial	0.4152	164.30	20.99	591.4	0.425
	anisotropic diametral	0.41205	139.10	17.64	517.96	0.421
1260°C/2h	isotropic	0.1812	104.15	5.81	540.11	0.289
	anisotropic axial	0.3684	96.49	10.94	589.07	0.389
	anisotropic diametral	0.3264	106.36	10.68	520.68	0.342

Table 1 Magnetic properties of sintered Sr-ferrite PIM samples. From paper by B.S. Zlatov etal, published in the proceedings of the PM2010 World Congress, Florence, 10-14 October

Titanium and titanium alloy Powder Injection Moulding: Matching application requirements

Titanium powder injection moulding (Ti-PIM) is coming ever closer to delivering its promise of penetrating high value markets, such as the aerospace and medical sectors. The biggest remaining challenge is to successfully match the specified mechanical and chemical requirements of final applications. As Éric Baril from Canada's National Research Council explains, the challenge of understanding and managing both the starting material and the various processing steps is no small challenge, but is essential to meet customer expectations.

Titanium and titanium alloys have several attributes that make them desirable for a large spectrum of applications. Strength-efficient structures and corrosion-resistant service are the two main areas of application where the unique set of characteristics justifies the selection of these materials.

The combination of high strength, stiffness, good toughness, low density and good corrosion resistance provided by various titanium alloys at very low to moderately elevated temperature allows weight savings in aerospace structures and other high-performance applications. The excellent corrosion resistance coupled with good strength make titanium and its alloys useful in chemical and petrochemical applications, and marine environment applications.

For medical applications, the ability to passivate allows titanium based materials to be nontoxic and generally biocompatible with human tissues and bones. This characteristic, coupled with its non-magnetic nature and Young's modulus close to that of bone, makes titanium the material of choice for biomedical implants among all metallic biomaterials.

Matching the application requirements can be a long journey when several variables are involved in the definition of the material properties. A good understanding of the effect of the key variables on the material attributes is, therefore, necessary in order to keep a firm control on the process and match customer expectations.

'the mechanical properties of dense titanium and titanium alloys are sensitive to the presence of interstitial solutes such as oxygen, nitrogen, carbon and hydrogen'

Material requirements

Each application has its own set of material requirements related to the relative importance of specific attributes of titanium and titanium alloys. Since the first commercial use of these materials for structural applications in the early 1950's, several specifications have been developed by the major standardisation bodies (ASTM, DIN, British Standards TA, Aerospace American AMS, Aerospace American MIL-T, and SAE). These standards mainly cover the wrought (billet/bar, plate, sheet, tube, wire, forgings) and cast materials. Table 1 summarises the main ASTM standards relating to titanium for general (B-series) and medical (F-series) applications. The primary specifications in these ASTM standards are the chemical and mechanical requirements. These requirements should be sufficient to predict some more complex behaviour, such as fatigue life and fracture toughness, since these attributes are somehow correlated to the chemistry and mechanical properties.

The reason for setting chemical requirements lies behind the fact that the mechanical properties of dense titanium and titanium alloys are sensitive to the presence of interstitial solutes such as oxygen, nitrogen, carbon and hydrogen. These interstitials increase the elastic modulus and the yield strength, this reducing the ductility of titanium and titanium alloys

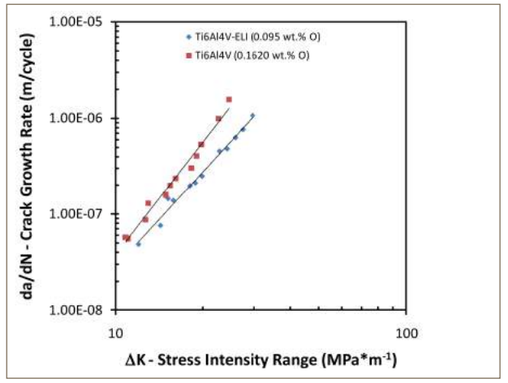


Fig. 1 Influence of oxygen content on fatigue crack propagation in Ti6Al4V in the annealed condition [5]

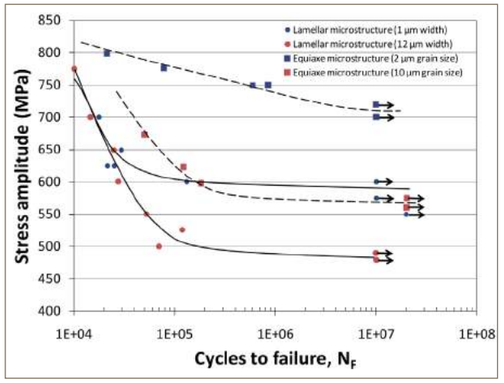


Fig. 2 Influence of microstructure on high cycle fatigue behaviour (R=-1) of Ti6Al4V [6]

[1]. Nitrogen generally has the most significant effect, followed by oxygen and carbon. While nitrogen and carbon are usually not found at high concentrations in dense titanium, oxygen is a common contaminant due to the high affinity of titanium for oxygen and its high solubility in titanium. At low concentration, oxygen occupies octahedral sites of the α-titanium crystal and increases the lattice parameters as well as the c/a ratio in the crystal, resulting in a volumetric change of 0.0013 nm^3 per atomic percent of oxygen [2,3]. The oxygen atoms interact with the hydrostatic stress field of the dislocations but also with the shear stress field, so that both edge and screw dislocation motion is affected. Therefore, increasing oxygen content results in an increase of the yield strength, hardness and fatigue resistance at a given stress level, whereas it decreases the ductility and impact resistance by restricting twinning and prismatic slip [4].

Fig. 1 shows that the crack growth rate is slightly higher for higher oxygen content [5]. However, a clear and unambiguous trend on the influence of oxygen on fatigue is difficult due to its effects on other microstructural features such as the lamella width of the typical lamellar microstructure of Ti6Al4V. The type of microstructure and the grain or lamella size have a direct impact on the fatigue strength (see Figs. 2 and 3) [6]. There is also a clear and direct correlation between

Standards	Title	Max.O (wt.%)	Max.N (wt.%)	Max.C (wt.%)	Min. Y.S. (MPa)*	Min. UTS (MPa)*	Min. Elongation (%)*
ASTM F67	Unalloyed titanium, for surgical implant applications						
	Grade 1	0.18	0.03	0.08	170	240	25
	Grade 2	0.25	0.03	0.08	275	345	20
	Grade 3	0.35	0.05	0.08	380	450	18
	Grade 4	0.40	0.05	0.08	483	550	15
ASTM-F1472	Wrought Ti6Al4V alloy for surgical implant applications	0.20	0.05	0.08	860	930	10
ASTM F136	Wrought Ti6Al4V ELI (extra low interstitial) alloy for surgical implant applications	0.13	0.05	0.08	795	860	10
ASTM F1108	Standard specification for Titanium-6Aluminum-4Vanadium alloy castings for surgical implants	0.20	0.05	0.10	758	860	8
ASTM B381	Standard specification for titanium and titanium alloy forgings (grade 5)	0.20	0.05	0.08	828	895	10
ASTM B348	Standard specification for titanium and titanium alloy bars and billets (grade 5)	0.20	0.05	0.08	828	895	10
ASTM B367	Standard specification for titanium and titanium alloy castings (grade 5)	0.25	0.05	0.10	825	895	6
ASTM B817	Standard specification for powder metallurgy (P/M) titanium alloy structural components (grade 5)						
	Density : 94%	0.30	0.04	0.10	814	903	8
	Density : 99%				862	958	13
ASTM WK26721	New specification for metal injection moulded Titanium-6Aluminum-4Vanadium net or near net parts for surgical implant applications	Work item – new standard under development					

Table 1 Selected ASTM standards for titanium products

**for annealed bar, billet, forging, wire and other forms*

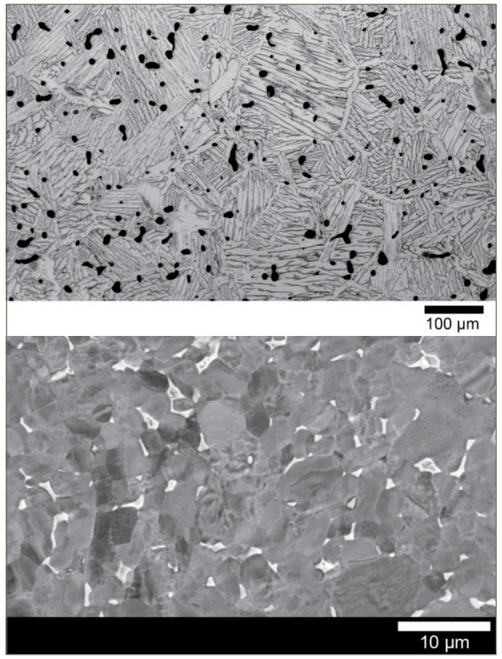


Fig. 3 Microstructure of Ti6Al4V; (a) Lamellar microstructure and (b) Equiaxe microstructure (Courtesy of Helmholtz-Zentrum Geesthacht – Orley Ferri and Thomas Ebel)

the fatigue life and yield strength which can be used as a predictor. Indeed, for wrought titanium and alloys, the rule of thumb is the fatigue strength is about 65% the value of the yield strength [1].

Even if the chemical and mechanical requirements seem to be sufficient to specify titanium alloys, in some cases, special requirements are also indicated in the standards. As an example, in F136 and F1462 standards, the microstructure requirements are stated: fine dispersion of alpha and beta phase without coarse, elongated alpha platelets. These requirements are in place most likely because of the effect of such microstructural features on the fatigue strength (Fig. 2), but also because thermo-mechanical processing can modify and improve the microstructure for a given chemistry. In the case of such standards, the titanium alloy is tuned to offer the best performance in fatigue both for minimal crack initiation and propagation rates.

The Powder Metallurgy (PM) processes have their own set of requirements in ASTM-B817. In this case, besides the chemical and mechanical requirements, relative density of the final material is also specified. It should be noted that the P/M standard allows the highest oxygen content in the final component (0.30 wt.%) for Ti6Al4V alloy. For this standard, the highest density also requires the highest mechanical requirements, which should give the highest fatigue strength.

Powder Injection Moulding (PIM) does not yet have its own standard. A work item is currently under development by ASTM F04.12 committee: Medical and Surgical Materials and Device – Metallurgical Materials. This standard will most likely set the chemical, mechanical and metallurgical requirements of Ti6Al4V alloy made by PIM for surgical implant applications. The exact values of the specifications will be a challenge between the Ti-PIM process historical capabilities and the decades of know-how on such application requirements.

In recent years several studies have been published reporting the Ti-PIM chemical and mechanical properties [7,8,9,10,11,12,13,14,15]. Prof. Randall German in the December 2009 issue of *PIM International* published one of the most comprehensive reviews of the current status of Ti-PIM [16]. From these publications, the current Ti6Al4V-PIM process capability can be drawn. Fig. 4 illustrates the process capability with regards to static tensile mechanical properties and equivalent oxygen content (O_{eq}). This value is defined by O_{eq}= O(wt.%)+2N(wt.%)+0.5C(wt.%).

These graphs show the expected trends between the mechanical properties and the O_{eq}. However, some large spreads of results are observed mainly due to variation in density for a given chemistry. A multivariate analysis has been performed on the dataset and confirmed that most of the variability is explained by the density and O_{eq} variabilities. Fig. 5 shows the predicted trend obtained with the multivariate model. Recently, Miura *et al.* demonstrated similar contour maps of ultimate tensile strength (UTS) as a function of relative density (ρ) and total oxygen content O_T [15]. They also determined the empirical equation: UTS (MPa)=700 O_T(wt.%)+10ρ(%)-315, provided that O_T<0.5wt.% and ρ>94.5%. When compared to Figs. 4 and 5, these equations slightly under estimate the UTS.

With the data of Fig. 4 and the predictive model of Fig. 5, the basic chemical, mechanical and metallurgical requirements can be proposed. Assuming that the targeted mechanical requirements for surgical implants made using PIM are somewhere between the one for cast and wrought Ti6Al4V (ASTM F1108 and ASTM F1462), the min. Y.S. would be between 758-860MPa, UTS between 860-930MPa and elongation between 8-10%. To match all these characteristics, the

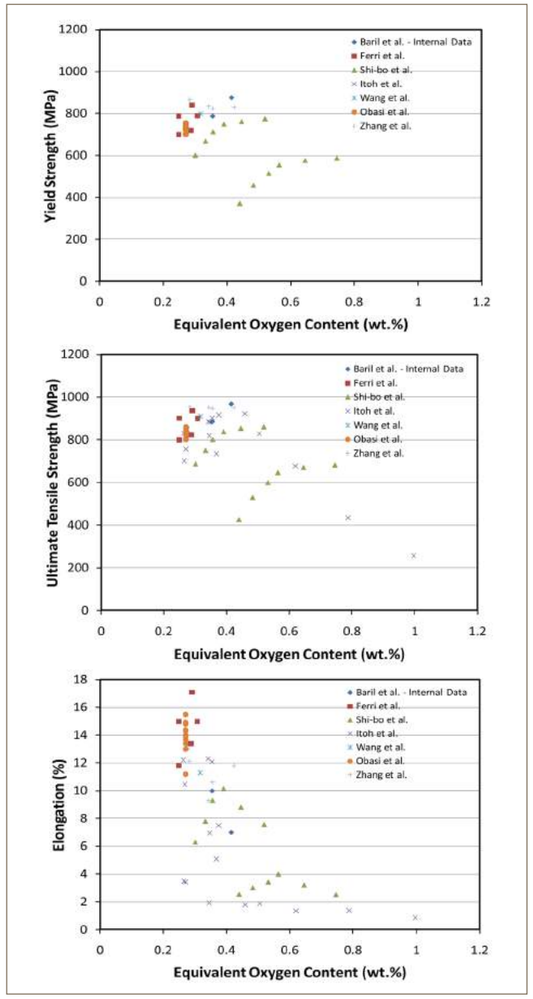


Fig. 4 Yield strength, ultimate tensile strength and elongation as a function of the O_{eq} from various sources of data

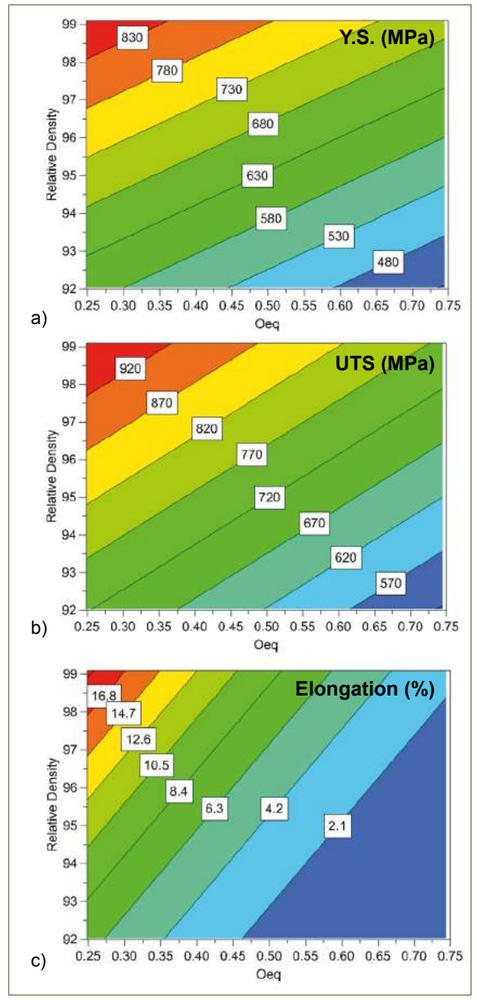


Fig. 5 Prediction of a) yield strength (MPa), b) ultimate tensile strength (MPa), c) elongation (%) for a range of relative density and O_{eq} from a multivariate model generated from Fig. 4

		Oxygen (wt.%)	Nitrogen (wt.%)	Carbon (wt.%)	Oeq (wt.%)	Comments
Based on the statistic of the dataset of Fig. 7 for O_{eq} <0.34wt.%	Minimum values	0.19	0.012	0.038	0.23	
	Maximum values	0.31	0.019	0.119	0.41	
	Average values	0.24	0.017	0.065	0.31	
	Max O, Ave N, Min C	0.31	0.017	0.038	0.36	Good debinding = low C pick-up -> Oxygen can't be above 0.3
	Ave O, Ave N, Max C	0.24	0.017	0.119	0.33	Bad debinding = high C pick-up -> improve oxidation control
	Ave O, Max N, Ave C	0.24	0.019	0.065	0.31	N range is narrow -> minimal impact even at upper limit
	Average O, Max N, Max C*	**0.24**	**0.019**	**0.119**	**0.34**	**Assuming worst conditions->0.24wt.% O is acceptable**
	ASTM-F1472	0.2	0.05	0.08	0.34	
	ASTM F136	0.13	0.05	0.08	0.27	
	ASTM F1108	0.2	0.05	0.1	0.35	
	ASTM B381	0.2	0.05	0.08	0.34	
	ASTM B348	0.2	0.05	0.08	0.34	
	ASTM B367	0.25	0.05	0.1	0.40	Industrial casting (alpha case and sand-oxide inclusions)
	ASTM B817	0.3	0.04	0.1	0.43	PM (HDH powder with high O content)

Table 2 Possible chemical requirements assuming an O_{eq} of 0.34wt.% compared to the ones of the ASTM standards reported in Table 1

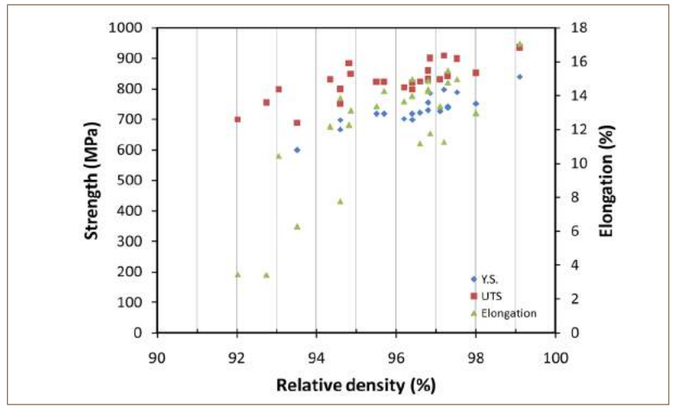


Fig. 6 Yield strength, ultimate tensile strength and elongation as a function of relative density for O_{eq} below 0.34wt.%

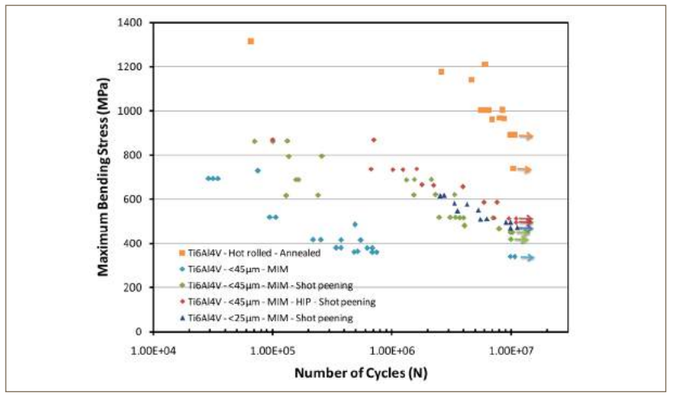


Fig. 7 Bending fatigue S-N curves of Ti6Al4V-PIM with different post-treatments [12,13,14]

equivalent oxygen content has to be below 0.34wt.%. When only the data from the conditions leading to O_{eq} below 0.34wt.% is taken, Fig. 6 can be drawn to show the effect of the relative density on the Y.S., UTS and elongation. To match the above requirements, especially for Y.S. and UTS, the relative density needs to be above 97%.

In summary, to match the actual requirements for a Ti6Al4V surgical implant, the O_{eq} should be below 0.34wt.% and the relative density above 97%. One should notice that the ASTM chemical requirements in the active standards for medical applications (F-series) give O_{eq} of 0.35wt.% or lower (Table 2).

More than one scenario of chemistry requirements could possibly give the required O_{eq} (Table 2). The acceptable scenarios should be within the oxygen, nitrogen and carbon ranges obtainable with Ti6Al4V-PIM processes. These ranges (minimum, maximum and average), given in Table 2, were estimated using the dataset of Fig. 6. The O_{eq} was calculated for the limits and the central points of these ranges. For conditions where O, N and C are at their upper limit, the O_{eq} (0.41wt.%) is above 0.34wt.%. A good scenario would be that debinding is difficult (thick parts) and nitrogen is high in the starting powder, in this situation, 0.24wt.% oxygen in the final part would lead to acceptable O_{eq}.

For steel based PM materials,

however, it has been demonstrated that the fatigue performance cannot be estimated reliably from the tensile strength using a fixed ratio, as is the case for wrought materials [17]. This is mainly due to residual porosity and surface roughness which influence the fatigue crack initiation. Therefore, the required yield strength is no longer an accurate predictor, unless the surface finish is modified and residual porosity eliminated.

There are very few studies of the fatigue behaviour of Ti PM material. In 2006, Wu *et al.* demonstrated the influence of surface finish on the fatigue strength of samples made by Ti6Al4V powder HIPping process [18]. They observed an increase in four-points bending fatigue strength after electro-polishing the as-HIPped surface. The as-HIPped surface gave fatigue strength of 360MPa while the electro-polished surface gave 510MPa, which is comparable to machining the as-HIPped surface. The fracture surfaces confirmed that the initiation sites were, indeed, the sintering necks on the as-HIPped surface. These necks were smoothed out or eliminated by electropolishing. More recently, Ferri *et al.* conducted a study on the high cycle fatigue behaviour of Ti6Al4V fabricated by PIM [12,13,14]. They looked at the effect of HIPping, shot peening and powder size on the four-points bending fatigue strength (Fig. 7). They first showed that the fatigue strength of PIM parts are significantly lower than wrought Ti6Al4V (hot-rolled) because of the much coarser microstructure and the presence of pores in the PIM microstructure. They demonstrated that shot peening offers the largest increase in fatigue strength of PIM-Ti6Al4V due to the reduction of the surface roughness and elimination of the surface porosity.

On the other hand, they found that HIPping also increases the fatigue strength by the elimination of the residual pores which removes stress concentration sites. Finally, they demonstrated that smaller Ti6Al4V powder (-25µm) gives slightly higher fatigue strength than large powder (-45µm). They attributed this increase to the higher oxygen content and higher yield strength of the parts made with -25µm powder.

Surface finish and post-processing treatments are not clearly specified in ASTM standards. These parameters are often specified by the customer,

Fig. 8 PIM knee implant parts made by Ti6Al4V-PIM (Courtesy of Maetta Sciences Inc., Canada)

but it is dictated by the expected life of the device and, therefore, the required fatigue strength. For load bearing surgical implants, the typical post-treatments are, after HIPping, bead blasting, polishing, electropolishing and anodising. Fig. 8 shows the common surface finishing required for Ti6Al4V-PIM knee implant parts currently under development.

The determination of chemical and mechanical requirements done above for Ti6Al4V surgical implants made by PIM could also be done for more general and less demanding applications (consumer and industrial parts, surgical tools, etc.). The development of a large property database linking chemical composition, density and grain size to mechanical properties would allow the development of more robust predictive models for the determination of the chemical and mechanical requirements. Obviously, the development of these new standards should be done with both the Ti-PIM process capability and the final application requirements.

The determination of the process capability will come with a better understanding of the key variables of the process. The increased knowledge of their influence on the material parameters determining the final mechanical properties is also essential. For titanium, this can be summarised by the determination of the influence of the process parameters

on both the densification (sintering and HIPping) and interstitial control. The following section gives more insight about the latter aspect.

Sources of interstitial contamination

PIM steps and related variables that may affect interstitial contamination are highlighted in Fig. 9. These sources are discussed in more detail in the following sections.

Analytical techniques

The analytical technique is an important aspect to consider when controlling the amount of interstitials in titanium components. Inert gas fusion and combustion techniques are most commonly used for the determination of oxygen, nitrogen and carbon in titanium. While these techniques are normalised by standards [20], the results are highly sensitive to the sampling and measurement procedures and can be affected by various measurement errors.

In order to verify the reliability of oxygen and carbon determination in titanium powders, a round robin testing campaign can be conducted between laboratories certified to serve the aerospace and medical sectors. Table 3 presents the results of such a campaign using -45µm powders (CpTi and Ti6Al4V) and shows the large variations observed from one laboratory to the other. The powder supplier was able to reproduce the results reported in the powders certificate of analysis. In addition, one laboratory (S) was able to give relatively accurate results for oxygen content but completely off for carbon content. While a second laboratory (G) was in the opposite situation with good carbon result but bad oxygen results. Other laboratories were, however, very far from the values reported by the certificate of analysis. The results clearly show that values from certified laboratories cannot be taken for granted unless their procedures have been validated and blind controlled to confirm their reliability. These observations also suggest that some laboratories have to be trained and monitored specifically for the analysis of titanium powders. As an example, NRC-IMI installed an inert gas fusion oxygen analyser (LECO TCH-600) and developed sampling, analytical and monitoring procedures for titanium powder.

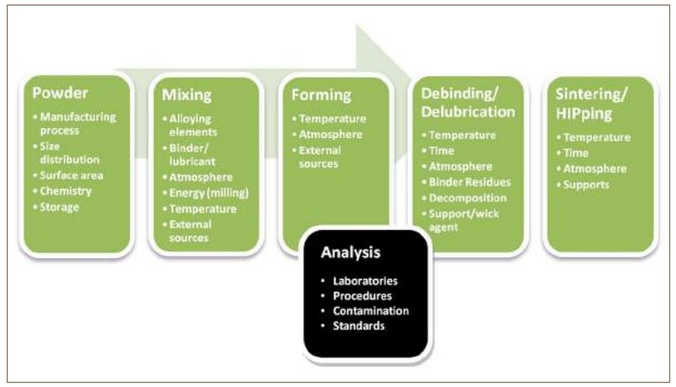


Fig. 9 Sources of interstitial oxygen contamination in typical PIM process [19]

Sample		Certificate of analysis	G	B	S	B2	Supplier	Average Labs	Standard deviation Labs
SP3-126 (Ti)	Oxygen	**0.25**	0.109	0.63	0.276	0.221	0.26	**0.30**	**0.20**
	Carbon	**0.007**	0.009	0.04	0.03	0.01	0.009	**0.0196**	**0.0145**
SP3-112 (Ti6Al4V)	Oxygen	**0.54**	0.220	0.66	0.570	0.503	0.53	**0.50**	**0.17**
	Carbon	**0.029**	0.029	0.056	0.046	0.038	0.032	**0.0402**	**0.0109**

Table 3 Round robin results of oxygen and carbon analyses (wt.%) on hydride/dehydride (HDH) -45µm powder conducted with 4 certified laboratories serving aerospace and medical sectors

Once the laboratory was trained and monitoring procedures were in place, the oxygen content measurement was identical to the certified value of SP3-126 (Ti) powder and the standard deviations of the analyses were down to 0.011 wt.%, which corresponds to a variability below 4.4%. These values are still, nevertheless, above the 1.5% variability values reported from the analytical equipment manufacturer [21]. A good monitoring practice for both internal and external laboratories is blind control with reference material (wire and/or powders) with interstitial contents close to the targeted ones. The analytical results could then be rejected if the controls are outside the established standard deviation.

Once the reliability of the analyses is established, the PIM production process can be followed and analysed to better understand the relative importance of the sources enumerated in Fig. 9. As an example, the tracking of the oxygen pick-up sources will be described below.

Contribution of the main process variables to the oxygen pick-up

In order to evaluate the relative contribution of different sources of oxygen, a study of a titanium PIM process has been carried out. For this case study, two Ti6Al4V powder particle size distributions were used: -25 and -45µm. The feedstock was composed of 66vol% of Ti powder in a PE, PW and SA binder system. The debinding was conducted for 10h between 100 and 450°C in repurified argon (4 l/min of argon with 10-8 ppm O_2). The sintering was done under vacuum for 3h at 1300°C.

In order to monitor independently the effect of each variable, reference powders were placed in a BN crucible to avoid any contamination from the binder or oxide support. Fig. 10 compares the absolute contributions of the powder, debinding, sintering and support on the total oxygen content in the component. The -25µm powder gave a higher oxygen content than the -45µm powder. The major contributors were the initial powder and the debinding process.

When normalised, the contributions can be ranked in a Pareto graph as presented in Fig. 11. This analysis indicates that the final oxygen content is mainly affected by the initial oxygen content of the powder and the interaction with the low amount of oxygen in the atmosphere in the vacuum sintering furnace.

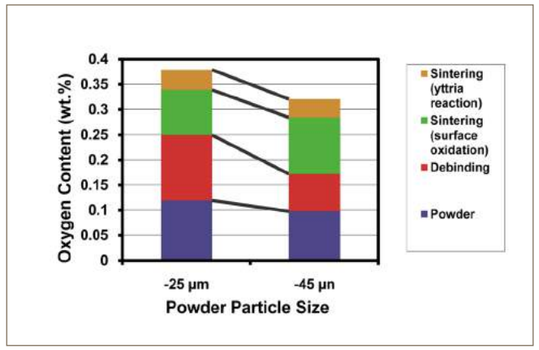


Fig. 10 Absolute contributions of powder, debinding and sintering cycles on the final oxygen content of titanium PIM components [19]

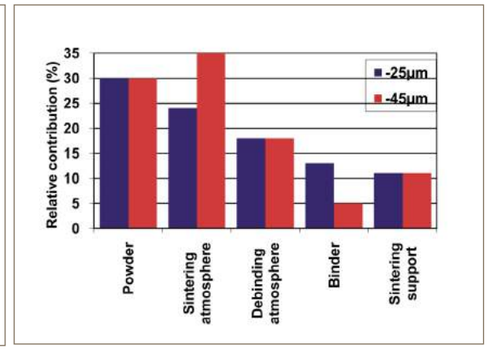


Fig. 11 Pareto graph of the contributions of the main titanium PIM variables to the final oxygen content [19]

Interestingly, the effect of the powder size and surface does not change the relative ranking of the powder, debinding and sintering support contributions. It does, however, impact the ranking of the binder and sintering atmosphere contributions. The binder contributes more significantly to the oxygen pick-up with the smaller particles. This might be due to the larger surface area available for the reaction with binder components. On the other hand, the relative contribution of the sintering atmosphere is less important with the smaller particles. This is related to their faster densification and the faster reduction of the specific surface area during sintering when compared to the larger particles. The reduction of the exposed titanium surface minimises the oxygen pick-up during sintering.

The Pareto graph gives areas of potential improvement to the process. Considering that the major contribution in oxygen comes from the powder, reduction of the powder oxygen content would be beneficial. However, for this case study, the Ti6Al4V powders were already low in oxygen (<0.11 wt.%). Considering that the major contribution of oxygen in high quality low oxygen content powder comes from the raw material, limited improvements are conceivable without significant cost penalty.

Any improvement on the sintering conditions will, however, contribute significantly to the reduction of the total oxygen content without major cost penalty. The optimisation of the sintering time-temperature and the installation of in-situ oxygen getters could further reduce the total oxygen content. Other improvements such as the reduction of the debinding peak temperature will also contribute to the reduction of the oxygen content in the final components.

Powder contribution

The oxygen content of the starting powder is mainly related to: the manufacturing process, size distribution, surface area, chemistry and storage conditions. These factors are affecting the two contributors to the total oxygen content: (1) surface oxide and (2) oxygen in solid solution. The oxygen in solution mainly comes from the chemistry of the raw material and the powder manufacturing process. The amount of oxygen in the surface oxide depends on the specific surface area of the powder (particle size distribution and shape) and thickness of the oxide layer. The oxide layer thickness, on the other hand, depends on the powder processing (exposition to oxygen at moderated temperature) and the storage conditions.

Fig. 12 presents the total oxygen content of various titanium powders and the effect of storage on the oxygen pick up. CpTi and Ti6Al4V powders from two manufacturers (RA = HDH and AP&C-Pyrogenesis = Plasma atomisation) were analysed over a period of 2.5 years of storage in normal conditions (unsealed steel containers filled with air of uncontrolled humidity between 20-60%).

The effect of particle size distribution and surface area can clearly be seen with the AP&C powders (Lot:5254-S1 and Lot:5254-S2). Both powders were from the same atomisation batch but were sieved at two different sizes: -25µm (S1) and -45µm (S2). The specific surface areas were 0.1233 m^2/g and 0.0717 m^2/g for S1 and S2 respectively. The effect of the surface area difference (i.e. 0.0516 m^2/g) results in an increase of the oxygen content by 0.0237wt.%. This represents an oxygen increase of 0.00459 g/m^2. Assuming that this increase is directly associated to surface oxidation (ρ=4.23 g/cm^3, O_{TiO2}=40.1 wt.%), this difference represents a 3 nm TiO_2 passivation layer. This is in the range of thicknesses observed on oxide layers naturally formed on titanium at room temperature (2-7 nm) [22]. With this oxygen tied up in the passivation layer, it means that the oxygen interstitial content (in solution in titanium) in these powders should be around 0.062 wt.%. This is close to high purity titanium commercially available (0.04 wt.%) and indicates that, apart from the oxidation of the new surfaces created during atomisation, there is practically no oxygen solubilised in the titanium matrix during the atomisation of the powder.

HDH powders show significantly higher oxygen content than the plasma atomised powders. The higher oxygen content is associated with both the higher surface area and higher soluble content. Indeed, the surface areas of the HDH powders are 0.137 and 0.176m^2/g for SP3-126 and SP3-112 respectively. The larger surface areas of the -45 µm HDH powders are associated to their irregular shape. When assuming a 3 nm TiO_2 passivation layer, it means the oxygen in solid solution represents 0.200 wt.% (SP3-126) and 0.484 wt.% (SP3-112).

Fig. 12 presents the oxygen content measured on the powders at different intervals for a period of 2.5 years. During that period, the containers

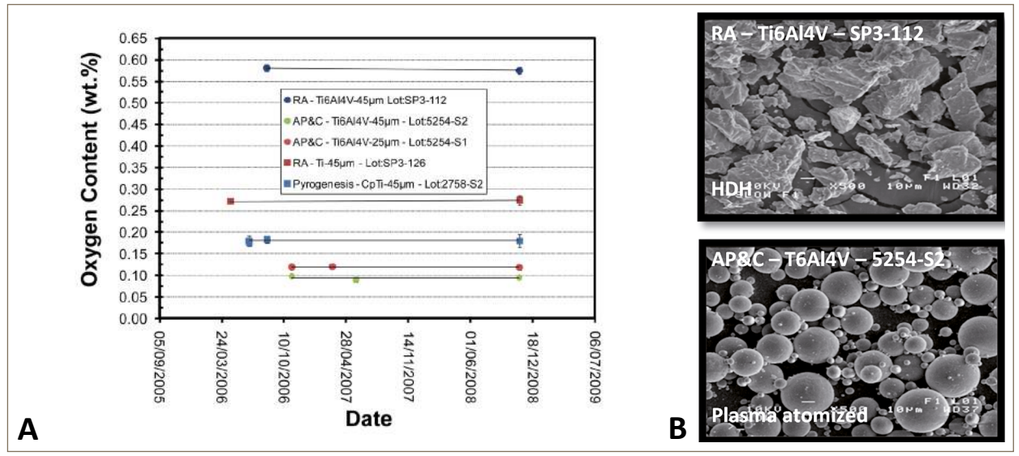


Fig. 12 a) Oxygen content of various powders (types and sizes) stored in unsealed steel containers in air under uncontrolled conditions and, b) morphology of HDH and plasma atomised powders [19]

were opened several times and closed without any purge with neutral gas. Consequently the powders were exposed to air. The results show the relative resistance to oxidation of the titanium powder when stored and manipulated in a laboratory environment without the use of a glove box or neutral gas cover.

Binder contribution

For PIM, the titanium powders need to be mixed with additives such as lubricants, binders and/or alloying elements. The contribution of the mixing procedure is usually negligible unless mixing is done at high temperature and/or energy. With high mixing energies, such as the ones involved in mechanical alloying for example, the titanium particles may deform and/or break. The deformation or rupture of the particles can lead to the exposure of new titanium surfaces that will be passivated when exposed to air. The creation of the new oxide film increases the oxygen content in the final powder mixture.

Additives such as binder and/or lubricant can also represent important sources of interstitial contamination. Consequently, these additives must be carefully selected when developing a powder formulation, to avoid important oxygen pick-up during processing. Unless the powder/additives mixture is exposed at high temperature in the presence of oxygen, the forming (moulding, compaction, extrusion and foaming) of titanium powders does not cause important oxygen pick up. The oxygen pick-up usually comes from the reaction with remaining oxygen in the debinding atmosphere and slightly from decomposition products from certain types of binder/lubricant. On the other hand, carbon pick-up may come from reaction with binder components and residues.

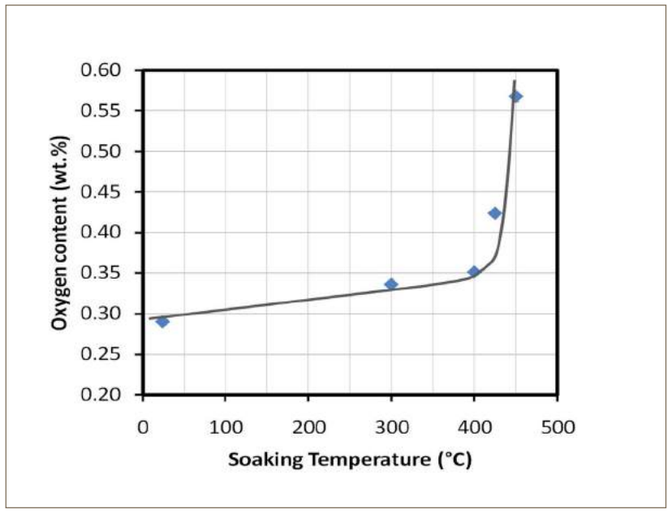


Fig. 13 Oxygen content in titanium foams exposed for 60 minutes at various temperatures in argon containing 20vol%O_2 [24]

The impact of debinding

Thermal processing is often used to decompose and eliminate binders and/or lubricants used during the forming of the powders. As the binder and lubricant are generally decomposed in inert atmospheres free of oxygen, these additives must have clean decomposition characteristics under inert atmospheres to avoid their reaction with titanium during debinding.

Several formulations have recently been developed for the powder injection moulding of titanium. These formulations generally include compounds among polyethylene (PE), polypropylene, polymethylmethacrylate, polyethylene glycol (PEG), ethylene vinyl acetate, paraffin wax (PW), naphthalene and stearic acid (SA) [16,23]. All these compounds have different decomposition temperatures, ranging usually between 200 to 500°C. Thus, the optimisation of the thermal debinding profiles must be done according to the composition of the binder system used. Some compounds such as PEG generally leave more residues (oxygen and carbon) if not sufficiently removed during the water based initial debinding treatment.

The thermal debinding treatments are usually done at moderate temperatures to ensure the complete decomposition of the binder while minimising the oxygen and carbon pick-up. Fig. 13 presents the oxygen pick-up of titanium foams (0.05m^2/g; initial oxygen content: 0.29wt.%) exposed for 60 minutes at various temperatures in Ar-20vol%O_2 [24]. Fig. 13 indicates that above 400°C, the oxidation dramatically increases. It should be noted that below that temperature, the oxidation of titanium is not as dramatic, even if the atmosphere contains 20vol.%O_2. This indicates that no special care need be taken when mixing or shaping the titanium at temperatures below 400°C to protect the powder from oxidation (except if very fine powders are used). It also indicates that the binder components have to be selected so as to be efficiently removed at temperature below 400°C.

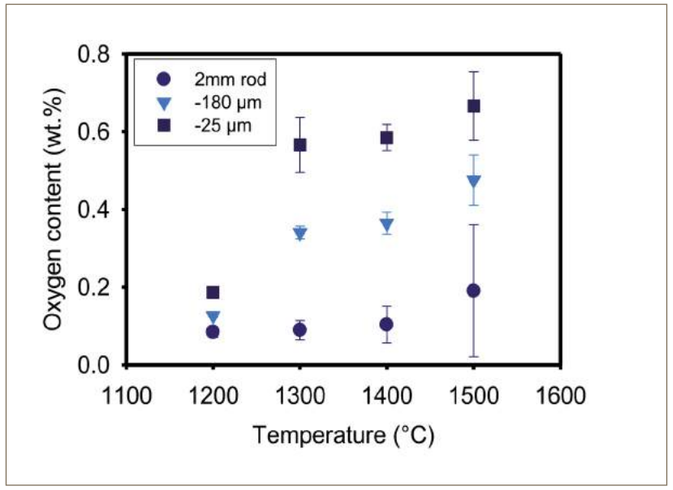


Fig. 14 Comparison of oxygen content in loose titanium powders and a 2mm rod after exposure for 60 minutes to various temperatures at 10^{-6} Torr vacuum [19]

The impact of sintering

High temperature vacuum sintering is generally preferred for the final consolidation of Ti-PIM components. Since sintering occurs at temperatures above 1000°C, the passivation layer is dissolved and the oxygen goes into solution at those temperatures [24]. The new titanium surface then becomes highly active and reacts with oxygen, even at very low concentration in the atmosphere. The initial surface area of the powder, the sintering time-temperature profile and the sintering support are the main factors affecting the oxygen pick-up during sintering. Fig. 14 presents the impact of the surface area (-25 µm and -45 µm powder and dense 2 mm rod) on the oxygen pick up at different temperatures (60 minutes in 10^{-6} Torr vacuum environment). The oxygen pick-up increases significantly with temperature but also with the surface area of the medium (powder or rod). Other variables, such as sintering time and supports, have also been analysed in other studies [24-27]. Fig. 14 shows that the oxygen pick-up rate increases significantly above 1200°C which suggest that sintering should be done at this temperature range. German reported that the median sintering condition observed in 33 R&D reports is a temperature slightly over 1250°C held for 3 hours [16].

Since most Ti-PIM process routes uses -45µm powder [7-16], high sintering energy is often required to reach densities above 97%. Zhang *et al.* demonstrated that, at 1320°C for 3 hours, density reached a plateau of 98.8%. But these fairly high temperatures will enhance titanium reactivity and lead to higher oxygen pick-up and reaction with the sintering support.

During sintering, the substrates are of a primary importance. As for conventional PIM, the substrates need to offer the possibility to securely set complex parts. Yttria and zirconia have been identified as better candidates than alumina because of limited reaction with titanium during sintering. However, zirconia substrate seems less stable than yttria at temperatures above 1100°C for extended time (8 hours) [15,16].

The surface of titanium is repassivated after exposure to air after vacuum sintering. This causes an additional oxygen pickup. This effect is minimal for dense components but can be important for porous components, as presented in [24]. The formation of this oxide film contributes to the total oxygen content but should not have an important impact on the final mechanical properties of the components as the effect of oxygen in solution is predominant. This oxide film, on the other hand, has positive effects on the corrosion resistance and biocompatibility of titanium and titanium alloys.

During the development of Ti-PIM thermal processes, especially when the temperature is above 400°C, the sample batch size is quite important. For a given furnace, the oxygen pick-up is significantly different between debinding and/or sintering a single part of 50g and a batch of several kilograms. The large furnace load will offer more titanium volume to dissolve atmospheric contaminants. Since titanium offers a large solubility to oxygen, reusable sacrificial titanium can be used in the furnace as internal gettering media to insure a good sintering atmosphere. The total load (part and getter) of titanium in the furnace should be significant and kept constant from one production run to the next in order to achieve reproducible conditions.

Conclusion

Titanium and titanium alloys have a unique set of properties which enable their use in several applications. However, the relative high cost of the raw material and processing routes will often only justify its use in higher-end applications with more demanding requirements. For such applications, several standards have been put together during the last 60 years to set the chemical and mechanical requirements for wrought material. These standards are based, independently

of the manufacturing process, on the relationship between the chemistry, the static properties and the dynamic properties. The goal is to achieve a compromise between the maximum interstitial content and the optimal static mechanical properties.

For Ti-PIM, this relationship between interstitial content and mechanical properties is more complex due the potential presence of residual porosity. In this case, the optimisation is about finding the best compromise between maximum densities, minimum interstitial content and optimal mechanical properties. An additional challenge is the absence of a clear relationship between yield strength and fatigue strength because of the presence of stress risers due to residual porosity.

The multivariate analysis of Ti-PIM data published during the last 10 years permitted to establish tentative chemical and density requirements to match the mechanical property requirements for surgical implant applications. The maximal equivalent oxygen should be 0.34wt.% and the minimum relative density 97%.
In order to maximise the fatigue strength, bead blasting or shot peening is required. HIPping should also be considered.

To reach those requirements, the following recommendations should be considered:

- Minimise oxygen from powders
- Keep the mixing, moulding and debinding temperatures below 400°C
- Keep the sintering temperature below 1200°C
- Use yttria or zirconia sintering setters
- Maximise furnace loads with sacrificial material
- Increase the density of the part surface and/or the part core.

These can be easily applied in standard PIM processes. The next important challenge is then demonstrating the economical benefits of going with Ti-PIM. This should come through better communication with designers. The value of Ti-PIM will be established with the introduction of innovative designs and functionalities created from strong collaboration between the end-user and the Ti-PIM industry.

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Ceramic injection moulded zirconia products enjoy success in high-value luxury applications

Coloured zirconia ceramics can be produced by the CIM process, yielding entirely dense sintered materials that are highly suited to high gloss polishing. As Johan ter Maat and colleagues from BASF SE explain, these materials have succeeded in attracting the attention of luxury goods producers. From watches and mobile phones to writing instruments and automotive interiors, the authors present some striking examples of the possibilities of injection moulded zirconia ceramics.

Tetragonal zirconia is a comparatively young class of ceramic materials which was only discovered in 1975 [1]. The yttria-stabilised polycrystalline version (TZP, tetragonal zirconia polycrystalline) appeared around 1980 and the first useful powder was produced by the Japanese company Tosoh on a commercial scale in 1983. This chemically derived powder is ultrafine and shows a very good sintering activity; with appropriate powder processing it can be readily sintered into practically theoretical density.

TZP exhibits an unusual combination of several favourable properties; it shows high strength, high toughness, high hardness, low thermal conductivity, a high volumetric density and a high refractive index (see Table 1 for typical values from several sources, notably [2, 3, 4]).

'TZP exhibits an unusual combination of several favourable properties'

It is rewarding to explore and understand the reasons for this set of properties. The high strength of TZP is associated with the very fine crystallite size of the sintered material, usually not more than 0.3-0.5µm, allowing a four point bend strength of 1000 MPa or more. It is essential that a high

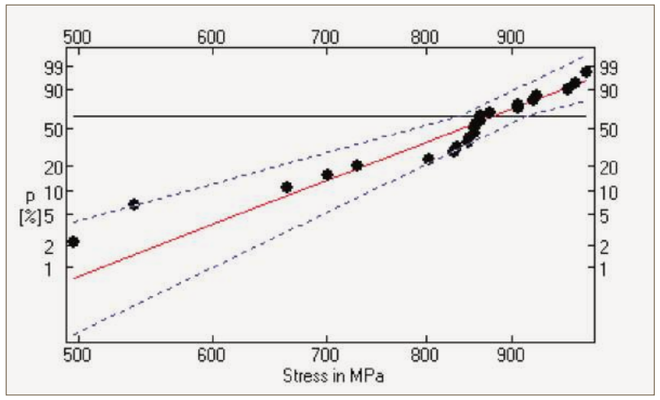

Fig. 1 Weibull plot of bend strength measurements of injection moulded black TZP bars

TZP ceramic materials properties	
Bend strength	1000 MPa
Toughness	6 - 8 MPa.√m
Hardness	1350 HV
Modulus of elasticity	200 GPa
Thermal conductivity	2 W/mK
Theoretical density	6.08 g/cm^3
Refractive index	2.2

Table 1 Materials properties of TZP ceramic

Fig. 2 Rado Integral watch utilising black TZP ceramic material

Fig. 3 Rado Sintra Jubilé watch utilising white TZP ceramic material

Fig. 4 Battery cover in black ceramic for an exclusive mobile phone

quality, high purity, ultrafine powder is used in order to achieve this. The high toughness is imparted by the metastable tetragonal crystal mode. TZP remains in the tetragonal state as long as the crystallite size is below 2µm the limiting grain size, the toughness becomes higher and the strength is slightly reduced [2].

Like all ceramic materials, TZP has a high hardness, which is innate to the strong ionic bonding prevalent in most ceramic materials. The low thermal conductivity is related to the zirconia defect structure as the incorporation of subvalent yttrium ions in the zirconia lattice creates a large number of oxygen ion vacancies. The yttrium ions and the oxygen ion vacancies act as lattice point defects interacting with phonons in the case of heat conduction [3]. The oxygen ion vacancies also provide a path for easy diffusion of oxygen ions at elevated temperatures (>600°C), leading to ionic conduction, another unusual zirconia property, not further discussed here, which is employed for oxygen sensors and fuel cells.

'TZP has a high hardness, which is innate to the strong ionic bonding prevalent in most ceramic materials'

since the surface region of small grains keep the interior under compression. Approaching and above this limiting grain size TZP tends strongly towards disproportioning into monoclinic and cubic phases. This metastable crystal condition is the reason for the high toughness.

When a crack approaches, the stress on the grain interior is suddenly released, allowing a spontaneous transition into monoclinic zirconia. This is associated with a volume expansion, so that the crack is blocked for further growth by the now larger monoclinic grain. As the grain size approaches

The high density and the high refractive index are both directly related to the high atomic number of zirconium, the atom is heavy and readily polarised.

The following set of properties demonstrate why TZP is an excellent material choice for decorative, hand touched objects:

- The absence of residual porosity allows a 'mirror finish' polished surface, very smooth and non-sticky to touch.
- The low thermal conductivity conveys a cool, but not cold impression.
- A high hardness imparts wear and scratch resistance to a polished object, a desirable feature if the object is in daily use.
- The high refractive index leads to a higher proportion of reflected light, making the polished surface look exceptionally brilliant.
- The weight of a hand held object, finally, is subconsciously associated with value.

However, the pure and dense TZP material is translucent and ranges from ivory to bone china in colour, which is rarely seen as an appealing colour for designer objects. Therefore, from the earliest days of TZP zirconia's development, the idea of colouring the material black by sintering in an inert atmosphere emerged in a patent by Kyocera [5]. Later on, patents on black or coloured TZP by using pigments were also filed and granted [6, 7].

The high hardness of TZP has, apart from the desired scratch resistance, also an unpleasant consequence for producing TZP parts. Since conventional ceramic powder pressing and sintering is limited in both tolerances and complexity, the production of complex designer objects presents a formidable challenge. Exact contours and tolerances would have to be achieved after sintering by diamond machining, which is extremely expensive.

For this reason ceramic injection moulding (CIM) was introduced very early in the 1990s for design dominated applications. The CIM process allows complex shapes, free surfaces and quite a good tolerance (+/- 0.2 - 0.3%). We are concentrating on the Catamold® process, which was launched in 1991 and was presented in detail a short time later [8].

History

The CIM process has been known for around 80 years, but it wasn't until the late 1960's that the technology began limited industrial practice with the production of thread guides in aluminium oxide. Recently a comprehensive review article has appeared [9]. Naturally, for very hard materials like ceramics, the motivation to use the CIM process is very high, much higher than for metals.

The problem with ceramics is the fine powder that must be used to achieve a sufficient sintering activity; in general the powders are below 1µm in size. This aggravates the general problems with binder removal and makes it very difficult to control and to reproduce the final results after sintering. Therefore the CIM process came much later in general use than MIM, because the reward in complexity and tolerances was paid for by a strongly varying yield with no clear cause.

The Catamold® process has proved in the last 15 years to be a significant improvement, especially for the ultrafine powders that are indispensable for TZP.

Formulation and processing

Blending ultrafine powders into a thermoplastic matrix requires a low volume fraction of powder, the use of dispersants and high shear mixing. The TZP powder has an average particle size of 0.3µm and even using effective dispersants a volume fraction above 50% is not possible. The Catamold® process employs polyacetal as the majority binder, which imparts a high green strength to the moulded green parts, which is especially valuable when producing large and/or thin parts. The dispersant system allows a volume fraction of 47% TZP powder; the dispersants fulfil the role of permanent binder as well, in order to maintain part integrity during the debinding process.

The debinding process employs catalytic binder decomposition using nitric acid vapour in a nitrogen atmosphere as described previously [8]. Sintering is performed under air at usually 1500°C. A dense TZP ceramic product is obtained and the density for unpigmented sintered material (6.07 g/cm^3) comes close to theoretical density (99.8%). The modest volume fraction of powder leads inevitably to a quite large linear shrinkage of 22.4%, which is nevertheless well controlled to a tolerance level of +/- 0.2 - 0.3%, depending upon the size of the article.

For a coloured product the TZP ceramic has to be pigmented. Of course the pigment must survive the sintering temperature without evaporating, melting or disproportioning and this limits the choice to inorganic pigments as used for tile and porcelain glazing. Broadly speaking, these pigments are mixtures of several transition metal oxides, notably iron, cobalt, nickel, manganese and chromium. This limits the choice of colours to shades of black, blue, green and brown.

'In order not to have a negative influence on the bend strength, all pigment particles should be smaller than 20µm'

Depending on the particle size of the pigment, a quantity of 1 - 10% by weight in TZP is sufficient for saturating the colour. Above 10% the densification process is increasingly impeded by the second phase pigment and a loss of gloss after polishing would be the consequence. In order not to have a negative influence on the bend strength, all pigment

Fig. 5 Luxury pen with black ceramic body

'Coloured TZP is a wonderful ceramic material, which delights designers and charms the public by its unique feel and brilliant look'

particles should be smaller than 20µm. Black zirconia, as in Catamold® TZP-F 315, is pigmented with 6% of a Ni-Fe-Co-Cr mixed oxide pigment.

Properties

Bend test bars were moulded on an Arburg 370C injection moulding machine using an end gated tool for the bars. The gate size was practically identical with the test bar cross section to avoid moulding problems like jetting, creating artefacts like air inclusions and knit lines.

Moulding conditions and further processing during catalytic debinding and sintering were done in accordance with the processing instructions available for Catamold® TZP-F 315. Debinding was done at 110°C with nitric acid in a 50 L Kendro debinding oven, sintering was done at a final temperature of 1500°C for 1 h in a Nabertherm sintering furnace.

The sintered bars were ground and polished into bend test bars in accordance with ISO 14704 and tested on an Instron 8562 at a cross head speed of 2mm/min. Fig. 1 shows a Weibull plot of the 23 strength values that were found.

The median four point bend strength was 876 MPa at a Weibull modulus of 9 (the red line in Fig. 1 - the dotted blue lines are the envelope values 6 and 11 for the modulus).

In addition fracture toughness (SEVNB, 7.4 MPa.√m), hardness (Vickers indenter, 1250 HV) and modulus of elasticity (195 GPa) were also determined on these bend test bars.

Fig. 6 Gear shift lever black ceramic inlay for an executive class automobile

In conclusion, we notice, that the addition of the black pigment causes a small, but tolerable decrease in strength and hardness compared to the host material TZP, whilst toughness and modulus of elasticity are largely unaffected (TZP properties in Table 1).

Applications

In all cases, the sintered parts are going through a polishing process which lasts many hours, if not several days [10]. Details about the polishing process are hard to find, but the equipment can be anything from rotating drums and stirred vessels to vibrating containers with a secret mixture of polishing media, diamond pastes and additives. If this sounds expensive, this impression is correct, polishing determines to a large extent the total cost.

After polishing, all parts go through a meticulous visual inspection to sort out defective parts, for example parts with pinholes, scratches or cracks. The power of a trained human eye should not be underestimated; a defect larger than 30µm in size can be detected on polished black TZP. This means that aesthetical ceramics must meet practically the same requirements as high tech ceramics.

Initially the application of black TZP ceramic materials was destined for watches. The watch brand Rado acted as the pioneer with the launch of the Rado Integral in 1986 (Fig. 2), featuring black zirconia bracelet elements. After the establishment of the CIM process, intricately shaped collections like Sintra (Fig. 3) were created and other colours than black were introduced.

For a long time, watches remained the only segment of industry employing decorative TZP ceramics, until the launch of the top range mobile phone brand Vertu in the year 2000 with an unprecedentedly large, mirror polished surface of approximately 40 x 80 mm serving as the battery cover (Fig. 4).

From then on, we have witnessed a gradual, steady expansion of the areas of application into other watch brands and writing instruments (Fig. 5). Recently, black TZP found acceptance in a top range executive class automobile [11]. In this case, extremely challenging shapes and part sizes were converted from plastic into black TZP ceramic, the masterpiece being an 80 g free shape inlay for the gear shift lever (Fig. 6).

Conclusions

Coloured TZP is a wonderful ceramic material, which delights designers and charms the public by its unique feel and brilliant look. With ceramic injection moulding the realisation of aesthetical design oriented applications for coloured TZP, which were previously impossible to produce by pressing techniques, have been put into practice. Although in most applications the TZP ceramic is in normal use not subject to any mechanical stress, the meticulous visual inspection procedures at the end of the production process lead to a ceramic product with a high tech character.

With the CIM process coloured TZP ceramic products can be produced on an industrial scale without a negative impact on the valuable property profile of TZP.

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AT&M: Pushing the boundaries of Metal Injection Moulding in China

China is rapidly becoming a powerful force in the global metal injection moulding (MIM) industry, with more than 30 part producers now competing in an ever expanding domestic and international market. AT&M is one of China's largest MIM part producers, and a major exporter to other parts of Asia as well as Europe and North America. *PIM International* reviews the development of the company, its MIM part and powder production facilities, and plans for the future.

Advanced Technology & Materials Co. Ltd (AT&M) was established in 1998 as a commercial arm of the Central Iron & Steel Research Institute (CISRI) Group, one of China's leading industrial materials research centres headquartered in Beijing. AT&M has since grown into a leading presence in the field of metallurgical materials and processing technology in China.

The company today supplies a wide range of industries with a diverse portfolio of products that includes magnetic materials and products, welding materials, atomised metal powders, porous filters, ultrahard and refractory materials, steel products, superalloys, tool steels, metallurgical processing equipment, ferroalloys, biomedical materials and MIM parts, to name just a few.

The company currently has more than 2400 employees and reported 2009 sales of RMB 3,663 million ($550 / €395 million*) across all divisions.

The story of MIM at AT&M

Although metal injection moulding is a relatively small part of AT&M's total business, accounting for around 2% of total sales, the company is the largest MIM producer in China and has ambitious growth plans. Research into metal injection moulding at CISRI dates back to 1985, when initial experimental work began. "We started looking at MIM technology in 1985 and achieved much early experimental success", Mr Jin Chenghai, General Manager of AT&M's Powder Metallurgy Division, told *PIM International*. "Then, in order to enlarge and commercialise our achievements, AT&M established a metal injection moulding plant in 1998 with an initial investment of around RMB 30 million ($4.5 / €3.25 million)".

'the company is the largest MIM producer in China and has ambitious growth plans'

Fig. 1 AT&M's manufacturing facility in the Zhongguancun Science & Technology area of Beijing, China

** All currency conversions are approximate, and based on exchange rates in November 2010*

Fig. 2 Injection moulding machines at AT&M. The machines at the far end of the manufacturing hall feature automated handling systems

In 2003 AT&M made a further investment of nearly RMB 50 million ($7.5 / €5.4 million) in a brand new MIM production line in the Zhongguancun Science & Technology area of Beijing. This new facility, stated Mr Jin Chenghai, features the most advanced international production equipment to enable MIM production to international standards.

'We continue to explore and optimise the MIM process, reducing production times whilst maintaining both quality and high volumes'

MIM production today

AT&M's MIM plant covers a manufacturing area of 2900m^2 and employs a staff of 114. There are currently 13 injection moulding machines in operation, capable of producing 780 million parts every year (Fig. 2). Nine of these machines are fitted with robotic pickup and handling systems, enabling the efficient production of high volume orders.

After moulding, parts are debound using a solvent and thermal process, before being sintered in five Japanese Shimadzu vacuum sintering furnaces. These furnaces have a volume of 400×400×1200 mm and are capable of sintering at up to 1500°C under vacuum, or with hydrogen, nitrogen or argon atmospheres (Fig. 3).

"We continue to explore and optimise the metal injection moulding process, reducing production times whilst maintaining both quality and high volumes. Our goal is to improve production efficiency and reduce overall energy consumption", stated Mr Jin Chenghai. "We are also committed to enhancing our product design capabilities to avoid the problem of shape distortion in complex products, and to enhance our machining capability."

Typical production volumes are five million parts per month, with the majority of products being consumer electronics, computer, telecom, medical, hardware and lock components.

The company also indicates that it has considerable in-house expertise when it comes to tooling for MIM. "We are committed to further improving our in-house tool making ability, and we are already able to manufacture around 35% of all new tools in-house. Our tooling shop has a team of nine people and we have spark erosion equipment, wire cutting and milling machines as well as grinding and polishing equipment. The tool material that we use is the Swedish ASSAB88 tool steel, which we have found is capable of 300,000 injection cycles. The maximum number of cavities per tool is currently 32."

AT&M also performs a wide number of post-sintering operations in house, including drilling, reaming, tapping, sizing and grinding. Heat treatment, coating and electroplating are also available.

Mr Jin Chenghai is optimistic about the future of MIM at AT&M, stating, "We are planning to double production volumes in the next five years. Our belief is that stainless steel and low-alloy steels will account for 70 tons per year, tungsten alloy and tungsten carbide alloys parts 35 tons per year and new materials such as titanium alloys will account for five tons per year".

The company is already planning to expand its MIM production facilities, using existing space available at the plant. It was indicated that there are no plans to add continuous sintering furnace technology, but rather remain with batch furnace solutions.

Feedstock

The majority of feedstock used at AT&M is manufactured in-house. Mr Jin Chenghai stated, "Over many years we have undertaken a lot of research and development in the area of feedstock for MIM and we believe that we have made great progress in this field. We imported MIM technology from America, however we have since optimised our binder systems, reducing debinding times from 35 to 20 hours. Today, around 90% of our MIM products are made using our own feedstock, with 10% manufactured using BASF's Catamold® system."

AT&M's binder technology is often combined with the company's own atomised metal powders, with typical materials being 316L, 440C, 420P and 17-4PH stainless steels. Other frequently processed materials include M2 tool steel, tungsten alloys (W-Ni-Fe-Cu, W-Ni-Cu), tungsten carbide, and soft magnetic materials.

"We continue to explore more new materials, such as Kovar, nickel free stainless steel and superalloys. There is also a lot of interest in titanium MIM in China, and we are now beginning to study and experiment with this".

Sales and markets

MIM producers in China have enjoyed strong growth over the past decade and AT&M is no exception. Between 2003 and 2006 the company's MIM part sales grew from RMB 12 million ($1.8/€1.2 million) to more than RMB 62 million ($9.3/€6.7 million), a remarkable 50% per year average growth. The company states that the global economic crisis had an impact on sales, largely due to a drop in demand for consumer electronics, but sales are now rebounding.

AT&M has to-date developed more than 500 different MIM parts. "We have become a certified supplier to more than ten major global corporations in the USA, Germany, Japan, Italy, Finland, Brazil and Thailand. Around 70% of our MIM products are now exported", Mr Jin Chenghai told *PIM International*.

"The main end-user markets we serve are test instruments, lock parts, surgical instruments, tools, IT, electronics and automotive. Because of confidentiality agreements with customers, the parts featured in this report do not comprehensively show our MIM production. The smallest parts that we produce weigh just 0.01g and have a minimum wall thickness of 0.3mm, whilst the largest parts weigh 150g and have a wall thickness of 10mm."

Commenting on the factors that are restraining the growth of the MIM industry, Mr Jin Chenghai stated, "The main obstacles to developing new MIM applications are firstly the high price of the raw material. After this, end-user industries know little about MIM and there is still a lot to be achieved as far as technology promotion is concerned. A lack of standards for material properties is also a problem. We also see the high tooling costs as a major obstacle for a customer whose requirement is for relatively small part volumes. Last, but not the least, there is still room to improve the dimensional accuracy of MIM mechanical parts."

Fig. 3 Shimadzu vacuum sintering furnaces at AT&M

Atomised powder production

As well as producing the majority of its own feedstock, AT&M has for many years manufactured both water and gas atomised metal powders. "In 2003 we invested more than $5 million in powder atomisation capability. The

Fig. 4 100Cr6 fleece clipper part, 100g

Fig. 5 17-4PH medical device jaw, 0.03g

Fig. 6 17-4PH fibre optic connector, 1.5g

Fig. 7 17-4PH lock part, 17.2g

Fig. 8 440C pliers, 48g

Fig. 9 Mobile phone part 17-4PH, 2g

Fig. 10 4605 special reamer, 13.12g

Fig. 11 One of several powder atomisation units at AT&M

production technologies that we have today includes high pressure (1000bar) water atomisation, vacuum gas atomisation and gas-water combined atomisation for low oxygen, high purity, spherical shape and ultrafine powders. Powder production capacity is 750 tons per year for water atomised powder and 250 tons of gas atomised powder per year. MIM grade powder makes up 5% of total output", stated Mr Jin Chenghai (Fig. 11).

Typical powders manufactured by AT&M include Fe-Ni, Fe-Si and Fe-Si-Al soft magnetic alloy powders, pure metal and pre-alloyed matrix powders for metal bonded diamond tools, catalyst powders for synthesising single crystal diamond, ultra-fine low alloy steel and stainless steel powders for MIM, high-speed steel and heat-resisting alloy powders and thermal spray powders. Export markets for AT&M's metal powders are Japan, and Europe. Fig. 12 shows micrographs of three hybrid atomised powders manufactured by AT&M.

Some powders needed for the company's MIM parts manufacturing facility are additionally purchased from established international suppliers.

Quality management

AT&M achieved ISO9001 status in 2000 and is currently undergoing certification to TS16949, which it hopes to receive in March 2011. The MIM plant's quality laboratory has a staff of six and is well resourced, with numerous testing machines for the analysis of raw materials and the dimensional accuracy and mechanical properties of MIM parts (Fig. 13).

Fig. 13 Testing equipment in AT&M's quality assurance laboratory

Awareness of MIM in China and outlook

There are now about 30 MIM companies with sales of more than $10million per year operating in China and the country's MIM industry is expected to develop rapidly, despite a limited awareness of the process.

"Customers in the mobile phone, IT and surgical device markets, all of which require high volume complex parts, have come to realise the importance of MIM. Customers in many other sectors, however, currently know little about the technology. In terms of important markets for MIM in China, the automotive industry is expected to be a strong growth area", concluded Mr. Jin Chenghai.

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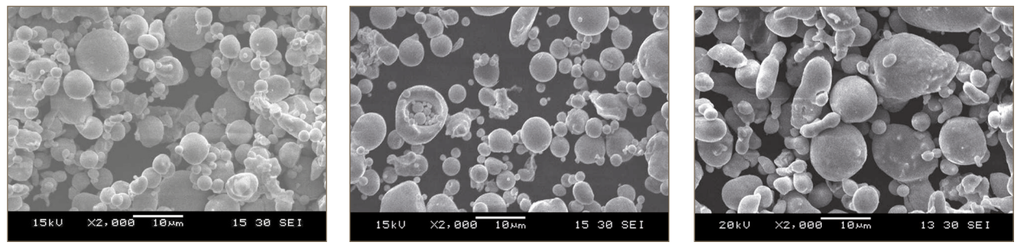


Fig. 12 SEM's of three hybrid atomised stainless steel powders produced by AT&M. Left: 17-4PH; centre: 316L; right 440C

PM2010 showcases the latest innovations in Powder Metallurgy and Powder Injection Moulding

Professor Alberto Molinari (University of Trento) and Alessandro Pasetti (Pometon SpA), Co-Chairmen of the PM2010 World Congress & Exhibition, welcomed 1300 participants from around the world to Florence in October. In addition to covering conventional powder metallurgy topics, the event also included a substantial number of technical sessions and seminars devoted to powder injection moulding (PIM). A significant number of exhibition stands also showcased PIM materials and production technology.

The PM2010 Powder Metallurgy World Congress, organised by the European Powder Metallurgy Association (EPMA) in the vibrant and historic city of Florence in Tuscany, Italy, attracted participants from nearly 50 countries around the world.

The high number of participants was a significant achievement given the challenging economic conditions the global PM industry experienced in 2008 and 2009. However, the recent sharp revival in demand for PM products plus the attraction of the latest innovations in PM through 500 oral and poster papers presented at PM2010, and a comprehensive 'market place' exhibition of 130 stands, including many devoted to materials and equipment supply for PIM, all combined to create a positive mood and helped to make PM2010 one of the most memorable PM events of recent years. Of course, Florence with its art treasures and World Heritage Site listed historic buildings was an additional irresistible attraction, which many PM2010 delegates and their spouses will no doubt also have enjoyed.

Eight of the 60 oral technical sessions at PM2010 were devoted to Powder Injection Moulding, with an additional sprinkling of PIM papers presented in other technical sessions.

Fig. 1 View of the PM2010 opening ceremony; the event attracted 1300 participants (Photo EPMA)

PIM was also well represented in the hundreds of posters set up just outside the meeting rooms. A series of Special Workshops on the concluding morning of PM2010 included one which reviewed MIM and CIM case studies from Asia, Europe and North America.

These PIM Case Studies are featured in a separate article in this issue of *PIM International*. Also included in this issue are summaries of a selection of the technical papers presented on PIM.

EuroMIM Open Meeting

As is now traditional at EPMA conferences, the main event is preceded by open meetings of some of the association's sectoral groups. The EPMA's EuroMIM group, co-chaired by Dr Bruno Vicenzi (MIMItalia) and Dr Frank Petzoldt (Fraunhofer IFAM), reviewed recent activities at its Open Meeting in Florence on Sunday afternoon, October 10, attended by some 60 participants. Dr Petzoldt said in welcoming

Fig. 2 Professor Alberto Molinari, University of Trento (left) and Alessandro Pasetti, Pometon SpA, (right) welcomed participants (Photos EPMA)

delegates that the EuroMIM group was now in its 10th year, and was supported by 32 member organisations of the EPMA.

Of these members, 18 are European MIM component producers, six are equipment and materials suppliers, and eight R&D related. Dr Petzoldt stated that the EuroMIM Group has, as its long term objective, to help widen market awareness of the potential and capabilities of MIM, and to promote MIM to end users in Europe and beyond. The group has also sought, albeit with little success so far, to enhance the process for gathering statistical and market information on MIM production in Europe. Some success has, however, been achieved with its annual Benchmarking of MIM companies reported on by Dr Vicenzi. The EuroMIM group has also sought funding for collaborative R&D projects from the European Union but has so far been unsuccessful with its most recent applications, said Dr Petzoldt. It will however continue to seek ideas for funded MIM projects.

Dr Petzoldt stated that a questionnaire had been circulated to members on the future activities of the EuroMIM group and how these activities should be prioritised and organised. About a third of EuroMIM group members responded with promotion of MIM technology to increase awareness among end-users coming out as the main priority. Roadshows, exhibitions and MIM technical courses were suggested activities. The respondents to the questionnaire also suggested increasing the property data lines for MIM materials in the on-line Global PM Properties Database (GPMPD) developed jointly by the three regional PM trade associations, EPMA, MPIF and JPMA, mainly for ferrous PM structural parts. Although more than 100 lines of property data for a limited range of MIM materials have been added to the on-line database, there is still a lack of data for MIM materials which are needed by the design engineer.

Dr Bruno Vicenzi reported on the annual benchmarking activities of the EuroMIM group in order to ascertain business trends in this sector. Dr Vicenzi stated that the benchmarking is now done on-line at the EPMA through 'blind' surveys covering both 'confidential' and 'open' questions. The blind survey makes it impossible to allow any responding company to be identified when the analysis is compiled at the EPMA. Only those companies participating in the survey are given the results, he said. The most recent 'confidential' analysis was increased from 15 to 16 questions in order to include the impact of the economic crisis which started in the second half of 2008 and went on through 2009. The 'confidential' survey included questions such as: number of employees directly used for MIM, MIM capacity utilised, number of moulding machines and use of robotic handling, MIM sales range, last six month sales and reason for any increase (decrease), expected 12 month forecast, which debinding strategy used, use of continuous sintering furnaces, in-house heat treatment facilities.

Fig. 3 Yoshiyasu Iino, President of the JPMA, presented an overview of PM activities in Asia (Photo EPMA)

Fig. 4 Michael Lutheran, President of the MPIF, reviewed the status of PM in North America (Photo EPMA)

Dr Vicenzi stated that the most recent 'open' results of the EuroMIM benchmarking for 2010 showed improving business confidence after the recent economic downturn. Around three-quarters of respondents said that business was currently fair (44%) to good (33%) and that a similar percentage indicated future improvements to good or very good with only 11% forecasting 'very poor' conditions. However, a fairly high percentage (30%) did not believe that the economic crisis is yet at an end.

Dr Vicenzi said that there was continuing concern among EuroMIM members at pressure on prices, growing competition from low cost MIM imports into Europe and also from competing manufacturing processes, and the long lead times in getting MIM parts to the market. Lack of knowledge of MIM technology among end-users and in particular among agents selling to end-users, needed to be reversed in order to maintain growth of MIM in Europe, he said. An interesting response to the impact of the economic downturn was that MIM companies significantly increased their efforts to look for new customers in different markets.

For collaborative research Dr Vicenzi reported that the most recent survey again showed a favouring of research into the relationship between defects and process parameters in MIM processing, and the modelling of the injection moulding process.

MIM industry optimistic about future

Keith Murray of Sandvik Osprey Ltd Powder Group located in Neath, South Wales, UK, reported on the status of the MIM component markets after a challenging 2009. The European MIM market was particularly badly affected due to its reliance on the automotive market, said Murray, and MIM part producers are reported to be seeking to reduce this reliance by broadening MIM applications in other areas such as medical and general engineering. He stated that Europe has a very strong MIM supply chain supporting technology development, and whilst MIM producers have seen a recent decrease in the dominance of the automotive sector, there remain significant opportunities for new MIM parts in vehicles. "The transition of turbocharger technology to petrol engines will open up new opportunities for high temperature MIM alloys, as will value added Ni-base superalloy MIM parts used in the aerospace sector", said Murray.

The North American MIM market was largely able to buck the downturn experienced in Europe and Asia, said Murray, thanks to buoyant demand from the firearms and medical sectors, and relatively low exposure to the automotive market at 9% compared to 43% in Europe and 16% in Asia (Fig. 8). Whilst it is the automotive sector which dominates in Europe, it is the IT sector

Fig. 5 Dr Stefano Maggi from Fiat Group spoke in the Plenary Session on future challenges for automotive materials (Photo EPMA)

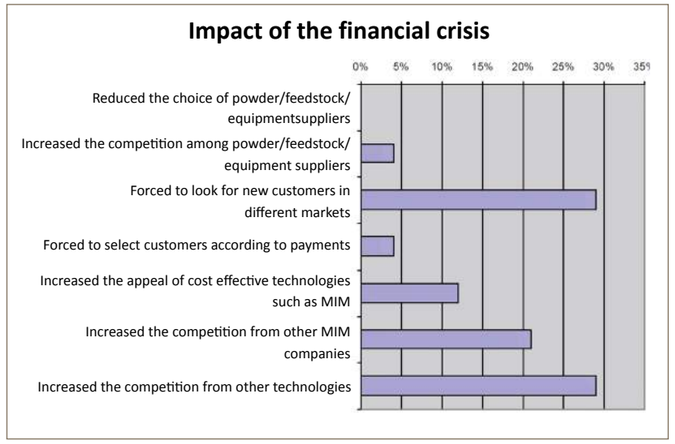


Fig. 6. A EuroMIM survey gave an insight into the effect of the financial crisis on the powder injection moulding industry (Courtesy EPMA)

Fig. 7. Benchmarking in the EuroMIM group showed that business confidence has returned (Courtesy EPMA)

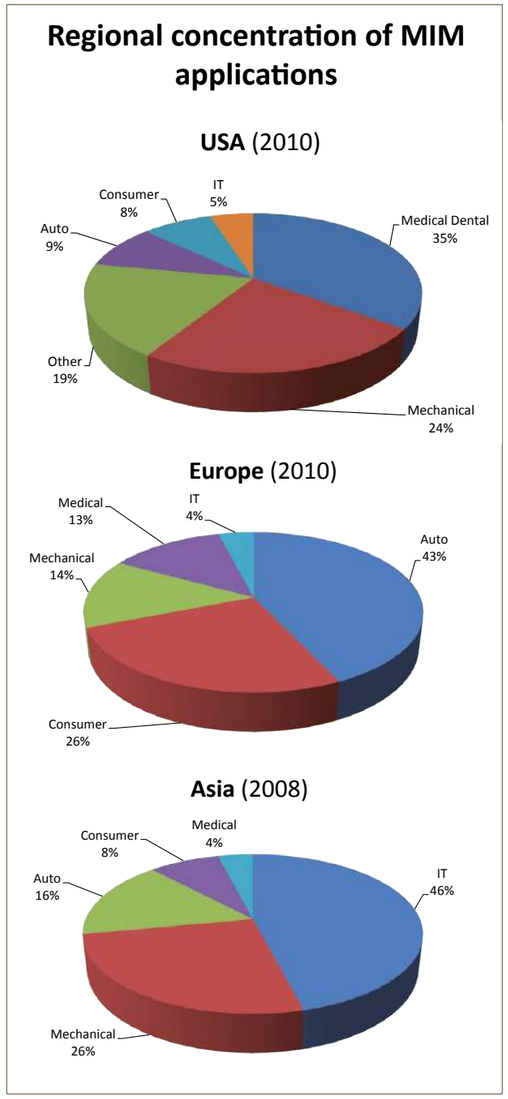


Fig. 8 Updated market segments for global MIM applications in different regions, as presented by Keith Murray, Sandvik Osprey Ltd, at the EuroMIM Open Meeting, October 10, 2010

Region	2009		2014		CAGR % 2009 - 14
	US$, M	% Share	US$, M	% Share	
Asia	460.8	48	959	51	**15.8**
Europe	279.7	28	484	25	**11.6**
N. America	231	23	424	22	**12.9**
RoW	13.4	1	33	2	**19.8**
Total	**984.9**	**100**	**1900**	**100**	**14.0**

Table 1 Global sales forecast of MIM components by region. RoW includes S. America, Australia & non-NATO Europe (inc. Russia). Presented by Keith Murray, Sandvik Osprey Ltd, at EuroMIM Open Meeting, October 10, 2010

which dominates in Asia, and the medical/dental sector in North America. A survey conducted by MIMA showed that 77% of responding members expect further increases in sales in 2010.

Murray stated that there is general optimism that the global MIM industry will continue to enjoy double digit growth over the next 5 years. Europe is expected to have the lowest regional growth averaging 11.6% (CAGR) and reaching sales of $484 million by 2014 (Table 1). Asia is expected to more than double its MIM sales to $959 million in the same period with CAGR of 15.8% and a 51% global market share. There are expectations for growth for MIM in the Asian automotive market, especially in China and India. Japan currently remains the largest MIM producer in Asia but has seen dramatic falls in 2008 and 2009 from the high of Yen15.7 billion ($194 million) in 2007. The JPMA is forecasting a recovery to Yen12.41 billion ($153 million) in 2012. N. America is forecast to reach $424 million and achieve a CAGR of 12.9%. The rest of the world (S. America, Australia and E. Europe) is expected to gain a 2% share of the market, taking it to an estimated $33 million.

The unprecedented strength of the recovery in global MIM production in 2010 in combination with growing demand for fine metal and alloy powders for non-MIM applications, led to some short-term powder availability issues, stated Murray. Part of the problem was capacity among the fine powder producers to meet the high demand for atomised prealloyed powders, and the prolonged strike at Vale's Canadian operations in 2009 and 2010 resulted in significant shortages of nickel powder grades such as Ni 123 and 4SP which are used in MIM alloy mixes. Murray reported that there is now a greater availability of stainless steel scrap, the key raw material for atomised powders, and Sandvik Osprey Ltd is increasing atomisation capacity for fine prealloyed powders in the final quarter of 2010. Vale reached a settlement in July 2010 to mark the end of a strike that began on July 13, 2009.

ISO MIM Standard on the way

According to W. Brian James, Hoeganaes Corp., and ISO/TC119 SC 5 Powder Metallurgy member, the draft ISO Standard for 'Sintered Metal Injection Moulded Materials –Specifications' has reached the final ballot stage within ISO. Dr James told the EuroMIM open meeting that there was no specific timeframe yet for the ballot to be conducted by the voting member organisations of ISO, but that it could be accepted within 'months'. The draft standard has been given the number ISO 22068 and normative values are included for low alloy steels (as-sintered and heat treated), 316L and 430 stainless steels (as-sintered), 17-4PH (as-sintered and heat treated), soft magnetic iron-base materials, and as-sintered Ti6Al4V alloys. The draft MIM standard can be viewed on www.iso.org.

MIMA (MPIF), the ASTM in North America and the JPMA, Japan, have already issued their own comprehensive Standard Specifications relating to MIM materials.

The PM2010 Exhibition

The PM2010 World Congress featured one of the largest PM exhibitions seen in Europe for many years, with 130 stands covering companies from all parts of the PM supply chain.

Initial feedback from exhibitors suggests that parts producers are once again investing in production equipment, following a difficult period for the industry.

PIM related exhibits were more prominent than ever, with a large number of European and international companies promoting powders, feedstock, debinding and sintering solutions and injection moulding machines. *(Photos EPMA / Inovar)*

PM2010: Case studies highlight global successes of Metal and Ceramic Injection Moulding

A Special Interest Seminar on the final morning of the PM2010 World Congress held in Florence brought together a number of industry leaders from around the world who presented case studies on successful, and in some cases not so successful, applications of metal and ceramic injection moulding technology in recent years. *PIM International* reports on some of the highlights of these presentations.

North America

Non-Medical applications

Matt Bulger of NetShape Technologies Inc and President of the Metal Injection Moulding Association (MIMA), covered a number of non-medical case studies on behalf of North American MIM producers.

He began by outlining some of the challenges MIM producers have to overcome vis-à-vis competing manufacturing processes such as investment casting, machining, fine blanking, etc. For a start, Bulger stated that MIM materials are typically more expensive, the process often has more processing steps and MIM equipment cost is high, especially sintering furnaces which involve long cycles and low output. "And the 15-20% shrinkage rate in MIM is a process variable that concerns customers", said Bulger. "Size is also an issue", he continued. "Whilst MIM can achieve better and finer detail (0.25 mm) than investment casting which struggles with 1 mm features, the bigger the piece then the better investment casting performs in both quality and price. Thus MIM usually wins for parts less than 100 g with <40 mm part envelope, and investment casting wins on parts larger than that."

Bulger said that one of the greatest motivations for some customers to use MIM is to see their competitors using the technology. "Fear of being left behind by your competition is highly motivating", he said. Examples of this came in the early 1980s when Remington and Millett Sights began producing MIM parts for firearms. By the early 1990s nearly all North American firearm manufacturers were using MIM parts. A similar story was given for MIM in orthodontics which made its breakthrough in the 1980s and is now routinely used for many orthodontic parts, and more recently MIM parts for medical and hand tool applications. Interestingly, US MIM producers have not focused their efforts to any great extent on the huge automotive components market, which currently makes up only a few percent of MIM parts sales in North America. Bulger put this down to the substantial investment that is required for continuous mass production of relatively low cost auto parts in a MIM industry focused primarily on the batch production of high added value materials and components.

He acknowledged nevertheless that there are many sizeable companies purchasing millions of dollars of metal components which would benefit from MIM technology. "The problem we have is that most of these companies don't even know MIM exists, and we struggle to find them", stated Bulger.

Among the case studies presented by Bulger was a trial MIM part developed by Megamet Solid Metals which has a complex internal geometry (Fig. 1). "This", he said, "was achieved by using an acetal core inserted in the mould around which the feedstock is injected. The core then dissolves during catalytic debinding. The resulting cavity could not be achieved using slides or lifters in conventional injection moulding", Bulger concluded.

Fig. 1 A MIM part by Megamet which has a complex internal geometry, achieved by using an acetal core (see inset image)

Fig. 2 A thin-wall MIM part produced from fine ~10 µm NiMoFe powder for use in a hearing aid receiver can. From presentation by M. Bulger at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

A MIM part produced by FloMet for the electronics sector showed how thin wall NiMoFe parts could successfully be made by changes to feedstock normally used in MIM. This involved using a lower viscosity binder and the use of 'high flow' fine powders (~10 µm instead of ~20 µm) in an optimised powder/binder ratio. The thin-wall MIM part is used in a hearing aid receiver can (Fig. 2).

MIM can also be a low cost route to producing prototype MIM parts for evaluation, stated Bulger. A lock pawl prototype component was produced by NetShape Technologies by inserting a pocket into an existing mould to produce the required shape in low volume and at low cost. Netshape Technologies also worked on a micro-MIM contact part weighing just 0.007g used in a medical pacemaker (Fig. 3). This part was to be made from MIM Alloy 42, stated Bulger. The base of the contact needs to be soldered to the circuit board and the posts must be strong enough not to deflect when wire is welded to them. However, despite cost and performance advantages of the MIM contact, the customer decided to stay with the existing fabrication process.

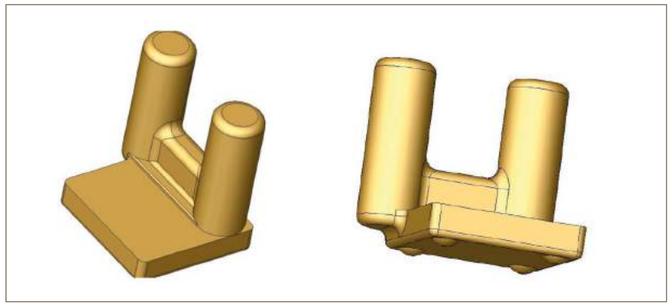


Fig. 3 MicroMIM contact part developed by NetShape Technologies weighing just 0.007g for use in a medical pacemaker. From presentation by M. Bulger at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

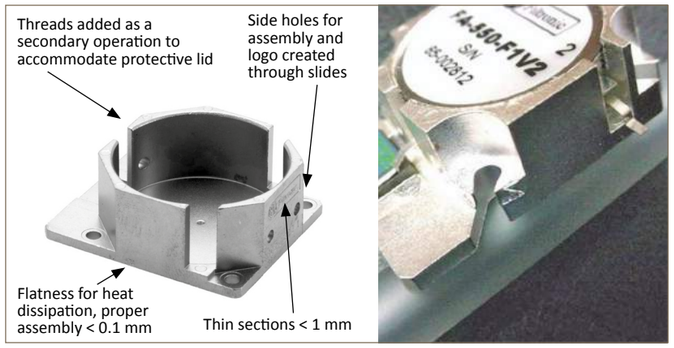


Fig. 4 MIM housing manufactured by NetShape Technologies and used in the telecommunications sector. From presentation by M. Bulger at PM2010 World PM Congress PIM Special Interest Seminars (Courtesy EPMA)

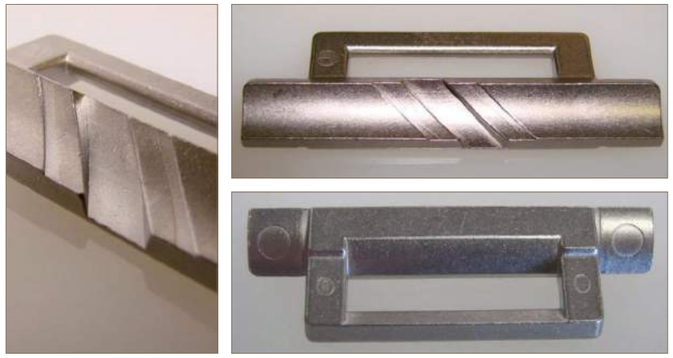


Fig. 5 Low alloy steel lock bolt manufactured by Kinetics Climax and used in a multi-joint gliding window lock system. From presentation by M. Bulger at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Bulger pointed to a successful MIM housing used in the telecommunications sector produced by his company. The housing (Fig. 4) must have good magnetic properties for shielding, good heat dissipation, and easy assembly. The 15 g housing is made from MIM 2700 Alloy and has thin sections of < 1mm. It is produced at a rate of 50,000 per month in a 4-cavity mould.

Further case studies given by Bulger included a low alloy steel lock bolt produced by Kinetics Climax for use in a multi-joint gliding window lock system (Fig. 5), and three MPIF award winning MIM parts in 2009. These were a stainless steel air nozzle produced by FloMet as two MIM parts co-sintered and laser welded, and two firearm parts produced by Parmatech and Megamet Solid Metal.

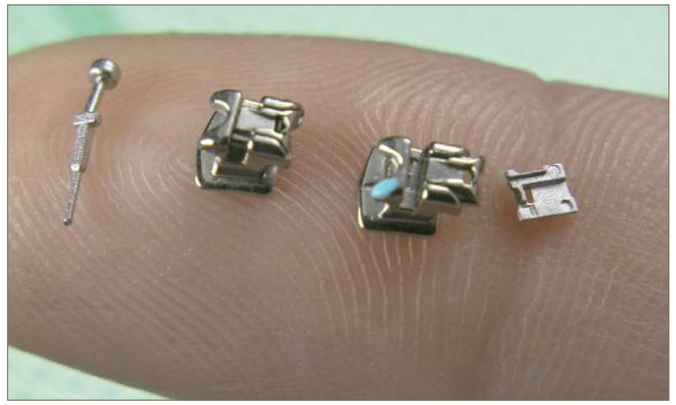


Fig. 6 Orthodontic system bracket, slide and hook produced by FloMet LLC and winner of the 2007 MPIF Grand Prize. From presentation by A. Bose at PM2010 World PM Congress PIM Special Interest Special Interest Seminar (Courtesy EPMA)

Medical Applications

Dr Animesh Bose of Materials Processing Inc. reviewed materials trends and applications for MIM in the medical sector, and gave a number of examples of where PIM has been successfully used to produce components with attractive combinations of cost savings, properties and shape complexity. Dr Bose stated that medical devices can be divided into three classes:

- Class I
  Unpowered devices that do not penetrate the body, diagnostic instruments, and surgically invasive devices for transient use.
- Class II
  Surgically invasive devices for short term use, radiotherapy devices, and long term use or implantable devices
- Class III
  Contacts central nervous system or heart, or is absorbed by the body.

Examples in Class I would include medical 'cutting' instruments such as knives, chisels, forceps, dissectors, scalpels, scissors, etc. 'Non-cutting' instruments include clamps, specula, cannulae, punches and skin hooks, clips, dilators, etc. Most of the above would be made from various grades of stainless steel, depending on property requirements, with Ti and Ti alloys and CoCr alloys also being used.

Dr Bose reported that the annual global market for biomedical devices is estimated at $28 billion of which only a tiny percentage, at around $112 million, are made by PIM. He said that one of the most significant success stories for PIM in the medical sector is in the production of orthodontic brackets. "PIM has successfully displaced investment casting and machining through its ability to produce small size (0.1 to 0.2 g) brackets with complex features including waffle patterns, blind pockets, square slots, and slides", said Dr Bose. 17-4PH stainless steel, Co-28Cr-6Mo and translucent alumina are the main powders used for the PIM orthodontic brackets. One example are three parts, a bracket, slide and removable drop hook, produced by FloMet LLC for use in the Damon 3MX self-ligation orthodontic tooth positioning system (Fig. 6).

Dr Bose also reported that some North American MIM companies such as Accellent Inc are looking to enter the market for medical implants including hips, knees, etc. There are over 1 million operations carried out annually worldwide involving metallic implants and this number is expected to rise as people live to an older age. Accellent is said to be developing MIM technology for this sector using both titanium, Ti alloy, and cobalt-chromium alloys. The chemistry and mechanical properties of MIM Ti CP materials are said to be close to ASTM F67 Grade 4 and Grade 2, whereas MIM Ti6Al4V alloy is also said to be close to ASTM Ti Grade 5 (Table 1). Accellent is participating in the development of ASTM MIM Standards for the Implantable Grades of Titanium and CoCrAlloys. Dr Bose stated that Ti6Al4V (Grade 5) is currently at the ballot stage and, pending acceptance, was expected to be published in November 2010. The same applies to MIM Co-28Cr-6Mo (F75).

Dr Bose gave examples of MIM parts used in the medical sector all of which had won MPIF awards. The first was a needle driver and Distal Clevis made by Smith Metal Products from 17-4 PH stainless and used in a minimally invasive endoscopic daVinci robotic surgical system. The second were laparoscopic surgical scissors with cautering capability also made from 17-4 PH by FloMet LLC consisting of a helical gear and two separate scissor blades. Thirdly, a 17-4 PH dental manifold used in a hand-held fibre-optic swivel dental system that delivers air, water, and fibre-optic light simultaneously into a patient's mouth made by MIMflow Technologies LLC, and finally an articulation gear made by Parmatech Inc from 17-4 PH for use in minimal invasive surgery.

Ti6Al4V Spec / Condition	UTS (ksi)	YS (ksi)	Elongation (% in 1 in)	Density (g/cc)
ASTM F1472	135	125	10	-
Proposed ASTM MIM Ti6Al4V	130	120	8	4.31
As Sintered [1]	132.00	126 [2]	13.5	4.3
As Sintered plus HIP'd	142.5	139 [2]	13.00	4.41

[1] Minimum observed values [2] YS estimated due to short tensile gagelength

Table 1 Comparison of mechanical properties of MIM Ti6Al4V proposed for a new ASTM Standard. From presentation by A. Bose at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Fig. 7 High precision MIM watch part made by Epson Atmix having large variations in section thicknesses. From presentation by T. Takahashi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Asia

High precision MIM watch part

Epson Atmix Corp. of Japan is both a MIM parts producer and powder producer. Dr Tomo Takahashi said that his company produces around 60 million pieces/year of MIM parts and around 3,000 tonnes of metal and alloy powders mainly for magnetic and MIM applications. His case study involved a high precision mechanical part used in a quartz watch (Fig. 7) made from a micro-grain 316L stainless steel powder. Dr Takahashi described micro-grain powder as having a particle size less than 10 µm, and small grain size powder having a particle size of >15 µm. The fine micro grade 316L powder is produced using Epson Atmix's advanced water atomisation process which yields both fine and spherical shaped powder particles, he said (Fig. 8). He further stated that these fine water atomised powders will become the mainstream powders used by his company for MIM parts manufacture in the future.

Despite the big variations in section thicknesses of the MIM watch part, Epson Atmix is able to achieve the high dimensional precision required, said Dr Takahashi. This is especially the case for the position and diameter of the hole and the sharp corner edges of the part as they are both critical for the assembly with other mechanical parts in the watch. Dr Takahashi reported that Epson Atmix selected Grade 316L PF-5F stainless steel powder to achieve the level of dimensional tolerances and smooth surface (0.6 µ Ra average) required on the MIM part. This powder has a particle size distribution of D_{10} = 2 µm, D_{50} = 4.2µm and D_{90} = 7.5 µm, a high specific surface area, and tap density of 3.89 g/cm^3. The injection moulded parts are sintered at 1305°C to reach a density of 7.9 g/cm^3. The level of precision achieved in sintering meant that no post-sintering operations are necessary.

'good elongation values allow the top of the endo tips to be bent if required. The MIM parts are simply polished and TiN coated'

MIM/CIM Dental Applications

Dr Seong Jin Park of Pohang University of Science and Technology in Korea reported on the development, in conjunction with CetaTech Inc. also in Korea, of three new dental applications for powder injection moulding – one for MIM and two for CIM. The first case study was for ultrasonic endo tips used for endodontic treatment, which Dr Park said were conventionally produced by machining, drilling, tapping, and diamond coating. These tips have short life due to poor diamond retention in the coating, and also health problems associated with nickel in the electrodeposited coating. The new MIM tips are produced from ultrafine water atomised 17-4 PH stainless steel powder (D_{50} = 8.3 µm) which is mixed with a binder to achieve 59% solid loading. After debinding and sintering the 17-4 PH alloy parts are heat treated to achieve high strength and hardness combined with good ductility. Dr Park gave examples of two MIM endo tips having 50 µm and 100 µm projections on the top section of the tip to eliminate the need for diamond coating (Fig. 9). The good elongation values allow the top of the endo tips to be bent if required. The MIM parts are simply polished and TiN coated and are then

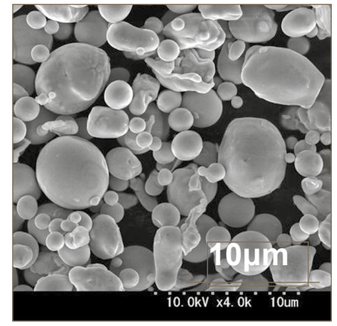


Fig. 8 Advanced water atomised powder (PF-5F) from Epson Atmix. From presentation by T. Takahashi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

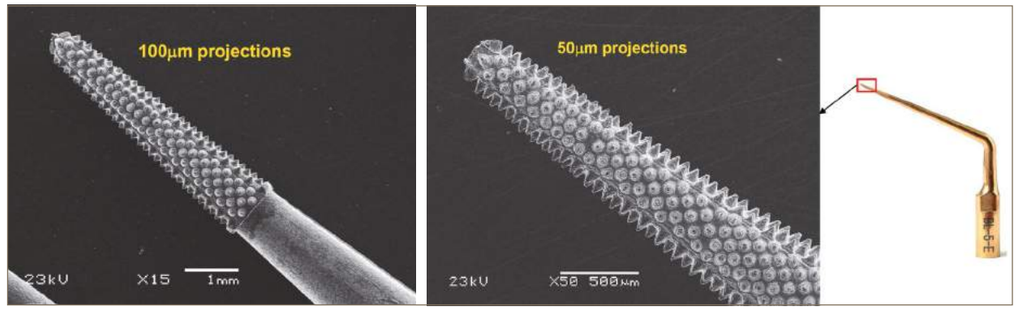


Fig. 9 MIM endo tips having 50 µm and 100 µm projections on the top section of the tip. From presentation by S. J. Park at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

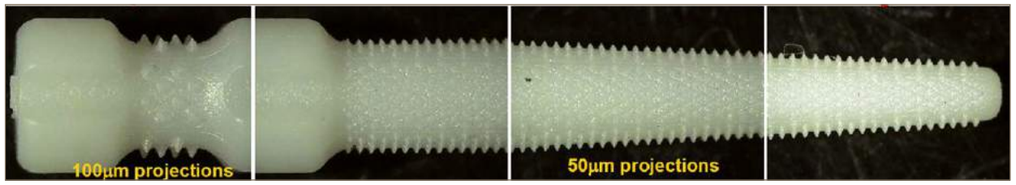


Fig. 10 CIM zirconia dental post with micro patterns to improve retention properties. From presentation by S. J. Park at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

ready for shipment to dentists around the world, he said.

The second case study given by Dr Park was a ceramic injection moulded zirconia dental post with improved retention properties (Fig. 10). The post was said to compete with metal and fibre-reinforced glass/plastic posts, but has the advantage in terms of biocompatibility, strength, corrosion, opacity, and aesthetics. Retention of the ceramic post has been improved, compared with earlier ceramic posts, by incorporating 50 µm and 100 µm micro patterns on the surface of the posts, which are said to measure 11.6 mm long by 1.2 mm diameter. The posts are produced by moulding zirconia feedstock with a 47% solid loading, debinding and sintering (in air at 1450°C) and HIPing to remove any residual porosity. A density of 99.9% is said to be achieved after HIPing.

The third case study was the development of a ceramic injection moulded dental burr tool tip used for cutting/grinding teeth or bone. Traditionally tungsten carbide or diamond coated tools have been used for dental burrs. Dr Park stated that the new CIM burr is made from a mixture of zirconia containing 20% alumina and 4.1% yttria which is sintered in air at 1550°C after solvent and thermal debinding. The parts are HIPed after sintering to reach a density of 5.49 g/cm^3 or 99.8% of theoretical density. As with the endo tips and dental posts, micro patters of just 50 µm have been incorporated to improve performance of the burr. Both the ceramic dental burr and posts are currently being field tested.

Fig. 11 Micro-MIM locking element part manufactured by Parmaco and used in an electronic door access system. From presentation by B. Vicenzi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Europe

Dr Bruno Vicenzi of MIMItalia and co-chairman of the EPMA's EuroMIM Sectoral Group, presented four case studies representing state-of-the-art in MIM in Europe today.

The first was a micro-MIM locking element part produced by Parmaco AG (Switzerland) for use in an electronic door access system developed by Simons Voss Technologies in Germany (Fig. 11). The locking element weighs just 0.23 g and is made from non-magnetic 316L stainless steel powder. Parmaco produces the locking parts in a 2-cavity split mould, and the parts are solvent debound and then vacuum sintering with H_2 partial pressure at 1360°C to reach 7.6 g/cm^3 (96%) density. After sintering the parts are treated with a unique 'colsterizing' process which allow the parts to reach a surface hardness of HV_5 1000-1050 to a depth of 0.03mm.The burr free MIM parts have a surface roughness better than Rz16, and in some areas better than Rz10. MIM provided the most competitive manufacturing route with cost savings of 70%.

The second case study was for a high-strength MIM seat belt component for the aerospace sector produced by MimEcrisa, Spain (Fig. 12). The 90 g complex shape is produced from an Fe7Ni0.6C steel alloy which, after heat treatment, provides a tensile strength greater than 1200 MPa. Dr Vicenzi stated that the 80mm diameter part was outside the traditional weight and size range for MIM parts. It was important to avoid closure of the open window/slides in the MIM part by deformation during processing.

Alliance Powder Inject Moulding (France) provided the third case study – a complex shaped backing case for a luxury watch (Fig. 13). Aimed at mimicking an aerospace turbine engine, the 36 mm diameter 316L stainless steel watch case is produced by assembling the individual 24 green injection moulded blades onto a green MIM support and then sinter-joining all the pieces during sintering (Fig. 14). Tolerances of the individual blades must be kept below ±0.01 mm for accurate assembly, and the joining quality after sintering must be sufficient to allow subsequent lathe machining and polishing.

Fig. 12 MIM low alloy steel seat belt component manufactured by MimEcrisa for the aerospace sector. From presentation by B. Vicenzi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

The final case study came from Dr Vicenzi's own company and covered the production of diamond injection moulding (DIM) to produce monolithic beads used in stone cutting (Fig. 15), and other types of diamond tools made by DIM. MIMitalia received an award from the EPMA for this technology in 2007. Dr Vicenzi stated that the company's DIM tools are produced by mixing diamond powder/grit (0.3-0.8mm particle size), metal powder binder and the plastic moulding binder. The technology for producing the DIM feedstock was developed in-house. In the case of the monolithic diamond tool beads production is carried out in a 4-cavity mould followed by solvent debinding and sintering under H_2 partial pressure at 900-1000°C to >95% density. Post-sinter HIPing is said to be unnecessary for this application. The as-sintered beads are assembled on wires used to form a multi-wire cutting frame to cut slices or slabs of marble or stone from large blocks.

Fig. 13 Complex shaped backing case manufactured by Alliance for a luxury watch mimics an aerospace turbine engine. From presentation by B. Vicenzi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Fig. 14 Production process for the aerospace turbine engine themed watch case. From presentation by B. Vicenzi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Fig. 15 Diamond injection moulded monolithic beads manufactured by MIMITALIA and used in stone cutting. From presentation by B. Vicenzi at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

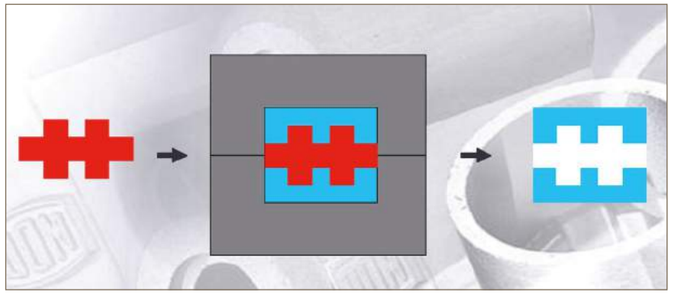


Fig. 16 Lost core technique increases the grade of complexity in MIM parts. From presentation by I. Langer & R. W-E. Stein at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Fig. 17 MIM levers manufactured by Schunk Sintermetalltechnik for adjusting vanes in aerospace turbine engines. From presentation by I. Langer & R. W-E. Stein at PM2010 World PM Congress PIM Special Interest Seminar (Courtesy EPMA)

Lifetime of the DIM beads compared with conventional diamond tools has been improved by 80% and the DIM beads have increased cutting speeds by 33 to 50%. "Around 1 million different diamond tools have been made by DIM since 2006", said Dr Vicenzi.

Broadening the appeal of MIM

The final presentation in the Special Interest Seminar by Dr Ingolf Langer of Schunk Sintermetalltechnik GmbH, Germany, focused on MIM materials and design in relation to competing technologies. He stated that in the past most MIM applications were pure substitutions of conventional parts with short term cost benefits for the end-user. Dr Langer stated that "the future success of MIM technology now depends on the ability to influence design engineers on other benefits of MIM, not just cost, in the early stages of design of new component projects". This was especially the case in the automotive sector which remains the market for MIM parts in Europe.

'the future success of MIM technology now depends on the ability to influence design engineers on other benefits of MIM, not just cost'

MIM offers an almost unlimited range of metals and alloys, said Dr Langer. The development of new fine atomised alloy powders and also recently introduced fine alloy powders produced by chemical reduction, to allow the production of complex shapes with thin structures. MIM parts offer homogeneous microstructures to near full density with stable dimensions during sintering", said Dr Langer. Additionally, MIM offers the design engineer intricate parts, or assembled parts, which cannot be produced by any other process. These include parts produced from a combination of metals and alloys using 2-Component injection moulding; MIM parts with complex hollow interior shapes produce by the 'lost core' process (Fig. 16); gas injection during moulding to increase part complexity; assembled structures where two or more MIM parts, or MIM + pressed and sintered parts, are joined together by diffusion bonding during sintering. Dr Langer concluded by showing a selection of MIM parts such as a drive wheel for a car bonnet locking mechanism, a soft magnetic sensor housing, a rocker arm lever for a 4-stroke engine, a system comprising three MIM parts used in a handbrake, a lever for a variable valve train, turbocharger parts, and an Fe-Ni-Cr-Mo-V-Mn-Si-C alloy designated MECO 26 used for a lever for adjusting vanes in aerospace turbine engines (Fig. 17).

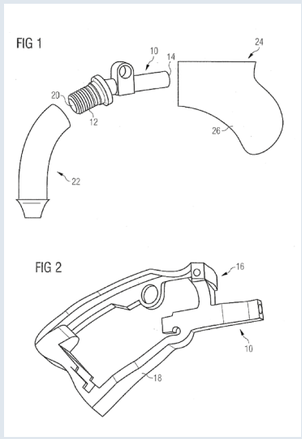
Global PIM Patents

The following abstracts of PIM-related patents have been derived from the European Patent Organisation databases of patents from throughout the world. Full information on individual patents (in the language of the country) is available through the *PIM International* editorial office

US2008273732 (A1)
CONNECTING ELEMENT FOR A CARRYING HOOK OF A HEARING DEVICE

Publication date: 2008-11-06
Inventor(s): W. Fickweiler et al, Siemens Corporation, USA

In order to connect a hearing device to a carrying hook, a connecting element is used, which has to satisfy high demands with regards to its precision and stability. To ensure this, the connecting element is designed as a powder injection moulded part, in particular as a ceramic injection moulded part or metal part, which is manufactured in a ceramic injection moulding process or a metal injection moulding process.



JP2008297603 (A)
SPLIT TYPE METAL POWDER INJECTION MOULDED PART AND PRODUCTION METHOD

Publication date: 2008-12-11
Inventor(s): Ozawa Tomomi; et al, Teibow Co Ltd, Japan

This patent shows a method of inexpensively and easily obtaining split bodies from a compact formed by a metal powder injection moulding process, even when a material with high toughness such as titanium alloy is used. The production method for a split type metal powder injection moulded part includes: step 1 where separate green compacts are formed; step 2 where the separate green compacts are made to adhere each other to form an integrated green compact; step 3 where the integrated green compact is debound and sintered to form an integrated silver compact having a pseudo joint at the adhered part; and step 4 where the pseudo joint in the silver compact is fractured and split to form the split bodies.

CN101293280 (A)
METHOD FOR PRODUCING MOLYBDENUM ALLOY GAS VANE WITH POWDER INJECTION FORMING

Publication date: 2008-10-29
Inventor(s): Jinglian Fan et al, Central South University, China

A powder injection moulding method is adopted to produce a molybdenum alloy gas vane with a complicated shape. Mechanical alloying is adopted for high performance ball grinding of Mo powder and one or multiple powders of Ti, Zr, Hf, Re, TiC and ZrC with the mass percent of 0.05-1.5%. The molybdenum pre-alloy powder and an organic binder are mixed and the feed is injected through an injection machine to form a gas vane injection billet. After the gas vane injection billet is debound by solvent, carbon control and presintering are carried out in a thermal decreasing furnace. Finally, high sintering is carried out on the samples.

EP1972419 (A1)
METHOD FOR MANUFACTURING PARTS BY PIM OR MICROPIM

Publication date: 2008-09-24
Inventor(s): L. Federzoni et al, Commissariat Energie Atomique, France

The process for making alumina pieces by injection moulding, comprises preparing a master mixture having a powder mixed with a polymeric binder (3-50%) and solubilized in an aqueous water solvent, injecting the master mixture in a mould under pressure, cooling the mould, removing the mixture from the mould and then washing, and sintering the mixture. The mixture is maintained at a temperature greater than an evaporation temperature of solvent during pressing, and has nanopowder, whose particle size is lower than 100 nm.

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PROCESS AND ASSEMBLY TO CRUSH METAL AND PLASTIC INTO POWDER FORM FOR METAL INJECTION MOULDING AND SINTER CASTING

Publication date: 2008-11-27
Inventor(s): R. Schoemann, Dorst Technologies GmbH & Co KG, Germany

In a process to prepare metal powder for metal injection moulding, the mixture ingredients consist of a metal and a thermoplastic component that are fed to a crusher that reduces the grains to a size in which they can be applied as a liquid spray. Also claimed is a commensurate grain crushing assembly that also functions as a spray assembly that creates droplets during the spray process and then dries the resulting casting.

Metal injection moulding of Ti-64 components using a water soluble binder

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Ti-6Al-4V powders with powder size of sub 45µm were mixed with a binder with a water soluble component and subjected to metal injection moulding studies. The binder system consisted of a major fraction of water soluble Polyethylene Glycol (PEG), a minor fraction of polymethylmethacrylate (PMMA) and some stearic acid used as a surfactant. A critical powder loading of 69 vol % was obtained which exhibited a pseudo-plastic flow. The injection moulding, debinding and sintering processes were studied. A low-cost, two stage and rapid debinding process which involved solvent debinding in distilled water at 55°C for 6 hours and then removing the remaining PMMA via thermal pyrolysis by heating in flowing argon was selected. Sintering was also carried out in flowing argon. Carbon and oxygen contents achieved were within ISO 5832 standard specifications for titanium, as were the mechanical properties of as-sintered specimens.

Introduction

Titanium and titanium alloys exhibit a high specific strength and stiffness, outstanding corrosion resistance and biocompatibility. This combination of properties makes titanium and its alloys an excellent choice for applications in watch parts and sports goods [1], and also provides a great potential for biomedical and aerospace applications. However, the processing of titanium is limited by costly, multi-step processes of fabrication and associated geometry design constraints [2]. Metal injection moulding (MIM) is a technique that can provide minimisation of such problems.

MIM is a well-established, cost-effective method of fabricating small-to-moderate size metal components. In this process metallic powders are injected into a mould. Plasticity and fluidity of the powder is essential for this to take place and this is achieved by the use of binder material. All binder systems are based on two important major groups of ingredients, polymers and waxes with minor additions of lubricants, surfactants and coupling agents. After injection moulding the binders are then removed in a process known as debinding and the remaining "brown" part is then sintered at elevated temperatures to achieve a densified part.

In the metal injection moulding of titanium, there have been serious challenges in recent years. Namely, the oxygen and carbon levels in the sintered parts have been too high for structural use [3]. Much of the early work on developing a viable titanium MIM process was plagued by the unavailability of suitable powder, less than optimum binders and debinding processes for a material as reactive as titanium, and inadequate protection of the titanium during elevated temperature processing [4,5]. During debinding, the decomposition mechanisms and chemical composition of binders play a major role in levels of residual contamination. Therefore in order to reduce contamination of Ti with carbon and oxygen due to debinding, the requirement is to reduce the amount of decomposable substances in the binder.

There have been a number of studies which investigated the effect of the binder type on the MIM of titanium [6] [7] [8] [9]. A binder system which uses water soluble PEG was first reported by Cao *et al* in 1992 [10] where they developed a binder made up of a

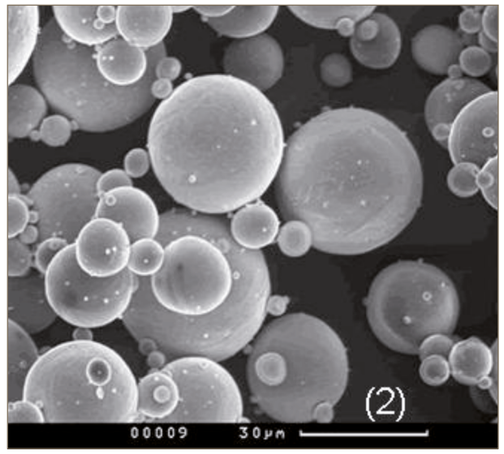

Fig. 1 Scanning electron micrograph showing the morphology of the Ti6Al4V

major fraction of polyethylene glycol (PEG) and a minor fraction of PMMA polymer. According to Cao *et al*, the binders with a water soluble component remain rigid during solvent debinding, giving excellent shape retention of the green part during debinding and the shrinkage from the mould dimension to the sintered part dimension is isotropic (equal in all directions). The difference in the amount of shrinkage along all directions within each part could be less than ± 1% for all sintered parts. Other uses of PEG as the primary water-soluble component have also been reported by Hens *et al*. [11].

The PEG based water soluble binder system has since been used widely with other metallic and ceramic powders [12], [13], [14], [15] . However, one report [16] discouraged the use of binder with a water soluble component in the MIM of Ti on the basis that such binders give increased oxygen content in the parts which in turn affect the mechanical properties.

In this study a binder consisting of polyethylene glycol (PEG), polymethylmethacrylate (PMMA) and stearic acid (SA) is investigated for its compatibility with Ti6Al4V and for its ability to reduce debinding time at a low cost. The debinding chemical reactions and the debinding mechanisms are discussed in detail.

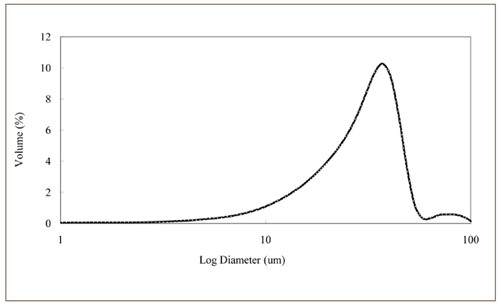

Fig. 2 Particle size distribution for Ti6Al4V

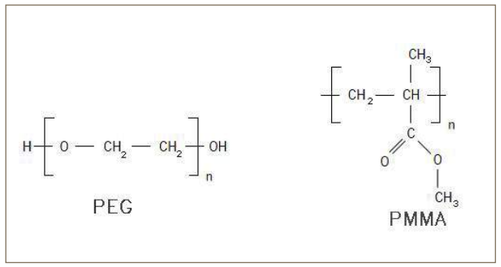

Fig. 3 Chemical Structures of PEG and PMMA

Experimental

The Ti6Al4V, powder used in this study was supplied by Advanced Powders and Coatings (Raymor Inc, Canada) and is produced by plasma atomisation. Table 1 shows the Ti6Al4V chemical properties that were obtained via XRF. Fig. 1 is a scanning electron micrograph (SEM) showing the morphology of the powder as spherical in shape. All the characterisations carried out via SEM were done on the Camscan Mk II (Cambridge Scanning, UK). The particle size distribution is shown in Fig. 2 as sub 45µm in size and this was obtained using a Coultier LS particle size analyser with sonication and diffloculant used to break up agglomerates.

The Ti6Al4V powder was mixed with a binder that consisted of a major fraction of water soluble polyethylene glycol with molecular weight of 1500 (PEG_{1500}) and a minor fraction of polymethyl-methacrylate with a molecular weight of 10^6 ($PMMA_{10^6}$) with stearic acid (SA) used as a surfactant.

The PEG was supplied by Sigma Aldrich and at the molecular weight of 1500 g/mol, the PEG is in a crystalline form. PEG, has in the crystalline state, a fairly open helical structure and this structure is responsible for the low melting temperature of 45-50ºC and its solubility in water [17]. The PMMA was supplied by Scott Bader Co. Ltd (Wellingborough, UK). The chemical structures of the PEG and the PMMA are shown in Fig. 3. The simplest degradation of PMMA occurs at very high molecular weights [18].

Handling of the materials was carried out in an inert argon atmosphere and the mixing was carried out in the centrifugal Speedmixer™ 800 FZ (Hauschild; supplied by Synergy Devices Ltd). The mixing speeds were increased every two minutes as follows: 800, 1200, 1400, 1400, 1600 rpm, leading to a total mixing time of 10 minutes. The weight ratios of the constituent binder materials were 87:11:2 of PEG, PMMA and SA respectively. A critical powder loading of 69 vol % was obtained via rheological studies carried out on a Rosand RH2000 capillary rheometer (Malvern Instruments, UK).

The mixed feedstock was granulated and then injection moulded in a 60 tonne Arburg 320 C (Arburg, Germany) injection moulding machine at 120°C. An injection pressure of 1500 bar, packing pressure of 1350 bar and injection speed of 30cm^3/sec were used. A MPIF Standard 35 mould was used to mould tensile bars and after injection moulding, the mouldings were visually inspected and each weighed for quality control.

Powder type	Mean size(µ)	Composition (%)							
		O	C	N	H	Fe	Al	V	Ti
Ti-6Al-4V	sub 45	0.148	0.04	<0.05	0.008	0.47	3.88	4.96	Bal.

Table 1 Ti6Al4V chemical properties

The green part mouldings were subjected to solvent extraction by immersing them in a heated water bath containing distilled water for 6 hours at 45°C, 55°C and 75°C. This stage of debinding was aimed at removing the PEG component of the binder. The MIM samples were then dried in air at 40°C for 12 hours.

The parts were then subjected to thermal debinding in order to remove the backbone PMMA component of the binder in a Centorr VI MIM-Vac M200 Series 3570 furnace (Nashau, USA). This was done by heating the parts in an argon atmosphere at a ramp rate of 2.5ºC/min to 350ºC, and holding for 1 hour after which they were heated up again at a heating rate of 2ºC/min to 440ºC, and again holding for 1 hour. The results of the study which was carried out en route to obtaining the optimum processing parameters of solvent and thermal debinding used here have been published elsewhere [19].

Sintering was carried out in the furnace during the same cycle as the thermal debinding. The sintering was carried out under the control of four sintering factors; sintering time, sintering atmosphere, heating rate and the sintering temperature. The conditions that were selected for the sintering of the Ti6Al4V parts were; sintering time of 3 hours, sintering in argon with a retort flow rate of 10 slpm, heating rate of 10°C/min and sintering temperature of 1300°C. The route used to arrive at these optimised sintering parameters was the Taguchi L9 experimental method and the details of this study have also been published elsewhere [20]. During thermal debinding and sintering, the partial pressure in the furnace was set at 300 Torr (~400 mbar).

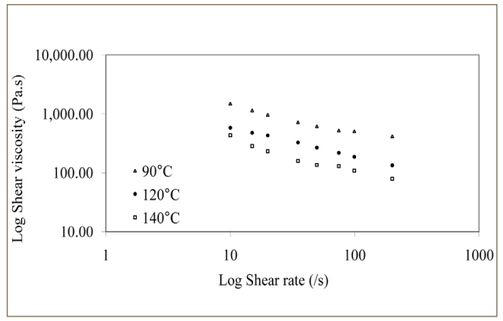

Fig. 4 Apparent viscosity vs apparent shear rate of 69 vol % Ti-64 feedstock at different temperatures

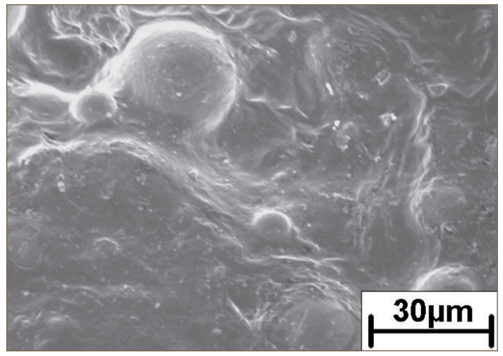

Fig. 5 Scanning electron micrograph of an as moulded component surface

Differential Scanning Calorimetry (DSC) studies, in order to observe phase transitions, were carried out on a Perkin Elmer DSC machine (Massachusetts, USA). Tests to determine changes in weight loss in relation to change in temperature and PMMA decomposition were carried out also using a Perkin Elmer TGA machine. Hg porosimetry to study pore distribution on leached samples was carried out on a Micromeritics Poresizer 9320. The chemical analysis of the sintered samples to determine the impurity levels of oxygen and carbon of MIM specimens was carried out using a conventional LECO melt extraction system by London & Scandinavian Metallurgical Laboratories (Rotherham, UK). Mechanical tests were carried out at room temperature according to ASTM E8 standards by NDT Ltd (Sheffield, UK).

Results

Rheology and Feedstock

Fig. 4 shows the evolution of the viscosity with temperature of the 69 vol % Ti6Al4V feedstock mixed with PEG, PMMA and SA at weight ratios of 87:11:2 respectively.

It can be seen from the shear viscosity vs shear rate plot that the flow is pseudo plastic with the viscosity decreasing with increasing shear rate, the viscosity being lower at the higher temperature of 140°C and increasing with lower temperature. It is desirable that the viscosity of the feedstock should decrease quickly with increasing shear rate during injection with no dilatants behaviour. This was the case with the Ti6Al4V feedstock and rheology indicates improved homogeneity of feedstock. This is confirmed in Fig. 5 which is a scanning electron micrograph of a moulding surface which shows the distribution of the Ti6Al4V powder within the PEG/PMMA/SA binder system. The binder, as can be seen, is evenly distributed throughout the sample body.

Solvent Debinding

Fig. 6 shows two scanning electron micrographs which illustrate the typical development of pores during the removal of PEG in heated distilled water at 55°C. After an hour of solvent debinding, it can be seen that there is still some residual PEG within the Ti/PMMA matrix. After four hours of solvent debinding, the SEM shows virtually no PEG with the remaining strands of binder consisting of PMMA.

Fig. 7 shows the Hg porosimetry result on a selected MIM sample after leaching of the PEG at 55°C. The Hg differential intrusion curve of the partially debound sample shows that the leached sample has a broad pore distribution and therefore confirms that the water molecules used for solvent debinding had diffused into the interior of the specimen. The average pore diameter is shown to range from 0.73µm to 2.3 µm. Therefore, all pores are smaller than the Ti6Al4V powder in which 97 % of powder is less than 45µm and 3 % over 45 µm. This is quite significant since small pores with a low coordination number are thermo-dynamically unstable and can easily be eliminated during the sintering process. The cumulative pore vs pore diameter plot in Fig. 7 shows that some large pores existed at low mercury pressures. These cavities were formed due to pullout of powders as the partially debound body was fractured. As the Hg pressure was increased during testing, it can be seen that a series of small pores were detected.

The complete removal of PEG was achieved at 55°C after 5 hours with no defects such as cracks. Fig. 8 shows the amount of PEG that was removed by water leaching from mouldings plotted against the leaching time at 55ºC. The rate of debinding is shown to have decreased with debinding time.

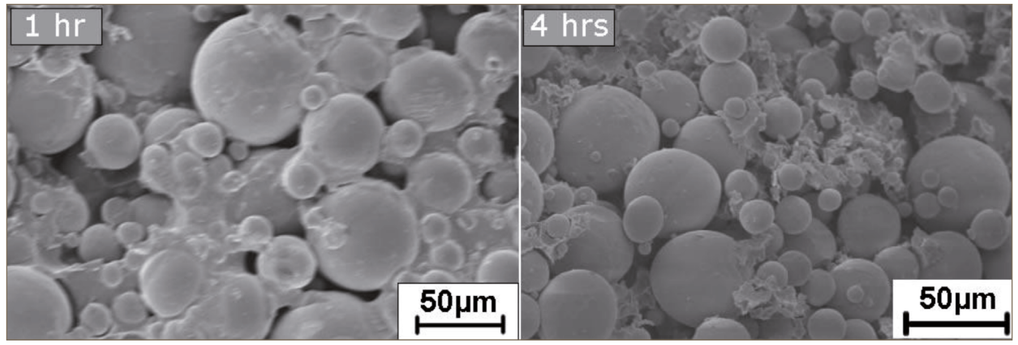

Fig. 6 Scanning electron micrographs showing the development of pores during the removal of PEG after 1 hour and after 4 hours at 55°C

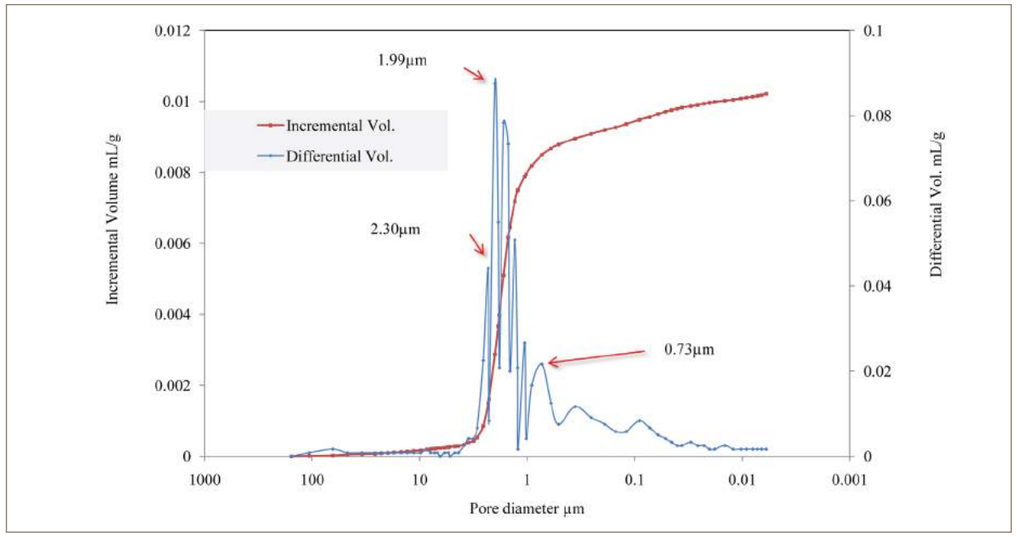

Fig. 7 Hg porosimetry result after leaching of MIM sample

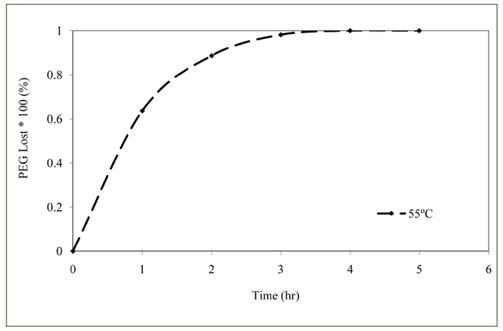

Fig. 8 Amount of PEG removed from the moulding versus the leaching time at 55°C

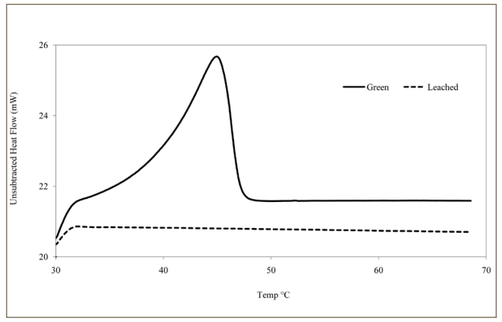

Fig. 9 DSC showing scans of an as moulded Ti6Al4V green specimen and that of a leached part after solvent debinding. The scans were carried out at 5°C/min from 30 to 70°C

Fig. 9 is a graph taken from a DSC and shows scans of a selected as moulded Ti6Al4V green specimen and that of a typical leached part after solvent debinding. The graph shows the absence of the PEG component in the leached samples as there is no peak corresponding to the heat flow as a result of PEG in the two traces. The DSC also shows the peak for the PEG at 44°C indicating the melting temperature of the green sample.

Thermal Debinding

Fig. 10 is a scanning electron micrograph which shows a typical brown part after the removal of the PMMA during thermal pyrolysis. The PMMA strands that were remaining behind as shown in Fig. 6 have disappeared, indicating successful debinding. The results can even be verified further by TGA analysis.

Fig. 11 is a TGA trace showing weight loss of Ti6Al4V/binder mix before and after thermal pyrolysis. It can be seen that there is no recorded weight loss from the brown part after thermal pyrolysis which confirms the complete removal of the PMMA binder component. Fig. 11 also shows the decomposition characteristics of the PMMA which degrades at 200-430°C. This information is useful in setting the thermal debinding process parameters. Binder unzipping under argon occurs over a shorter period than in air.

Sintering

The Ti6Al4V feedstock used here contains a relatively high volume of binder at 31%. Therefore, after the complete removal of the binder, the shrinkage after sintering is also relatively high at around 10%, taking into consideration the size of the powder which is sub 45µm. Fig. 12 is a photograph illustrating the linear

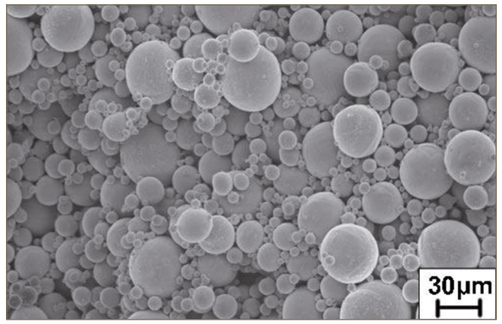

Fig. 10 Scanning electron micrograph which shows the brown part after the removal of the PMMA during thermal pyrolysis

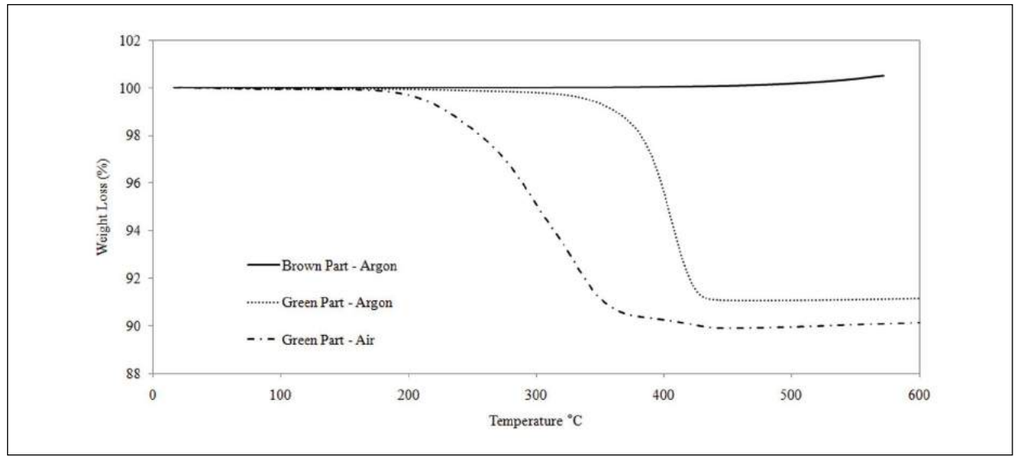

Fig. 11 Weight loss curves for PMMA at a heating rate of 5°C/min for Ti/binder mix in Ar and air before and after thermal pyrolysis

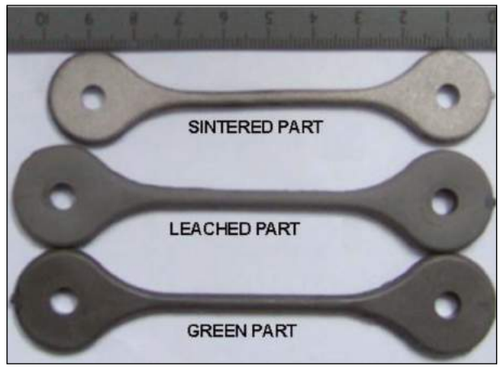

Fig. 12 Photograph illustrating the linear shrinkage undergone by a MIM sintered Ti6Al4V part

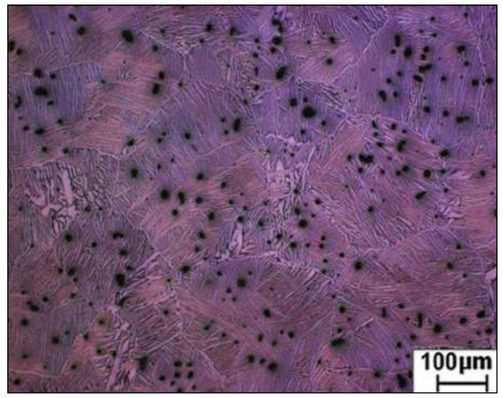

Fig. 13 The pore structures and microstructure of the Ti6Al4V MIM components

Sample	Tensile Strength (MPa)	Elongation (%)	Oxygen (%)
1	880	14	0.21
2	876	16	0.20
3	852	8.5	0.19
4	876	15.5	0.19
5	873	9.5	0.21
6	878	11.5	0.21

Table 2 Ti6Al4V injection moulded component mechanical and chemical results

shrinkage undergone by a sintered Ti6Al4V MIM tensile sample. The dimensional change of the MIM sample after injection moulding, solvent debinding and sintering is shown with good shape retention.

The final mechanical and chemical properties of Ti6Al4V injection moulded standard tensile bars are shown in Table 2. From Table 2, it can be seen that Ti6Al4V properties for oxygen impurity levels are that of specifications according to ISO 5832-3 standards [21]. The elongation for Ti6Al4V varies, showing 4

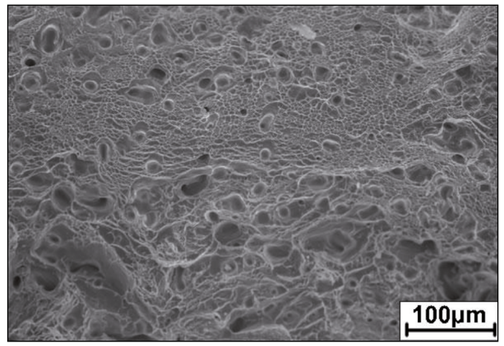

Fig. 14 Fracture surface of a Ti6Al4V MIM-tensile test sample after mechanical test showing a honeycomb structure which signifies a typical sign for a ductile break

samples meeting ISO requirements whereas the tensile strength is above ISO standards for all samples except one. The residual carbon level was 0.04% in one of the sintered Ti samples analysed. The maximum requirement for carbon is 0.08%.

The tensile strength and elongation of MIM products are

improved significantly as the porosity decreases. Shown in Fig. 13 is the pore structure and microstructure of a selected Ti6Al4V MIM component which indicates a low void ratio of round unconnected pores. Fig. 14 is an SEM of the typical fracture surface of a Ti6Al4V MIM-tensile test sample after mechanical test showing a honeycomb structure which signifies a typical sign for a ductile break.

Discussion

Solvent Debinding

The first debinding process, i.e. solvent debinding, does not involve polymer decomposition. The chemical analysis results shown in Table 2 confirm that leaching Ti6Al4V MIM samples in water does not increase oxygen levels detrimentally. Titanium metal contains a surface layer of titanium oxide that prevents chemical reactions. When the layer is damaged it is usually restored rapidly. Titanium only reacts with water after its protective titanium oxide surface layer is destroyed. It is therefore water insoluble.

Pertaining to kinetics, solvent debinding is a two-stage process consisting of dissolution and diffusion. Initially, solvent dissolves the polymer phase, thus forming a porous surface. The solvent then gets into the pores by capillary action. This is followed by diffusion of dissolved polymeric substances out of the green body. The process can be formulated using Fick's diffusion-based model [15][22]:

$$\ln\left(\frac{1}{F}\right) = \frac{D_e t \pi^2}{(2L)^2} + K \qquad (1)$$

where F is the fraction of the remaining soluble polymer, D_e is the inter-diffusion coefficient of polymer and solvent, t is time, 2L is the thickness of the specimen and K stands for the change in the mechanism controlling the debinding behaviour.

Equation 1 can be utilised to explain solvent debinding behaviour of PEG for the injection moulded Ti6Al4V powder. In order to demonstrate that solvent debinding is a two stage process, results have been included in Fig. 15 for the debinding temperatures of 40, 55 and 75°C, where ln(1/F) is plotted against leaching time. At 40°C, it is clear that the solvent debinding is a two-stage process. The dissolution of PEG is the rate limiting step in the beginning of debinding up to a leaching time of 3 hours. As the process proceeds, a longer diffusion distance through porous channels formed after initial debinding slows down the process and diffusion becomes the rate-determining step.

Thermal pyrolysis

The backbone PMMA is removed by decomposition. The PMMA retro-polymerises into monomers with the production of a gaseous product but leaves no residue. The range of monomer (MMA) yielded in the process is from 95 to 100% in vacuum or inert atmospheres [23]. The residual oxygen and carbon levels obtained in the sintered samples suggest that the titanium surfaces do not interact significantly with PMMA or its degradation products. During the process, several mass transport processes often occur simultaneously during binder removal but, in the case of the Ti/PMMA body, it is the pore structure of the partially debound body which influences the resistance to mass transfer. The pre-existing porosity allows for fast vapour transport, making the body relatively easy to debind.

Apart from the pore structure, the carefully controlled heating rate and the partial pressure in the furnace, on which the mean free path depends, are designed to control the capillary forces and limit defect formation. At the set partial pressure of 300 Torr or 400 mbar, the inert (argon) gas molecules flow at sufficient velocity

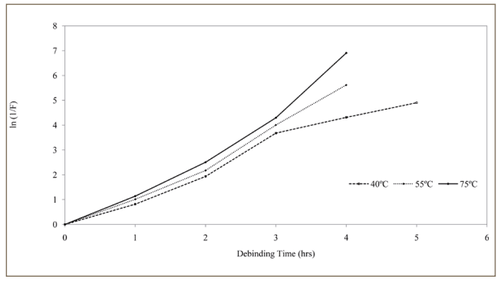

Fig. 15 ln(1/F) with leaching time at 40, 55 and 75°C. F is the remaining fraction of PEG

to flow smoothly and evenly over surface irregularities. This creates an even flow and no shadow effects, much as if the parts were submerged in a liquid [24]. At an atmospheric pressure of 760 Torr, the gas molecules would flow at high pressure and velocity, colliding with each other whereas at a molecular flow of 1 Torr or less, the gas molecules are known to collide with each other randomly and gas flow becomes unpredictable.

The transport of gaseous species through empty pores occurs by either Knudsen slip, or viscous (Poiseuille) flow [25,26,27]. Knudsen flow [28] occurs when the average pore radius (r) is much smaller than the mean free path (λ_g), i.e. $r/\lambda_g \leq 0.1$. Slip flow occurs when gas transport is intermediate between viscous flow and Knudsen flow, i.e. r/λ_g is in the range of 0.1 to 10 and, finally, viscous flow occurs when $r/\lambda_g > 10$ [29].

The process of gas transport through the pores can be estimated using an expression developed by Wakao *et al* [30] to estimate K, the transport coefficient for a single gas through a capillary of radius r:

$$K = \frac{1}{RT}\left[\frac{\frac{2r}{3}\sqrt{\frac{8RT}{\pi M_W}}}{1+2r/\lambda} + \frac{1}{1+\lambda(2r)}\left(\frac{\pi r}{6}\sqrt{\frac{8RT}{\pi M_W}} + \frac{r^2 P}{8\eta}\right)\right] \qquad (2)$$

where R is the gas constant, *T* is temperature, *MW* is molecular weight of the gaseous species, *P* is pressure, and η is the viscosity of the gas given by:

$$\eta = \frac{M_W \bar{\nu}}{3\sqrt{2N_0\pi\sigma^2}} \qquad (3)$$

where $\bar{\nu}$ is the mean molecular speed, N_0 is the Avogadro constant, and σ is the effective molecular collision diameter. This term K can then be adjusted to predict the effective transport coefficient (Keff) of a single gas through a porous body. Using this approach should show that the presence of a porous, PMMA free outer layer gives rise to a moving boundary with a variable concentration of diffusant that depends upon the surface flux, gas transport coefficient, and thickness of the porous layer [29].

Conclusion

The use of a binder with a water soluble component comprised of a major fraction of PEG, a minor fraction of PMMA and small amounts of stearic acid in the metal injection moulding of Ti6Al4V has been successfully carried out. The two stage debinding process was carefully controlled to eliminate defects and contamination in the final sintered specimen and reduce the debinding time. Details of the debinding process have been discussed in terms of chemical reactions and also in terms of debinding kinetics. In the first stage of debinding, the distilled water got into the pores by

capillary action and then dissolved the PEG out of the green body by diffusion. In the second stage, the backbone PMMA degraded cleanly and with negligible carbon over a narrow temperature. The final sintered products were evaluated against ISO standard requirements. The tensile strength, elongation and oxygen levels within specification were achieved using the specially controlled debinding and sintering process to meet the requirements for ISO 5832-3 titanium.

Therefore, the Ti6Al4V components fabricated exhibit potential for biomedical applications because the binder is completely removed before sintering. After sintering at high temperatures the parts are absolutely clean due to the protected atmosphere at high temperature.

Acknowledgements

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High temperature properties of MIM processed superalloys

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Two Ni-based PM superalloys (Inconel 713C & Udimet 720), which have been processed by metal injection moulding (MIM), were analysed with respect to their high-temperature properties. This included tensile tests at temperatures up to 900°C and evaluation of oxidation resistance up to 1100°C. The first test series lead to promising results when compared to other processing routes; however, optimisations concerning impurity contents are necessary to improve the high-temperature performance.

Introduction

There is a continuous demand for shifting the operating temperatures to higher values, especially in the automotive and aircraft industry, combined with the need for cost-effective mass production of the respective parts. With respect to suitable high-temperature materials, these are subject to complex thermomechanical loads at service temperatures. One of the most promising material classes to fulfil all the requirements are Ni-based superalloys, which have been focused on in R&D as well as in production of the respective parts for many years due to their excellent combination of mechanical strength and corrosion resistance.

Regarding cost-effective production routes, the metal injection moulding (MIM) process offers an advantageous route for production of large numbers of near-net-shape parts. Therefore, MIM-processed superalloys are one of the most promising candidates for next-generation parts in high-temperature applications.

There is knowledge available on how to process superalloys by MIM and their room-temperature properties [1, 2]. However, in order get a more profound understanding on how these MIM-processed alloys are going to perform at temperatures in the range of actual service conditions, their high-temperature properties need to be analysed. This study has the aim of providing first results for selected alloys.

Experimental

Two Ni-based PM alloys (Udimet 720 and Inconel 713C) were evaluated for their properties at elevated temperatures. These alloys contain significantly more Al (up to 6 wt%) than previously used MIM-materials (typical compositions see Table 1). Therefore, they are able to form γ' precipitates, which lead to an increase in, for example, tensile and creep strength at high temperatures [3].

Samples were provided by Schunk Sintermetalltechnik GmbH as MIM tensile bars (Fig. 1). Both alloys underwent a HIP treatment after the MIM process. Furthermore, Udimet 720 was subjected to an additional heat treatment in order to adapt the morphology and size of the precipitates (parameters see Table 2). As Inconel 713 is used in the "sintered+HIP" condition, no heat treatment of this kind was applied for this alloy.

Mechanical testing was done using a Zwick universal testing machine 1476. This machine is equipped with a furnace (HTO-08, Maytec), which operates under air, and a high-temperature extensometer (PMA-12/V7/1, Maytec). Prior to testing, the MIM samples were machined in order to fit into the sample holder. The

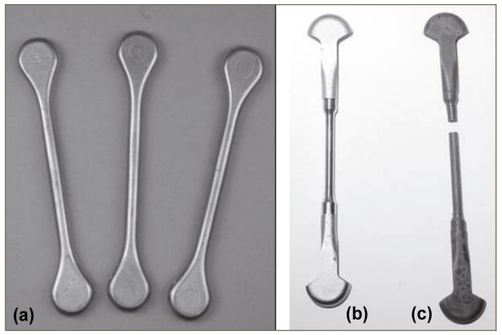

Fig. 1 (a) MIM tensile bars, (b) MIM tensile bar, machined for HT testing, (c) MIM tensile bar after HT mechanical test (tensile test)

	Ni	Cr	Al	Co	Mo	Ti	W	Nb
U720	bal.	18	2,5	15	3	5	1,25	
IN713C	bal.	12,5	6,1		4,2	0,8		2

Table 1 Typical chemical composition of studied superalloys (wt%)

Alloy	HIP	Heat treatment
Inconel 713C	1200°C, 100 MPa, 4h	---
Udimet 720	1130°C, 140 MPa, 4h	solution anneal: 1100°C, 1h ageing: 650°C, 24h + 760°C, 16h

Table 2 Post-processing of studied alloys

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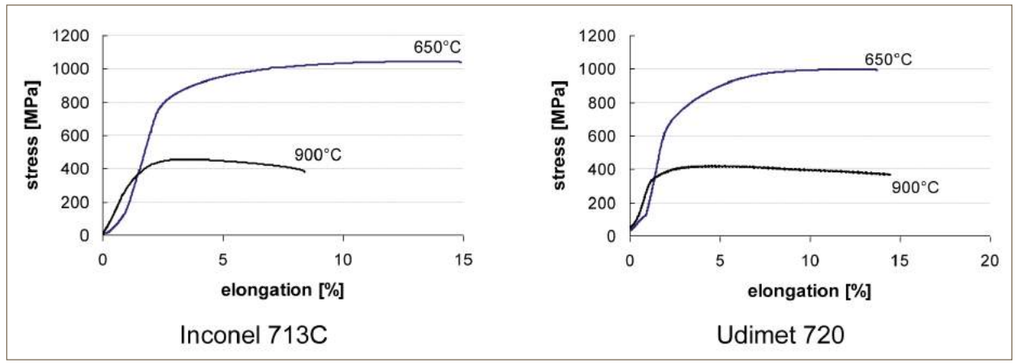

Fig. 2 Typical stress-strain curves at elevated temperatures for alloys of this study

assembly was then heated to the respective target temperature, which was in the range of 650°C – 900°C, at a rate of 15 K/min. In order to ensure a homogeneous temperature along the sample, a holding time of 60 min was inserted before the actual test started. For the tensile test, the machine speed was 0.05 / min and the test was finished when the force dropped below 80% of its maximum value.

The oxidation resistance was analysed by different tests under air. In one isothermal test, samples were exposed to air at temperatures between 900 and 1100°C for up to 100h. Additional analysis included gas analysis for impurities (carbon, oxygen, nitrogen), SEM for microstructure, SEM-EDX for composition and element distribution.

Results and discussion

Density & impurity contents

Density measurements using the Archimedes method indicate that all samples are fully densified (> 99% of theoretical density). Typical impurity contents for both alloys are summarised in Table 3.

Hot tensile test

Fig. 2 shows typical stress-strain curves for both alloys in the temperature range 650 – 900°C. Values for the yield strength $R_{p0.2}$ and the tensile strength R_m are given in Table 4. By comparing the values of Inconel 713C with those obtained by investment casting [4] and on cast samples [5] it can be concluded that the MIM samples yield comparable values at 650°C. However, at the test temperature of 900°C, the tensile properties obtained for the MIM samples are lower.

For alloy Udimet 720 tensile properties are inferior to previous tests on PM [10] and cast samples [6] (see also Table 5 for additional values at other temperatures).

The most likely reasons for the differences in tensile properties are the following:

(1) <u>High carbon content for both alloys</u>

Table 3 shows that the C-values are substantially higher for this first series of MIM samples and also above specification values (IN713C [1], U720 [11]). Fig. 3 and Fig. 4 show that substantial amounts of carbides are formed. Although carbides on grain boundaries contribute beneficially to high-temperature strength [3], increased amounts of high-temperature stable carbides on grain boundaries and inside grains can have detrimental effects on tensile properties by e.g. being initiation sites for cracks [12, 13, 14, 15].

Alloy	C (%)	N (%)	O (%)	Remarks
Inconel 713C	0.32	0.02	0.25	C = 0.17% , N = 0.02%, O = 0.04% [1]
Udimet 720	0.09	0.002	0.26	C = 0.02% [8] C = 0.04% [9] C = 0.01 – 0.04 % [10]

Table 3 Impurity contents (carbon (C), nitrogen (N) and oxygen (O)) for MIM samples in the as-sintered condition; values from literature are given for comparison

Alloy	T [°C]	$R_{p0.2}$ [MPa]	R_m [MPa]	Remarks
IN713	650	800	1043	$R_{p0.2}$ = 650 – 670 MPa [4] $R_{p0.2}$ = 550 – 850 MPa [5] R_m = 660 – 940 MPa [5]
IN713	900	373	455	$R_{p0.2}$ = 400 MPa [4] $R_{p0.2}$ = 320 – 460 MPa [5] R_m = 600 – 780 MPa [5]
U720	650	677	1000	$R_{p0.2}$ = 1050 MPa [6] $R_{p0.2}$ = 880 – 1103 MPa [10], depending on heat treatment R_m = 1367 - 1476 MPa [10], depending on heat treatment
U720	800	595	656	$R_{p0.2}$ = 880 MPa [6]
U720	900	343	390	

Table 4 Tensile properties of MIM-processed alloys Inconel 713C & Udimet 720 at elevated temperature; values from literature are given for comparison

T [°C]	$R_{p0.2}$ [MPa]	R_m [MPa]	Remarks
600	675 - 830	1190 - 1290	[7], values depend on grain size
700	705 - 824	800 - 1225	[8], values depend on test speed
704	690 - 850	1040 - 1190	[9], values depend on heat treatment
760	780 - 1069	1103 - 1180	[10], depending on heat treatment

Table 5 High-temperature tensile properties of alloy Udimet 720 at temperatures other than those investigated in this study

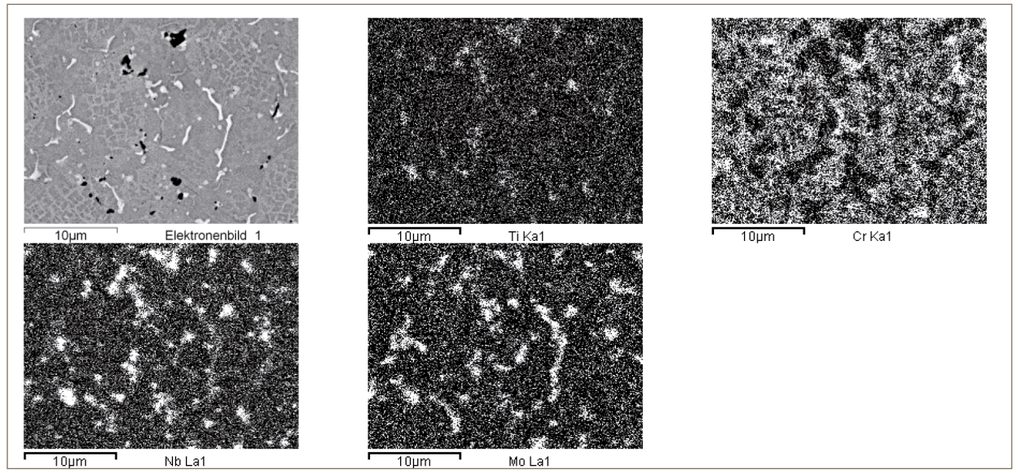

Fig. 3 Element distribution (Ti, Cr, Nb, Mo) in MIM sample of alloy IN713C (condition as sintered)

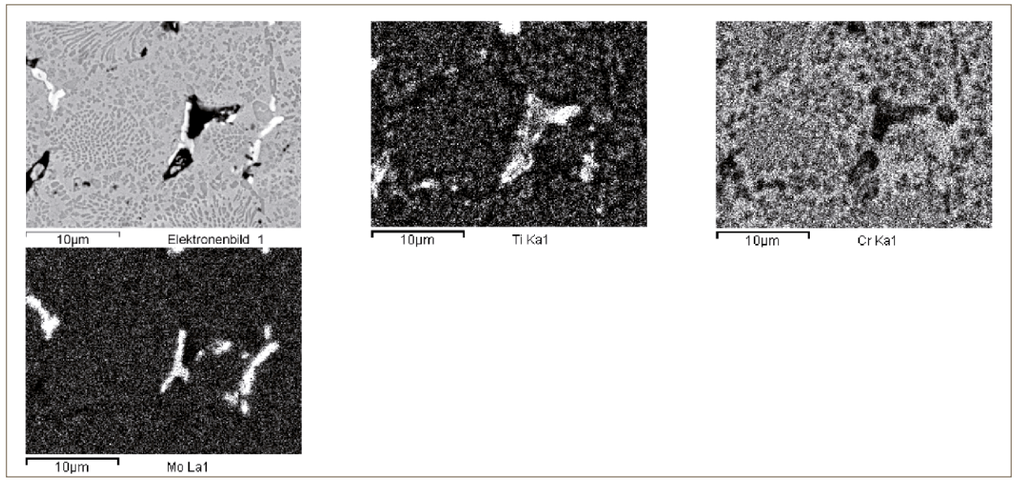

Fig. 4 Element distribution (Ti, Cr, Mo) in MIM sample of alloy U720 (condition as sintered)

(2) <u>High oxygen content for both alloys</u>

This can lead to formation of, for example, unwanted oxides, which have similar detrimental effects on tensile properties as carbides.

(3) <u>Heat treatment parameters (U720)</u>

Effects on high-temperature mechanical properties are reported: [10, 16], also a beneficial effect on strength is found by modifying the precipitate morphology and size distribution [7, 17].

Oxidation resistance

Figs. 5 - 7 show the element distributions at the edge of a MIM-bar (alloy IN 713C) after isothermal oxidation between 900 - 1100°C for 100h. All samples are in the as-sintered condition. In this temperature range, Al_2O_3 as well as Cr_2O_3 can form as protective oxide scales. At 900°C, alumina is pronounced, while at 1000°C and 1100°C both oxides form. Fig. 8 shows overview images of the edge up to the middle region of oxidised MIM bars (alloy IN 713C). Based on these images the thickness of the overall oxide scale (i.e. the closed scale on top and the porous oxidised region below) can be estimated: it increases with temperature from 136µm (900°C) up to 264µm (1100°C). Below the scales and the porous edge region no further internal oxidation takes place. Therefore it is stated that the alloy IN 713C is able to passivate under oxidising conditions.

Conclusions

A test series has been started on alloys Udimet 720 and Inconel 713C which were processed by MIM in order to evaluate their high-temperature performance. First tests included tensile tests up to 900°C and isothermal oxidation tests up to 1100°C.

Concerning high-temperature strength, IN 713C shows a high potential compared to other processing routes. U720 however needs improvement with respect to mechanical strength.

It is concluded that in order to increase the high-temperature tensile strength, the primary effort needs to be the significant reduction of impurities, namely carbon and oxygen. This can be achieved by optimising the thermal debinding regime. Current tests with new regimes show that reductions down to the level of impurities in the alloy powders are possible. Furthermore, new powder variants with reduced carbon contents (Inconel 713LC &

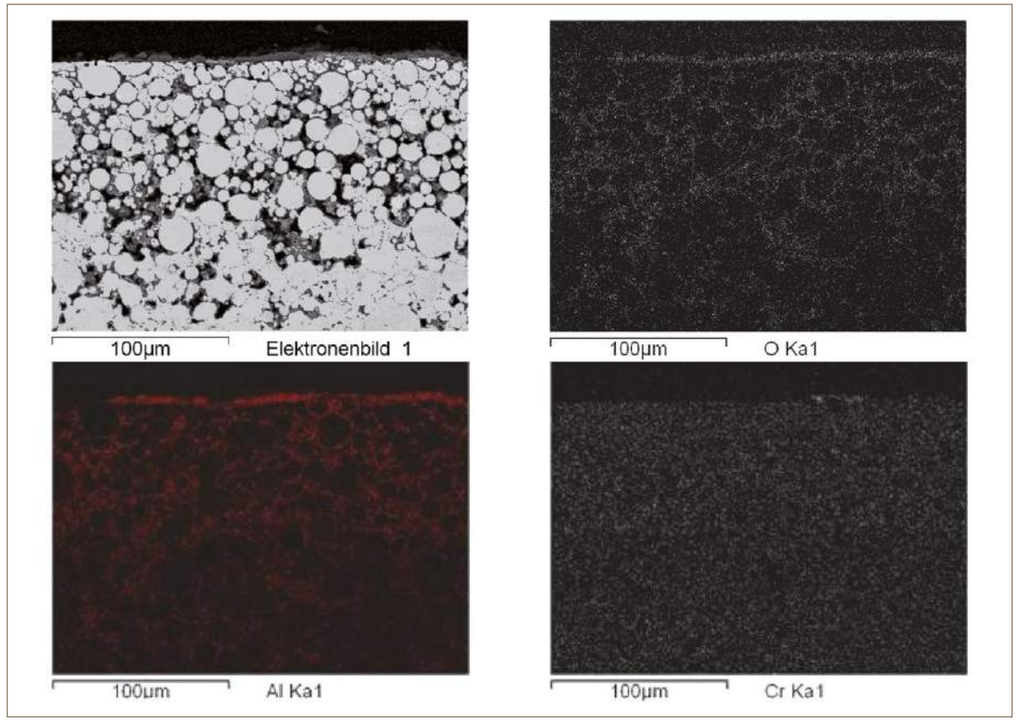

Fig. 5 Element distribution in alloy IN 713C after isothermal oxidation (900°C, 100h, air)

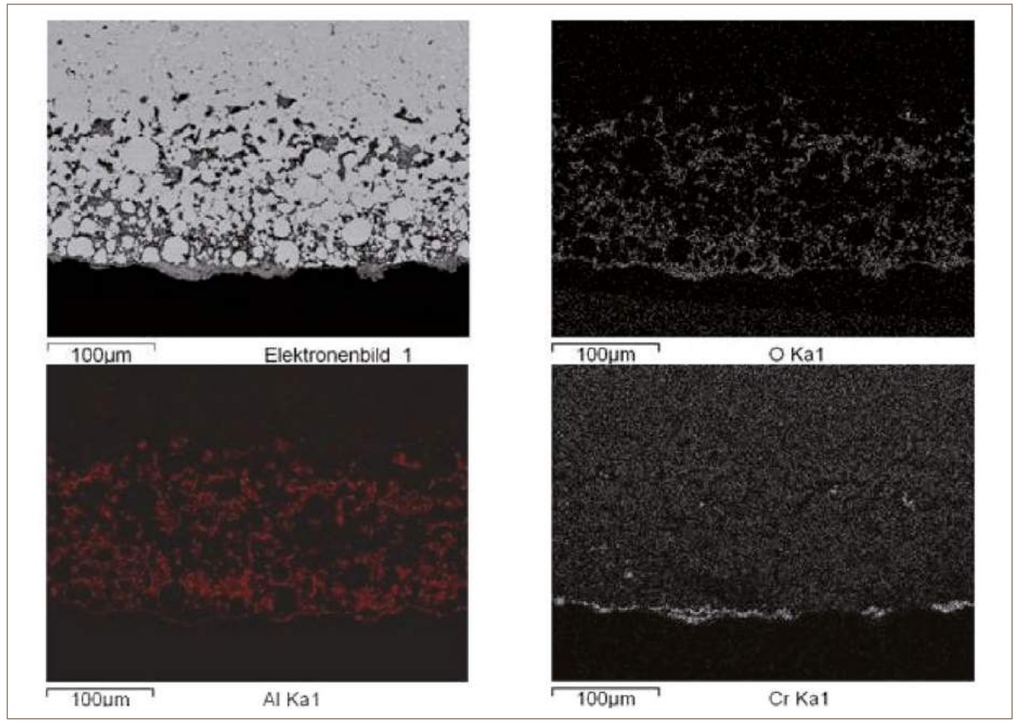

Fig. 6 Element distribution in alloy IN 713C after isothermal oxidation (1000°C, 100h, air)

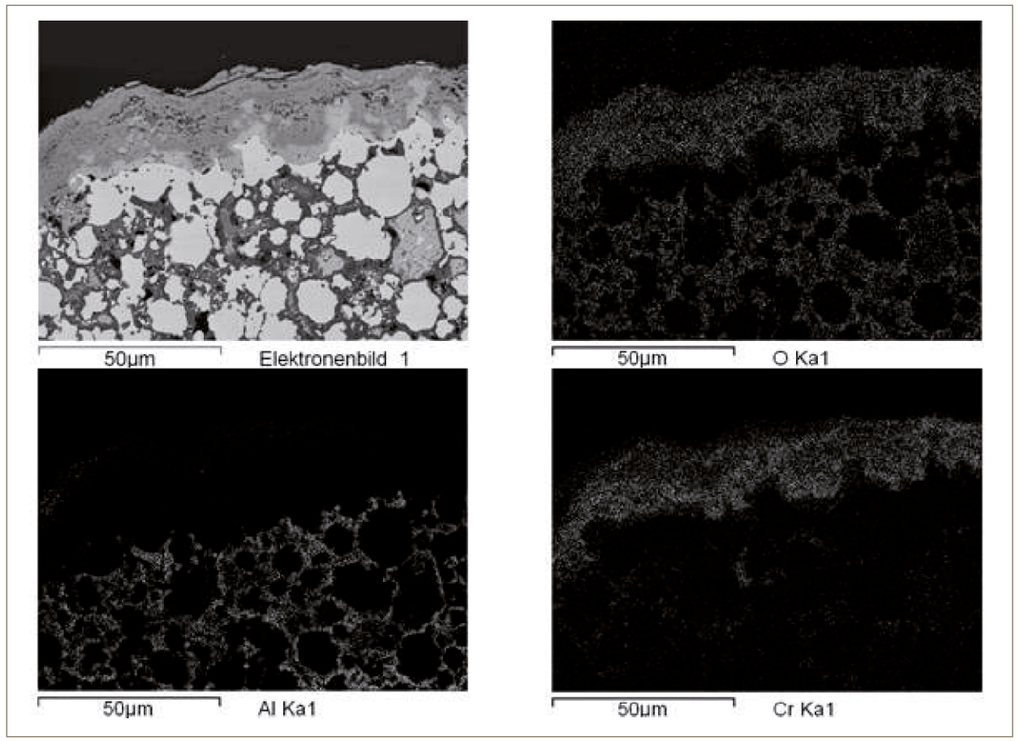

Fig. 7 Element distribution in alloy IN 713C after isothermal oxidation (1100°C, 100h, air)

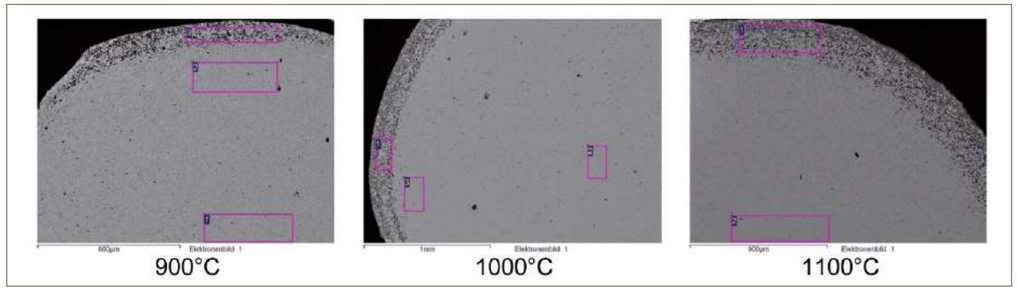

Fig. 8 SEM images of alloy IN 713C after oxidation for 100h at different temperatures

Udimet 720Li) will be included in subsequent tests. Concerning high-temperature oxidation resistance, first tests under isothermal conditions indicate a good performance of alloy IN 713C. Further tests (thermogravimetry, thermocycling conditions) on both alloys will help to get a better understanding of the overall high-temperature performance of these Al-containing MIM-superalloys.

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High temperature and fatigue properties of injection moulded superalloy compacts

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Inconel 718 is a representative Ni-base superalloy. However, it is not easy to produce complex shaped parts at low cost due to the material's poor workability. In this study, the Metal Injection Moulding (MIM) process, one of the near net-shape forming methods for such powders, has been applied for fabricating Inconel 718 compacts using both gas and water atomised powders. By optimising the MIM process, the obtained relative density was near full density (98~99%) and the tensile property of as-sintered compacts had a strength of 1000MPa and elongation of around 10%, properties which are similar to those of wrought materials. High temperature and fatigue properties of heat treated MIM compacts are presented in detail.

Introduction

Superalloys have been used especially for aerospace and atomic energy applications because of their excellent attributes of high corrosion and oxidation resistance, and high temperature strength. Inconel 718 is one representative Ni-base superalloy. Inconel 718, however, has a high nickel content. It is not easy, therefore, to manufacture complex shaped parts at low cost due to the material's poor workability.

Powder metallurgy is an effective way to produce the complex shaped parts at low cost. However, with die press moulding of the powder it is also difficult to obtain high density, so it is hoped that metal injection moulding (MIM) will be a suitable processing technique for complex shaped parts even with poor workability materials.

In this paper, MIM of Inconel 718 pre-alloy powders is conducted and the various mechanical properties of the injection moulded compacts are discussed as a function of the type of powders, processing techniques, sintered densities and chemical compositions.

Experimental

Three types of pre-alloyed Inconel 718 powders were used in this study. Table 1 shows the characteristics of the selected powders. Water and gas atomised powders with different particle size and composition were used. In this paper, these powders were designated as W2, W10, and G22 by the differences in atomisation method and particle size. Fig. 1 shows electron micrographs of the selected raw powders. The powders and wax based binders were compounded and pelletised for injection moulding. The solid powder loading was 62 vol.% for the W2 specimen, and 65 vol.% for the W10 and G22 specimens.

In order to investigate the mechanical properties, tensile and rotating bending fatigue test specimens were produced by injection moulding. Green compacts were debound in a heptane atmosphere, followed by thermal debinding in a nitrogen atmosphere. Sintering was performed at 1100~1250°C for 1~6 hours using sintering furnaces in a vacuum (10^{-1}Pa).

Density measurement by the Archimedes method, hardness testing (HV), elemental analysis for carbon and oxygen, and the testing of mechanical properties were performed for each sintered compact.

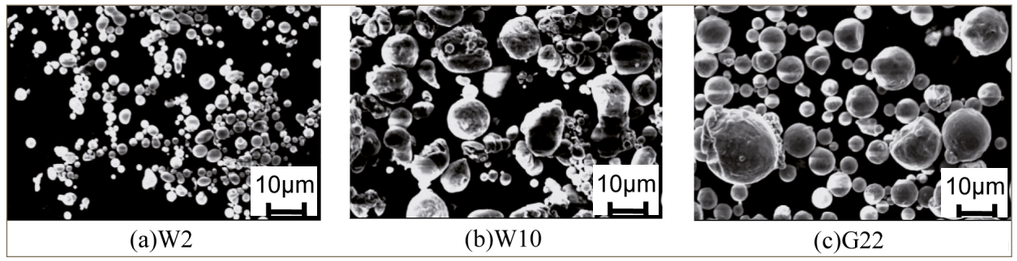

Fig. 1 Electron micrographs of Inconel 718 alloy raw powders

Symbol	Atomisation	Particle size	Ni	Cr	Nb	Mo	Ti	Al	C	O	Fe
W2	Water	<2μm	49.86	17.91	5.01	3.02	0.73	0.27	0.05	0.60	Bal.
W10		<10μm	49.86	17.91	5.01	3.02	0.73	0.27	0.05	0.49	Bal.
G22	Gas	<22μm	53.42	18.94	5.14	3.12	0.98	0.66	0.05	0.046	Bal.

Table 1 Chemical composition (mass%) of raw powders (Inconel 718)

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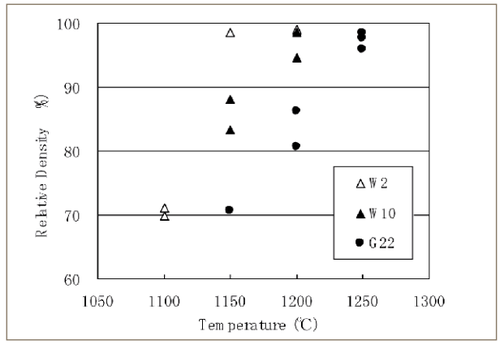

Fig. 2 Relationship between relative density and sintering temperature for Inconel 718 specimens

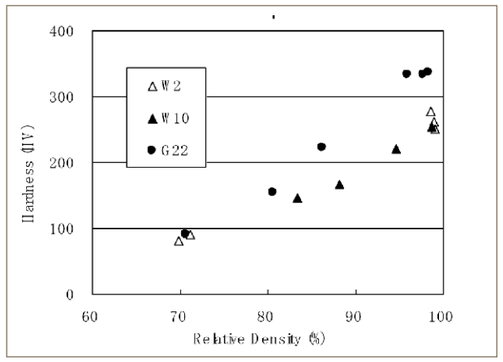

Fig. 3 Relationship between hardness and relative density for Inconel 718 specimens

Results & Discussion

Relative density, hardness, and grain size

The relationship between the relative density and the sintering temperature is shown in Fig. 2. The sintered densities of all specimens increased by elevating the sintering temperature and decreasing the particle size, and nearly full densities were obtained in all powders. The relationship between hardness and the relative density is shown in Fig. 3. Hardness also increases by increasing the relative density. In the high density specimens, the G22 specimen showed the highest hardness value of 340HV which is the same level as wrought materials. On the other hand, the W2 and W10 specimens showed a relatively low hardness value of about 250HV.

Fig. 4 shows the optical micrographs of non-etched (A) and etched (B) cross sections of high density specimens (98~99%). The grain sizes of sintered specimens shown are as large as the particle size of raw powders.

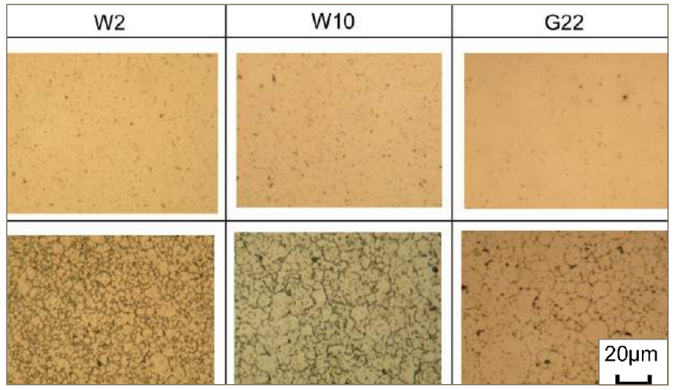

Fig. 4 Optical micrographs of Inconel 718 high density specimens; non-etched (A) and etched (B)

Chemical composition

The relationship between the carbon content and the relative density of sintered specimens is shown in Fig. 5. Also, the relationship between the oxygen content and the relative density is shown in Fig. 6. In both results, carbon and oxygen content are little related to relative density. Their carbon content is very low level and is approximately the same level (0.06-0.09 mass%) for each sintered specimen. The significant difference in oxygen content between gas atomised powder (G22) and water atomised powders (W2,W10) is directly affected by the original oxygen content of the starting powders.

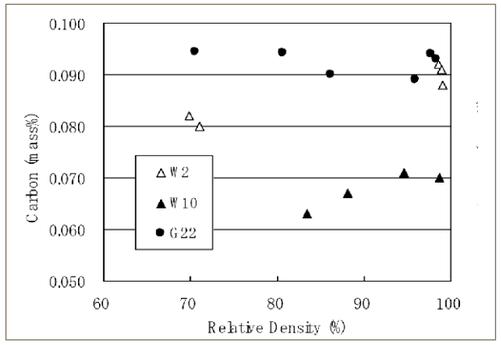

Fig. 5 Relationship between carbon content and relative density for Inconel 718 specimens

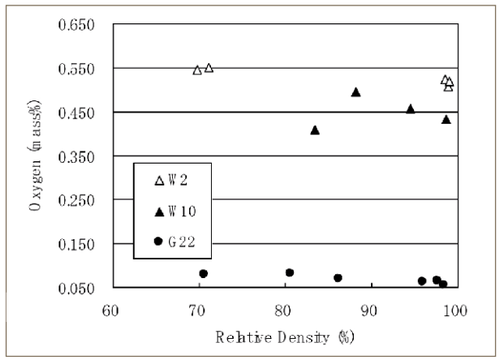

Fig. 6 Relationship between oxygen content and relative density for Inconel 718 specimens

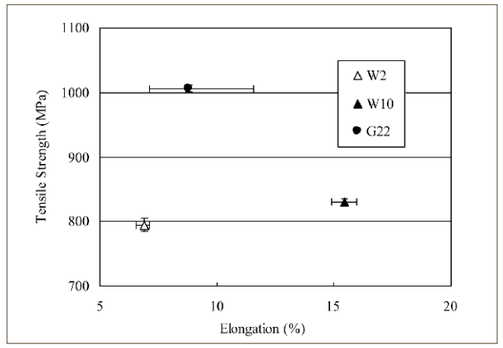

Fig. 7 Relationship between tensile strength and elongation for Inconel 718 high density specimens

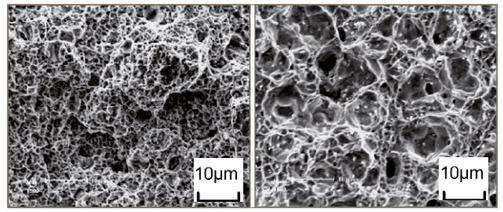

Fig. 8 Electron micrographs of fractured surfaces, W2 sample on the left, G22 sample on the right

Tensile property

The relationship between tensile strength and elongation for Inconel 718 high density specimens is shown in Fig. 7. The tensile test was performed to the specimens with the relative density of 98~99% in each powder. Compared with wrought material, the tensile strength of the W2 and W10 specimens was about 70% (800MPa) and the G22 specimen showed about 80% (1000MPa). The elongation value of W10 specimen reached 15%, which was better than wrought material. Even though W10 and W2 specimens showed a similar tensile strength, the elongation is very different, which seems to be influenced by oxygen content.

Fig. 8 shows the electron micrographs of fractured surfaces of the W2 and G22 specimens. Both W2 and G22 specimens showed average elongation of 7%. Dimples can be seen in both fractured surfaces, however the fractures size is similar to the grain size for each specimen. Therefore it can be concluded as grain boundary fracture. Both W2 and G22 specimens show the same fracture morphology and value of elongation, however there are significant differences in their tensile strengths. Since there is a difference in the oxygen content, it is considered that fewer precipitation strengthening elements such as Ti and Al exist in the water atomised powder than in the gas atomised powder, giving a significant influence on the decrease in the tensile strength.

Fatigue strength

The G22 specimen has the highest tensile strength of the three powders. This G22 specimen was used for the rotating bending fatigue test. An S-N curve of a high cycle fatigue test is shown in Fig. 9. The fatigue strength obtained was approximately 50% of the value of forged material. Compared with the tensile strength behaviour, fatigue strength was much lower. It is thought that the residual pores after sintering strongly affected the fatigue strength. Even porosity of 1 or 2% significantly decreases the fatigue strength in high strength materials.

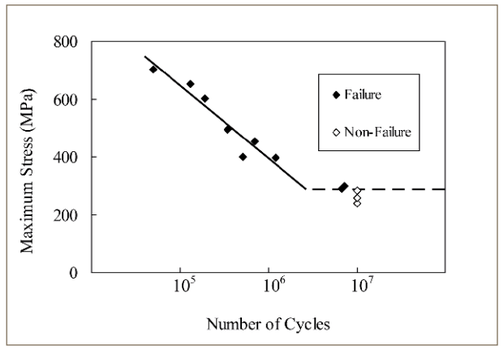

Fig. 9 An S-N curve for high cycle fatigue test at room temperature (G22 specimen)

High temperature fatigue tests were conducted on the as-heat treated G22 specimens. The heat treatment process consists of holding at 991K for 8 hours followed by furnace cooling (FC) to 894K and holding at 894K for 8 hours then air cooling (AC) to room temperature. High temperature tension-compression fatigue tests were carried out at 811K under air atmosphere conditions. The high cycle fatigue strength obtained was approximately 70% of forged material.

Conclusion

In this study, MIM of three types of pre-alloyed Inconel 718 powders with different particle size and composition were conducted. The sintered properties and mechanical properties were investigated. The relative density of small grain size specimens was higher than the others in low sintering temperature conditions, but with standard sintering conditions all powder specimens showed near full density (98~99%). The gas atomised powder specimen shows high tensile strength and hardness. On the other hand, in the case of water atomised powder, ductile specimens were obtained. Inconel 718 is a precipitation hardened alloy, therefore the quantity of elements such as Ti, Al and Nb is important. The difference between gas and water atomised powder seems to have an affect on the tensile strength. For the improvement of the mechanical properties of water atomised powder, it will be useful to increase the amount of Ni, Cr and precipitation hardening elements, or decrease the amount of oxygen. Additionally, an improvement in the fatigue strength could be expected by reducing the number of pores, for example, in combination with hot isostatic pressing (HIP).

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