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SURFACE OXIDE SOFTENING OF SINGLE CRYSTAL NiAl

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Introduction

The effects of surface oxide films on the mechanical properties of single crystal and polycrystalline body-centered cubic refractory metals have been extensively investigated by Gibala and co-workers (1-5). Their results have shown that thin surface films on the order of tens to a few hundred nanometers enhance the ductility and decrease the flow stress of these metals at low homologous temperatures. For the temperature range over which this phenomenon occurs in bcc metals (less than two tenths of the absolute melting temperature), macroscopic plastic deformation is controlled by the low intrinsic mobility of screw dislocations. By contrast, the mobility of non-screw dislocations is much higher over this temperature range, such that these dislocations are responsible for controlling deformation only during microstrain or pre-macroyield events. However, this normal balance between deformation-generated edge and screw dislocations can be altered in bcc materials by the presence of phase boundaries or other interfaces, such as the film-substrate interface of oxide-coated bcc metals (6). For example, during deformation of a film coated material, the effect of elastic and plastic constraint at interfacial steps between the substrate and the oxide film results in a localized build-up of stress. This increased stress state at the interface is subsequently relieved in part by the generation of non-screw dislocations which contribute to plastic flow of the material at reduced flow stresses compared to the uncoated material, for which macroscopic deformation is controlled by less mobile screw dislocations (7).

The structure of B2 ordered intermetallic alloys is related to that of the body-centered cubic metals, with resultant similarities in dislocation core structures and dislocation mobilities, including examples of edge dislocation/screw dislocation mobility differentials. Consequently, the general plastic flow behavior exhibited by B2 alloys is also in many respects analogous to that observed in bcc metals. This includes such features as a large temperature dependent flow stress, a ductile-brittle fracture transition and deviations from Schmid's law (8). In our present research, the similarities between bcc metals and these bcc-based ordered alloys were carried a step further by experimental determination of surface film softening effects in single crystal NiAl. Such experiments were conveniently accomplished at room temperature, in the vicinity of which the flow stress begins to increase substantially with decreasing temperature.

Room temperature deformation of NiAl typically occurs by {110}<001> slip of perfect dislocations (9), and crystal orientations away from [001] where this type of slip occurs are normally referred to as soft orientations. On the other hand, if single crystal NiAl is oriented such that the [001] direction is parallel to the deformation axis, <001> slip is constrained and deformation occurs by <111> slip of superdislocations (10). Since the flow stress for [001] oriented single crystals is several times higher than that for other orientations it is normally referred to as a hard orientation. Therefore, using NiAl as a model B2 ordered alloy presented us with the opportunity to investigate film softening effects in a single material which exhibits two significantly different types of slip behavior.

Materials and Methods

The as-received NiAl was originally cast by TRW Inc., Cleveland, Ohio and was obtained from J.K. Doychak (11). The material is part of the same lot utilized by Doychak in his investigations of the oxidation behavior of NiAl (11,12). Chemical analysis was performed by National Spectrographic Laboratories and is provided in Table I. The material is non-stoichiometric (nickel-rich) and contains residual impurities totaling less than one atomic percent. Zirconium was intentionally added in order to improve thermal oxide adherence.

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Single crystal samples with an axial orientation near [$\bar{1}$23] or [001], as determined by Laue x-ray diffraction, were cored from the ingot using a standard ram-type electric discharge machine equipped with a Cu/W electrode. These samples were subsequently centerless ground to a uniform diameter and electropolished in a 2:1 methanol:nitric acid solution. Final dimensions of the cylindrical samples were 4 mm in length by 2 mm in diameter. All mechanical testing was performed in compression at room temperature and at an initial strain rate of 2×10^{-4}/s on a screw-driven Instron machine. Samples were tested either as-electropolished (uncoated) or after receiving a thermal oxidizing treatment.

Table I
Composition of NiAl (at%)

Ni	Al	Si	Fe	Cr	Zr	Cu	O	Mg
52.10	47.13	0.52	0.09	0.05	0.03	0.03	0.03	0.02

All specimens were oxidized in air using a laboratory furnace at temperatures of 800, 1000 or 1200°C. These treatments result in the expected formation of several distinct types of thermal oxide films (11-15), as summarized below. Oxide thicknesses ranged from 40-700 nm and were determined from kinetic data.

Oxidation of NiAl at 800°C results in the formation of a duplex oxide film which exhibited excellent adherence to the substrate even after considerable deformation. Doychak (11,12) has determined that the inner layer of this oxide is $NiAl_2O_4$ or a solid solution of $NiAl_2O_4$ and gamma-Al_2O_3 with a high epitaxial relationship to the metal. Above this inner layer of oxide grows a layer of delta-Al_2O_3 and/or gamma-Al_2O_3 which thickens with time while the $NiAl_2O_4$ spinel remains incorporated as the inner layer of the oxide scale.

The oxide formed at 1000°C has not been determined as definitively as that formed at 800°C. At short oxidation times ($\lesssim$8 hours) it is thought to be delta-Al_2O_3 which at longer oxidation times undergoes a transformation to alpha-Al_2O_3 (13). For thicknesses of less than 400 nm, this type of oxide coating displays considerable ductility and adherence, even on samples deformed to strains of greater than 20%.

Samples oxidized at 1200°C form a mature alpha-Al_2O_3 scale (14) which initially grows as a submicrocrystalline oxide but recrystallizes during growth to a textured alpha-Al_2O_3 film (15). These alpha-Al_2O_3 films were extremely brittle and did not perform as satisfactory coatings since they cracked and spalled after only slight deformation.

Results and Discussion

[$\bar{1}$23] NiAl - Soft Orientation

Of the three types of oxide coatings investigated, the delta-Al_2O_3 oxide films formed at 1000°C produced the most pronounced softening effects observed in [$\bar{1}$23] oriented crystals. Figure 1 shows several examples of this softening behavior for specimens oxide coated to the thicknesses indicated. In general, the oxide coated materials exhibited a reduction in yield and flow stresses and a concomitant increase in ductility compared to the uncoated material. As observed for the bcc metals investigated previously (4,6), there exists an optimum film thickness for which there occurs a minimum in yield stress and a corresponding maximum in ductility. For [$\bar{1}$23] single crystal NiAl with a delta-Al_2O_3 oxide coating, this optimum thickness occurs at approximately 350 nm resulting in an average 20% decrease in offset yield stress and a four-fold increase in ductility. This behavior is portrayed in the inset of Figure 1 which is a plot of the average 0.2% offset yield stress as a function of delta-Al_2O_3 oxide thickness. The data which are plotted represent mean values obtained from 3-5 samples per oxide thickness while the bars represent one standard deviation displayed by the data.

Figure 2 shows the stress-strain behavior for samples coated with optimum thicknesses of all three types of oxide films discussed in the previous section. In general, the mechanical behavior of NiAl specimens coated with the duplex oxide formed at 800°C was qualitatively similar to that of samples coated with the delta-Al_2O_3 scale. On the other hand, samples coated with the alpha-Al_2O_3 oxide displayed almost no significant difference in behavior compared to the uncoated material. Even though an initial decrease in yield stress was occasionally observed for the alpha-Al_2O_3 coated material, the flow stress quickly reached or exceeded that of the uncoated material. This behavior can be explained by the film cracking which was observed upon deformation of samples coated with an alpha-Al_2O_3 oxide. When the film cracks, compatibility stresses at the interface are relieved and consequently the oxide film is not effective at generating dislocations. However, the hard, brittle nature of this film would enable it to act as an effective barrier to dislocation motion. This would not only account for the small initial softening effect but also the observed increase in flow stress.

It is significant that film softening effects are observed for this orientation. In bcc metals the film softening effect is a direct result of the difference in intrinsic mobility between edge and screw dislocations and the preferential generation of the more mobile species. For $[\bar{1}23]$ oriented single crystal NiAl and all other soft orientations, a large intrinsic difference in dislocation mobility apparently does not exist. Both mobility calcualtions based on a Peierls model (16,17) and atomistic calculations of the core structure of <001> screw dislocations in a model CsCl lattice (18,19) indicate that a large difference in mobility between <001> edge and screw dislocations in NiAl should not be expected. These calculations imply that the surface film effects observed in this soft orientation could be due to an increase in total mobile dislocation (edge and/or screw) density and not necessarily the effect of preferential generation of a specific species characterized by high mobility. This result would be analogous to the findings of Ruddle and Wilsdorf (20) who observed softening in nickel-plated copper single crystals and rationalized their results in terms of an increased mobile dislocation density due to activation of surface sources. In such a circumstance, softening effects are observed because a dislocation-"starved" material becomes overwhelmed with mobile dislocations which are efficiently produced at the film-substrate interface. Therefore, increasing the total dislocation density in this soft orientation of NiAl could be in itself enough to produce softening effects.

[001] NiAl - Hard Orientation

NiAl single crystals tested in compression along [001] deform by <111> slip (10). Other than deformation occurring by slip of superdislocations, as opposed to unit dislocations, low temperature deformation of NiAl single crystals of this orientation occurs quite similarly to that of typical bcc metals. This similarity is due to the equivalent nature of the core structure of <111> dislocations in NiAl and bcc metals (8). The core of the screw dislocation in both structures is nonplanar and spread onto three intersecting {110} planes, while the non-screw dislocations possess less complicated planar cores (21,22). Therefore screw dislocations with their high Peierls stress and low mobility compared to non-screw dislocations control the low temperature deformation of [001] oriented single crystal NiAl.

Our experiments on single crystals of this hard orientation demonstrate that oxide coating has such a tremendous effect on the mechanical behavior of NiAl that it dwarfs the significant effect observed in $[\bar{1}23]$ single crystals, as shown in Figure 3. For [001] oriented samples, the delta-Al_2O_3 oxide coating results in as much as a 60% decrease in yield stress and up to a four-fold increase in ductility over uncoated samples. Because the yield stress of the uncoated material is intrinsically high, the film softening effect amounts to more than a 800 MPa decrease in yield stress for oxide coated samples! In agreement with these results, mobility calculations for <111> type slip in NiAl indicate that edge dislocations are mobile at stresses which are also about 60% less than those needed to move screw dislocations (17). Therefore, as in the case of bcc metals, the film-related generation of extremely mobile edge dislocations (as compared to screw dislocations) results in the greatly enhanced softening effect observed in NiAl of [001] orientation.

Conclusions

The phenomenon of surface film softening, observed previously for several bcc metals, occurs as well in single crystal NiAl of both soft and hard orientations. The magnitude of the surface film effects, i.e. a decrease in yield stress and increase in strain to fracture, is dependent on oxide thickness as well as the type of oxide coating applied. A much greater surface film effect occurs in the hard [001] oriented single crystals, for which previous theoretical investigations suggest there exists a large difference in mobility between edge and screw dislocations.

Acknowledgement

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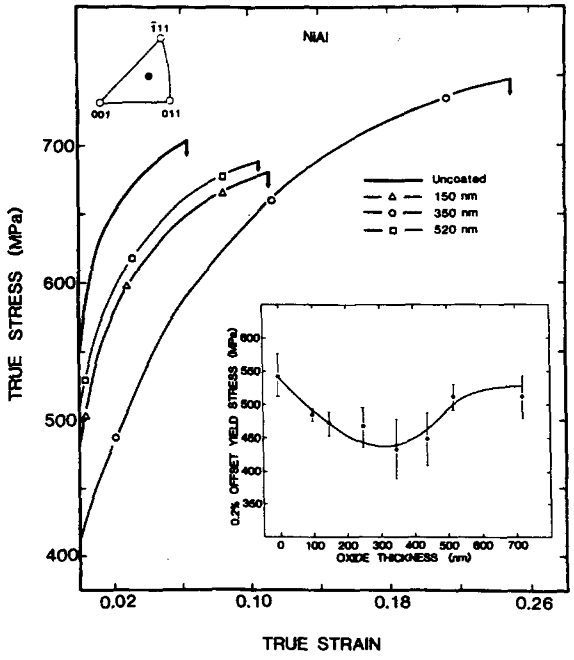

Fig. 1. The effect of delta-Al$_2$O$_3$ oxide films on the mechanical behavior of $[\bar{1}23]$ oriented single crystal NiAl tested in compression at room temperature. Inset shows the dependence of surface oxide softening on oxide thickness as revealed by its effect on the 0.2% offset yield stress.

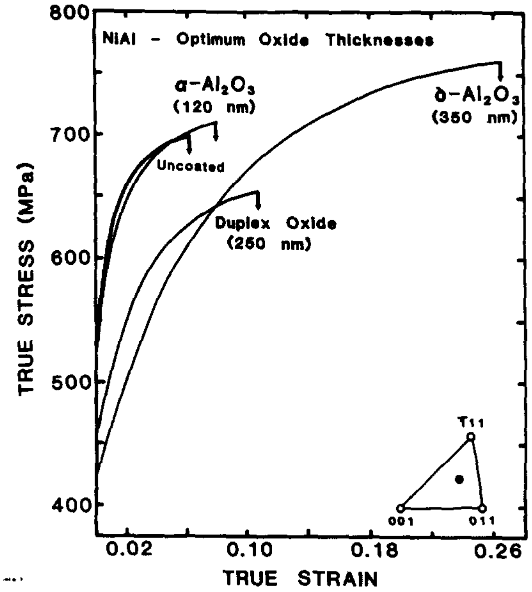

Fig. 2. The effect of different thermal oxide films of optimum thickness on the mechanical behavior of single crystal NiAl.

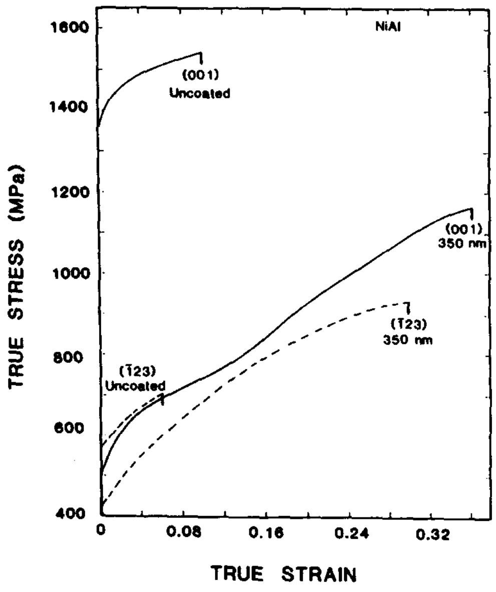

Fig. 3. The effect of orientation on the surface oxide softening of delta-Al_2O_3 oxide-coated NiAl tested in compression at room temperature.