



CHEMICAL ETCHING OF DISLOCATIONS AND GRAIN BOUNDARIES IN ORDERED Ni₃Al CRYSTALS

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Introduction

Ni₃Al and other ordered intermetallic alloys have been the subject of intensive investigation for more than three decades. The reason for that is not only their superior mechanical properties at high temperatures but also their extraordinary temperature dependence of the flow stress. Unlike most other materials, some intermetallics demonstrate a flow stress increase with increasing temperature over a rather wide range of temperatures. In particular, such an anomaly has been observed and studied long ago in Ni₃Al (1). Despite a great deal of experimental and theoretical work, we still do not possess sufficient knowledge of the processes responsible for such anomalous behavior even in the most widely studied intermetallic, Ni₃Al. All researchers agree that it is an unusual structure of dislocations and their specific dislocation dynamics that can explain the anomaly. However, we still do not know if the mobility of dislocations or their multiplication behavior (or both) is responsible for such exceptional mechanical properties. Quantitative studies of the mobility of individual dislocations in intermetallics could provide a way to elucidate the nature of the phenomena.

In such studies, a proper technique for identifying the dislocation displacements must be employed (2). This is most commonly achieved using the so-called selective etching which produces etch pits at the points where dislocation lines cut the surface of the specimen. The etch pits are formed because of faster local dissolution near the dislocations. Such a "dislocation" etchant should meet several requirements for dislocation mobility measurements. The most important among them are (a) a one-to-one correspondence between etch pits and the dislocation positions; (b) a possibility to reveal as-grown, aged and new individual dislocations, as well as dislocations in subgrain and grain boundaries; and (c) a high contrast of etch pits to define clearly the dislocation position and motion (2).

Since the pioneering investigation of Gilman et al. (3) on etching properties of dislocations, many appropriate selective etchants have been developed for a variety of crystals including many metals (4). To the best of our knowledge, the dislocation etch pits in Ni₃Al have been observed only in two studies using electrolytic etching (5, 6). Kear and Hornbecker (5) developed an electrolyte of 10% H₂SO₄ in methanol for revealing dislocation etch pits in polycrystalline Ni₃Al. An electrolyte containing H₃PO₄, HNO₃ and FeCl₃ · 6H₂O in methanol has been suggested by Qin and Chou (6).

Recently the mobility of dislocations in Ni₃Al single crystals was studied by the selective etching technique for the first time (7). The dislocation velocities were measured at different temperatures applying a simple chemical etchant, a mixture of HCl + HNO₃ (8). However, we found that the etchant (7) as well as the other etchants available in the literature (5, 6) had limitations in their application. In particular, all the etchants form only very small etch pits with a relatively low contrast, and they are able to etch the dislocations intersecting {001} surfaces only.

In this paper we report a new selective etchant for revealing dislocations in Ni₃Al single crystals. The etchant is a chemical solution, and hence more practical than an electrolytic procedure. The etchant reveals both aged and fresh individual dislocations as well as dislocations in grain boundaries, with etch pits large enough to distinguish moving dislocations and measure experimentally the dislocation displacement. Finally, the etchant is able to reveal dislocations on surfaces other than {001}.

Experimental Procedure

The specimens were cut from a bulk Ni₃Al single crystal with a composition of Ni-22.9 at. % Al (kindly provided by Dr. D.M. Dimiduk, Wright Laboratory, Wright-Patterson AFB). The orientation of the specimens was determined by the Laue back-reflection X-ray technique. Parallelepiped specimens with either all {001} or {001} and {110} side faces were first mechanically ground and polished on several types of Emery silicon carbide papers. They were then polished on a soft cloth with diamond pastes, and finally with 6 μm diamond and 0.3 μm alumina suspensions. To decrease the dislocation density, the specimens were annealed at 1470 K for at least 120 h in flowing argon and then cooled in the furnace at 10 K/min. After mechanical polishing and again after annealing, the surface damage was removed by electrolytic polishing in a 10% solution of H₂SO₄ in methanol for 5 ÷ 10 min at a voltage of 12 V and a current density of 0.3 A/cm² (6). The preparation of the specimens and their deformation have been described in more detail elsewhere (7). The size and depth of etch pits were measured by an optical interferometric microscope.

Results and Discussion

All of our attempts to improve the existing alcohol-based electrolytic etchants (5, 6) by varying the ratio of components, the temperature of the solution or the current density proved to be unsuccessful. In all cases the size of the etch pits did not exceed 2-4 μm even after a long etching time. Instead of upgrading electrolytic etchants, we used a different approach to develop merely chemical dislocation etchants based not on electrochemical but chemical dissolution. Specifically, we tested aqueous solutions of several acids and their mixtures, such as HNO₃, HCl and H₂SO₄, together with complex-forming additives and oxidants. A similar approach has been used for developing a selective dislocation etchant for Ni (8).

As shown earlier (9,10), the formation of dislocation etch pits in metals in an oxidizing solution often begins with a process referred to as the surface decoration. It is suggested that oxidizing gaseous agents provide selective dissolution of the metals by enhancing short-time adsorption at the dislocation sites where the local energy of the metal has been increased by dislocations. Therefore, there was good reason to believe that the aqueous solutions of strong acids, such as HNO₃ + NaNO₂ or HNO₃ + HCl, might also be used for dislocation etching of Ni₃Al crystals.

Nitric acid HNO₃ and sodium nitrite NaNO₂ interact to create the oxidation-reduction medium while producing gaseous nitrogen oxides so that the process might originate local dissolution near dislocations (9). Upon dissolving in water, they start developing etch pits on the {001} surfaces of Ni₃Al just at the instant the brown gas of NO₂ is released from the solution. However, we found that the mixture could

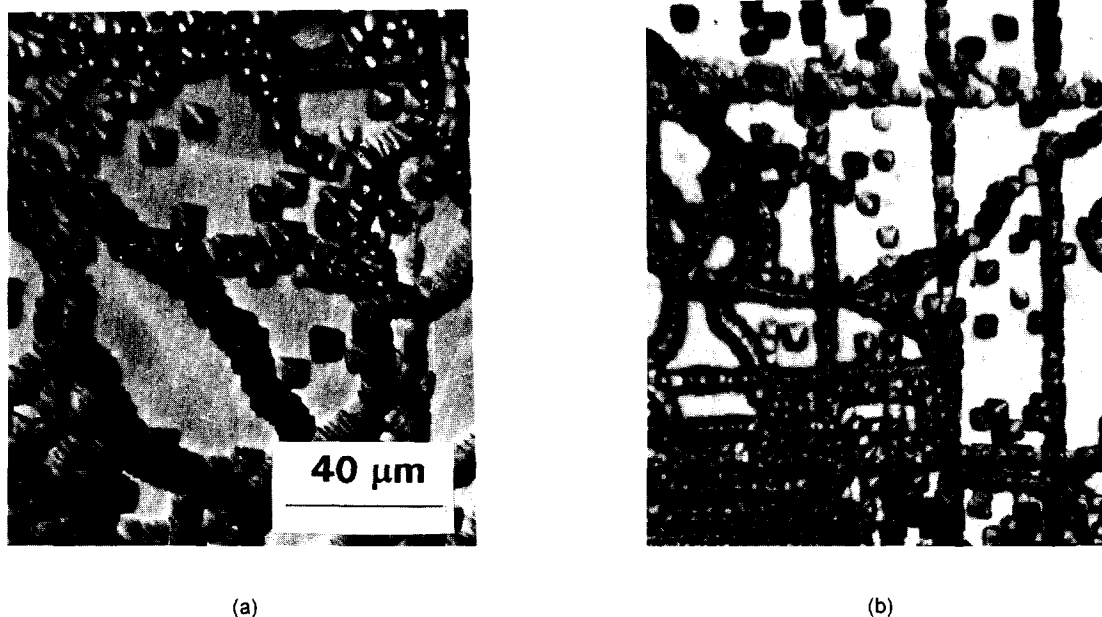


Figure 1. Etch pits on the {001} surfaces of Ni₃Al (a) without any deliberate deformation and (b) with local deformation by indentation. (The scale shown in Fig. 1a is the same for the other Figures.)

produce only low-contrast round-bottomed etch pits that were not appropriate for double etching. The measurements of the normal etch rate V_n (along the dislocation line) and tangential etch rate V_t gave $V_n = 1.2\mu\text{m}/\text{min}$ and $V_t = 20\mu\text{m}/\text{min}$. Such etch rates were also too high and beyond the required range for dislocation mobility experiments since the suitable ratio V_n/V_t should be close to 0.2 (2, 4).

We obtained better etching results using a mixture of nitric and hydrochloric acids in water (7, 8). The reaction in this case, $\text{HNO}_3 + 3\text{HCl} = \text{Cl}_2 + \text{NOCl} + 2\text{H}_2\text{O}$, produces such strong oxidants as gaseous chlorine and nitrosyl chloride. Usually the reaction begins in 5-10 min after mixing as evidenced by an orange coloring of the solution. The contrast of the dislocation etch pits and the etch rates turn out to depend heavily on the nitric acid to hydrochloric acid ratio.

It is known that the contrast and the shape of dislocation etch pits can also be radically changed by some additives, such as ions of variable valence, in particular, Fe, Al and Cr (3, 4). Their action may be attributed to the formation of complexes that are adsorbed on the host crystal (4, 8). The complexes are believed either to retard the transfer of host ions into the solution or directly impede the kink (step) motion during etching. The associated changes in the relationship between V_n , V_t and the polishing rate (or average dissolution rate) V_p can improve the contrast of etch pits.

To check the effect of such ions, we studied mixtures of nitric and hydrochloric acids in water with added $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ of different concentration between 0.1 M to 0.001 M. The samples with introduced dislocations were etched at room temperature and a stirring rate of 2 rev/s. We found that the additive indeed not only improved the contrast of the etch pits but also increased their size. The best contrasting dislocation etch pits of a reasonable size of 3 to 15 μm were produced in a mixture of equal volume parts of HNO_3 , HCl and H_2O with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, in the range from 0.01 to 0.002 M depending on the composition of Ni₃Al.

The etching solution described above reveals as-grown, aged (annealed) and fresh dislocations on the {001} surfaces of Ni₃Al as distinctive square etch pits. The etch rates are measured to be $V_n = 0.3\text{-}0.5$

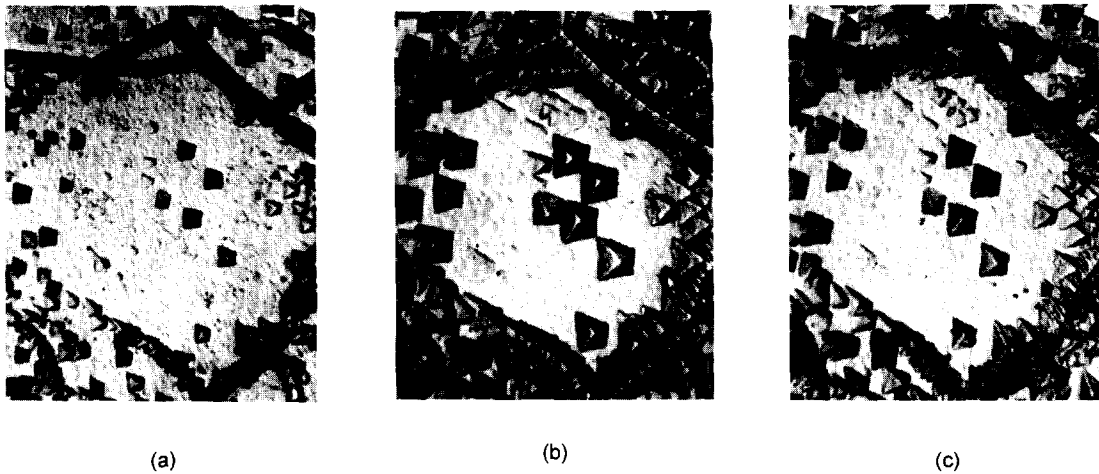


Figure 2. The same site on the {001} surface of annealed Ni_3Al shown after (a) being etched for 1 min, (b) etched additionally for 2 min, and (c) polished and etched again for 2 min.

$\mu\text{m}/\text{min}$ and $V_t = 2-3 \mu\text{m}/\text{min}$ giving the ratio $V_n/V_t = 0.15$. The etching is accompanied by overall dissolution of the {001} surfaces with a rather high rate of $V_p = 0.8 \mu\text{m}/\text{min}$. We also found that the etching occurs at the same rate on both the free surfaces of the sample and the slopes of the etch pits, and it is this feature that maintains rather high etching contrast. The etchant reveals dislocations not only on the {001} surface but also on all surfaces that are off by not more than 15° in any direction. Since any deviation from the {001} surface changes the square shape of the dislocation etch pits, it is also easy to verify the orientation of Ni_3Al samples with the etchant.

To study the possibilities of the new etchant, we used it to reveal the dislocation structure of Ni_3Al before and after various types of deformation. Fig. 1a shows the {001} etched surface of an annealed sample. The etch pits correspond to as-grown individual dislocations (randomly distributed square etch pits) and dislocations in subgrain boundaries formed during annealing. Fig. 1b demonstrates the effect of local deformation of the same surface at room temperature. The dislocations are produced by the Vickers indentation (near the lower left-hand corner of the picture) under a load of 0.25 N. The vertical and horizontal rows of etch pits correspond to the new dislocations moved along $\langle 110 \rangle$ and $\langle \bar{1}10 \rangle$ directions. Since the primary glide system in Ni_3Al is $\langle \bar{1}10 \rangle \{111\}$ (1), the etching pattern confirms that such indentations create and move dislocations in four {111} glide planes intersecting the {001} surface along the observed directions.

The reproducibility of the etchant is rather good so that the same place of the crystal under study can be etched many times without the loss of quality including successive polishing and etching. The sequence in Fig. 2 shows the same place on a surface close to the {001} surface of an annealed sample after etching for 1 min (a), additional etching for 2 min (b), and polishing and etching again for 2 min (c). The arrangement of five etch pits revealing dislocations near the center of a small subgrain is practically the same in all of the pictures. As also seen, the etch pits increase proportionally as the etching time increases without the noticeable modification of the etch pit shape. Although the surface of the sample does not correspond exactly to the {100} plane as evident from the shape of the etch pits, the etchant is able to reveal the dislocations on the tilted surface.

Fig. 3 illustrates the effect of bending deformation of a sample with the longest side oriented along the $\langle 110 \rangle$ direction and a light scratch made along this direction on the {001} surface. The sample was loaded at room temperature by three-point bending about the $\langle \bar{1}10 \rangle$ axis so that slip lines were nucleated and

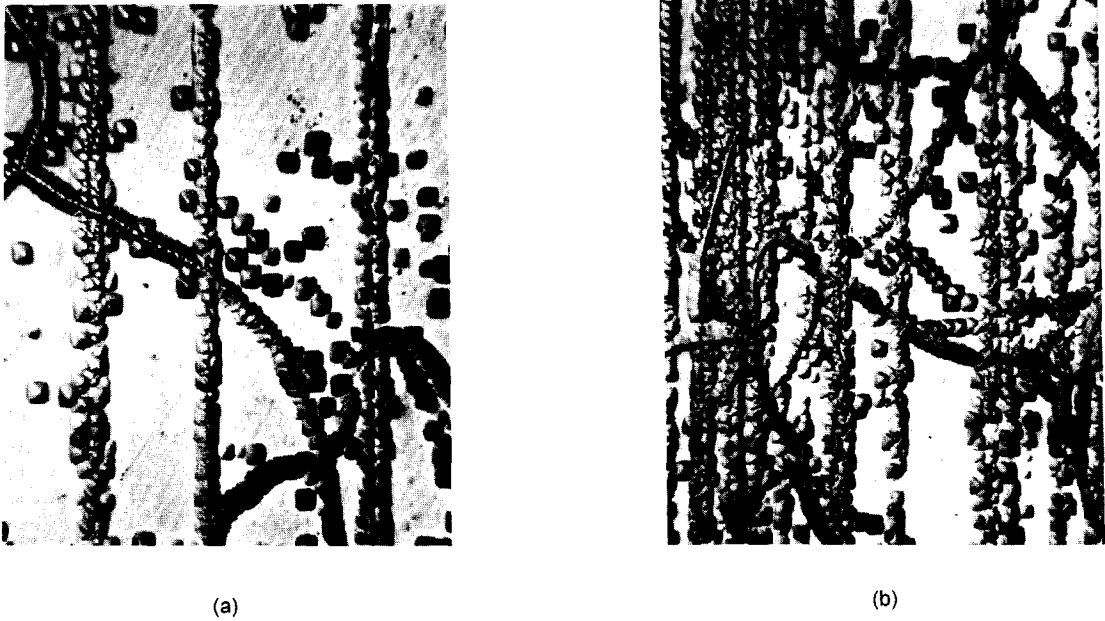


Figure 3. Dislocation etch pits in slip lines produced in Ni₃Al by three-point bending at room temperature in the areas of low (a) and high (b) applied shear stresses.

moved from the scratch. Figs 3a and 3b show the surface sites where the applied resolved shear stress is either low (about 30 MPa) or high (about 60 MPa), respectively. As can be seen from the etching patterns, the dislocations move and multiply in the $\{111\}$ and $\{\bar{1}\bar{1}1\}$ glide planes intersecting the sample surface (001) along the common $\langle\bar{1}10\rangle$ direction. The glide planes correspond to two primary easy glide systems with non-zero Schmid factors. Besides the glide, some indication of the dislocation cross slip can also be observed in Fig. 3a: the etch pit centers are located not exactly along a $\langle\bar{1}10\rangle$ line but deviated from it. Finally, Fig. 3 demonstrates that the density of dislocations in the rows depends strongly on the applied stresses indicating multiplication processes: the higher the applied stress the higher the dislocation density in the rows.

The arrangement of dislocation slip lines inside the deformed samples also confirms the operation of two primary glide systems with equal Schmid factors. After polishing and etching again a sample with individual dislocation slip lines (similar to those shown in Fig. 3a), we observed the splitting of each line into two. Since bending promotes dislocation nucleation and multiplication mainly from the topmost (001) surface, the splitting indeed demonstrates the operation of the two primary glide systems.

As can be seen from all the pictures above, our Ni₃Al specimens are single crystals composed of subgrains with relatively small misorientation. We have also found several samples that include grains of larger misorientation. Such samples have provided a simple way of checking the applicability of the etchant for other than $\{001\}$ surfaces. Fig. 4 demonstrates the ability of the etchant to reveal dislocations on a $\{711\}$ surface. In contrast to the $\{001\}$ surface (Fig. 1 and Fig. 3) where square etch pits are observed, the etchant reveals etch pits of other, irregular shapes on this surface (Fig. 4a). Fig. 4b shows how several dislocation arrays are changing during passing through a grain boundary between the $\{001\}$ and $\{711\}$ surfaces. Since such boundaries are typically obstacles to moving dislocations, some arrays in Fig. 4b have disappeared in the misoriented grain.

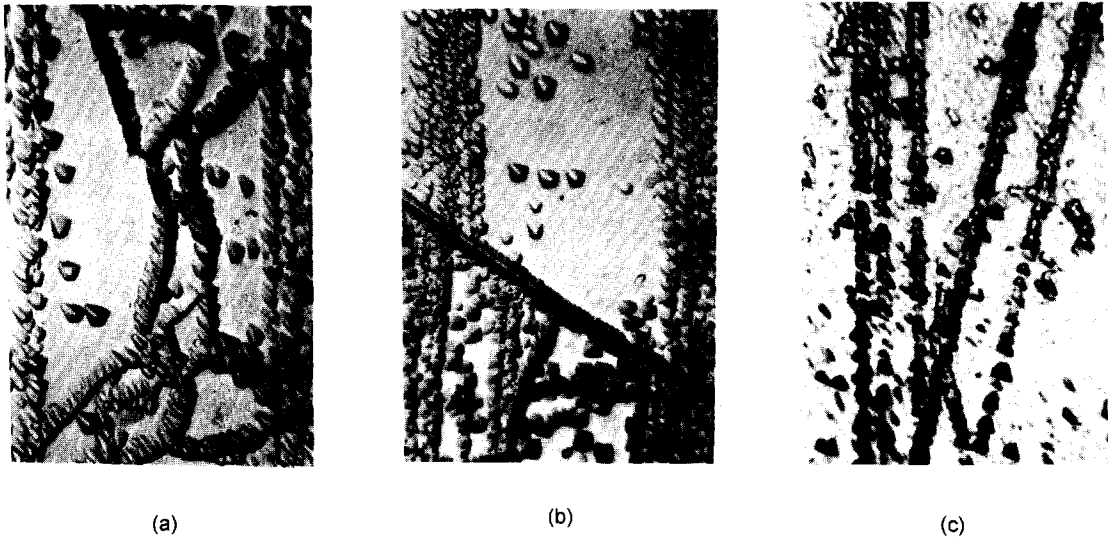


Figure 4. Dislocation etch pit patterns on a $\{711\}$ surface of Ni_3Al show (a) individual dislocations, subgrain boundaries and slip lines; (b) dislocation rows crossing the grain boundary dividing $\{001\}$ and $\{711\}$ surfaces, and (c) dislocation rows moving in two different glide planes, $\{111\}$ and $\{\bar{1}\bar{1}1\}$.

After passing over such boundaries with large enough misorientation, the slip lines may not only change their direction (Fig. 4b) but also intersect differently with the etching surface. Unlike Fig. 3 for the $\{001\}$ surface, where all dislocation rows oriented along the same $\langle 0\bar{1}1 \rangle$ direction, the rows on the $\{711\}$ surface (Fig. 4c) are not parallel anymore. The two operating primary glide planes, $\{111\}$ and $\{\bar{1}\bar{1}1\}$, should intersect the $\{711\}$ surface along $\langle 0\bar{1}1 \rangle$ and $\langle \bar{1}\bar{4}3 \rangle$ directions and make the angle 13.9° between the intersections. The angle between the dislocation rows in Fig. 4c is about 14° , in a very good agreement with the crystallographic estimation.

Conclusions

A new selective chemical etchant is developed and tested for its ability to reveal dislocations in Ni_3Al single crystals. The best results have been found for the mixed solution of $\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}$ (1 : 1 : 1 volume ratio) with the aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (over a range of 0.01 - 0.002 M). The etchant forms etch pits with the properties typical of dislocation etch pits. The etchant reveals both individual dislocations and dislocations in grain boundaries before and after different types of deformation of Ni_3Al samples. The features of the etchant, such as retaining the desired high contrast, the increase of the etch pit size with etching time, repeatability and practical convenience, make the developed etchant a good candidate for various applications, such as revealing dislocation structures on $\{001\}$ and close surfaces and measuring dislocation mobility in Ni_3Al crystals. When combined with chemical polishing, the etchant is of prime interest, among other things, for studying the dislocation structure and its modification in the bulk of plastically deformed samples. The etching patterns demonstrate that the macroscopic motion of dislocations in Ni_3Al under local or bending deformation takes place mainly in the $\langle 110 \rangle / \{111\}$ primary glide systems. Some indication of dislocation cross slip and multiplication was also observed in the studied samples.

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