INJECTION MOLDED TUNGSTEN HEAVY ALLOY ①

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ABSTRACT 97W-2Ni-1Fe heavy alloy feedstocks with different powder loadings were prepared for injection molding. The rheological behavior of these feedstocks was studied. The mechanical properties of as-sintered parts and the shrinkage during sintering were measured. The results showed that the rheological behavior of these feedstocks could be described as pseudoplastic fluid. The mechanical properties of the injection molded alloy are superior to those of alloy prepared by conventional press/sinter process. There is an optimal powder loading 47% (volume fraction) with the best mechanical properties. The shrinkage during sintering is isotropical and the tolerances of products are small.

Key words injection molding heavy alloy powder loading

1 INTRODUCTION

Metal Injection Molding (MIM), which is derived from plastic injection molding, is a kind of newly developed powder metallurgy forming process. It has the advantage of direct forming metal or ceramic parts with complex shapes. Furthermore, the products prepared by MIM processes can avoid the density gradient in conventional press/sinter process due to the feedstock's uniform filling into mold[1-3].

Tungsten heavy alloy parts are widely used in fields of medical instruments, ordnance industry and scientific experiment apparatus etc[4, 5]. With the development of the technology, the requirement for tungsten heavy alloy parts with more and more complex shapes is increasing. The cost of machining after press/sinter has become too high for these kinds of complex shaped tungsten heavy alloy parts. The occurance of metal injection molding processes provides a way to solve the problem. Because the tungsten powder used in MIM processes is the same as that used in press/sinter processes, the heavy alloy MIM parts have the cost effectiveness compared to low alloy steel parts and stainless steel parts produced by MIM processes. In this paper, 97W-2Ni-1Fe heavy alloy feedstocks with different powder loadings were prepared for injection molding. The MIM standard tensile bars, and a kind of cartridge cores were prepared.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The powders used in the experiment were elemental tungsten, iron and nickel powder. Their characteristics are shown in Table 1. The binder components were polystyrene (PS), polypropylent (PP) and vegetable oil(VO).

Table 1 Characteristics of metal powders

	Particle size / μm	Apparent density / (g·cm^{-3})	Tap density / (g·cm^{-3})	Shape	Impurity/ %		
					C	O	N
W	2.9	3.64	6.00	Irregular	0.02	0.005	-
Ni	2.6	0.75	1.95	Spherical	0.1	0.3	0.1
Fe	4.0	1.64	2.99	Spherical	1.5	1.5	0.3

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W, Ni and Fe powders were premixed in a V type mixer in a weight ratio of 97∶2∶1. The basic binder was composed of PS, PP, VO in a weight ratio of 50∶30∶20. The feedstocks were produced by mixing the binder with premixed powder in a LH60 roller mixer for 4 h. The powder loadings were 45, 47, 50 and 55(volume fraction, %) for feedstock F1, F2, F3 and F4 respectively.

2.2 Injection molding, debinding and sintering

MIM parts were injection molded on a SZ-28/250 injection molding machine at 185 ℃ after granulation on a LSJ 20 plastic extruder. The debinding was divided into two steps. First, the as-molded parts were immersed into dichoromethane for 2~3 h to remove PS and VO. After drying for 1 h, the subsequent debinding and sintering were carried out in a hydrogen atmosphere. The sintering was performed at 1530 ℃ for 2 h. MIM standard tensile bars recommended by MPIF, and a kind of cartridge cores were prepared by this MIM process, and conventional press/sinter 97W-2Ni-1Fe tensile bars were prepared by press/sinter process for comparison.

2.3 Properties determination

An Instron 3211 capillary rheometer was used to measure the viscosities of feedstocks. It had a diameter D of 1.27 mm and a length L of 76.2 mm, giving a ratio L/D of 60. The tensile properties of as-sintered MIM tensile bars and P/M tensile bars were determined on an Instron material tester. The shrinkage of the cartridge core after injection and sintering was measured.

3 RESULTS AND DISCUSSION

3.1 Rheological properties of feedstocks

In MIM processes, the rheological properties of the feedstock are key features which influenced the steady flow and the uniform filling into the mold. The evaluation of rheological properties of the feedstock was based on the viscosity of the feedstock and its shear sensitivity and temperature sensitivity. The viscosities of the feedstocks F2 are shown in Table 2. The viscosity data indicated the flowability of the MIM feedstocks. The lower the value of viscosity, the easier it is for a MIM feedstock to flow. It could be found from Table 2 that the viscosity of the feedstock decreased with the icrease of shear rate and the increase of temperature, which accorded with the pseudoplastic behavior. For a pseudoplastic fluid, there is

$$\eta = k\dot{\gamma}^{n-1} \qquad (1)$$

where η is the viscosity, $\dot{\gamma}$ is the shear rate, k is a constant, n is a flow behavior exponent < 1. The value of n indicates the degree of shear sensitivity. The lower the value of n, the more quickly the viscosity of the feedstock changes with shear rate. Injection molding of MIM feedstocks is conducted under pressure and temperature. It is desirable that the viscosity of MIM feedstocks should decrease quickly with increasing shear rate during injection process. This high shear sensitivity is especially important in producing complex and delicate parts which are leading products in MIM industry. Plotting log viscosity stress against log shear rate as in Fig. 1, values of n of 0.409, 0.423, 0.458 at the temperature of 170, 180, and 190 ℃ respectively could be determined.

Table 2 Viscosities of the feedstock with the powder loading of 47% (Pa·s)

Temperature/ ℃	Shear rate/ s^{-1}					
	3.543	11.81	35.43	118.1	354.3	1181
170	1761	1028	604.9	318.5	112.4	47.94
180	1588	924.9	454.9	246.6	107.6	47.28
190	1216	962.0	446.9	170.9	161.3	39.71

The dependence of feedstock viscosities on temperature can be expressed by an Arrhenius equation[6],

$$\eta(T) = \eta_0 \exp(E/RT) \qquad (2)$$

where E is the flow activation energy, R is the gas constant, T is temperature, η_0 is reference viscosity. The value of E experesses the influence of temperature on the viscosity of MIM feedstocks. If the value of E is low, the viscosity is not so sensitive to temperature variation, then any small fluctuation of temperature during injection molding will not result in a sudden viscosity change that can cause undue stress concentrations in the molded parts, resulting in cracking and distortion. On the condition that the shear rate is 1 181 s^{-1} which fell in the normal range of shear rate during injection molding of MIM feedstocks, by plotting the logarithm of viscosity against the reciprocal of temperature, as in Fig. 2, the flow activation energy of feedstocks could be determined. $E = 16.1$ kJ/mol.

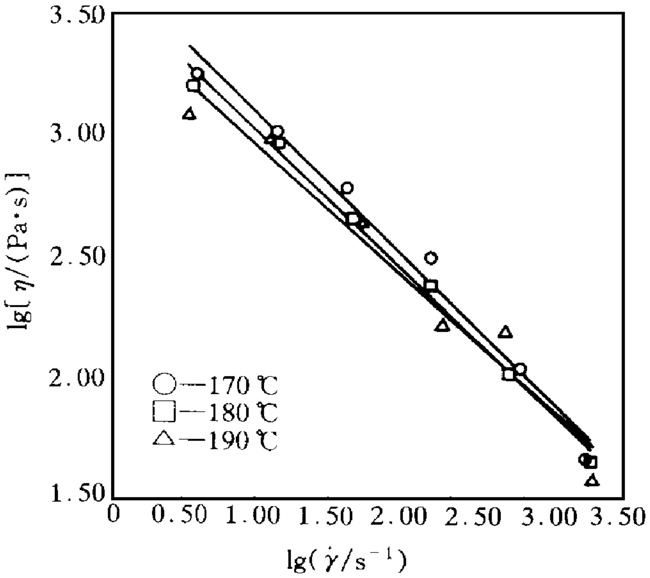

Fig. 1 Correlation of viscosity and shear rate

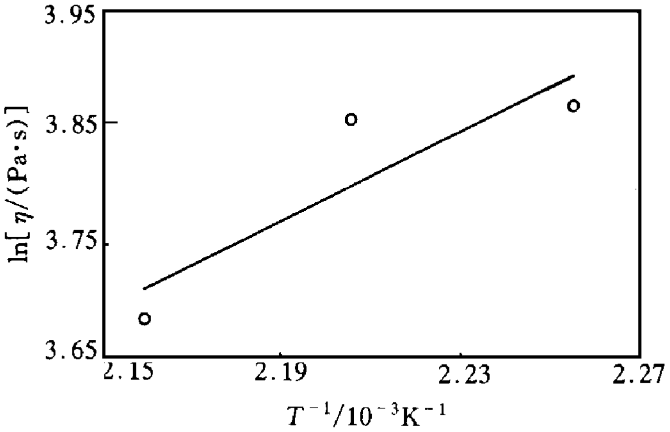

Fig. 2 Correlationof viscosity and temperature

3.2 Mechanical properties of injection molded tungsten heavy alloy

The ultimate tensile strength (UTS), elongation, hardness and density of MIM tensile bars prepared by feedstocks with different powder loadings are shown in Fig. 3. It could be seen from Fig. 3 that the ultimate tensile strength first increased with the powder loading and achieved the highest point at 47% powder loading. Then, it decreased with the further increase of the powder loading. The value of the elongation and the hardness of the MIM tensile bars were also the highest at 47% powder loading. The density continuously increased with the powder loading. Fig. 4 shows the optical photograph of the tungsten heavy alloy prepared by feedstocks with different powder loading.

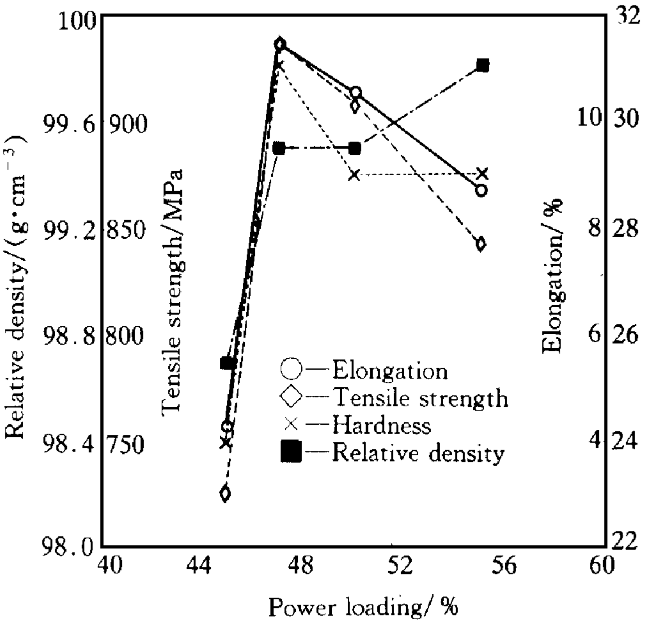

Fig. 3 Correlation of the mechanial properties and powder loading

The extent of densification during sintering heavily influenced the mechanical properties of powder metallurgy products. The densification of injection molded parts with low powder loadings during sintering was difficult. The density of 97W-2Ni-1Fe alloy prepared by feedstock F1 was only 98.7 percent of the theoretical density (TD), whereas the alloy prepared by feedstock F2 achieved 99.5% TD. The difference of the density contributed to the differences of the mechanical properties. The UTS, elongation and hardness of the alloy prepared by feedstock F2 were higher than the alloy prepared by feedstock F1. On the other hand, although the sintered parts had a higher density and lower porosity with the higher powder loading, but the grain was coarse, because of the shorter migration distance and the higher sintering rate. It could be seen from Fig. 4 that the grain size increased with the powder loading at the same sintering temperature and the same holding time. The density of sintered MIM tensile bars was 99.5%, 99.6% and 99.8% TD for the powder loading of 47%, 50% and 55% respectively. It indicated that the density only increase slightly from 47% to 55% powder loading. But the grain size increased from 40 μm to 80 μm when powder loading increased from 47% to 55%. This was the main cause of the decrease in the UTS, elongation and hardness properties with the powder loading increasing from 47% to 55%. Another possible cause for the decrease of mechanical properties was the heterogeneous distribution of binder in molded parts with high powder loading, which resulted in non-uniform shrinkage during debinding and sintering and resulted in stress concentrations.

Table 3 shows the mechanical properties of the parts prepared by MIM process and press/sinter process. It could be found that the mechanical properties of MIM samples were superior to those of press/sinter samples at the same sintering schedule. Fig. 5 shows the fracture surfaces of these samples. The fracture of press/sinter samples was the typical intergranular fracture dominated by the fracture at tungsten-tungsten interfaces, while that of MIM samples was the

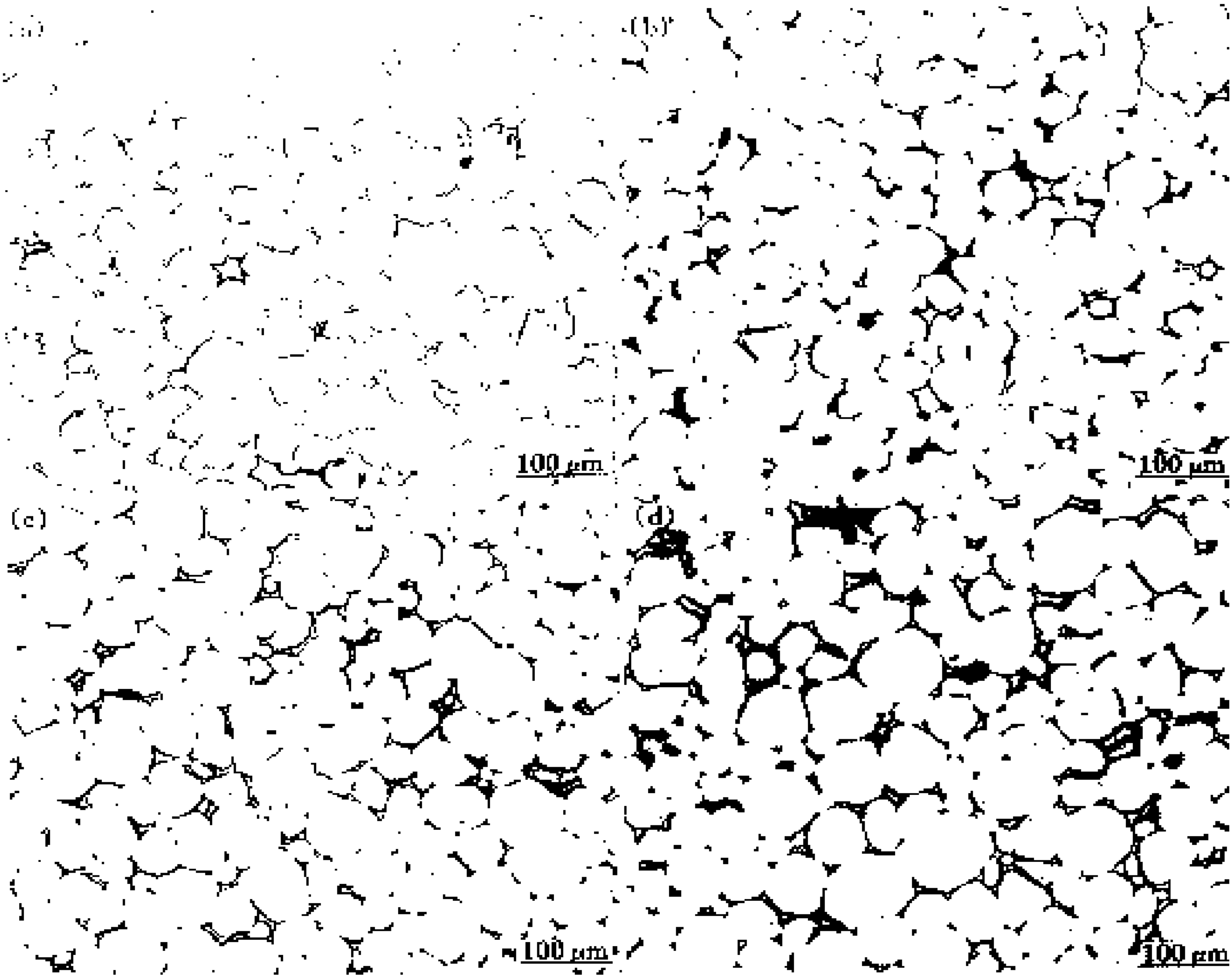

Fig. 4 Optical photographs of 97W-2Ni-1Fe alloy prepared by feedstocks with different powder loadings
(a) —45%; (b) —47%; (c) —50%; (d) —55%

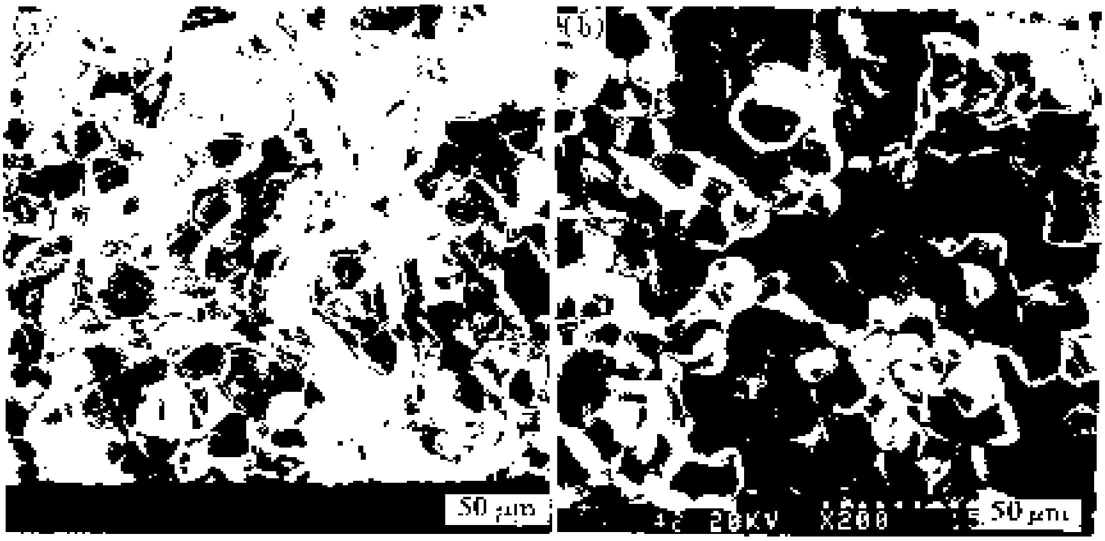

Fig. 5 SEM photographs of tensile test bars fracture surfaces
(a) —MIM; (b) —Press/ sinter

Table 3 Mechanical properties comparison of parts prepared by MIM process and press/ sinter process

Process	σ_b/ MPa	$\sigma_{0.2}$/ MPa	δ/ %	HRC
MIM	936	649	11.4	31
Press/ sinter	604	524	3.0	24

mixture of intergranular fracture and transgranular frature. Parts of cracks passed through tungsten grain, which caused in tungsten grain cleavage, resulting in high ductility and strength.

The tungsten-tungsten interfaces was the most possible place for the crack initiation. Decreasing the tungsten grain contiguity was an effective way to increase the mechanical properties of tungsten heavy alloy, especialloy for 97W-2Ni-1Fe alloy with high tungsten content. Compared to conventional press/ sinter process, there was an additional wet mixing of powders with organic binders at elevated temperatures for MIM process. This wet mixing made tungsten powder dispersed more uniformly due to the addition of the large volume of organic binders and surface agents, which avoided the gravity segregation in the dry mixing step of press/ sinter process. The nickel, iron, and fine tungsten powders dispersed uniformly around large tungsten powder, which formed uniform liquid phase around tungsten grains during sintering. It was probably the reason that the mechanical properties of MIM parts were superior to that of press/ sinter parts.

3.3 Dimensional tolerance

The schematic figure of the cartridge core is shown in Fig. 6. The shrinkage rates of several main dimensions for the cartridge prepeared by feedstock F2 are shown in Table 4.

From Table 5, it was seen that although there was some differences in shrinkage rate of each dimension, but the deviation of dimensions was very low. The shrinkage rate difference for different dimension should be taken into considering the design of MIM toolings.

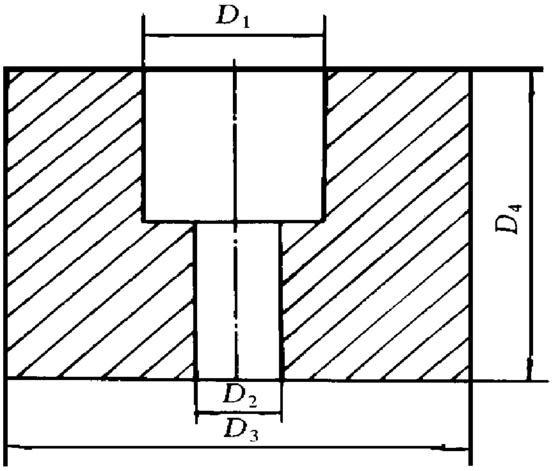

Fig. 6 Schematic figure of cartridge core

Table 4 Shrinkage rates of several main dimension

	D1 (Big hole)	D2 (Small hole)	D3 (Outer diameter)	D4 (Height)
As-molded/ mm	3. 85	1. 80	9. 70	7. 75
As-sintered/ mm	3. 02	1. 41	7. 60	6. 06
Shrinkage rate/ %	21. 56	21. 67	21. 65	21. 80
Deviation of dimension/ mm	±0. 01	±0. 01	±0. 02	±0. 02

4 CONCULSIONS

(1) The viscosity of the feedstock decreases as the non-newtonian shear rate increasing. The rheological behavior of the feedstock can be discribed as psudo-plastic fluid because the power index n that is in formutation: $\eta = k\dot{\gamma}^{n-1}$ is less than 1.

(2) 97W-2Ni-1Fe heavy alloy had optimal mechanical properties that the yield strength, the tensile strength, the elongation and the hardness reach 649 MPa, 936 MPa, 11. 4% and HRC31, respectively, when the powder loading of feedstock is 47%.

(3) The wet mixing makes tungsten powder dispersed more uniformly due to the addition of the large volume of organic binders and surface agents, which avoid the gravity segregation in the dry mixing step of press/ sinter process, the nickel, iron and fine tungsten powders disperse uniformaly around large tungsten powder, which form uniform liquid phase around tungsten grains during sintering. It is probably the reason that the mechanical properties of MIM parts are superior to those of press/ sinter parts.

(4) The shrinkage rate of MIM parts during sintering is isotropical and the deviation of as-sintered parts' dimension was very small.

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