ACTIVATED SINTERING OF TUNGSTEN AND MOLYBDENUM POWDERS

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The sintering of powder compacts to a relative density of 85-90% necessitates the use of high temperatures (0.7-0.8 T_m). At such temperatures, metal atoms are highly mobile, and diffusion-viscous flow of material is the main mechanism of densification of powder compacts. However, sintering is very often performed at temperatures below 0.7 T_m, while activated sintering is possible even below 0.5 T_m. At such temperatures, the values of the coefficients of self-diffusion and mutual diffusion are low, and the rates of material transport by the diffusion-viscous mechanism constitute a fraction of the observed rates of densification.

In the present investigation an attempt was made to compare the degree to which diffusion takes place during the sintering of specimens and the degree of densification of specimens. A mixture of tungsten and molybdenum powders was selected for study; up to 0.5 wt. % nickel was added to the mixture of activate sintering, since it is known that such an addition of nickel leads to active sintering of both tungsten and molybdenum [1].

The systems W-Ni and Mo-Ni have similar properties, and the following is known about them: Both W and Mo dissolve in nickel with the formation of solid solutions (up to 40% W and 37% Mo). Nickel forms eutectics with both tungsten (at 1495° C) and molybdenum (at 1350° C) [2]. At these temperatures the eutectics contain up to 0.8% Ni. As temperature is lowered, the solubility of nickel decreases. The coefficients of volume diffusion into nickel are $D = 1.13 \exp (73{,}000/RT)$ for tungsten [3] and $D = 1.6 \cdot 10^{-3} (50{,}900/RT)$ for molybdenum [4]. The coefficients of diffusion of nickel into these metals are not known, but qualitative evaluations have indicated that the permeation of nickel into W and Mo is negligible [1, 5]. Thus, the W-Ni and Mo-Ni pairs exhibit pronounced unipolar diffusion.

The system W-Mo forms a continuous series of solid solutions in both the liquid and solid states.

The following experiments were performed. Specimens compacted from a mixture of W and Mo powders (50 vol. %) were impregnated with an aqueous nickel nitrate solution in amounts calculated to introduce up to 0.5 wt. % Ni into the specimens. They were then annealed for 1 h at 600° C to reduce the nickel. Specimens from the pure mixture were sintered for 2 h at 1200° C and for 1 h at 1800° C. Specimens from the nickel-containing mixture were sintered at 1200° C. For comparison, pure tungsten and molybdenum specimens were sintered at 1200° C.

Both before and after sintering, the relative density of specimens was determined and profile diagrams of the lines (321) were recorded. Photography was performed in a URS-50I apparatus, using monochromatized copper radiation. The results obtained are presented in the table and figures.

Change in Relative Density of Specimens after Sintering

Specimen composition	Sintering temp., °C	Sintering time, h	Initial rel. density, %	Rel. density after sintering, %
Pure tungsten	1200	2	60	60
Pure molybdenum	1200	2	65	70
Tungsten + molybdenum ..	1200	2	52	65
Tungsten + molybdenum + nickel	1200	2	52	90
Tungsten + molybdenum ..	1800	1	54	85

Mean values of three results are quoted.

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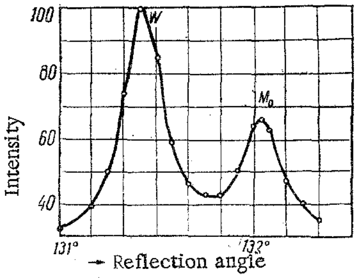

Fig. 1. Profile diagram of lines (321) of specimen after sintering of 1200° C. Relative density of specimen 65%.

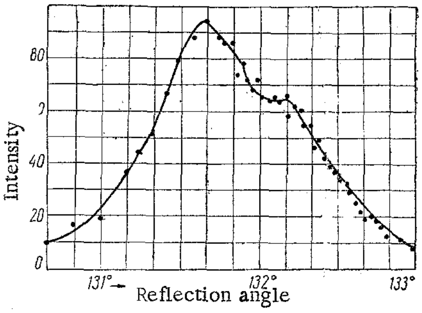

Fig. 2. The same as for Fig. 1, after sintering at 1800° C. Relative density of specimen 85%.

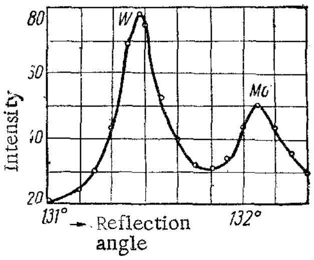

Fig. 3. Profile diagram of lines (321) of specimen with nickel addition after sintering at 1200° C. Relative density of specimen 90%.

As can be seen from the table, a relative density of 90% may be attained at 1200° C by adding nickel to the specimen. At this temperature neither the pure powders nor their mixture exhibited such a degree of densification. It was only at 1800° C that the relative density of the powder mixture reached 85%. The coefficient of self-diffusion of tungsten and molybdenum atoms at 1200° C does not exceed 10^{-20}–10^{-22} cm^2/sec. These values are too low to enable diffusion-viscous flow to secure a significant densification of the specimen. At 1800° C, the coefficients of mutual diffusion of W and Mo are $2.30 \cdot 10^{-8}$ and $3.80 \cdot 10^{-9}$ cm^2/sec, respectively [7]. At such values of the coefficients of diffusion, a solid solution is formed between W and Mo. This claim is fully supported by profile diagrams of the lines (321) (Figs. 1 and 2).

Figure 1 presents line profile diagrams obtained for compacts from the powder mixture before and after sintering at 1200° C; the lines virtually coincided. The maxima of the tungsten and molybdenum lines were distinctly separated, the distance between them being equal to the value obtained from tables, namely, an angle of 37' [8]. Figure 2 shows a line profile diagram for a specimen sintered at 1800° C. As can be seen from the shape of this curve, a W-Mo solid solution forms at this temperature; the maxima are no longer clearly divided, and the distance between them has decreased. Figure 3 illustrates a line profile diagram for a sintered specimen with a nickel addition. Although the relative density of the specimen was 90%, the shape of the curve indicates that no solid solution has formed, and the distance between the distinct maxima has remained unchanged (37'). The results obtained demonstrate that material transport during densification at high temperature takes place by the diffusion mechanism.

It is apparent that mutual diffusion processes enable compacts to attain a relative density of 85% at 1800° C. In fact, calculations showed that the time required for the consolidation of a specimen from 65 to 85% relative density at 1800° C by the mechanism of diffusion-viscous flow without allowing for mutual diffusion is 200 h. The method of calculation was the same as in [9], while the coefficient of viscosity for the mixture was calculated by the method proposed in [10]. Calculation was performed on the assumption that tungsten and molybdenum do not react with each other during sintering. The block size was determined experimentally and found to be $4.0 \cdot 10^{-5}$ cm; the surface tension was computed by Pines' method [11].

The values of the coefficients of diffusion at 1800° C, employed in the calculation, were: $D = 1.0 \cdot 10^{-12}$ cm^2/sec for tungsten and $D = 6.8 \cdot 10^{-12}$ cm^2/sec for molybdenum. These values are some four orders of magnitude smaller than the coefficients of mutual diffusion. Because of this difference between the coefficients of diffusion and also as a result of boundary diffusion, the rate of densification of W-Mo specimens is substantial at 1800° C. The sintering of a mixture of tungsten and molybdenum under these conditions is diffusional in character, as indicated by the formation of a solid solution.

During sintering with a nickel addition, the process exhibited no diffusional characteristics. In spite of the high degree of densification (to 90% relative density), the shape of the profile of the lines (321) pointed to an absence of a solid solution in the sintered specimen.

On the basis of data available for the systems W-Ni and Mo-Ni it may be expected that a virtually unipolar diffusion of tungsten and molybdenum into nickel must be a source of a large quantity of excess vacancies. Their concentration will greatly exceed, as a result of diffusion, their equilibrium level. Excess vacancies may be annihilated through coalescence into microvoids (caverns). Both excess vacancies and caverns promote vacancy climb at relatively low temperatures [6], the process taking place at stresses below the yield stress of the material. Such a growth and climb of dislocation loops as a result of vacancy absorption was observed in zinc, in which excess vacancies were formed in consequence of the diffusion of zinc into an oxide layer undergoing nucleation [13]. In addition, excess vacancies may be annihilated on dislocations, and, at a sufficient degree of supersaturation with vacancies, this process must lead to a continuous evolution of dislocations capable of limited slip [12]. It is, in fact, these processes that will cause the material to yield. During the sintering of W-Mo specimens with an addition of nickel, this appears to be the principal mechanism of densification.

CONCLUSIONS

1. The sintering of specimens from a mixture of tungsten and molybdenum powders takes place by the diffusion mechanism at temperatures at which the values of the coefficients of mutual diffusion attain 10^{-9}-10^{-8} $\mathrm{cm}^2/\mathrm{sec}$.

2. An addition of up to 0.5% nickel activates the sintering of W-Mo specimens at 1200° C and enables a relative density of 90% to be attained after holding for 1 h.

3. During the activated sintering of W-Mo specimens, no solid solution formation was observed. It is probable that the dislocation mechanism is chiefly responsible for densification during activated sintering.

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