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TECHNICAL PAPER

Micro injection molding of micro gear using nano-sized zirconia powder

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Abstract Powder injection molding (PIM) is well established in macro molding. Scaling down to micro-PIM (μPIM) opens a new arena for cost effective production of micro components. One potential application is the manufacture of cutting tools with sharp edges for machining. However, scaling down to such a level produces challenges in raw material preparation, injection molding and thermal treatment. In this report, near dense (>98% of theoretical density) tensile bars and 3 mm micro gears were produced using 50 nm Yttria Tetragonal Zirconia Polycrystal (Y-TZP). The sintered gear teeth were well defined and visually defect free.

1 Introduction

Powder injection molding (PIM) is a near net shape forming technology that combines the cost effective attributes of plastic injection molding with the superior properties of engineering materials. The PIM industry has grown rapidly since the onset of its commercialization in the 1980's. As of 1998, worldwide PIM related industries involved 300 manufacturers and 5,000 subcontractors (Yoshikawa and Ohmori 2001). The potential market for 2010 is estimated to be greater than $2.1 billion (Kirkland 1997). PIM is suitable for a wide range of powder materials including metals and ceramics. With PIM capable of producing micro components, small tools like end mills and drills of fine diameters can be mass produced at reduced cost which is an $8 billion US market (Cornwall and German 1997).

PIM, driven by miniaturization, is in demands with μPIM bucking the trend. To study μPIM with good mechanical properties, a 3 mm micro gear produced from Yttria Stabilized Zirconia (Y-TZP) was selected. Y-TZP is well recognized for its high toughness and its stability at temperatures of up to 1500°C. Scaling down to nanometers, study of Y-TZP is mainly focused on the synthesis of nano-sized particles, their sintering behavior and microstructure analysis via powder metallurgy (PM) (Theunissen et al.1993; Ran et al. 2006; Zych and Haberko 2006). PIM of nano powder has the potential to mass produce complex and micro components. Rheological properties of the feedstock are important for PIM; the viscosity of the melt needs to be carefully controlled together with the solid loading. Reduced powder size is associated with more binder or higher viscosities. Reported works (Xie et al. 2005; Song and Evans 1995) mainly focus on rheological studies of nano powder feedstock. The scope of this project includes the de-agglomeration, solid loading, injection molding and debinding methods. These areas will be addressed in this report and a micro gear was produced successfully by μPIM.

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2 Experimental

2.1 Raw material

Y-TZP powder with average size of 50 nm is used in this study. It can be observed from Fig. 1 that the spherical

powder is narrowly distributed. Agglomeration is the critical problem of fine powder. De-agglomeration methods will be addressed in the following section.

2.2 Feedstock

Feedstock was prepared by double planetary mixer. Special binder compositions were formulated to impart flowability and moldability. The binder was first melted at 150°C followed by addition of powders in small consecutive loading. After reaching the desired solid loading, the feedstock was mixed at 30 rpm under vacuum for 1 h to increase the homogeneity. The blend was then allowed to cool down and mechanical crashed into fine granules.

2.3 Injection molding

PIM of mini tensile bars with green dimensions of 17 mm in length and thickness of 1.2 mm were first demonstrated. Scaling down to μPIM, a micro gear with 3 mm outer diameter and 20 teeth was selected. The mold insert was manufactured by high precision micro milling of harden steel with 56 HRC. PIM of mini tensile bar and micro gear were carried out using Battenfeld Micro Molding Machine.

2.4 Debinding and sintering

Multistep thermal debinding was adopted to remove the binder components progressively. A slow heating rate and long holding time are preferable to prevent defects such as blistering and slumping from occurring during debinding. As the debound parts were very fragile, the debinding was schedule with pre-sintering to 900°C. The specimens were isothermally sintered at 1500°C for 1 h. In this study, CM box furnace is used for both debinding and sintering. The thermal cycle is shown in Fig. 2.

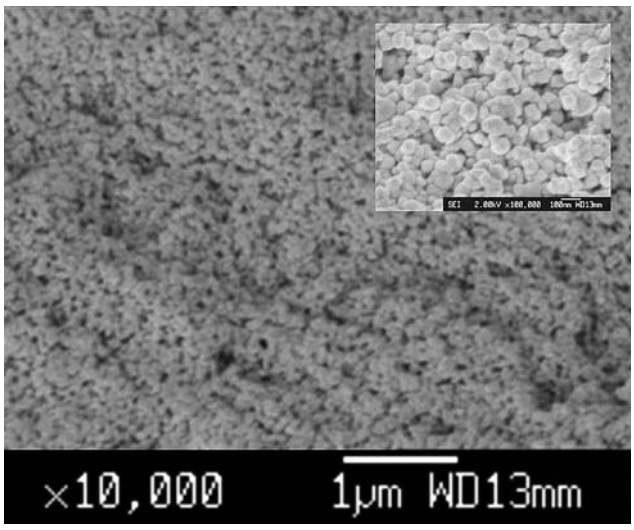

Fig. 1 Microstructure of nano-sized Y-TZP reveals the near mono-size distribution spherical particles, with the insert picture shows the average size is at about 50 nm

2.5 Characterizations

Sintered tensile bars were evaluated through linear shrinkage, density and Vickers hardness. The shrinkage percentage was measured through the dimensional change of green and sintered body, according to $\Delta L/L_o$ for both the length and thickness. The density was measured using Archimedes method. Vickers Hardness test was conducted using Mitutoyo Machine at 1 kgf load on polished surface. Sintered micro gear was visually inspected for defects and shaped retention.

3 Results and discussions

Although μPIM is an adaptation of PIM that comprises of the same processes of feedstock preparation, injection molding, debinding and sintering, the requirements for μPIM are far more stringent and require additional precautions. De-agglomeration, optimization of solid loading versus flowability, injection molding profile, demolding and debinding will be discussed in this section.

3.1 De-agglomeration

μPIM often involves powders in the submicron or even nano-meter range. Agglomeration becomes the first critical issue (Trunec and Hrazdera 2005; Bukaemskiy et al. 2006; Chen and Mayo 1993). Highly agglomerating powders lead to severe defects. Voids and cracks are clearly observed in Fig. 3a for specimens produced without the de-agglomeration step. Several attempts such as high compaction

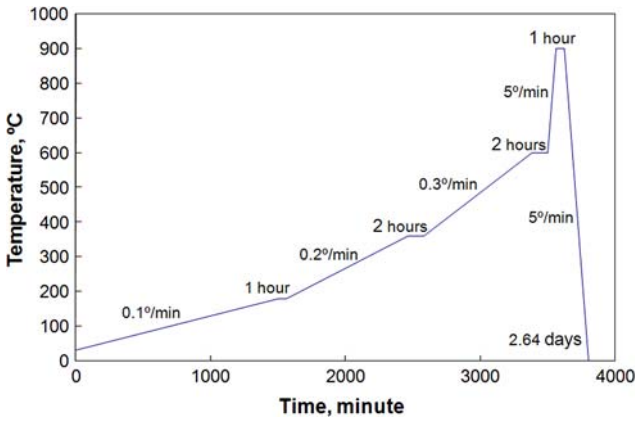

Fig. 2 Slow thermal debinding profile used in the report

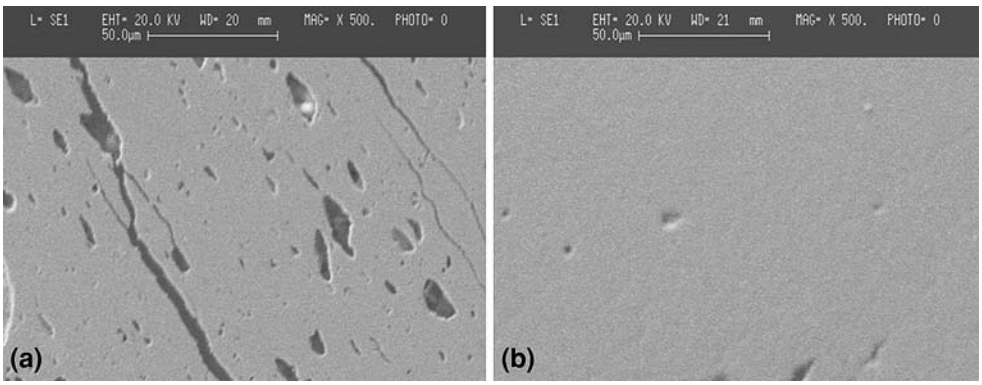

Fig. 3 Microstructure of compact from NANO powder (**a**) without and (**b**) with pre-heat treatment. The microstructure is improved significantly with heat treatment

pressure; high sintering temperature and duration; addition of binder and additives were unsuccessful in eliminating defects. Agglomerates form inter-particulate bonds that are strong enough to resist compaction pressure and remain as flaws. Several methods have been reported to be able to overcome agglomeration problem. Zhu and Fan (2005) pre-heated the powder to 500°C prior to pressing to remove the surface hydroxyl group, while Wu and Wei (2004) pre-heated the ball milled powder to 300°C. In this experiment, heat treatment to 150°C was used. Figure 3b shows tremendous improvement after heat treatment at 150°C for 1 h. The agglomerates' existence in fine powder is mainly induced by the presence of hydroxyl group when exposed to atmospheric moisture. The hydroxyl group creates attractive forces strong enough to flocculate the fine powder. Pre-heat treatment of the powder above 100°C evaporates the moisture that causes agglomerations. Slightly higher temperatures were used for heat treatment to compensate the efficiency of oven and also the possibility of impurities that increased the evaporation temperature of water.

3.2 Solid loading

Solid loading is the volumetric ratio between powder and polymeric binders. Scaling down powder size corresponds with the increase of total surface area per unit volume. This means the same viscosity is to be achieved by reduced solid loading. High powder contents are necessary in PIM samples to retain the shape. Reducing the solid loading will cause high shrinkage and possible shape distortion after sintering. Optimizing the solid loading and viscosity is thus critical. Typical solid loading for PIM falls around 60 vol.% (German and Bose 1997). Feedstocks with various solid loadings were prepared in comparison with commercially available BASF Catamold® TZP-F 106A feedstock. Figure 4 compares the properties of shrinkage, weight loss, density and hardness for various feedstocks. At

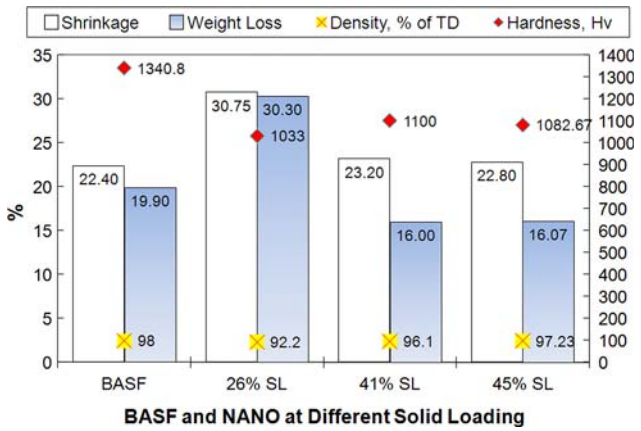

Fig. 4 Effect of the volumetric solid loading on properties of shrinkage, weight loss, density and hardness

26 vol.% solid loading, the high binder concentration assists in the injection process. However, the low solid loading is insufficient to retain its net shape with visible sink marks observed after sintering. A 45 vol.% solid loading was prepared to overcome this problem. Although the immediate purpose was achieved, the high viscosity impeded the injection process. A feedstock of 41 vol.% solid loading was then mixed and found to be optimum without sink marks with relatively smooth injection and increased hardness. A measure of 41 vol.% solid loading was hence defined as the critical solid loading for this 50 nm Y-TZP.

3.3 Injection molding

As the viscosity increased, injection molding becomes difficult. It is found that insufficient filling often occurs especially at micro features. As viscosity is temperature sensitive, the molding temperature has to be carefully controlled. Several degrees differences in the respective heating zones are observed to significantly affect the

Table 1 PIM temperature profile at different heating zones

Temperature (°C)	PIM of BASF	PIM of tensile bar	μPIM of micro gear
Mold	50	50	60
Nozzle	180	130	165
Front barrel	190	135	170
Rear barrel	190	140	170

moldability. Referring to Table 1, it is observed that temperature profiles vary with binder system, powder size and the complexity of the micro features. For the tensile bar, temperature profile for rear barrel/front barrel/nozzle/mold was 190/190/180/50 for conventional BASF feedstock and 140/135/130/50 for nano powder feedstock. With micro gear features, the temperature profile for later is increased to 170/170/165/60. PIM of micro gear using BASF feedstock was not successful due to the coarse powder size.

3.4 Demolding

Demolding is a step when shaped molten feedstock solidifies and ejects from the die. Demolding of the tensile bar was easy. Figure 5a shows the green and sintered tensile bars with the size relative to a paper clip. For μPIM, however, even with complete filling, defects can often generate during demolding. Adhesive force between the feedstock and micro-cavities can exceed the material strength resulting in incomplete demolding. The use of the variotherm mold is recommended to ensure complete filling of the micro features and high green strength for demolding (Loh et al. 2008). Fleischer et al. (2006) on the other hand suggested the development of a special ejection system with ejector pins of inner diameter 525 μm, surrounding the inner core of feature to ensure shape retention during demolding. In this study, the die set that is initially designed for plastic injection molding was modified by inserting a thin layer of plastic gear base into the mold cavity. With this support base the ejector pin transfers the force to the whole die cavities, promoting the ejection of the micro gear and teeth. Figure 5b shows the molded green parts with an attached layer of plastic gear that decomposed during heat treatment.

3.5 Debinding

Polymeric binders are the temporary vehicles for flowability. A proper debinding process is necessary to avoid defect formation (Hwang and Hsieh 1996). Several debinding methods were tested on the 26 vol.% feedstock, as depicted in Fig. 6, for the most desirable density and hardness. The solvent debinding process utilizes both heat and polymer dissolution to remove the binders. Oliveira et al. (2005) in particular studied solvent debinding kinetics for PIM specimens. Although solvent debinding can effectively shorten the debinding cycle, it was found to be less effective for small specimens as the turbulence produced by the solvent can be relatively strong to generate flaws. Surfaces were found to be severely cracked, and the resulting hardness was low. The wicking method adopts both thermal and absorbent effects. Samples subjected to wicking are submerged under an absorbent powder and

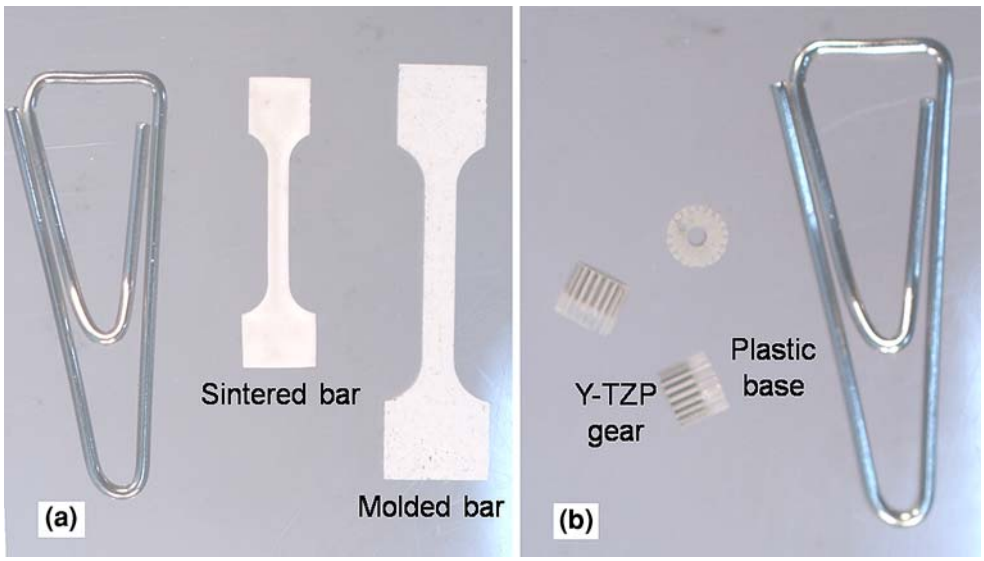

Fig. 5 Photographs showing (**a**) green and sintered tensile bar and (**b**) green micro gear with attached plastic gear base for ease of ejection. Specimen size is visually compared with a paper clip

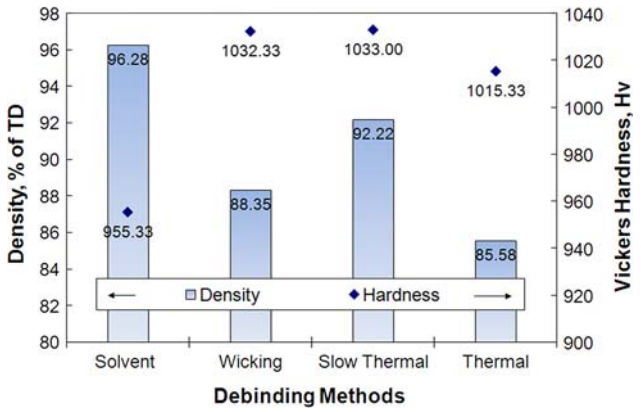

Fig. 6 Density and hardness as a function of debinding methods

subsequently heated in a furnace. The hardness of samples debound by this method is increased significantly. Slow thermal debinding processes heat up the sample in a furnace using a very slow heating rate, typically at a rate of 0.1°C/min. This method results in the best combinations of density and hardness. However, this method is extremely time consuming. Recently, Thomas-Vielma et al. (2008) reported an optimized 18 h thermal cycle for 0.8 μm alumina with high density polyethylene binder system. To speed up the process, another thermal debinding cycle with faster heating rate of 5°C/min was attempted. The sample was found to be more prone to defects as compared to that produced by the former. Hence, the slow thermal debinding is identified as the optimum debinding method and will be used subsequently. It is concluded that fine powders and features increased the difficulties of binder removal and the handling of the brown part. The debinding method that is used for coarse powder and macro parts is not suitable for nano powder and micro parts.

3.6 Characterizations

It is found that sintered samples experience isotropic shrinkage around 23% with 15% weight loss. Relative density was calculated based on theoretical density (6.06 g/cm^3) for tetragonal Zirconia. Near dense (>98%) tensile bar achieved hardness of 1121 Hv. Figure 7 shows the sintered 3 mm micro gear with 20 teeth. The gear teeth shrunk to about 73 μm after sintering. Visual inspection observed overall isotropic shrinkage and good shape retention with the gear teeth well defined. Injection molding of fine and complex features do not affect material properties. Vickers hardness of the micro gear yielded the same hardness as the tensile bar. The arrow in Fig. 7c pointed to the typical indentation of a Vickers hardness test. The well defined diamond shape without crack lines at the tips demonstrated the high hardness and toughness of the micro gear. As powder of at least one magnitude smaller than the micro features is necessary for good shape retention (Liu et al. 2001), the moldability and sinterability of 50 nm powder demonstrated in this report suggested that μPIM of features as small as 0.5 μm was feasible.

4 Conclusions

Micro-PIM (μPIM) of nano powder was found to differ from conventional PIM of coarse powders. In this study, the problems arising from μPIM have been addressed. The problem of agglomeration was resolved by pre-heat treatment. Special binder system with 41 vol.% of 50 nm Y-TZP powder was found to provide good dimensional control and flowability. Injection molding is temperature sensitive and complex shape demands higher temperature profile. Solvent debinding of small parts can be detrimental and thermal debinding at slow ramp rates is preferred. The production of micro gear with 50 nm powder suggests that micro features as small as 0.5 μm with interesting properties is possible in near future.

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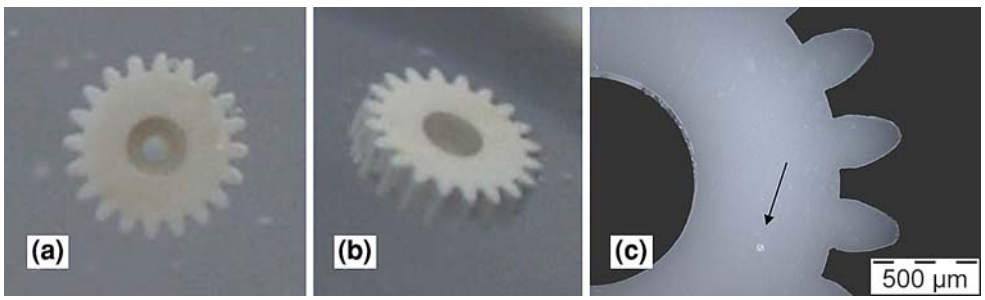

Fig. 7 Optical microscopic photographs showing (**a**) the top and (**b**) isometric views of a sintered micro gear revealing excellent shape retention, (**c**) shows well defined gear teeth and the arrow pointed an indentation mark of Vickers hardness test

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