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Cutting Apart of γ'' Precipitates by Dislocations Emitted from Nanoscale Surface Notches in Ni-Base Alloy 725

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We present a high-resolution transmission electron microscopy study that gives evidence for cutting apart of DO_{22} Ni_3Nb γ'' precipitates by dislocations emitted from nanoscale notches on free surfaces in Inconel[®] 725. This finding suggests that the surface morphology influences the rate of cutting apart of sub-surface precipitates in Ni-base alloys under mechanical loading.

Keywords: Ni-Base Alloys, Electron Microscopy, Surfaces, Precipitates

Inconel[®] 725 is a Ni-base alloy with exceptional resistance to pitting, hydrogen embrittlement, and stress corrosion cracking in corrosive environments, such as those found in deep oil wells [1]. Because it is age-hardened during heat treatment by precipitation of nanoscale Ni_3M γ' and γ'' phases ($\text{M} = \text{Al}, \text{Ti}, \text{Nb}$) rather than by cold work, alloy 725 also displays high strength along with excellent ductility and toughness [2–4]. Coherency strains from γ' and γ'' precipitates are thought to be the main strengthening mechanism in alloys such as Inconel[®] 718 [5,6] and 725 [7]. If these precipitates are destroyed, the mechanical properties of the alloy are degraded. For example, cyclic loading in Inconel[®] 718 gives rise to planar bands that have been cleared of precipitates [8–12]. Slip along these bands is easier than in the virgin material and their formation is therefore believed to soften Ni-base alloys under cyclic loading and reduce fatigue life.

Planar slip bands are known to form by dislocation glide-assisted breakup of precipitates [9] and are thought to initiate from dislocation sources at grain boundaries [11]. In this paper, we present evidence that nanoscale notches on free surfaces in alloy 725 also emit dislocations that cut apart γ'' precipitates, suggesting that surface morphology influences the rate of cutting apart of sub-surface precipitates in Ni-base alloys and may ultimately

affect mechanical behaviors that depend on the integrity of these precipitates, such as the initiation of planar slip bands.

The Inconel[®] 725 used in this study was supplied by Special Metals Corp. Its chemical composition was measured by energy dispersive spectroscopy (EDS) in a transmission electron microscope (TEM) and the size of the grains was measured using electron backscatter diffraction (EBSD). To prepare TEM specimens, 3 mm diameter discs (for conventional TEM samples) or rectangular sheets of $11.5 \times 2.5 \text{ mm}^2$ (for straining samples) were cut out from 50 to 100 μm thick foils and electrochemically polished to electron transparency by twin jet thinning using a 7 vol.% perchloric acid in methanol electrolyte at -50°C with a current of $\sim 50 \text{ mA}$. We carried out a structural investigation in a JEOL 2010F TEM using a conventional double-tilt holder. The phase identification was carried out using selected area electron diffraction (SAED), electron energy loss spectroscopy, and EDS. *In situ* tensile straining was performed using a Gatan 654 single-tilt straining holder (Supplementary information, Figure S1) inside a JEOL 2011 TEM operated at 200 kV.

Alloy 725 has been studied much less extensively than alloy 718, so we first carried out a detailed

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Table 1. Composition of Inconel® 725 samples.

Element	Ni	Cr	Fe	Mo	Nb	Ti	Al	C
Wt.%	56.9	21.3	8.8	7.3	3.8	1.6	0.3	< 0.1

microstructural investigation of alloy 725. Its composition is reported in Table 1. The EBSD-determined grain size was in the 30–80 μm range (Supplementary information, Figure S2). The TEM analysis (Figure 1) shows that the fcc Ni-Cr solid solution γ matrix contains numerous bct (DO_{22}) Ni_3Nb γ'' particles. These particles are coherent with the γ matrix and typically ~ 10 nm thick and 20–40 nm in diameter. A smaller number of coherent L_{12} $\text{Ni}_3(\text{Al}, \text{Ti})$ γ' particles were also found, often contiguous with γ'' precipitates. Reflections 1 or 2 in Figure 1(c) are actually composed of a point, which is a $\langle 100 \rangle$ reflection from all the γ' precipitates, and a streak, which is a (002) reflection from one of the three sets of γ'' precipitates with differently oriented c -axes. A dark-field micrograph using one of these spots, therefore, shows all of the γ' particles and only one of the three systems of γ'' particles. Thus, by imaging with different reflections, the γ' and γ'' precipitates may be distinguished. The stress-free lattice parameters of γ , γ' , and γ'' are $a_\gamma = 0.352$ nm, $a_{\gamma'} = 0.356$ nm, and $a_{\gamma''} = 0.362$ nm and $c_{\gamma''} = 0.741$ nm, respectively [13]. However, because all three phases are strained to coherency with each other, $a_\gamma \approx a_{\gamma'} \approx a_{\gamma''} \approx c_{\gamma''}/2$ in alloy 725. Additionally, 100–200 nm Nb-rich carbides were observed within grains and at grain boundaries (Supplementary information, Figure S3), where they appeared either as isolated particles or as continuous films, respectively. Finally, cuboidal 0.5–10 μm Ti carbonitrides were also occasionally observed (Supplementary information, Figure S4).

Dark-field images of the alloy 725 sample (Figure 1(a) and 1(b)) acquired using superlattice reflections '1' and '2' shown in the SAED pattern in Figure 1(c) reveal uniform distributions of γ' and γ'' precipitates. γ'' precipitates are typically shaped as oblate ellipsoids with the shortest principal axis aligned with $[001]$ directions. In addition to isolated γ'' precipitates, such as those in Figure 1(d), high-resolution TEM also revealed coherent composite γ'/γ'' precipitates. For example, in Figure 1(e), γ' is sandwiched between two γ'' layers with cube-on-cube orientation relationships between all components: $(001)_{\gamma''} // \{100\}_{\gamma'} // \{100\}_{\gamma'}$ and $[100]_{\gamma''} // (100)_{\gamma'} // \{100\}_{\gamma'}$ [13]. Similar precipitates have been observed in Inconel® 718 [13,16]. In another common γ'/γ'' morphology, shown in Figure 1(f), cubic γ' 'cores' with edge lengths 10–15 nm are coated with a 'shell' of γ'' on all six $\{100\}$ faces. The extensive similarities in microstructure that we have observed in alloy 725 compared to that previously reported in alloy 718 suggest that similar mechanisms of mechanical deformation and environmental degradation are likely to be operative in both.

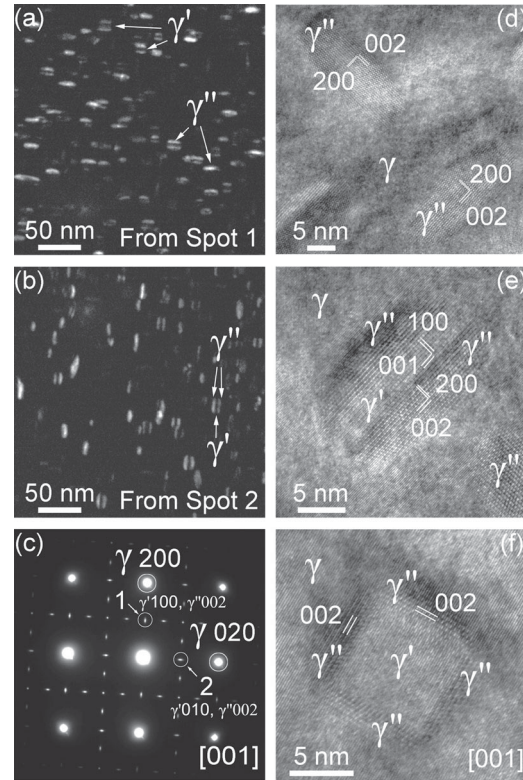


Figure 1. (a) and (b) Dark-field images of Inconel® 725 sample using '1' and '2' diffraction points in the SAED pattern (c) respectively, revealing the distribution of γ'' and γ' precipitates of specific orientations. The two γ'' precipitates indicated in (b) are parts of a single sandwich composite particle with γ' in the middle, similar to the one shown in (e). (c) SAED pattern along the $[001]$ zone axis, showing γ matrix as well as γ'' and γ' superlattice reflections. (d) High-resolution TEM image of two γ'' particles oriented perpendicular to each other. (e) A composite γ''/γ' precipitate with the sandwich morphology and (f) one with a 'core-shell' morphology.

Next, we used *in situ* TEM tensile straining experiments to investigate crack propagation in alloy 725. When tensile loading is applied to the TEM samples, transgranular cracks originating from the edges of the electropolished hole propagate along $\{111\}$ planes into the foil, as illustrated in Figure 2(a). Some cracks were found to cross multiple grain boundaries and no crack was observed to propagate exclusively along grain boundaries, indicating that the boundaries in thin foils of alloy 725 are not intrinsically weak. Stereoscopic and contrast analysis showed that the opening mode of most of these cracks was either mode II ('sliding') or, more frequently, mode III ('tearing') [16,17]. Propagation of such cracks in fcc metal TEM foils is known to proceed by the emission of glide dislocations on conventional $\{111\}\langle 110 \rangle$ slip systems from the crack tips: edge dislocations in mode II and screw dislocations in mode III [16]. Therefore, these cracks may be viewed as sources of dislocations with known glide planes and Burgers vectors.

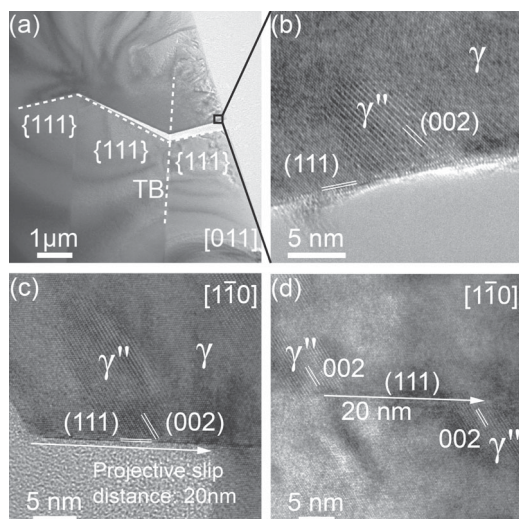


Figure 2. (a) TEM image showing a crack propagating in alloy 725 along $\{111\}$ planes across two twin boundaries. (b) High-resolution TEM image of the crack surface indicated by a black square in (a) contains part of a γ'' precipitate. (c) A nanoscale surface notch with slip displacement of 20 nm along the (111) plane. (d) A γ'' precipitate ahead of the notch shown in (c) that has been cut into two halves along the same (111) plane forming the notch. The amorphous structures above the scale bar in (b) and below the arrow in (c) are organic contaminants.

High-resolution examination of the region close to the crack surface (shown in Figure 2(b) and indicated by the black square in Figure 2(a)) demonstrates that the crack surface is nearly atomically flat and lies on a $\{111\}$ plane, as expected. We note that the amorphous structures observed on the surface (above the scale bar in Figure 2(b) and below the arrow in Figure 2(c)) are organic contaminants, which may adsorb during sample transfer as well as during the TEM investigation itself. They do not reflect the structure of the sample or affect its mechanical properties. Interestingly, we frequently observed evidence of cutting through of γ'' precipitates by cracks (Figure 2(b)); however, these may in fact be cut by dislocations emitted from the crack tip or from surface notches well in advance of a crack propagating through them. Therefore, we focus on examining γ'' precipitates ahead of such surface notches.

Figure 2(c) shows a notch that grows by the emission of edge dislocations. The sliding displacement along the notch in the $\langle 110 \rangle$ projection is ~ 20 nm, corresponding to ~ 80 glide dislocation Burgers vectors. γ'' precipitates directly ahead of this notch were found to be cut into two parts: one lying above the $\{111\}$ plane parallel to and aligned with the notch surface, and the other lying below it, as shown in Figure 2(d). These matching parts of initially disc-shaped γ'' precipitates have identical crystallographic orientations and are displaced from each other by the notch size, i.e. ~ 20 nm. These observations indicate that upper and lower halves of γ'' precipitates,

such as those in Figure 2(d), initially belonged to a single particle and were cut apart by dislocations emitted from the growing notch.

The fact that surface features such as nanoscale notches emit dislocations that cut apart γ'' precipitates suggests that surface morphology influences the rate at which sub-surface precipitates in Ni-base alloys are destroyed under mechanical loading. Thus, the state of free surfaces in alloys 718 and 725 may affect the evolution of sub-surface microstructure and, ultimately, mechanical behaviors that depend on the integrity of γ' and γ'' precipitates, such as initiation of planar bands. Stress concentration factors between 2 and 4 have been found at the tips of isolated surface notches [18] and pits [19,20] as well as for arrays of pits [21], supporting the view that dislocations are most likely to nucleate in their vicinity. Large pits have even been shown to nucleate cracks in steels [22].

A wide range of factors, especially mechanical contact with other solids, influence the state of free surfaces of engineering components. The surface morphology also depends on the chemistry of the operating environment. For example, in alloy 725, we find that selective etching of γ' and γ'' precipitates in sour environments may contribute to the formation of nanoscale notches on free surfaces. To simulate conditions that might be encountered in sour environments, we immersed TEM foils of alloy 725 into 20 vol.% sulfuric acid in methanol. Figure 3 shows that all the γ' and γ'' precipitates have been selectively etched, leaving behind nanoscale holes whose shapes, sizes, and distributions are the same as those of the precipitates. Most of the holes are, therefore, shaped as sections of oblate spheroids. The selective etching of the precipitates is further confirmed by the absence of corresponding superlattice reflections in the SAED pattern for the etched foil (Figure 3, inset). In a bulk alloy 725 component, such holes would only intersect one surface

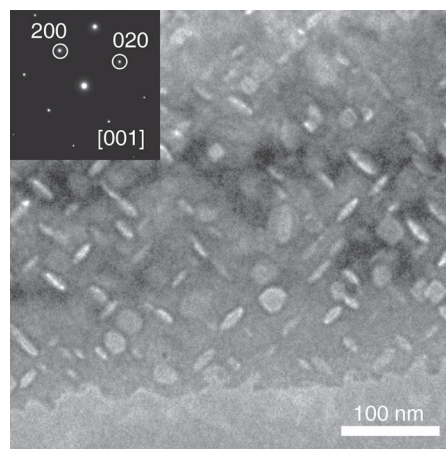


Figure 3. Bright-field TEM image of alloy 725 etched in an acidic solution showing selective etching of γ''/γ' precipitates. Inset: corresponding SAED shows only γ reflections.

(as opposed to two in the TEM foil) and would, therefore, form nanoscale surface pits.

Khantha et al. [23] proposed a classification of DO_{22} compounds into two types: those that deform by twinning on $\{111\}$ planes (e.g. Al_3Ti or Ni_3V), and those that deform by glide of $\langle 110 \rangle$ superdislocations on $\{111\}$ planes (e.g. Al_3V). Since we did see cutting apart of DO_{22} Ni_3Nb precipitates and never found any evidence of twinning, our work suggest that the deformation of DO_{22} Ni_3Nb is likely more akin to DO_{22} Al_3V rather than Al_3Ti or Ni_3V . In planar slip band formation under cyclic loading, precipitates are thought to be repeatedly cut by dislocations into segments so small that they may no longer be detected in TEM and may even re-dissolve into the matrix. Some controversy remains as to whether dislocation cross-slip is [9,24] or is not [8] essential to the breakup of the precipitates. The TEM results presented in Figure 2 suggest that cross slip is not necessary for cutting apart of γ'' precipitates by glide dislocations, at least at room temperature.

In summary, we presented tensile straining and high-resolution TEM evidence for the cutting apart of γ'' precipitates by glide dislocations emitted from nanoscale notches on free surfaces in Inconel[®] 725. This finding suggests that the state of free surfaces in alloy 725 may affect the evolution of sub-surface microstructure and, ultimately, mechanical behaviors that depend on the integrity of γ' and γ'' precipitates. Selective dissolution of γ'' precipitates in acidic environments is one example of a process that may provide copious surface pits capable of emitting dislocations that cut apart sub-surface γ'' precipitates.

Supplementary online material. A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2013.775187>

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