Effect of Ni and Ni$_3$Al Additions on Sintering of Molybdenum Powders

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Sintering of molybdenum powders normally requires very high temperatures to obtain high achieved densities. A small addition of pure nickel powders, however, not only lowers the sintering temperature of Mo but also remarkably increases its sintered density. For example, a 2 mass% addition produces a 94% achieved density even at one-half of the homologous temperature for Mo, the achieved density strongly depending on the sintering temperature. The sintering proceeds quickly with a lower activation energy (143 kJ/mol) compared to the Mo bulk diffusion energy, and the entire sintering is accomplished in a rather short period of time.

On the other hand, when Ni–10 mass% Al powders mostly comprised of an f.c.c. Ni$_3$Al phase are added, the sintering temperature is further lowered compared to the case of Ni addition, and the achieved density is greatly increased at a much higher rate. The activation energy for densification (104.8 kJ/mol) is less than that obtained by adding Ni.

A Mo–5 mass% (Ni–10 mass% Al) powder mixture sintered at 1573 K exhibits excellent flexural and tensile strengths at ambient temperature. The tensile strength of 880 MPa at room temperature is reduced by only 9% even at 773 K, suggesting a possible application of this material at elevated temperature.

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I. Introduction

Molybdenum is known as a metal difficult to be sintered, and its powders are normally sintered by passing current at and above 2500 K. A significant amount of work has been carried out to obtain high-density sintered products at lower temperatures. It is known that the addition of elemental metal powders such as Au, Pt, Pd and Ni into Mo powders results in achieving higher densities even at temperatures as low as 1573 K. The effect of Ni, Fe and Co additions was also confirmed by one of the present authors.

In this study, the effect of Ni addition on sintering of Mo is re-examined from a different point of view of Ni as a sintering promoter. A light is shed to a Ni-Al alloy system as the additive to Mo. It can be expected to be a sintering promoting agent since the Ni$_3$Al phase predominantly existing in a Ni–10 mass% Al Alloy has an f.c.c. crystal structure and a lattice parameter (0.35655 nm) similar to pure Ni (0.35167 nm). Since sintered Mo with Ni$_3$Al powders exhibits a significant improvement in sintered density, its mechanical properties are also evaluated at ambient and elevated temperatures.

II. Materials and Experimental Procedures

Molybdenum powders were obtained from Nippon Tungsten Co. that have the mean particle size of 4.3 μm; nickel powders from INCO, type-124 of 4–7 μm mean particle size; water-atomized Ni–10 mass% Al powders from Japan Atomizing Co., the exact composition and mean particle size being 10.26 mass% Al and 10.63 μm, respectively. This alloy is supposed to have 98.8 mass% Ni$_3$Al (from Ni–Al binary phase diagram), and was confirmed by X-ray analysis.

Pure Mo powders and powder mixtures of Mo and Ni and Ni$_3$Al were weighed and placed in a metal die with the inner wall surface lubricated with an ethanol-zinc stearate solution prior to pressing. Cylindrical cold-compacts (11.28 mm in diameter) were made by uniaxially applying a 490 MPa external force. Then, the cold compacts were sintered in a vacuum of less than 10$^{-3}$ Pa at temperatures for periods.

The sintered density was measured using Archimedes technique, and the microstructure was observed under SEM along the longitudinal section at the center of a sintered body. The same cross-section was used for the area analysis by EPMA operated at 20 kV and 0.03 μA to determine the constituent diffusion and compound decomposition from the concentration distribution profiles for respective elements.

The mechanical properties of Mo sintered with Ni$_3$Al addition, among other characteristics, were the major concern in this study. Test specimens were prepared by cold-pressing the powder mixture with an external pres-
sure of 490 MPa and sintered at 1573 K. Flexial strength test was conducted by a 3-point bending at a cross-head speed of 0.05 mm/s on the Shimazu Autograph (Instron type screw-driven machine) for the specimens having a dimension of 10 mm width, 10 mm thickness and 55 mm length. Cylindrical tensile specimen was prepared by machining from a sintered block of 10 mm × 10 mm × 90 mm to have a gauge section of 5 mm in diameter and 80 mm in length with two gripping ends of 8 mm in diameter. Tensile tests were conducted on Shimazu Autograph at a cross head speed of 0.05 mm/s from ambient temperature to 1173 K in air. Also, micro Vickers hardness measurements were carried out with a 0.98 N load for a holding time of 30 s on a polished cross section cut along the longitudinal direction of a sintered block.

III. Results and Discussion

1. Sintering of Mo powders mixed with Ni powders

Figure 1 shows the achieved density versus sintering temperature for a 3.6 ks holding time for pure Mo powders, compared to Mo mixed with 2 mass% Ni powders. Both powders were cold-pressed to have the same green density of 70%. It is clearly seen that a 2 mass% addition of Ni powders to Mo exhibits a significant increase in achieved density with increasing sintering temperature. The Ni-mixed powder reaches to a relative density of 94% at 1573 K (a half of the homologous temperature for Mo). Especially in a temperature range of 1573–1623 K, the densification rate is quite high, and the sintered density reaches 98% at 1673 K even after a short sintering time, 3.6 ks. Further increase in sintering temperature does not appear to promote further increase in sintered density for Ni-mixed powders, while pure Mo needs much higher temperatures to attain higher sintered densities.

SEM micrographs are shown in Fig. 2 for Mo–2 mass% Ni mixed powders sintered in the temperature range from 1373 to 1673 K for 3.6 ks. Although the bonding of powder particles can be clearly recognized at 1373 K, the growth of powder particles is rather insignificant up to 1573 K and the pore shape is irregular. At 1673 K, however, the particle growth is quite significant, the enclosed pores being of a round shape. Further increase in sintering temperature appears not to increase sintered density anymore.

The increase in sintered density strongly depends on temperature, as seen in Fig. 1. However, high sintered densities after 3.6 ks sintering suggest that sintering in Ni-mixed powders may proceed in a rather short period and at a higher rate. So, the influence of holding for a long period may not be as great as that of the sintering temperature itself. The sintered density was measured as a function of the holding time, for 0.3, 0.6, 1.2 and 3.6 ks. Figure 3 depicts the sintered densities for pure Mo powders and Mo powders with a 2 mass% Ni addition versus sintering time as a function of the sintering temperature. These sintering temperatures were chosen so that the effect of the holding time could be clearly observed. Molybdenum powder compacts show rather limited increases in density at these sintering temperatures, while Mo–2 mass% Ni mixed powder compacts exhibit sharp increases in density in the first 0.3 ks at all the temperatures, and then they saturate at the asymptotic densities approximately after 1.2 ks at much higher levels compared to those for pure Mo. Namely, a small addition of Ni powders contributes to a very swift densification of Mo powders in a shorter time at lower temperatures.

Since the increase in the sintered density with time is parabolic in Fig. 3, it is expected that the densification

\[ \Delta \rho = (\rho_s - \rho_p) \times t^B \]

where \( B \) is a constant \((<1)\). Accordingly, the densification is plotted against time in a log-log scale in Fig. 4. It is clearly seen that the relationship is almost linear except for the data point at the longest time and the slope \( B \) has temperature dependence as described by

\[ \log(\Delta \rho) = A + B' \log(t) \]

where \( A \) and \( B' \) are constants. This dependence of \( B \) on temperature may be related to an Arrhenius equation

\[ B' = K \exp\left(-\frac{Q}{RT}\right) \]

where \( K \) is a constant, \( Q \) is the activation energy for densification, and \( R \) and \( T \) are gas constant and absolute temperature, respectively. In Fig. 5 the logarithm of the densification rate, \( B' \) is plotted against the reciprocal of temperature, and the data points align on a single straight line. From the slope of the curve, the activation energy
Fig. 2 SEM micrographs for the Mo-2 mass% Ni mixed powder compacts sintered at indicated temperatures for 3.6 ks.

Fig. 3 Sintered density for pure Mo powders and mixed Mo-2 mass% Ni powders sintered indicated temperatures is plotted against sintering time.

Fig. 4 Densification is plotted against the holding time in a log-log scale for a Mo-2 mass% Ni powder mixture as a functional of temperature.

...can be calculated to be 143 kJ/mol for the sintering process of Mo powders mixed with a 2 mass% addition of Ni powders. The activation energy of 143 kJ/mol currently obtained is significantly smaller than that for Ni diffusion into Mo (269.4 kJ/mol) so that it is considered that other diffusion mechanisms than a simple bulk diffusion may be simultaneously taking place. Further research will be conducted to clarify this situation.
2. Sintering of Mo powders with Ni<sub>3</sub>Al powder additions

Powder mixtures of Mo with either Ni–3 mass% Al (Ni<sub>3</sub>Al 39.1%), Ni–10 mass% Al (Ni<sub>3</sub>Al 98.8%) or Ni–20 mass% Al (Ni<sub>3</sub>Al 88.4%) alloy powders were prepared for the mixture to have 0 to 5 mass%Ni in total and sintered at 1573 K for 3.6 ks. The sintered density is plotted in Fig. 6 against the total Ni content added as Ni–Al alloys powders. An increase in the total Ni content results in an increase in the sintered density in all mixtures. But the increase in rates, when Ni–10 mass% Al and Ni–20 mass% Al alloys are added, are greater than that when Ni–3 mass% Al alloy powders are added. At any values of the total Ni content, the densification appears to be strongly influenced by the Ni:Al ratio in the additive alloy, leading to the speculation that the total content of Ni<sub>3</sub>Al in the alloy predominantly influences the densification. Accordingly, Fig. 7 is reproduced to show the relation between the sintered density and total concentration of Ni<sub>3</sub>Al for three different additive alloys for sintering at 1573 K for 3.6 ks. It is clearly seen that the densification curves for three different alloys' additions are indistinguishable. It is then concluded that the Ni<sub>3</sub>Al phase existing in Ni–Al alloys' powders, as the additive to Mo powders, really plays an important role in its densification.

Figure 8 shows the densification behavior of Mo with a 5 mass% addition of Ni–10 mass% Al alloy powders (mostly Ni<sub>3</sub>Al). The densification rate is much higher and quickly saturate in a short time of sintering (1.2 ks), compared to the case of pure Ni additions to Mo powders (Fig. 3). The saturation level depends on sintering temper-
ature but it is greater than 96% of theoretical even at 1623 K before 1.2 ks. The densification is plotted in Fig. 9 against sintering time in a log-log scale for three temperatures. Then the densification rate in a log-scale is plotted in Fig. 10 against the reciprocal of sintering temperature. Three data points at three sintering temperatures align on a straight line, and the activation energy for the sintering process can be calculated from the slope to be 104.8 kJ/mol. This value is about 30% less, compared to the activation energy obtained for a Mo–2 mass% Ni powder mixture.

The sintering process is featured in SEM micrographs shown in Fig. 11 for a Mo–5 mass% (Ni–10 mass% Al) that has been sintered isochronally for 3.6 ks at respective temperatures. The sintering at 1373 K has already produced good particles' bonding. The particle growth becomes apparent even at 1473 K while that was not obvious at the same temperature for a Mo–2 mass% Ni mixture (Fig. 2). Compared to a Mo–2 mass% Ni case, the particle growth is significant even at 1473 K, and at and above 1573 K it becomes almost saturated. The other significant feature observed on the fracture surfaces of a Mo–mass5% (Ni–10 mass% Al) mixture in Fig. 11 (especially at 1573 and 1673 K) is appearance of small dimples that indicate the ductile nature of transgranular fracture. This was not observed for a Mo–2 mass% Ni mixture in Fig. 2, and it appears to be due to the existence of Ni₃Al phase in the additive. The element distributions in a Mo–5 mass% (Ni–10 mass%Al) mixture sintered at 1523 K for 3.6 ks were examined using EPMA. Figure 12 shows a SEM micrograph and element characteristic images of Mo, Ni and Al. Mo has penetrated into the Ni-rich particle, while diffusion of Ni atoms into Mo particles can be seen, too. Also the Al distribution is not confined within the Ni-rich particle but also found in Mo particles as a result of Mo diffusion into this compound particle. Accordingly, it is considered that the sintering of Mo powders was promoted by the mutual diffusion of Mo into Ni₃Al and Ni and Al into Mo. However, further research will be conducted to make clear this situation in future.

3. Mechanical properties of sintered Mo with Ni₃Al alloy powder addition

The results of bending test for Mo–x mass% Ni and Mo–x mass% Ni₃Al sintered at 1573 K for 3.6 ks are shown in Fig. 13, where the flexial strength is plotted against the total addition of Ni, in mass%. A huge increase in flexial strength is observed when a 5 mass% of Ni–10 mass% Al is added to reach a maximum of about 900 MPa followed by a gradual decrease. On the other hand, the effect of Ni addition on increasing the flexial strength is less significant to reach a maximum of only approximately 300 MPa at 2 mass% addition again followed by a gradual decrease. A gradual decrease in flexial strength beyond the maximum may indicate that any excess amount of additive powders would not improve the sintered density since the amount of Mo diffusion into them is simply temperature dependent. A big difference in the maximum flexial strength does not appear to be due to the difference in the achieved density (96% for Ni₃Al versus 94% for Ni). But it may be due to a difference in the sintered structure (substantial particle growth in Ni₃Al mixture versus premature growth in Ni mixture). This significant particle growth by Ni₃Al addition may be a result of the two-way diffusion of Mo into Ni₃Al and Ni and Al from Ni₃Al into Mo (refer to Fig. 12).

Figure 14 shows the results of tensile and hardness testing for Ni₃Al addition as a function of the total Ni content. The trend in tensile and hardness increases is very similar to that seen in the flexial strength (Fig. 13). The maximum are observed at 5 mass% addition followed by very slight decreases in tensile strength and hardness. An increase in the amount of Ni–10 mass% Al to Mo beyond
5 mass% does not appear to contribute to the strength of the sintered compact, but the high strength observed here may be due to cohesivity between Mo and additive particles and deformability in the additive matrix. Also, a substantial increase in ductility is observed beyond 3 mass% addition and the attained ductility of about 3% is sustained beyond 5 mass% addition. This may be due to the ductility observed in the additive particles (Fig. 11).

The sintered density of Mo has been greatly improved by adding Ni₃Al to result in higher strength and some ductility. Ni₃Al itself is known for high strength at elevated temperatures. Thus, it is expected that the addition of Ni₃Al would improve high-temperature strength of Mo.

Figure 15 compares the tensile strengths and ductilities of wrought and recrystallized Mo and sintered Mo–5 mass% (Ni–10 mass% Al) at temperatures from ambient to 1173 K. Sintered Mo–5 mass% (Ni–10 mass% Al) exhibits a very small decrease in tensile strength up to 573 K followed by a little steeper drop beyond 773 K (9% drop from the ambient strength). But even at 1173 K, it still sustains a tensile strength of 550 MPa (63% of the ambient strength) which is as 3.7 times higher as the strength of recrystallized Mo at 1173 K. It appears that Ni₃Al inhibits the grain growth of Mo to sustain the sintered strength while recrystallized Mo loses its strength by grain growth. Therefore, Mo sintered with Ni₃Al may find a
possible application at elevated temperatures. The elongation was achieved 3% at 273 K. It was remarkably lower than that of recrystallized Mo and decreased with elevated temperature.

The Ni addition of only 2 mass% lowers the sintering temperature of Mo and significantly improves the sintered density. For example, a 94% sintered density could be attained even at one-half of the homologous temperature of Mo. The sintering proceeds quickly with a lower activation energy (143 kJ/mol), compared to the activa-
Effect of Ni and Ni₃Al Additions on Sintering of Molybdenum Powders

Fig. 15 Tensile strength at elevated temperatures of wrought and recrystallized Mo and sintered Mo–5 mass% (Ni–10 mass% Al).

The activation energy associated with Mo diffusion into Ni (269 kJ/mol).

When Ni–Al alloy powders were mixed with Mo, sintering of Mo was further promoted to result in lowering the sintering temperature and accelerating the densification rate. For example, a sintered density of 95% could be attained at 1623 K after about 1 ks. This pronounced effect can be signified by a lower activation energy of 104 kJ/mol (a 30% reduction from that for a 2 mass% Ni addition) for the sintering process due to the enhanced diffusion of Mo into Ni₃Al and counterdiffusion of Ni and Al from Ni₃Al into Mo.

A 5 mass% addition of Ni–10 mass% Al to Mo produced, by sintering at 1573 K, excellent flexural and tensile strength at ambient temperature. The tensile strength of 880 MPa at room temperature is reduced by only 9% even at 773 K and a further increase in temperature to 1173 K results in a 35% reduction of the ambient strength (3.4 times as high as the strength of recrystallized Mo). The results indicate a possible application of this material at elevated temperatures.

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REFERENCES