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NOVEL ETCHING AND POLISHING TECHNIQUES FOR Ni$_3$Al CRYSTALS

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Introduction

Ni$_3$Al and other ordered intermetallic alloys have been extensively studied because of their extraordinary mechanical properties at high temperatures and anomalous temperature dependence of the flow stress (1). Numerous investigations have been undertaken to elucidate the nature of this unusual behavior. A direct measurement of the dislocation velocities over a wide temperature range is one of the most efficient approaches to the problem. Reliable experimental techniques to reveal the dislocation displacements are required for such investigation (2). The average dislocation velocity in Ni$_3$Al has recently been measured experimentally for the first time at temperatures ranging from 300 K to 873 K (3). Several selective chemical etchants available in the literature have been used to reveal dislocation positions. The work clearly demonstrated an anomalous temperature dependence of the dislocation mobility. At the same time, the results have indicated that a more dependable selective etching technique is needed to study the dislocation motion in Ni$_3$Al in more detail.

Commonly used dislocation etching takes advantage of a larger chemical potential near a dislocation. A proper etchant forms etch pits centered at the points of emergence of the dislocations on the specimen surface. Several dislocation etchants have been specifically developed for Ni$_3$Al (3–6), but none of them form large enough etch pits to ensure good contrast. Recently we have developed a selective etching procedure that produces larger etch pits near dislocations in Ni$_3$Al (7). Although the method was found useful in revealing the dislocation structure, it could not be successfully applied to the dislocation mobility studies. The contrast of the etch pits was still not good enough to reveal the dislocation displacements under applied stresses. Another limitation of the method was its inability to produce dislocation etch pits in boron-doped Ni$_3$Al, whereas a better understanding of the boron doping effect (8–10) is of great importance in controlling various mechanical properties of Ni$_3$Al, including its brittleness.

It is desirable, therefore, to develop a dislocation etchant that would (a) mark clearly both the initial and the final displaced dislocation positions; (b) reveal individual dislocations of all types, such as "fresh" and "aged" and as-grown dislocations; and (c) form high-contrast etch pits in both boron-free and boron-doped samples.

Polishing techniques that are complementary to the selective dislocation etching provide a way to locate dislocation displacements inside a sample (2). Ideally, such a technique should preserve the sample surface orientation during successive etching and polishing. Although an electrolytic polishing procedure for Ni$_3$Al was developed by Kear and Hornbecker (4) as far back as 1965, the suggested

743

solution and its modifications (3,6) showed remarkably strong anisotropic behavior on different surfaces which resulted in significantly distorted samples after polishing. It would be beneficial to develop a chemical solution that could be combined with selective dislocation etching to repolish etched surfaces without any noticeable change in the sample shape.

Finally, an "orientation" etchant available for some metals would also be of great importance since it can allow a fast and simple check on sample orientation making use of characteristic shapes of etching figures.

In this paper we report three novel techniques for chemical selective dislocation etching, polishing, and orientation etching of Ni₃Al single crystals, both boron-free and doped. In particular, the dislocation etchant allows us for the first time to keep track of the motion of each dislocation in this material.

Experimental Procedure

Sample preparation is described in detail elsewhere (3,7). A majority of the samples used in this study are similar to those in (1), namely, Ni₃Al (Ni-22.9 at. % Al). In addition to such "boron-free" samples, Ni₃Al crystals doped with B (of about 650 wppm as cast) were also tested. The polish and etch rates were measured with an optical interferometric microscope. All quantitative measurements were performed immediately after preparation of the corresponding solutions. The standard X-ray diffraction (the Laue back-reflection technique) was used to define sample orientations needed for developing the orientation etchant.

Chemical Polishing Results

Instead of electrolytic solutions (3,4,6) with a highly anisotropic action, we propose a simple and convenient method of chemical dissolution in a mixture of equal volume parts of HNO_3, H_2SO_4, and H_2O. The polish rate of the solution is about 10 μm/min and practically independent of the surface orientation. It takes typically several minutes of polishing to make the surface reasonably flat. It should be noted that the surface remains flat even after a longer polishing time, and it preserves its orientation after numerous etching - polishing runs. The best surface quality is achieved immediately after preparation, when the solution is still warm. However, reasonable results can also be accomplished in the polish even after several days if the solution is heated to about 45°C immediately before polishing. At higher temperatures not only does the polish rate increase dramatically but also the solution reveals shallow individual dislocation etch pits and grain boundaries.

As illustrated in Fig. 1, the 30-second polishing of a {100} surface with dislocation etch pits transforms the 15-μm etch pits (Fig. 1a) into flat-bottomed etch pits of a smaller size (Fig. 1b). After additional 3-minute polishing, the etch pits disappear completely leaving a flat surface without any visible traces of previous etching (Fig. 1c).

Orientation Etching Results

It is known that the dissolution rate of a solid can be radically changed by some additives, such as Al, Cr or Fe ions, that form complexes with dissolved solid ions. For instance, the complexes can initiate preferable dissolution near surface imperfections resulting in the "selective" etching of the solid surface instead of its uniform polishing describe above. This ability of the complexes to transform polishing into etching have been employed in developing numerous dislocation etchants for many solids, see, for instance, (11). In our study we also utilize another property of the complexes, their high sensibility to
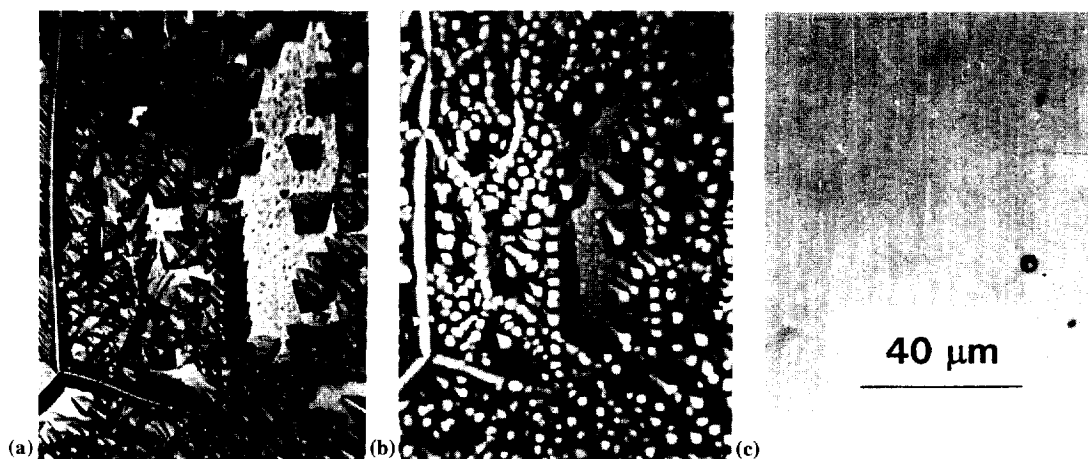
Figure 1. The same surface area (a) of a boron-free Ni₃Al sample with dislocation etch pits after chemical polishing for 30 s (b) and 3 min (c). The scale shown in Fig. 1c is the same for all other figures.

the type of such imperfections. In particular, it is feasible to find a complex that can create the so-called "orientation" figures instead of dislocation etch pits converting the dislocation etching into "orientation" etching. We have investigated the effect of Fe^{3+} ions on the etching rate of Ni₃Al to verify that it is possible to switch between the two etching modes.

The same polishing solution described above becomes susceptible to the surface orientation after adding a small amount of $FeCl_3 \cdot 6H_2O$. The dissolution rate of various surfaces in such a solution is changed differently. For instance, after adding 0.02 M of $FeCl_3 \cdot 6H_2O$ to the polishing solution, the polish rate of the {001} and {011} surfaces has decreased from 10 to 7 μm/min. In contrast, the polish rate of the {111} surface has increased up to 15 μm/min. Such a change promotes formation of well-defined orientation etch figures on the main crystallographic planes, with the {100} and {110} facets determining the morphology of these etch figures. Instead of the dislocation etch pits, however, the orientation figures are produced only on macroscopic defects, such as small scratches, local indentations, precipitation colonies, and so on.

Using comprehensive tables and calculations done by Buerger (12), one is able to find the orientation of the etched surface with a precision of 1–2 degrees. The method of orientation etching is also applicable for the evaluation of grain and even subgrain misorientation. Some typical orientation figures on the main crystallographic planes, {001}, {110}, {111}; and {117}, identified by the X-ray Laue technique, are shown in Fig. 2. All the pictures were taken after etching in the above solution with 0.02 M of $FeCl_3 \cdot 6H_2O$ for several minutes.

It should be noted that these orientation etch figures do not reveal dislocations and therefore can be used only for orientation purposes. Similar technique has been developed for other materials (11,13) but was unknown before for Ni₃Al.

Dislocation Etching Results

We have found that the most convenient and reliable selective etchant for multiple etching of dislocations in Ni₃Al is a solution that can increase the ratio of the normal etch rate V_n along dislocations to the tangential rate V_t of the etch pits. In particular, a solution that provides the best contrast for dislocation etch pits in both boron-free and boron-doped samples is a mixture of HNO_3,
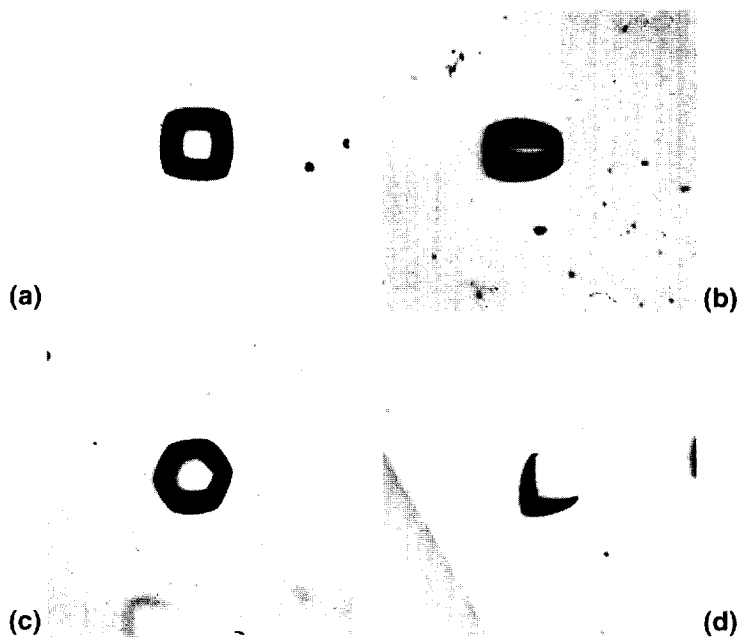
Figure 2. Orientation etch figures on various surfaces of Ni$_3$Al, {001} (a); {110} (b); {111} (c); {117} (d).

HCl and H$_2$O (1:3:3 volume parts) with 0.05 M of FeCl$_3$·6H$_2$O. The corresponding etch rates are V$_n$ = 0.4–0.6 μm/min and V$_t$ = 2–3 μm/min, while the average polishing rate V$_p$ is about 0.5 μm/min.

It should be noted that the preparation procedure for an efficient dislocation etchant is important. It is described below in more detail. A 1:3 volume mixture of concentrated nitric and hydrochloric acids is prepared and kept standing for 1–2 hours until intense yellow-brown coloring and gaseous bubble formation is observed in the solution. This indicates a formation of strong oxidants, such as gaseous chlorine and nitrosyl chloride, by the reaction HNO$_3$+3HCl = ClNO + Cl$_2$+ 2H$_2$O. Then the mixture is diluted by water with the ratio 1: 2–3 to form a basic solution. Finally, FeCl$_3$·6H$_2$O is added to the basic solution to produce a required concentration of 0.05 M. The best results (in terms of contrast and reliability) are achieved with a fresh solution (or stored no longer than one day) at room temperature. This etchant allowed us to reveal "fresh" and "aged" and as-grown individual dislocations, as well as those in grain boundaries. Several examples of the dislocation etching are shown in Fig. 3.

Discussion

We have developed several solutions to provide a convenient tool for the studying of dislocation structure and dislocation motion in ordered Ni$_3$Al. So far we have tested the solutions on boron-free samples of only one composition (Ni$_{77}$Al$_{23}$) and on boron-doped samples of only one boron concentration (Ni$_{76}$Al$_{23.5}$B$_{0.5}$). We have observed no considerable difference in their action. The dislocation etchant reveals the dislocations in both types of samples, and the etch pits have practically the same size and contrast. On the other hand, it is well known that different stoichiometry and doping of a solid can change its dislocation energy. As a result, the dissolution rates may reach such a level that the dislocations can not be revealed anymore. However, our preliminary results indicate that the developed solutions can also work on samples of different stoichiometry and doping, as long as the dislocation energy does not vary too much and the solution is adjusted to a proper concentration of Fe ions. Recent

Figure 3. A surface of boron-free Ni$_3$Al after the first selective dislocation etching for 2 min (a), and after additional etching for 2 min (b, c). Note that all three types of dislocation etch pits (revealing the initial position of a moving dislocation, its final position, and the positions of the dislocations that have not moved) can be seen in (c) (marked respectively as A, B and C).

results have shown that the total dislocation energy in a boron-doped Ni$_3$Al samples (10) and after Ta alloying (14) may be higher than in boron-free stoichiometric crystals, although the difference is not very large (less than 50%).

The selective dislocation etchant we have developed is quite promising for a comparative study of the dislocation mobility in both boron-free and boron-doped samples, when one uses the double-etch-pit-pulse-loading technique. Such experiments can provide a better understanding of the nature of both the anomalous flow behavior and the effect of boron doping in Ni$_3$Al. As seen from Fig. 3c, the double etching allows us to identify moving dislocations (larger flat-bottomed etch pit A and corresponding smaller sharp-bottomed etch pit B) and immobile dislocations (sharp-bottomed etch pits C of a larger size). The technique allows one not only to mark the initial and final dislocation positions and therefore to measure the dislocation displacements and velocity in Ni$_3$Al but also to determine the slip systems at various temperatures and to study the contributions made by the dislocation motion and dislocation multiplication into the flow strength anomaly of both boron-free and boron-doped Ni$_3$Al. The possibility of such contributions has been found in the preliminary study of dislocation mobility in boron-free Ni$_3$Al samples (3).

TABLE I
Polishing and Etching Features of Ni$_3$Al Crystals

Solution #	Composition Volume Parts	Typical Time, min	Features
1	HNO$_3$+H$_2$SO$_4$+H$_2$O, 1:1:1	3–6	Polishing, all surfaces
2	HNO$_3$+H$_2$SO$_4$+H$_2$O+FeCl$_3$·6H$_2$O, 1:1:1 + 0.02M	3–6	Orientation etching, all surfaces
3	HNO$_3$+HCl+H$_2$O+FeCl$_3$·6H$_2$O, 1:3:3+ 0.05 M	1–3	Selective dislocation etching, {001} surfaces

The three different compositions are summarized in Table 1. Each solution corresponds to completely different dissolution processes occurring on the surface of Ni$_3$Al samples:

a) uniform dissolving leading to uniform polishing of a given crystallographic plane (Table 1, Solution #1);
b) anisotropic dissolving of the surface, with macroscopic defects serving as nucleation centers and leading to the formation of the orientation figures (Table 1, Solution #2); and
c) anisotropic selective dissolving of the {001} crystallographic planes, with dislocations serving as permanent nucleation centers and leading to the formation of the etch pits (Table 1, Solution #3).

Conclusion

New water solutions of HNO$_3$ with HCl, H$_2$SO$_4$, and FeCl$_3$·6H$_2$O have been developed for chemical polishing, orientation etching, and selective dislocation etching. The solutions have several important advantages: (a) they do not require electrolytic techniques for either etching or polishing; (b) the selective dislocation etchant reveals dislocations of any type, both in pure and boron-doped crystals; (c) the contrast of the dislocation etch pits is high enough to distinguish between mobile and immobile dislocations; (d) the polish dissolves all the crystallographic planes uniformly; and (e) the "orientation" etching allows a simple identification of sample orientation by the characteristic shape of "non-dislocation" etch figures.

Acknowledgments

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