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EFFECT OF ANODIC OXIDE FILMS ON LOW TEMPERATURE MECHANICAL BEHAVIOR OF NIOBIUM SINGLE CRYSTALS

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EFFECT OF ANODIC OXIDE FILMS ON LOW TEMPERATURE MECHANICAL BEHAVIOR OF NIOBIUM SINGLE CRYSTALS

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ABSTRACT. The effect of thin ($\lesssim$ 1500Å) anodic oxide films on the mechanical behavior of single crystals of niobium at low temperatures ($T \lesssim 0.15T_M$) was investigated. Oxide films affect mechanical behavior in two ways: the yield stress is reduced and the stress-strain curves are serrated over an appreciable range of strains. When oxide-coated specimens are also prestrained into stage I at 300°K, the serrations observed at low temperatures disappear, the flow stress is further reduced, the ductility is increased, and a three-stage work hardening behavior occurs. A model involving generation and motion of non-screw dislocations from the oxide-metal interface is used to explain the results.

1. BACKGROUND

The mechanical behavior of bcc metals at temperatures T below $\sim$ 0.15 of the melting temperature T_M is characterized by several important features: (a) a large (often $\geq$ 30-fold) increase in flow stress as $T \to 0$°K; (b) a sharp decrease in ductility over the same temperature range; (c) a pronounced asymmetry of slip [1]. These and other related features can be explained in terms of two important strengthening mechanisms: dislocation-interstitial solute interaction and intrinsic lattice (Peierls-Nabarro) strengthening.

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The tetragonal distortion of an interstitial solute in bcc crystals interacts strongly with both screw and edge dislocations. The screw dislocation-interstitial interaction causes a very rapid change in yield stress at low temperatures with just small ppm-level additions of interstitial in solid solution [2]. This interaction affects all of those features mentioned above. However, of greater importance is the fact that bcc metals have large temperature-dependent intrinsic flow stresses at low temperatures. There is at least a 20-fold difference in yield stress of unalloyed niobium tested at 300°K and at 77°K [2-4].

The intrinsic contribution to the strength of bcc metals has been successfully rationalized in terms of a high Peierls-Nabarro stress of screw dislocations [1]. The core of the screw dislocation has a characteristic three-fold symmetry arising from its localized dissociation into three non-coplanar partial dislocations on intersecting {112} or {110} planes. There are no such complicated core structures of edge and mixed dislocations, and their high mobility permits microstrain deformation at stresses much lower than the macroscopic yield stress [5]. Thus the plastic flow of bcc metals is understood in terms of a two-dislocation model: non-screw dislocations move easily at relatively low stresses and give mainly microstrain deformation until they are exhausted into the screw orientation. Thereupon macroflow commences and is controlled by the movement of comparatively immobile screw dislocations at much higher stresses.

The preceding discussion suggests that the macroflow stress of bcc metals at low temperatures could be very low if it were possible to avoid deformation effected by the movement of screw dislocations. We have investigated this possibility and have found such a method of altering the basic dislocation dynamics of bcc metals. The method involves injection of a high density of mobile non-screw dislocations into a bcc metal by prestrain at temperatures $T \gtrsim 0.15T_M$ coupled with the introduction of an efficient multiplication source of non-screw dislocations, viz. a thin, highly self-stressed surface oxide film [6].

The remainder of this paper reports details of the experiment and several results on niobium single crystals. We have also obtained identical results on tantalum [3,4].

2. EXPERIMENTAL METHODS

The experimental procedures to prepare high purity single crystals of niobium have been reported in detail elsewhere, cf. [2-4]. The crystals are $\sim$ 2.6mm diam. and $\sim$ 13mm long with the tensile axis oriented parallel to [321] for single slip. The 300°K/4.2°K resistivity ratio of the crystals is $\sim$ 2000. All mechanical testing was done in tension at a resolved shear strain rate of 5.5×10^{-4} sec^{-1}.

It is well-known that prestrain of bcc metals at temperatures $T \gtrsim 0.15T_M$ introduces mainly non-screw dislocations and can enhance the extent of microstrain by non-screw dislocation movement at $T < 0.15T_M$ [1,5,7]. For niobium, 300°K is a convenient "high" prestrain temperature. If the prestrain is limited to stage I deformation in crystals oriented for single slip, one obtains predominantly edge dislocations in various dipole and multipole configurations [8].

It is also well-known that deposition of surface films, particularly oxides on metallic substrates, introduces large stresses in the films and in the substrate by epitaxy and by stresses associated with misfit dislocations [6,9]. That large stresses are generated by surface oxides on niobium has been demonstrated by Pawel and Campbell [10]. They observed extensive bending, corresponding to stresses well above the low temperature flow stress, of thin ($\sim$0.4mm thick) foils of niobium oxidized on one surface. In thick crystals, which are elastically and plastically constrained by their size and by uniform deposition of the oxide over the entire surface, such a surface film can serve as a nucleation source for dislocations during deformation. We have employed anodically deposited oxide films in these experiments because of the simplicity and control offered by the technique [11]. Oxide films of thickness $\sim$100-1500Å were easily and reproducibly deposited over the course of the investigation.

3. EXPERIMENTAL RESULTS

We have made extensive measurements of the yield stress of niobium single crystals at low temperatures as a function of test temperature, strain rate, prestrain and oxide thickness [4]. The stress-strain curves given in Fig. 1 represent a simple summary of our findings.

The stress-strain curve for uncoated, unprestrained niobium (curve A) is typical of results obtained by several investigators on high purity niobium. Prestraining this material $\sim$ 10% at 300°K decreases the yield stress and reduces the rate of work hardening at large plastic strains (curve B), but the differences between A and B are not much greater than those encountered among various investigations on pure niobium.

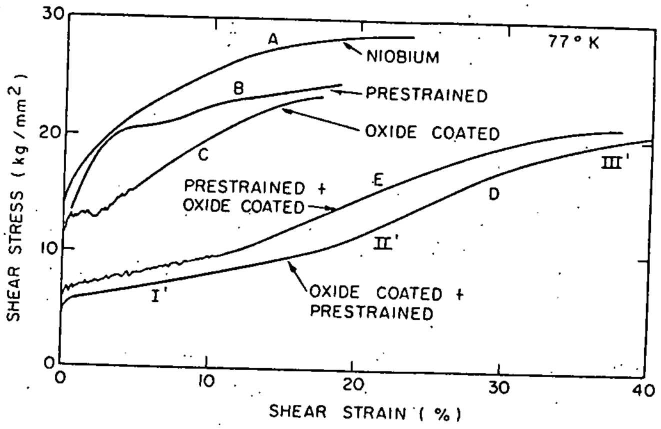

Fig. 1. Effects of oxide coating and prestraining on mechanical behavior of Nb single crystals.

When unprestrained niobium is coated with a 650Å oxide film, the yield stress is reduced (from 18kg/mm^2 to 12kg/mm^2 at 2% shear strain) and the stress-strain curves are initially serrated over several percent strain, as in curve C. If the oxide-coated niobium is also prestrained into stage I at 300°K (curve D), there is an additional substantial decrease in flow stress, a three-stage work hardening behavior developes, and the ductility, measured as the extent of uniform elongation, is greatly increased. Curve E is included to show that the order in which the oxide coating and prestraining are applied to the material is not significant. Crystals that are first prestrained and then oxide-coated exhibit slightly higher flow stresses and the serrated flow characteristic of unprestrained, oxide-coated materials.

The experiments depicted in Fig. 1 have been performed at several test temperatures below 300°K. Fig. 2 shows the dramatic effect of oxide coating plus prestraining by comparing the temperature dependence of the resolved shear stress (RSS) at 2% shear strain for pure niobium and the same material with a 650Å oxide film and prestrained 10% at 300°K. At all temperatures below ~ 200° K there is a two- to three-fold difference in the RSS of the two materials. Note that at high temperatures (T $\gtrsim$ 300°K), the oxide film hardens rather than softens niobium, as often observed in fcc crystals, cf. [12].

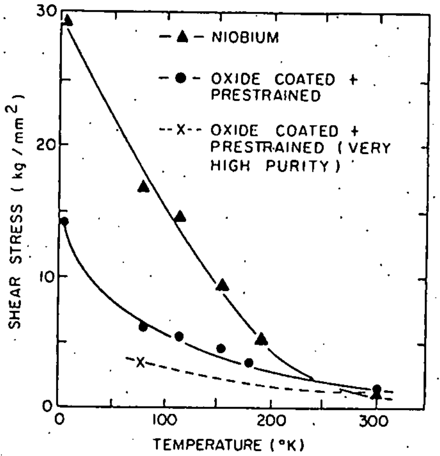

Fig. 2 Temperature dependence of the yield stress of uncoated Nb and oxide-coated+prestrained Nb of different purities.

Fig. 2 also includes some results obtained on the effect of substrate purity. Niobium crystals were outgassed for several days in ultra-high vacuum at temperatures as close to the melting point as possible to reduce residual interstitial impurities to a minimum. These crystals were oxide-coated and prestrained in the same manner as other materials, and were tested at 77°K. The mechanical behavior was much the same as indicated in Fig. 1, except that the flow stress was reduced by an additional 40-50%. The RSS at 2% strain at 77°K was in the range 3-4 kg/mm^2 for these crystals.

Several experiments were performed to establish that the behaviors observed in Figs. 1 and 2 were caused by the coating/prestrain treatment and not a result of contamination or other artifactual effects. Fig. 3 gives results from experiments involving removal of oxide films from deformed specimens which exhibited the pronounced softening. If the low temperature deformation is interrupted and the oxide film is removed by etching, the subsequent flow stress and stress-strain behavior at the same temperature are quite similar to that for prestrained, uncoated specimens.

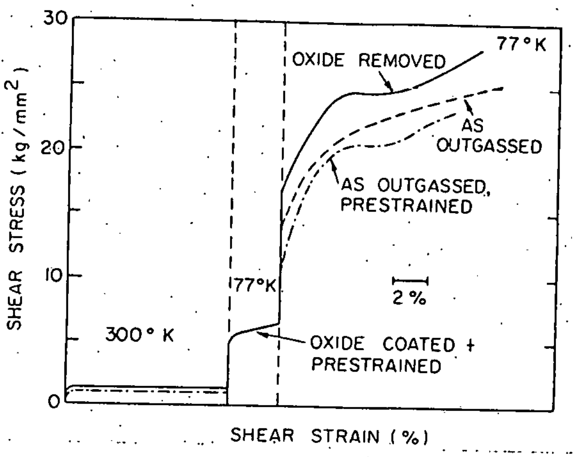

Fig. 3. Effect of film removal on the softening behavior caused by oxide coating + prestraining.

4. DISCUSSION

It is most reasonable to interpret the above results in terms of the model experiment hypothesized earlier: a high purity bcc metal can be deformed macroplastically at very low stresses at low temperatures if movement of non-screw dislocations is responsible for the deformation. Thus prestrained niobium (B in Fig. 1) deforms at only moderately reduced stresses (by 0-4 kg/mm^2) because the pre-injected non-screw dislocations are quickly exhausted into the screw orientation. The exhaustion process can better be avoided in oxide-coated niobium for which the self-stressed oxide generates large tensile residual stresses in the substrate, allowing nucleation of non-screw dislocations during deformation. The serrated flow in curve C of Fig. 1 is probably a manifestation of heterogeneous activation of surface sources. However, again the reduction in flow stress is not extremely large because the surface sources alone can not adequately supply non-screw dislocations across the entire glide plane of the specimen.

The combination of prestraining and oxide coating is so effective in reducing the flow stress and increasing ductility because it eliminates the difficulties associated with each of the operations performed separately. Prestraining introduces a high initial density of mobile dislocations across the entire glide plane that are not produced during deformation by oxide coating alone. Oxide coating supplies fresh non-screw dislocations during deformation that prestrain alone can not.

The dominant role of non-screw dislocation motion in the proposed model requires that the three-stage work hardening observed in curves D and E in Fig. 1 be interpreted differently than in normal work hardening theories. These stages are labeled I', II' and III' in Fig. 1 to distinguish them from the usual designations I, II and III. The specific interpretations of stages I', II' and III' are the basis of another investigation in which we have examined the dislocation substructures of these materials.

The additional softening observed in the very high purity niobium in Fig. 2 shows that interstitials interact strongly with edge dislocations and stop their movement. This behavior is no different than observations made on the importance of edge dislocation-interstitial interaction in microstrain deformation of uncoated bcc metals [5], except that in the present work the observations and interpretations apply to the macrostrain regime.

5. SUMMARY

We have proposed that macroflow of bcc metals at low temperatures can occur at greatly reduced applied stresses and with enhanced ductility if plastic flow can be carried primarily by edge dislocations rather than screw dislocations. To test this proposal experiments have been performed on niobium single crystals which were oxide-coated to give an important source of non-screw dislocations during deformation and also prestrained at temperatures high enough that a large density of non-screw dislocations was present prior to deformation. Such materials exhibited very small temperature dependences of the flow stress and large ductilities at low temperatures. The basic concept of using surface films to enhance ductility should be applicable to many other bcc materials.

ACKNOWLEDGMENTS

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