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Powders for Metal Injection Molding

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Abstract

Metal injection molding (MIM) uses powders which differ considerably from the ceramics powders used for ceramic injection molding. Metal powders are hardly available in the sub-micron ranges that are almost standard in ceramics. The reason for this lies in the ductility and reactivity of the metals which make it difficult and very expensive to produce fine powders. In this paper the specifications for MIM powders are discussed with reference to the different materials processed by MIM and the resulting properties of the materials. Subjects will include stainless steel, tungsten alloys, intermetallics and titanium. The paper will deal with the activation and characterisation of the powders as well as with their processing by MIM. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Metal powders for metal injection molding (MIM) are produced by different methods listed in Table 1. The medium particle size may be in the range between around 1 μm for hardmetals up to 45 μm for stainless steels and speciality materials. Coarser powders are usually not used because they lack sintering activity. Finer metal powders are hardly used for two reasons: for many metals there exist no production methods for sub-micrometer powders. If a method is available the handling of the powders becomes difficult as they tend to oxidise very easily.

The work horses of todays MIM production are carbonyl–iron and carbonyl–nickel powders as well as gas atomised and water atomised stainless steel powders. The carbonyl powders are produced by thermally decomposing gaseous compounds composed of the metal and carbonmonoxide. These fine powders often form the basis of powder mixtures for metal injection molding. These can be simple mixtures of iron and nickel but also materials like heat treatable steels or even stainless steels have been produced from powder mixtures.

The atomised powders are produced by atomising a stream of molten metal using an intense stream of gas (often argon) or of water. The water atomisation leads to irregular particles with a good yield of the particle fraction below 45 μm. The gas atomisation leads to mostly spherical particles but often yields only a small fraction below 45 μm. The atomisation process can be used for any metal or alloy that may be homogenously melted.

Today the MIM process has been developed for a wide range of other materials. The list is continuously enlarged by producers and research institutes as the materials are needed. Examples for the different powders and for their application for MIM are given in the following case studies.

2 Stainless Steel

Nowadays, a broad range of stainless steels are available as MIM powders. Most often they are produced by gas atomisation or by water atomisation. Figure 1 shows the morphology of the spherical gas atomised powder while Fig. 2 presents the irregular shaped water atomised powder. Figure 3 gives the corresponding particle size distributions. Both kinds of powders have their advantages and disadvantages.

Gas atomised powder has a higher packing density and thus needs less binder for injection molding leading to low shrinkage and distortion during sintering. The spherical morphology also guarantees a more isotropic shrinkage as the particles cannot take a preferred direction during injection molding. The disadvantages of this kind of powder is its higher price and the lower strength of the molded part during debinding. After the stabilising binder has been removed the spherical particles easily flow if sintering has not begun yet. Any

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Table 1. Methods for producing MIM powders

No.	*Production method*	*Used for*
1	Chemical methods	Ta, W
2	Electrochemical methods	Cu, Fe, Ni
3	Thermochemical method	Carbonyl–Fe, Ni
4	Mechanical methods (milling, atomisation)	Steels, titanium, intermetallics

handling or vibration can destroy the brown part in this state.

The advantage of the water atomised powder lies in its lower price. Also, the brown strength of parts produced with this kind of powder is fairly high as the irregular particles cannot flow past each other. Disadvantages are the low tap density resulting in high sintering shrinkage as well as the tendency of the irregular particles to slightly align during injection molding and thus causing anisotropic shrinkage. This is why some companies 'activate' the water atomised powder by milling which produces a less irregular, slightly rounded powder.

Mixtures of gas atomised and water atomised powders of 316L and 17-4PH have been tested for

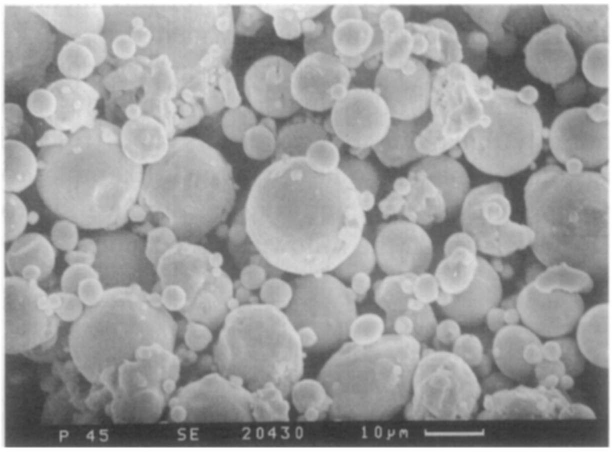

Fig. 1. SEM micrograph of a gas atomised 17-4PH stainless steel powder [HCST].

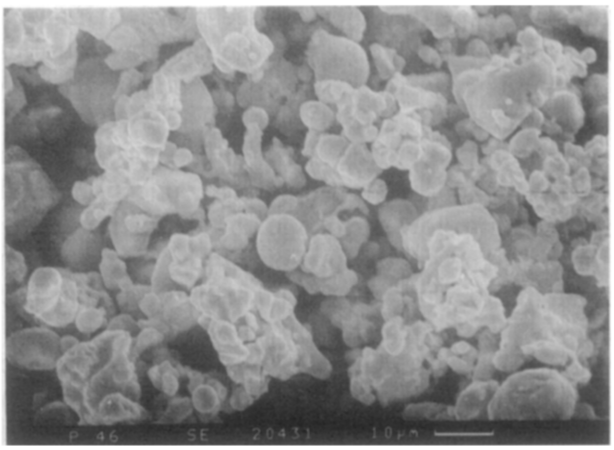

Fig. 2. SEM micrograph of a water atomised 17-4PH stainless steel powder [HCST].

the resulting properties of MIM parts in order to be able to adjust shrinkage, mechanical properties and price of the resulting component. Figure 4 shows the linear shrinkage of such powder mixtures as a function of the composition, the shrinkage increasing more or less with the amount of water atomised powder. Curves like this allow to adjust the shrinkage of a MIM feedstock to a value necessary for producing parts to given dimensions with a given mold. Said tendency in Fig. 4 reflects the lower tap density which causes higher shrinkage to reach similar densities as the gas atomised powder. The mixture with 25% water atomised powder is an exception to this trend. This mixture had a higher tap density than the pure gas atomised powder and could be sintered to over 99·6% of theoretical density at 1420°C. At lower sintering temperature the water atomised fraction in that mixture prevents perfect mechanical properties (Fig. 5). Activating the water atomised powder by milling improves the properties of the resulting MIM parts (Fig. 5). The tensile strength is increased by more than 10% for the mixtures with large fractions of water atomised powder.

Similar experiments using powder mixtures of 17-4PH stainless steel produced slightly different results. The shrinkage increased almost linearly with the fraction of water atomised powder (Fig. 6). The two 17-4PH powders did not form a mixture with a specially high tap density. The high tensile properties of this material can be seen in Fig. 7. The tensile test specimens were sintered at the given temperature, solution treated in argon for 1 h at 1050°C, followed by a water quench. Aging was performed at 480°C for 4 h, again followed by water quenching.

3 Tungsten Heavy Alloy

For the MIM of tungsten heavy alloy a mixture of elemental powders is used. Figure 8 presents the morphology of the powders, the polygonal particles being the chemically produced tungsten mixed with small amounts of round carbonyl–nickel and iron powder particles. This material allows liquid phase sintering to full density forming a W–Fe–Ni matrix for the tungsten particles. This powder was used to prepare feedstock using a wax/polymer binder with 20% of EVA, 10% carnauba wax, 1% stearic acid and 69% paraffin wax. After injection molding most of the binder was extracted in hexane and the remaining polymer thermally decomposed. Sintering was performed in flowing hydrogen. The sintering program had to be carefully adjusted to the part to be produced (Fig. 9) the fairly large size combined with the high density

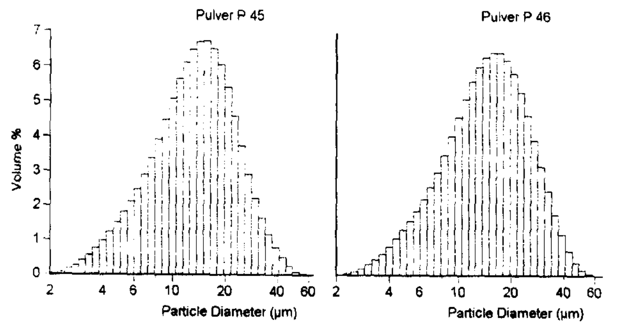

Fig. 3. Particle size distribution of 17-4PH powder measured by laser diffraction: left, gas atomised powder; right, water atomised powder.

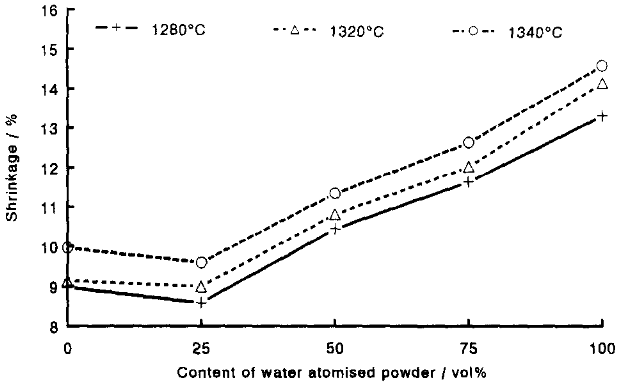

Fig. 4. Linear shrinkage after sintering of mixtures of gas atomised and water atomised 316L powders.

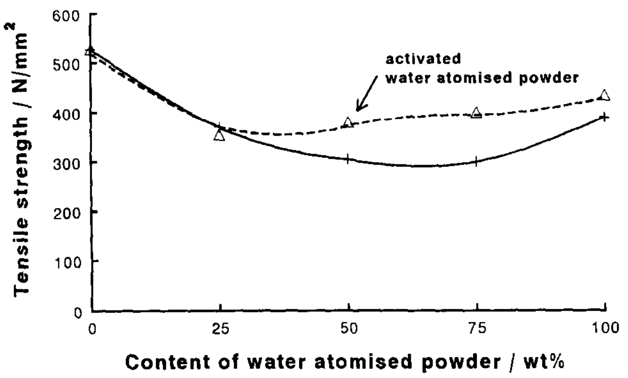

Fig. 5. Tensile strength of sintered 316L powder mixtures. The broken line shows the effect of activation of the water atomised powder.

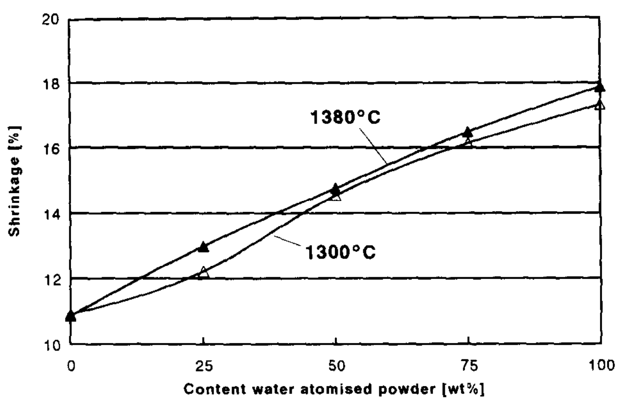

Fig. 6. Shrinkage during sintering of powder blends of gas atomised and water atomised 17-4PH powders. Sintering was performed at the given temperatures.

of the material of around 18 g cm^{-3} caused distortion of the part especially in the liquid phase. Pilot scale production of the part became possible when an optimised sintering fixture was used.

4 Titanium

For titanium and titanium alloy applications most often the low weight and the resulting high strength to weight ratio is of particular importance. Other applications need the excellent corrosion resistance against seawater and other environments. An essential problem in using the MIM technology for small and complicated titanium parts is the high affinity of the powder towards carbon, oxygen and nitrogen. These elements are easily picked up during processing and embrittle the material. Thus they are strictly specified for the different qualities of titanium and its alloys (Table 2). The highly active powders that are necessary for MIM of titanium obviously pick up the contamination easily and have to be processed very carefully.

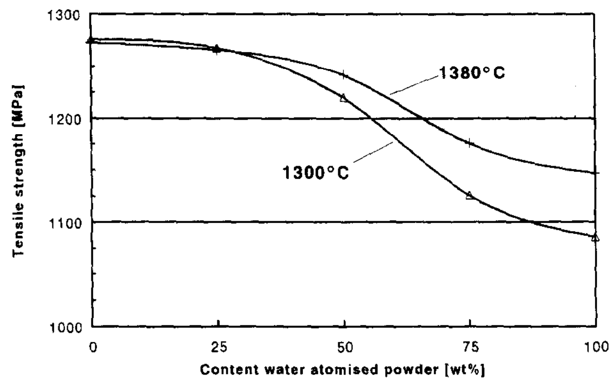

Fig. 7. Tensile strength of heat treated MIM 17-4PH (1 h at 1050°C, water quench, 4 h at 480°C, water quench) sintered at the given temperatures as a function of the percentage of water atomised powder in the powder blend.

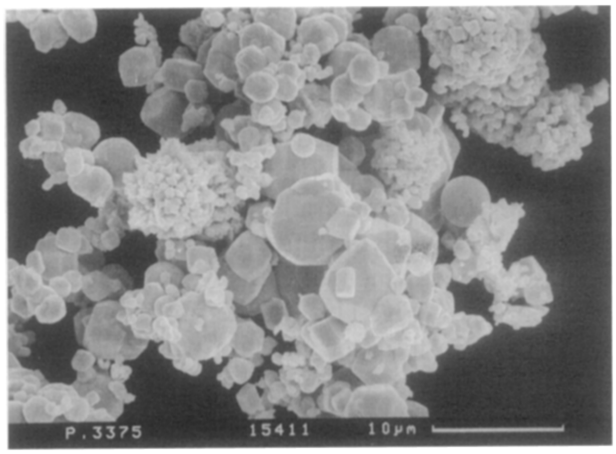

Fig. 8. Powder morphology of W–Fe–Ni powder.

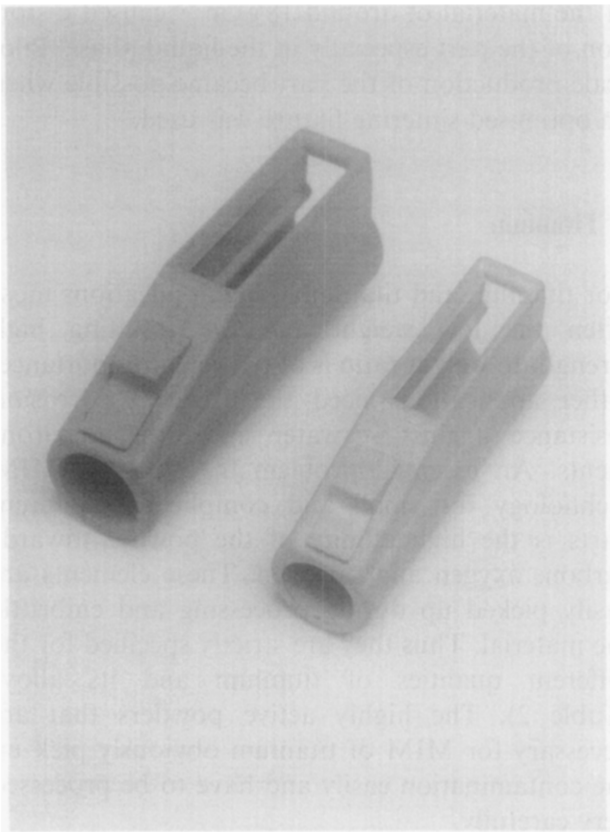

Fig. 9. W–Fe–Ni radiation shield, courtesy Advanced Technology Projects, ATP, Freilassing, Germany; left, green part; right, sintered part.

Table 2. Comparison of titanium specifications ASTM grade 3 and ASTM grade 4 with values obtained after MIM processing of gas atomised powder

	ASTM titanium		
	Grade 3	*Grade 4*	*MIM-Ti*
Oxygen content (%)	max. 0·35	max. 0·40	< 0·25
Carbon content (%)	max. 0·1	max. 0·1	< 0·1
Yield strength (MPa)	377–520	min. 480	445
Tensile strength (MPa)	min. 440	min. 550	550
Elongation (%)	min. 18	min. 15	26

There exist three different kinds of titanium powder: sponge fines, hydride–dehydride and gas atomised powder. Sponge fines are produced after reducing $TiCl_4$ with magnesium and removing the $MgCl_2$. The remaining sponge is crushed yielding some 'fines' (Fig. 10). The larger fraction of the sponge or any billets produced from it for refining the metal may be crushed by hydriding-dehydriding. Here, the metal is reacted with hydrogen to TiH_2. This brittle material can easily be crushed and milled. On dehydriding a highly porous material is obtained which can easily be broken into single particles (Fig. 11). All the process steps can lead to oxygen/nitrogen pick-up which cannot be removed during powder processing and thus ends up in the final part. This means that for MIM a powder with very low contamination of the interstitial elements C, O, N and H is needed. Also,

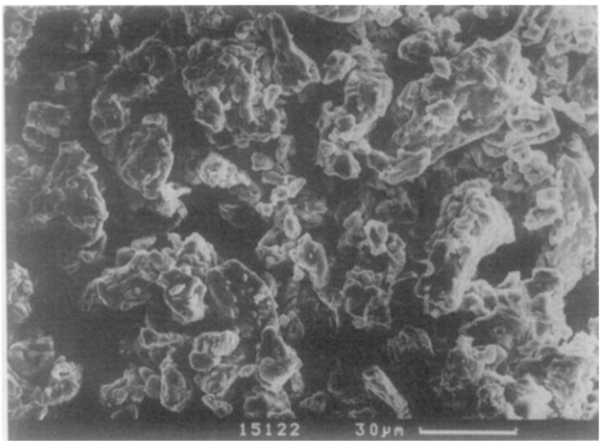

Fig. 10. SEM picture of titanium sponge fines.

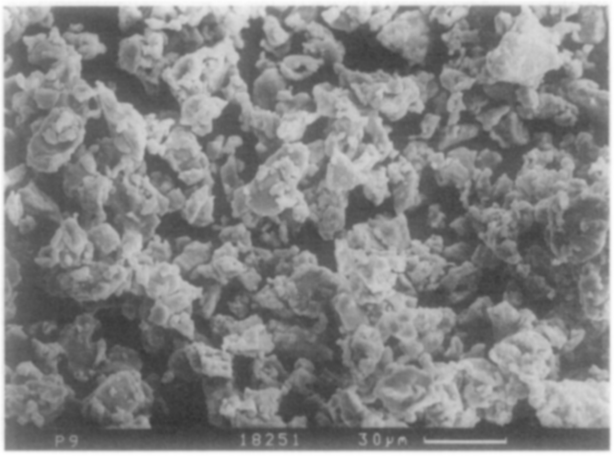

Fig. 11. SEM picture of titanium hydride dehydride powder.

careful handling and processing as well as a binder which does not react with the powder is needed to reach titanium MIM parts. Sintering has to be performed in high vacuum or good qualities of argon at temperatures between 1150 and 1400°C.

Some good gas atomised powder of tianium grade 2 can be sintered to a density of 97% of theoretical density reaching mechanical properties which are comparable to the specified grades of wrought titanium (Table 2). The gas atomised powder is still very expensive which makes it desirable to use the cheaper sponge fines or the HDH powders. These powders are more difficult to process as their irregular morphology reduces the possible powder loading in the MIM feedstock. Also these powders mostly contain more oxygen to start with. These facts necessitate slightly higher sintering temperatures. Nevertheless test parts of titanium grade 4 have already been produced using a grade 3 HDH powder.

5 Intermetallics

Here two materials have been investigated, NiAlCr and $MoSi_2$. For NiAlCr the gas atomised powder shown in Fig. 12 was used. The powder fraction of

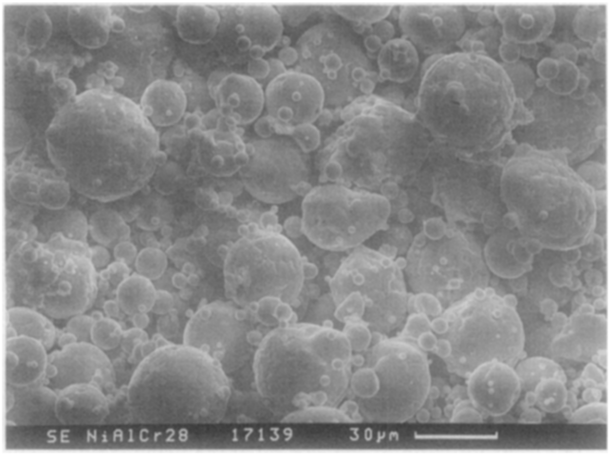

Fig. 12. SEM picture of gas atomised NiAlCr27 powder.

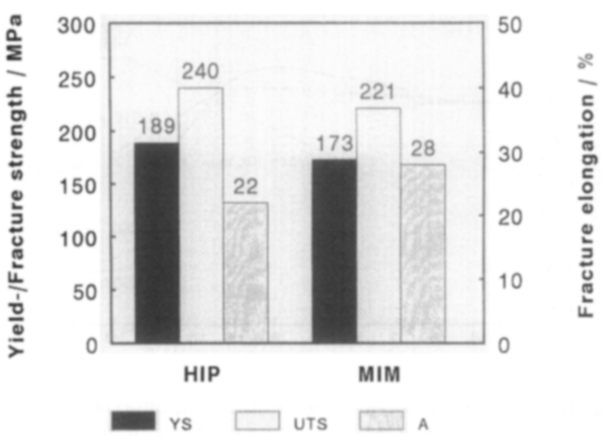

Fig. 14. Comparison of the mechanical properties at 900°C of HIP samples with MIM samples (tensile test bars).

$-45\,\mu m$ was separated for the experiments. The dendritic microstructure of the powder is shown in Fig. 13 and may lead to problems. The larger particles of another powder batch with a very similar chemical composition had a highly porous surface and thus needed much more binder for processing via MIM. The reason for this may be a different cooling rate or the effect of some surface active additive in the melt.

For processing a wax/polymer binder was adapted in such a way that up to 85% of the binder could be removed by solvent extraction. This helped to reduce the carbon contamination of the sintered parts to less than 0·05 wt%. Sintering was performed at a maximum temperature of 1417°C and led to densities of 96–97% of theoretical density. Tensile test bars produced by MIM showed very similar properties as those produced by hot isostatically pressing the powder (Fig. 14). After optimising the mold design by a simulation using the Moldflow® software the hollow turbine vane shown in Fig. 15 could be produced. The high sintered density after MIM processing allowed HIP without extra encapsulation. In a burning chamber test the resulting part exhibited perfect thermal cycling stability using heating and cooling rates of up to $35\,K\,s^{-1}$ and excellent corrosion resistance up to 1000°C.

Other problems had to be solved in order to process molybdenum disilicide with MIM. The commercially available powder was produced by crushing and milling billets resulting in a particle size of less than $45\,\mu m$. This powder could not be sintered to closed porosity by pressureless sintering. Some activation of the powder was needed in order to lower the sintering temperature to less than 1500°C and in order to reach high densities. Here, different additives were tested producing some temporary liquid phase or reducing the silicon oxide layer on the surface of the particles. Both techniques had their drawbacks, the one producing phases which lowered the strength of the $MoSi_2$, the other resulting in powders which could not be safely handled in air any more. As a third technique system inherent sintering additives of activated Mo–Si elemental powder mixtures have been successful. The mixture of molybdenum and silicon powder was ball milled resulting in a finely

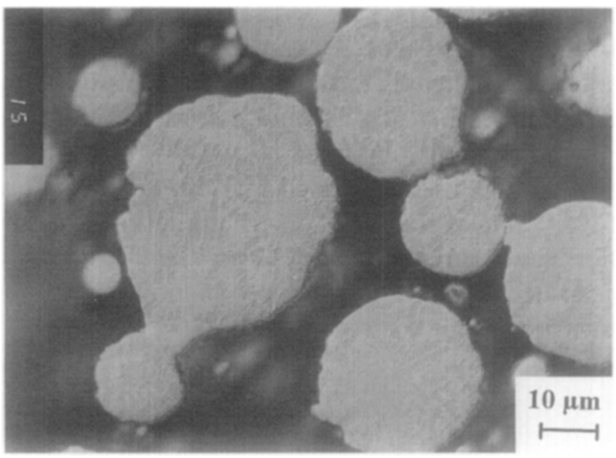

Fig. 13. Microstructure of the gas atomised NiAlCr powder. The dendritic microstructure may lead to porous particles which need large amounts of binder.

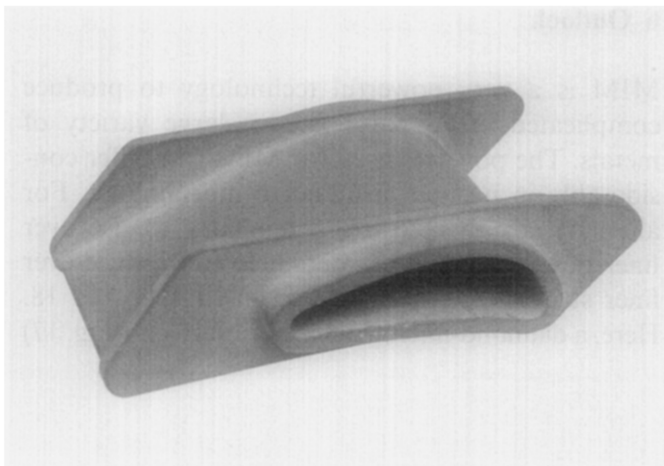

Fig. 15. Hollow turbine vane produced by MIM (design by MTU, München).

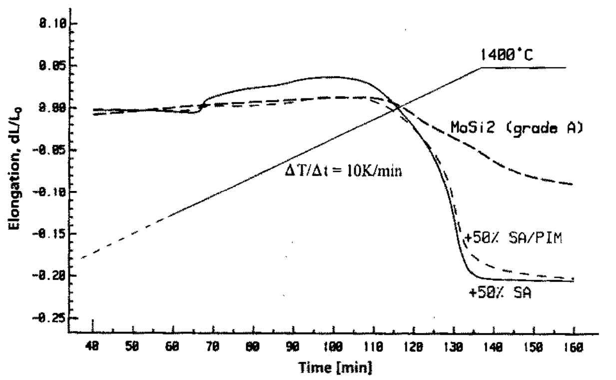

Fig. 16. Sintering behaviour of commercial, uniaxially pressed $MoSi_2$ powder (Grade A) and of two mixtures of grade A with 50% milled Mo–2Si additive SA (+50% SA: uniaxially pressed, +50% SA/PIM: produced from MIM feedstock).

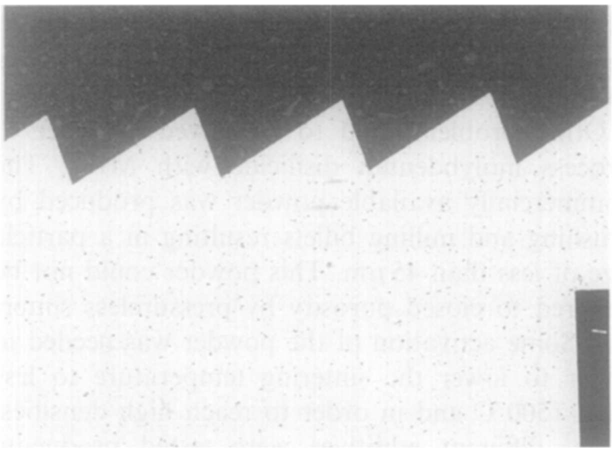

Fig. 17. Diamond micromachined fresnel lens.

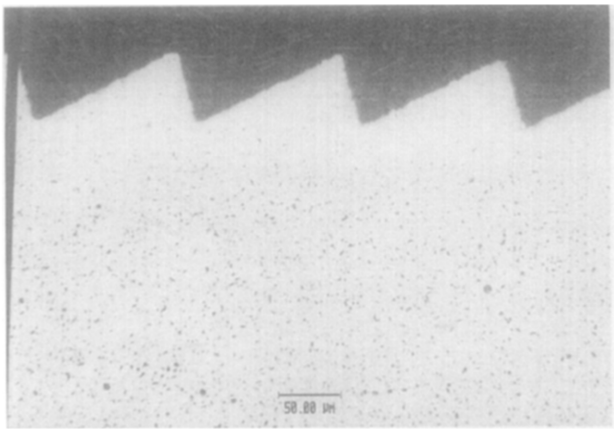

Fig. 18. Reproduction of the lens by MIM using stainless steel powder.

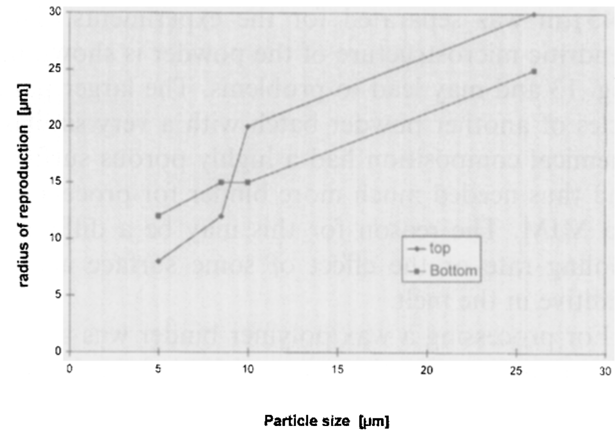

Fig. 19. Radii at top and bottom of the teeth in the reproduced lenses as a function of the particle size used in the MIM feedstock.

intermingled and highly active powder. This was added to the $MoSi_2$ base powder before feedstock preparation and helped to reach a closed porosity at 96% of theoretical density already at a sintering temperature of 1350°C. The shrinkage curves of $MoSi_2$ powder compacts with 50% of Mo–2Si additive are compared in Fig. 16

6 Outlook

MIM is a very powerful technology to produce complicated metal parts from a large variety of metals. The powders used for MIM can differ considerably in particle size and in morphology. For all materials there exists a tendency to use ever finer powder. These powders help to produce ever finer structures as can be seen in Figs 17 and 18. Here, a diamond-micromachined fresnel lens (Fig. 17) was used as a mold for MIM. Feedstocks were made of different powders and injection molded using the lens (Fig. 18). The quality of reproduction of the original microstructure was measured and is given in Fig. 19 as a function of the medium particle size of the powders. The finer powders lead to sharper corners and higher sintered density in the structure. On the other hand the processing of the powders becomes more difficult as the higher surface area of the fine powders necessitates a large amount of binder. This again increases the shrinkage during sintering and often leads to cracks and distortion. Here the right compromise between particle size and processing difficulties combined with the right mixture of very fine metal powders is needed. This may offer new markets for MIM in the future as a cheap technique for mass production of microstructures or microstructured parts.