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Advantages and Limitations of Using Nano Sized Powders for Powder Injection Molding Process: A Review

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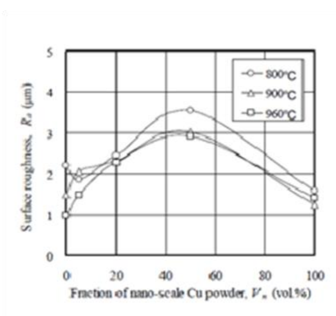
Graphical abstract



Abstract

Powder injection molding (PIM) is among the most known forming techniques that use material powders. This technique has been widely evaluated for the production of large scale and small components using metal and ceramic powders. Nano particles have larger surface-to-volume ratio compared with large-sized particles, thus they display high surface area. Some merits in the application of nano-sized particles in the PIM process includes increasing its comparative density at a low sintering temperature, decreasing sintering temperature, decreasing grain size of sintered bodies, increasing hardness value, and improving surface properties. However, it also has several disadvantages, which include increasing the viscosity behaviour of feedstock, oxidation, and agglomeration. This article reviews current studies on the effects of nano-sized particles on the PIM process and finding solutions to address its disadvantages.

Keywords: Nano sized powders; powder injection molding process; relative density; sintering temperature; surface properties

Abstrak

Proses pengacuan suntikan logam adalah proses yang amat berpotensi bagi menghampiri bentuk akhir. Pembentukan logam untuk struktur 3D yang komplek geometri, persis geometri disebabkan keupayaan pengeluaran dalam jumlah pukal, menyebabkan penjurangan secara mendadak kos seunit berbanding proses-proses yang lain. Kebelakangan ini, serbuk logam atau seramik yang bersaiz nano telak menarik minat penyelidik dalam PIM. Antara kelebihan menggunakan zarah bersaiz nano dalam proses PIM ialah dapat meningkatkan ketumpatan bandingan pada suhu pensinteran yang rendah, dapat mengurangkan suhu pensinteran dan saiz ira pada bahagian yang disinter serta dapat meningkatkan sifat permukaan. Tetapi disebabkan, kekurangan yang terdapat dalam proses ini ialah meningkatkan kelikatan bahan suapan, pengoksidaan dan pengaglomeratan. Justeru itu, objektif kajian ini adalah untuk mengkaji struktur perkembangan kesan bahan bersaiz nano terhadap proses PIM dan mencadangkan kajian dimasa hadapan bagi topik ini.

Katakunci: Serbuk bersaiz nano; proses pengacuan suntikan logam; ketumpatan relatif; suhu pensinteran; sifat permukaan

1.0 INTRODUCTION

Powder injection molding (PIM process) is a combination of plastic injection molding and conventional powder technology. It has five main sub processes, namely raw materials selection (powder/binder), feedstock preparation, injection molding, debinding, and sintering [1, 2]. During the process, the powder is mixed with a blend of diverse materials called a "binder" to form the "feedstock". After shaping the parts in the injection molding step, the binder is removed in the debinding process by either one or sequential combination of several procedures including solvent extraction, thermal degradation, or catalytic cracking. The particles are then welded together by sintering after the binder is completely removed to obtain the final product [3-7].

The prefix 'Nano' comes from the Greek word "Nanos" (meaning dwarf) and represents one-billionth of a unit (e.g. 1.0nm=10^{-9}m). A great impetus was given to the field of nanotechnology research by the groundbreaking speech of Richard Feynman, where he stated "there is plenty of room at the bottom" and discussed the possibility of controlling materials at atomic and molecular levels [8, 9]. A common question in the field of nanotechnology is, "If the material units are so small, how can they be very useful?" The answer depends on the application. In some applications, nano materials can be added to other materials, thus lending some of their unique properties to the overall performance of the composite [10].

A number of studies have focused on nano-particles(nanoparticles are sized between 100 and 1 nanometers)due to its strong potential for application in research fields and high technology industries. In this study, the advantages and disadvantages of using nano-sized powders in the PIM process are investigated. In addition, new methods for decreasing and removing the limitations on using nano-sized powders are reviewed.

■2.0 ADVANTAGES OF NANO-SIZED POWDERS IN THE PIM PROCESS

2.1 Increasing Relative Density At A Low Sintering Temperature

Sintering rate (densification rate) increases with the decrease of particle size and increase in sintering time. The effect of particle size on sintering is explained by Herring's scaling law as shown in Eq. 1:

$$\left(\frac{t_1}{t_2}\right) = \left(\frac{D_2}{D_1}\right)^m \qquad (1)$$

Where t (sintering time) and D (particle size) refer to particles 1 and 2, respectively, and m is the dimensionless scaling-law exponent [11, 12].

Based on equation 1, utilizing Fe powder with a diameter of about 50 nm, relative density bodies about 94% to 97% were achieved even at a range of low sintering temperatures (600°C to 700 °C), which are half of the normal sintering temperature. On the contrary, a Fe-sintered body using about 3 µm Fe powder displayed a relatively low density of about 93% at 1100 °C, which is lower than the value of the nano powder sintered at 600 °C. These results confirmed the view that nano-sized Fe powder can markedly decrease sintering temperature due to its high specific surface energy. Table 1 shows that the highest relative density for a 55(Fe–Ni)/45(binder) sintered at 900 °C was 99.5%. The contact distance between the powders after debinding was closer than that of the other compositions, resulting in denser sintered bodies via the sintering process [13, 14].

Studies have also focused on feed stock, which include BASF and Nano Yttria-stabilized zirconia (YSZ). These studies determined that Nano YSZ powders exhibited better homogeneity and sinterability at lower temperature because the surface area per volume of nano particle is high. The density of Nano YSZ was measured at 98%, whereas that of BASF was 95.6% at approximately 1100 °C. The high density indicates that Nano YSZ has reached intermediate sintering stage and that the material has acceptable strength. The density also decreased with large particles due to their slower sintering kinetics [15, 17].

2.2 Soaring Hardness Value And Decreasing Grain Size

The final grain size G depends on the peak sintering temperature, hold time, and initial grain size. The effects from porosity and pore drag are in conformity with the relation:

$$G = D + Kt^{1/3}\left(\frac{p_g}{1-p_s}\right)^{1/2} \exp\left(\frac{-Q_G}{T}\right) \qquad (2)$$

Where D is the initial particle size, K is a collection of material constants, t is the isothermal time at absolute temperature T, Pg is the fractional green density, Ps is the fractional sintered density, and Q_G is the activation energy for grain growth [17].

The grain size was more than 200 µm in diameter when approximately 3 µm Fe powder was used, whereas the grain size was about 0.5 µm in diameter when the nano-sized Fe powder was sintered at 700 °C. The hardness of the sintered bodies was inversely reduced as the grain size increased. Table 1 shows that the hardness increased from 75 Hv to 216 Hv (T= 600 °C and D = 50 nm) as the grain size decreased from 200 µm to 0.89 µm [13] .Nevertheless, studies on displayed Nano YSZ can be injection moulded and sintered to uniform microstructure with finer grain size and obtained compatible hardness about 836 *HV* at 1100 °C compared with commercial BASF via 451 *HV* [15].

Figure 1 shows that the initial 50 nm particles grew to 200nm because of unstable nano particle size. The nano particles have very high surface energy due to its high surface area-to-volume ratio. Nano particles will coalesce into a single large particle to minimize its surface energy to obtain a more stable stage [15].

Table 1 A summary of investigations using nano particles in PIM process.

Material	Powder Size(µM)	Sintering temperature(°c)	Sintering density(%)	Grain diameter(µM)	Hardness (HV)	Ref
Fe	0.05	600	94	0.89	216	**[13]**
		650	95.5	0.97	203	
		700	96.5	2.4	202	
	3	1100	93	200	75	
Fe-50%Ni	0.08	900	99.5	0.4	312	**[14]**
YSZ	0.05	1100	98	0.2	836	**[15]**
	BASF	1100	95.6	2	451	
3YSZ	0.1	1300	-	0.26	-	**[18]**
	0.4	1500	-	0.47	-	

The sample sets were manufactured with pure nano powder Yttria-stabilized zirconia (YSZ) is a zirconium-oxide based ceramic (10 nm to 100 nm); thus, the sintering temperature can be reduced to 1300 °C, resulting in a finer microstructure and smaller grain size of 0.26 and 0.32 µm compared with 0.47 µm at 1500 °C for submicron scaled 3YSZ (0.4 µm)[18].

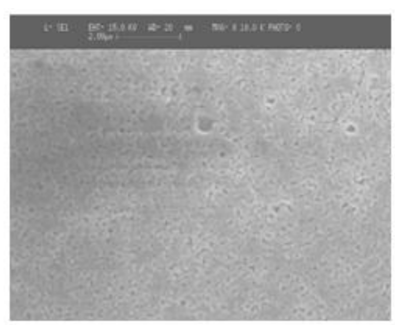


Figure 1 Micrograph of Nano YSZ sample after sintering 1100°c that shows uniform distribution of particles measured around 200 nm [15]

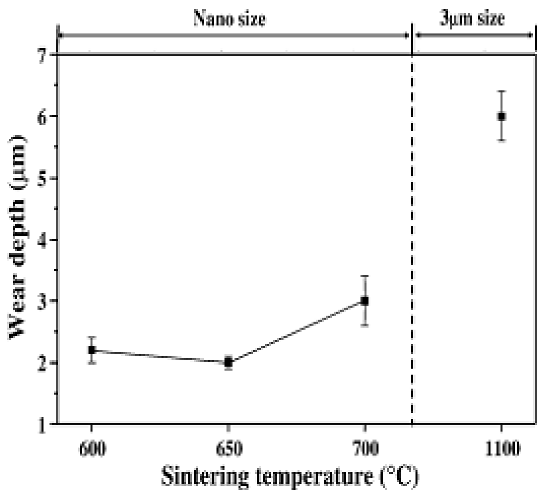


Figure 2 Wear depths of Fe sintered bodies using nano and about 3 μm powders after wear test depending on the sintering temperature [13]

2.3 Improving Surface Properties

Using finer metal powders is one of the solutions to the issues of dimensional accuracy and better surface property control, which are significant considerations in μMIM products. Finer metal powders are also expected to inhibit grain growth by reducing the sintering temperature [19, 20].

a) *Wear depth:* Figure 2 demonstrates that the wear depth of Fe-sintered bodies decreased as the particle size of raw Fe powders and grain size of sintered bodies decreased because of decreasing sintering temperature. Utilizing nano powder sintered at 650 °C resulted in a minimum value of wear depth of about 2.1 μm due to its comparatively high relative density of 96% and fine crystalline size of 0.97 μm, whereas the powder with 3 μm had about 6.2 μm at 1100 °C [13].

b) *Surface roughness:* The surface roughness of the sintered part created from the nano powder was around 280 nm. On the contrary, the 3 μm in diameter metal powder produced surface roughness of around 400 nm to 500nm [21]. Figure 3 shows that surface roughness deteriorated significantly in the hybrid powder with a large amount of nano-scale powder addition because of a sintered shrinkage mismatch between the micro- and nano-scale powders. However, surface roughness was modified for a full nano-scale powder specimen due to finer and homogeneous particles [19].

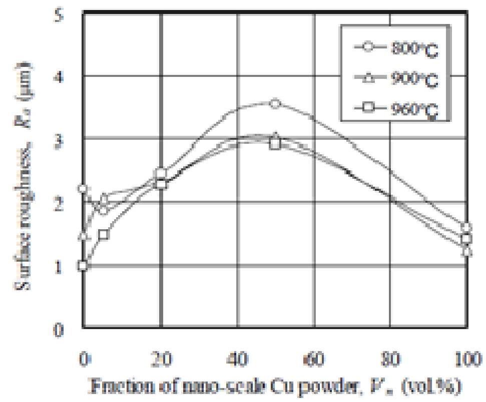


Figure 3 Surface roughness of sintered parts via adding Cu nano powders [19]

3.0 LIMITATIONS OF NANO SIZED POWDERS ON THE PIM PROCESS

3.1 Agglomeration

Agglomeration is the first critical problem in the PIM process. Agglomerates shape inter-particulate bonds that are strong enough to resist compaction pressure and remain as defects. Several methods have been reported to address agglomeration. For instance, powder was preheated to 500 °C prior to pressing to remove surface hydroxyl group, and ball milled powder was preheated to 300 °C and 150 °C. Figure 4 (b) shows the improvement obtained after heat treatment at 150 °C for 1 h. Existence of agglomerates in the fine powder is mainly induced by the presence of hydroxyl group when exposed to atmospheric moisture. The hydroxyl group produces attractive forces that are sufficiently strong to flocculate the fine powder. Pre-heat treatment of the powder above 100 °C evaporates the moisture-causing agglomerations. Slightly higher temperatures were utilized for heat treatment to compensate for the efficiency of the oven and the possibility of impurities increasing the evaporation temperature of water [22-24].

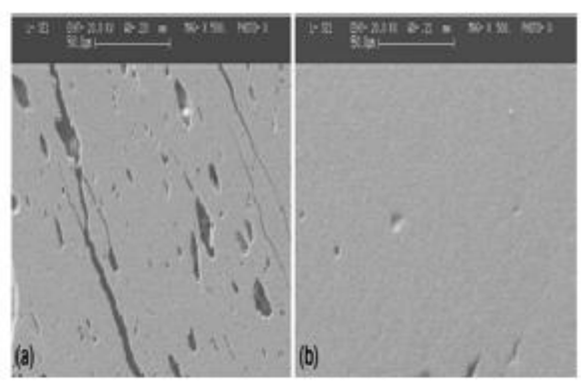


Figure 4 Microstructure of compact from nano powder (a) without and (b) with pre-heat treatment [24]

3.2 Oxidation of the Nano-Sized Metal Powder During Process

One significant problem in the PIM process using nano powders is the oxidation of nano particles having high surface area. Hanyang Educational Institute suggested a method that involved coating a binder to the nano-sized metal powder to inhibit the explosive oxidation of the nano-sized metal powder and improve the complete compaction of the product. The first step in manufacturing below 100 nm-sized metal fine particles involves applying electric currents that alternated periodically in direction and magnitude with time, supplying a small amount of alkali metal ions into a container filled with at least one water or organic solvent, and concurrently arranging at least two metal electrodes in the container. The second step involves the addition of an organic binder for powder injection molding into the container that had passed through the first step. The third step involves solving the added organic binder and mixing it with the fine particles uniformly. The final step involves pulverizing the organic binder and fine particle mixture in the container after removing the water or organic solvent from the container [25, 26].

Mixing the nano powders with binders in the mixing step utilizes temperature higher than 100 °C. Nano powders could burn in such temperatures, thus, they should always be fed below 100 °C during the mixing to prevent burning [21]. For instance, stainless steel nano powders were mixed with binder below 100 °C to prevent burning. Mixing temperature can then be increased to achieve the desired temperature after the nano powder has been covered by the binder [27].

■4.0 CONCLUSIONS

The advantages of using nano powders in the PIM process include an increase in comparative density at low sintering temperature, a decrease in sintering temperature, reduction in the grain size of sintered bodies, an increase in hardness, and improvement in its surface properties. Its limitations include oxidation of nano-sized metal powder and agglomeration. These limitations can be overcome by coating a binder to the nano-sized metal powder, mixing the nano-sized metal powder and the binder solution, and then wet-milling simultaneously and pre heating ball milled powders to remove the surface hydroxyl group.

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