The Thermally Activated Solid Solution Hardening
of the Ternary System: Nb-Mo-W

by

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Abstract

The temperature dependence of the flow stress of ultra-high vacuum degassed Nb-Mo-W single crystals has been investigated between 77 and 900 K. Tests of alloys containing up to 9.4 at/o (Mo+W) show that the thermal component of the flow stress exhibits little or no increase with increasing ternary solute content for most of the alloys tested. Solid solution softening is observed in the Nb-4.2 Mo-W alloys at 77 K. The results are interpreted utilizing a phenomenological analysis of the solid solution hardening of ternary alloys in terms of binary alloy hardening increments. The analysis of the results suggests that a non-random solute distribution is responsible for reducing the thermal activated flow stress component, especially in concentrated alloys in which the Mo to W ratio is near unity.

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INTRODUCTION

Low temperature deformation behavior of bcc ternary alloys has been studied in detail only in those systems in which at least one of the solutes is an interstitial type. Little is known about the thermally activated deformation of substitutional solid solution ternary alloys. Ulitchney, Vasudevan, and Gibala¹ report low temperature yield stress results for three Nb-1.7Re-Mo alloys; the results suggest a small solid solution softening effect may occur, but the data is not conclusive.

The purpose of this study is to examine the thermal component of the flow stress for a series of high purity Nb-W-Mo alloy single crystals. The Nb-W-Mo system is attractive for several reasons. Unlimited solubility of the components is reported.² The W and Mo atoms possess similar atomic size and misfit parameters and therefore have nearly the same obstacle strength to dislocation motion, resulting in similar hardening rates per solute addition in binary Nb alloys.^{3,4} Such behavior permits use of a straightforward analysis⁵ of solid solution hardening of the ternary Nb-W-Mo alloys in terms of binary alloy (Nb-Mo and Nb-W) hardening increments. Finally, athermal solid solution hardening of Nb-W-Mo has been studied by Mizia and Koss,⁵ and the interpretation of their athermal results has implications pertinent to the present investigation.

EXPERIMENTAL

Single crystals of the Nb-W-Mo alloys had specimen axes near the [421] direction. In order to minimize the complications due to interstitial effects, the alloy single crystals were given an ultra-high vacuum ($\sim 5 \times 10^{-10}$ torr) degassing treatment at approximately 2575 K for ten hours. Following the degassing heat treatment, the specimens were cooled rapidly by radiation. Chemical analysis indicates that the (O+N) interstitial content is about 100-160 ppm (atomic) with no dependence on substitutional content. The following alloys were tested: Nb-2.1Mo-3.1W, Nb-1.9Mo-5.2W, Nb-4.4Mo-3.0W, and Nb-3.9Mo-5.5W (compositions are atomic percent). All mechanical tests were performed in compression at an axial strain rate of $1 \times 10^{-4} \text{ sec}^{-1}$.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the concentration dependence of the difference flow stress between 900 K and either 298 K or 77 K ($\tau_{298} - \tau_{900}$ or $\tau_{77} - \tau_{900}$). The data is plotted as flow stress differences because the flow stress at 900 K is essentially athermal,⁵ and thus $\tau_{298} - \tau_{900}$ or $\tau_{77} - \tau_{900}$ may be regarded as the thermally activated component of the flow stress. All data were obtained at axial strains between about 1 and 4%, and the shear stresses were calculated assuming maximum resolved shear stress slip, which is observed at 900 K.⁵ No significant change in slip plane is observed for the sample re-strained at low temperatures.

Fig. 1. The concentration dependence of the flow stress differential between 77 or 298 K and 900 K for (Nb-Mo)-W single crystals.

Fig. 2

The concentration dependence of the flow stress differential between 77 or 298 K and 900 K for (Nb-W)-Mo single crystals.

In order to present the data in terms of constant W or constant Mo contours, small adjustments have to be made to the composition of the alloys tested and to the experimentally observed flow stresses. A method⁶ of successive approximations was used, and composition adjustments resulted in flow stress changes of always less than 5%. For example, the Nb-3.0W-4.4Mo was adjusted to Nb-3.1W-4.4Mo (for purposes of Fig. 1), and the value of $\tau_{77} - \tau_{900} = 23.4$ changed to $\tau_{77} - \tau_{900} = 23.6 \text{ kg/mm}^2$.

The results in Figs. 1 and 2 show that the ternary alloys exhibit a small but positive rate of hardening per ternary solute addition at 298 K. However at 77 K, little or no ternary hardening is observed with the exception of one alloy (Nb-5.2W-1.9Mo). Solid solution softening is actually observed at 77 K in the Nb-4.2Mo-W alloys. Among the alloys tested, only the Nb-5.2W-1.9Mo alloy shows an appreciable flow stress increase upon the addition of the ternary (Mo or W) element to the binary alloy (Nb-W or Nb-Mo, resp.). The data from this alloy is the cause of the different appearance of Figs. 1 and 2.

The thermally activated deformation behavior presented in Figs. 1 and 2 is in direct contrast to the rapid rate of hardening per solute addition that Mizia and Koss⁵ observed in the same Nb-W-Mo alloys at 900 K. Thus while the athermal component of the flow stress increases rapidly with ternary solute content, the thermally activated component shows little or no increase for most of the alloys tested. However,

the low temperature behavior of the Nb-1.7Re-Mo alloys is similar in that a small amount of solid solution softening is observed, and this is followed by a small (when compared to binary Nb-Mo) increase of the flow stress with increasing Mo content.¹

Figs. 1 and 2 also show that the dependence of the flow stress on solute concentration is nearly linear for both the binary Nb-Mo and Nb-W alloys.^{3,4} The rate of hardening per solute addition is about the same for the Nb-W as for the Nb-Mo alloys. It is reasonable to assume that in Nb alloys, Mo and W atoms possess nearly identical strengths as obstacles to dislocation motion and thus cannot be distinguished from each other by the dislocations. This is not surprising since both Mo and W are electronically similar, about 5% smaller than Nb, and elastically much stiffer by a comparable degree than Nb (see Table II of ref. 3).

A phenomenological analysis has been presented for ternary alloy hardening in terms of binary alloy hardening increments for the case in which solute atoms are of equal strength.⁵ The analysis replaces the Mo and W atoms with equivalent atoms whose concentration C_{MoW} is equal to the total solute concentration in the ternary alloy or $C_{MoW} = C_{Mo} + C_W$, where C_{Mo} and C_W are the atomic fractions of Mo and W, resp. Because Mo and W possess equal obstacle strengths, the equivalent atoms also will have the same strength and should result in the same hardening behavior (similar harden-

ing rate and concentration dependence) if the distribution of solute atoms in the ternary alloy is the same as in the binary alloy. The ternary solid solution hardening behavior should thus be that of a concentrated binary alloy. For the concentrations considered, this means that for the thermally activated solution hardening of a ternary alloy, the increment in flow stress $\Delta\tau_3^*$ has the same form as the athermal stress⁵ or:

$$\Delta\tau_3^* = K(C_{Mo} + C_W)^{1.0} = \Delta\tau_{Mo}^* + \Delta\tau_W^* \quad (1)$$

where K is the hardening rate per unit solute (which is the same as in the binary alloys), C_{Mo} and C_W are the Mo and W concentrations in the ternary alloy, and $\Delta\tau_{Mo}^*$ and $\Delta\tau_W^*$ are the thermally activated components of the solution hardening increment due to Mo and W in binary Nb alloys.

The rule of mixtures relationship expressed in eqn. 1 means that the ternary data in Figs. 1 and 2 should be displaced to higher stress but parallel to the binary alloy data. Agreement between predicted behavior (eqn. 3) and observations is adequate at 298 K for total solute concentrations of less than about 7%. At both 298 K and the Nb-5.2W-1.9Mo alloy does not behave anomalously but rather behaves according to predictions. The other alloys all show much less thermally activated solution hardening than expected from eqn. 1.

The deviation between predicted and observed behavior is shown in Fig. 3 for both the athermal component (900 K)

Fig. 3

The difference between the thermal component of the flow stress at 77 K ($\tau_{77} - \tau_{900}$) or the athermal 900 K yield stress (τ_y) and the yield or flow stress (τ_3 or $\Delta\tau_y^*$) predicted from eqn. 1 plotted as a function of the fraction of the solute atoms which are Mo atoms in the Nb-Mo-W alloys tested.

and the thermally activated component of the flow stress at 77 K. The most significant feature is small but definite positive deviation at 900 K at large total solute concentrations (>6 at.%) (reflecting the rapid rate of athermal hardening), which is accompanied by a large negative deviation at 77 K (which reflects the little or no increase in thermal component upon ternary solute addition for most of the alloys). Both deviations increase with increasing total solute content, the thermal component deviating much more rapidly. Fig. 3 shows that the maximum deviation occurs at a C_{Mo}/C_W ratio of about one. Thus, the "ideal" behavior of the Nb-5.2W-1.9Mo alloy may be a result of the small ratio of C_{Mo}/C_W .

A rapid rate of athermal hardening at large solute concentrations is observed not only in Nb-W-Mo⁵ but also in Nb-W-Hf alloy single crystals.⁶ The athermal strength of concentrated Nb-W-Hf crystals is sensitive to heat treatment even though second phase precipitates are not expected and are not observed by transmission electron microscopy techniques.⁶ A non-random solute distribution, sensitive to heat treatment at least in the Nb-W-Hf alloy, was suggested as the cause of the observed rapid athermal hardening in these alloys,^{5,6} and the low temperature behavior of the Nb-1.7Re-Mo alloys. In the ternary alloys in which at least one of the solutes is an interstitial, a non-random solute distribution in the form of solute association is likely to be the cause of solid solution softening in Nb and Ta alloys.^{1,7-9}

The present low temperature data also suggest that solute association occurs and is especially important in affecting the thermal component of the flow stress. The solute association may take the form of Mo-W rich zones or might change any local or short range ordering already present. Fig. 3 implies that such association is maximum at a C_{Mo}/C_W ratio of about one, and that the degree of association increases with increasing solute content.

A comparison between athermal and thermal activated deformation behavior is also consistent with the concept of non-random solute distribution. As solute association sites form, they slowly create obstacles to dislocation motion whose interaction is sufficiently long range to preclude thermal activation. Hence, athermal hardening occurs and is more rapid than expected but only is observed at large solute concentrations ($C_{Mo} + C_W \gtrsim 6$, See Fig. 3) where the site density or strength is sufficiently large. However, the athermal hardening occurs at the expense of the thermal component. The change in solute distribution prevents (or "scavenges") some Mo and W atoms from forming barriers which are overcome by thermal activation.

Thus athermal hardening is accompanied by a decrease in the thermally activated flow stress (see Figs. 1, 2, and 3). The data in Fig. 3 suggests that the solute redistribution process occurs at small ternary solute concentrations affecting the thermal component much more quickly than the athermal component.

SUMMARY

The low temperature flow stress of a series of high purity Nb-Mo-W alloy single crystals shows little or no increase with increasing ternary solute content. Solid solution softening is observed in the Nb-4.2Mo-W alloys deformed at 77 K. An analysis of the ternary alloy behavior in terms of binary alloy hardening increments suggests that a non-random solute distribution, probably in the form of solute association. The association sites or zones are responsible not only for a rapid increase in athermal hardening⁵ but also cause a reduction of the thermally activated flow stress component, possibly by a "scavenging" process of Mo and W atoms. The rapid athermal hardening and the decrease of the thermally activated component is most pronounced in concentrated alloys in which the Mo to W ratio is near unity.

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