Heterogeneous Process of Disordering and Structural Refinement in Ni₃Al during Severe Plastic Deformation by High-Pressure Torsion

Octav Ciucă¹,* , Koichi Tsuchiya¹,², Yoshihiko Yokoyama³, Yoshikazu Todaka¹ and Minoru Umemoto¹

¹Department of Production Systems Engineering, Toyohashi University of Technology, Toyohashi 441-8580, Japan
²Hybrid Materials Center, National Institute for Materials Science, Tsukuba 305-0047, Japan
³Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The process of grain refinement in Ni₃Al by high-pressure torsion (HPT) was investigated up to 100 turns. The entire diametric sections of the deformed samples were analyzed by optical microscopy and image processing methods in order to evaluate both the spatial distribution and the volume fractions of the nanocrystalline and coarse grains. A thick band of nanocrystalline phase was formed in the middle section of the samples, and a structure containing mainly coarser ordered fragments was present in the vicinity of the top and bottom surfaces. Pseudo-twinning along {111} was observed at the boundaries of coarse-fragmented grains as well as the inside of the fragments and is put forward as a possible mechanism for disordering and nanocrystalline structure formation in Ni₃Al.

Keywords: disordering, twinning, high-pressure torsion, nanocrystalline materials, intermetallic compound

1. Introduction

The effect of SPD on the microstructures and properties of bulk metallic materials has been a subject of extensive investigations with the main goal of reducing the average grain size of the processed materials down to nanometer scale in order to improve their mechanical properties. A majority of those investigations, however, concern almost exclusively pure metals or solid solutions. Meanwhile there are much fewer reports on the severe plastic deformation of intermetallic compounds, and this is mainly due to the inherent brittleness of this class of materials. The High-Pressure Torsion (HPT) method opened a pathway to investigate these compounds since the large torsion deformation is applied under quasi-hydrostatic conditions which significantly suppress the fracture. A number of intermetallic compounds, such as TiNi,¹² Ni₃Al,³–⁶ Cu₃Au,⁷ ZrCu⁸ and Zr₂Al⁹ have been subjected to HPT deformation which, aside from the expected grain refinement, resulted in various interesting phenomena, e.g. amorphization, disordering, and/or shear band formation. Ni₃Al represents a very attractive group of intermetallics from a technological point of view, used mainly as a strengthening phase in superalloys. In recent years continued interest has been manifested towards the improvement of the mechanical properties, e.g. their ductility. HPT deformation of Ni₃Al has been studied by various workers. Languillaume et al.⁵ reported almost full disordering and grain refinements to 50 nm as well as the formation of the strong torsion texture. Korznikov et al.⁵ pointed out that the addition of B increases the thermal stabilities of the nano-grained structures in HPT-deformed Ni₃Al. The process of nanocrystalline structure formation during HPT deformation was studied by Korznikov et al.⁵

They reported a heterogeneous structure composed of highly misoriented nanocrystalline areas and microcrystalline areas with high densities of defects including dislocations and twins. They have found that the first stage of the nanostructure formation is the fragmentation of grains by the formation of deformation twins, followed by the development of misorientation between the fragments and eventually leading to disordered equiaxed nano-grains. They have also reported the formation of the heterogeneous structure, and indicated that grain fragmentation occurs along {111} planes, with the fragments separated by sharp boundaries. They concluded the boundaries have a character of dislocation boundaries. Local disordering at the boundaries has been found. The present authors have studied the nano-grain formation and its relation to the micro hardness. The deviation from Hall-Petch behavior in the hardness was related to the activity of Shockley-partial dislocations and to the appearance of deformation twins in the disordered nano-grains.¹¹

Therefore the process of nanostructure formation in Ni₃Al is still controversial, particularly the presence and importance of deformation twinning and the dominant mechanism of disordering. To shed a new light on these uncertainties, we have performed a systematic investigation on the evolution of microstructures in Ni₃Al. It will be shown that the deformation process during HPT can be inhomogeneous throughout the samples and that the pseudo-twinning may be one of the mechanisms of disordering.

2. Experimental

The material used in the present study was a single-phase binary Ni₃Al, arc-melted and cast into a cylindrical ingot of...
10 mm in diameter. The ingot was sliced into 0.85 mm thick discs, which were homogenized for 3.6 ks at 1173 K followed by furnace cooling. The samples were deformed at room temperature using a high-pressure torsion (HPT) apparatus with anvils having a depression depth of 0.25 mm. The details for the apparatus can be found elsewhere. The turning speed was set at 0.2 rpm and the applied pressure was 5 GPa. Both the planar and diametric sections of the plastically-deformed disc samples were prepared for optical microscopy; the planar samples were mechanically ground down to roughly the median plane and, along with the diametric samples, carefully etched with a mixture of 25 vol% nitric acid, 25 vol% sulfuric acid and 50 vol% water. Observations were performed on a Nikon Eclipse LV150 microscope in the dark-field (DF) and differential-interference contrast (DIC) observation modes. In the DF mode only reflections from surfaces at an angle different from 90° to the optical axis are allowed and these surfaces appear bright, while completely flat surfaces perpendicular to the optical axis appear dark. The DIC configuration uses the optical path difference of the beams reflected by surfaces at different relative heights to emphasize topological features on the sample surface. These two observation modes were used to characterize the topology of the etched specimen surfaces. Secondary-electron images of the etched sample surfaces were also obtained using a JEOL JSM-7001F scanning electron microscope. Images of the etched sample surfaces were also obtained. Two observation modes were used to characterize the topological features on the sample surface. These observation modes were used to characterize the topography of the etched specimen surfaces. Secondary-electron images of the etched sample surfaces were also obtained using a JEOL JSM-7001F scanning electron microscope operated at 15 kV. X-ray diffractometry (XRD) was performed on the diametric sections of the deformed discs using a RINT 2500 diffractometer (Bragg-Brentano geometry) with Cu-Kα radiation (40 kV–250 mA), 1/2 divergence and scattering slits, and an exit monochromator (graphite [0002]). The beam width varied between ~2–9 mm at the sample position for the chosen range of diffraction angles; this ensured the beam is wider than the diffracting surfaces of the samples. Disc samples (3 mmφ) for transmission electron microscopy (TEM) analysis were cut from the edge and central regions of the deformed samples so that the electron-transparent areas are situated near a radial distance of ~3.5 mm and 0 mm, respectively. Electropolishing was done using a Tenupol-5 with an electrolyte consisting of 20 vol% sulfuric acid and methanol at a temperature of 258 K with an applied voltage of 10 V. TEM investigations were performed on Hitachi H-800 and JEOL JEM-2000FX, both operated at an accelerating voltage of 200 kV. High-resolution TEM analysis was performed on a JEOL JEM 2100F microscope operated at 200 kV.

3. Results

The X-ray diffraction patterns measured on the diametric sections of the HPT-deformed discs are plotted in Fig. 1. Figure 1(a) shows the entire diffraction patterns, and Fig. 1(b) gives an enlarged view of the patterns in the lower angle region containing two superlattice reflections (100 and 110). The samples are identified in the plot by the number of turns N in HPT deformation. The diffraction pattern of the as-homogenized structure was also included. Two main trends can be noted. Firstly, the fundamental reflections show significant broadening and decrease in peak intensity during the first HPT turn, indicating significant structural refine-

Fig. 1 (a) Evolution in X-ray diffraction patterns of HPT deformed Ni$_3$Al, measured on the diametric sections of the disc samples. N: number of turns in HPT deformation. (b) Enlarged view of lower angle range.

![Fig. 1](image1.png)

Fig. 2 Lattice parameter, $a$, as a function of number of turns, N, in HPT deformation.

![Fig. 2](image2.png)
Crystallite size for the HPT-deformed samples was estimated from the measured broadening of the X-ray diffraction peaks using the Hall-Williamson equation, and appear to indicate an evolution with $N$ similar to the one reported by Korznikov et al. The average crystallite size determined in the present data, measured in the diametric sections, is consistently larger ($\sim 20 \text{ nm}$) than the value determined by the same experimental method on the planar section ($\sim 15 \text{ nm}$). The difference indicates that the grain refinements are more significant in the direction perpendicular to the plane of shear than within the plane.

DF optical images of the entire diametric sections used for XRD are presented in Fig. 3. The etching revealed regions with strongly different appearances. Dark bands can be seen running horizontally in the middle section of the HPT deformed samples, forming sharp interfaces with a much brighter structure. An increase in the thickness of the dark bands with $N$ is readily apparent. It is also apparent that their thickness increases at a higher rate in the edge than in the center of the discs. Details of the diametric section of the sample processed by $N = 1$ can be seen in Fig. 4. Structural features specific of the edge region are shown in Fig. 4(a) in DF mode. The dark areas with a predominantly horizontal orientation in the image are observed to be nearly-flat, almost featureless regions in the corresponding DIC image (Fig. 4(b)), while the bright regions in (a) are seen as a finely-fragmented structure in (b). These two significantly different appearances of neighboring regions of the etched surface suggest a clearly different reaction to the etching solution and are an indication of structural heterogeneity. Figures 4(c) and (d) show comparative secondary-electron images of the etched structure in the center and edge regions of the same sample respectively, at positions roughly around the median section of the discs. In both images, dark-gray regions which correspond to the dark areas in Fig. 4(a) and the featureless areas in Fig. 4(b) are covered by submicron etch pits, while the lighter areas seem to be relatively flat. Based on these observations and TEM observations in the previous works, it is inferred that the dark-gray areas covered by etch pits are nano-grained regions, which are disordered and thus less resistant to etching, and that the lighter, relatively flat areas correspond to coarse-grained volumes in which long-range order is retained, making them more resistant to etching. Figure 4(c) shows fragmented coarse grains apparently separated by thin bands of nanograins, which run parallel to the plane of shear. The fragmented aspect of the coarse grains suggests that the division caused by plastic deformation becomes increasingly finer with strain, with the fragments locally reaching submicron size. In the edge region of the sample where the theoretical strain is highest (Fig. 4(d)), the nanograined bands form a matrix completely surrounding remnant fragments of the coarse grains.

The area fraction of the nanocrystalline structure across the diametric section was estimated by image analysis techniques, by taking advantage of the strong contrast between the optical appearances of the two structures in DF mode. The results indicated a monotonic increase of the area fraction with straining, with maximum values for the sample deformed by 100 turns, of 36% for the entire section and of 58% in smaller edge areas.

Structural aspects of the edge regions of HPT-deformed samples as viewed in the planar section (parallel to the shearing plane and roughly in the median plane of the sample) were also analyzed by OM in the DIC mode and are presented in Fig. 5. The structure after the initial compres-
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A complete illustration of the microstructural evolution with plastic deformation of the binary alloy used in this study, as observed in TEM studies, is shown in Fig. 6. The initial compression ($N = 0$) leads to the accumulation of a large number of dislocations gliding along the $\{111\}$ slip planes.$^{17}$ The shear strain resulting from the rotation of the bottom HPT anvil initiates the fragmentation of the original grains and the formation of thin bands of nanocrystals, as seen in the structure characteristic for the $N = 1$ sample (Fig. 6(b)). As will be shown later, it is also in this stage that disordered nanograined bands are observed running along crystallographic boundaries. Further deformation ($N = 5$, Fig. 6(c)) leads to the formation of a nanocrystalline matrix in which fragments of coarse grains are completely isolated and maintain only a limited degree of LRO. The electron diffraction pattern of the nanocrystalline matrix assumes the typical ring shape with a uniform intensity distribution and it shows no superlattice reflections. At strain levels of more than 10 turns the structure becomes uniformly nanograined. These observations are consistent with the OM results presented in Fig. 5.

The edge region of the sample subjected to a moderate level of strain ($N = 1$), shown in Fig. 7, exhibits a finely fragmented grain surrounded by nanograined bands. This is in good agreement with the SEM observations on the diametric section discussed above (Fig. 4(d)). The fragments have large aspect ratios, and their widths are of the order of tens of nanometers. The fragmented structure is viewed along the $[011]$ direction, with two sets of $\{111\}$ planes end-on. The spreading of fundamental reflection spots in the diffraction pattern of the fragmented grain indicates relatively small azimuthal misorientation angles ($<$ 5°) between...
neighboring fragments. Superlattice reflections, although weaker than in the as-homogenized structure, indicate that LRO is still retained. The diffraction pattern of the surrounding bands shows almost perfect Debye rings, characteristic of nanograined structures, and no superlattice reflections, suggesting large misorientations and complete chemical disordering.

The details of the fragmented structures are shown in Figs. 8(a)–(d). Figures 8(a) and (b) show a BF image and the corresponding SAD pattern of the fragmented structure in the $N = 1$ sample, respectively. The appearance of the $g_{110}$ spot in Fig. 8(b) indicates that the long range order is still retained. Boundaries between the fragments are noted as the discontinuity in bend contours and strain contrast and are parallel to $\{111\}$ in Fig. 8(a). Similar features can be seen in a dark field (DF) image with a fundamental reflection of $g_{220}$ shown as Fig. 8(c). Figure 8(d) is a DF image of same area obtained with the $g_{110}$ superlattice reflection. The fragment boundaries appear dark in the image, although no contrast can be seen at the corresponding locations in Fig. 8(c), indicating the local disordering at the boundaries. The thickness of the disordered boundaries is as much as 5 nm. These results are similar to those found by Rentenberger et al.\textsuperscript{3}

Similar fragmented plate structures but with a different boundary structure were also found. Figure 9 shows a BF image (Fig. 9(a)), the corresponding SAD pattern (Fig. 9(b)) and a DF image (Fig. 9(c)) obtained from central region of $N = 1$ sample. As shown in Fig. 9(a) the fragments are separated by the long thin strips with thicknesses of less than 10 nm along the $\{111\}$ planes. Streaks perpendicular to the $\{111\}$ planes are visible in the corresponding diffraction pattern (Fig. 9(b)), caused by the reduced thickness of these structural features. Weak twin spots for the fundamental reflections ($g_{111}$ and $g_{200}$) are also visible, with $\{111\}$ as the twinning plane, but no twinning spots are seen on the

Fig. 5 Differential-interference contrast images of the edge regions of Ni$_3$Al samples deformed by HPT (plane view). a: $N = 0$ (compression only); b: $N = 1$; c: $N = 5$; d: $N = 10$.  

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superlattice reflections (e.g. $g_{011}$). Figure 9(c) is a DF image with the $g_{200}$ twin spot, which shows the strips appearing brighter, thus confirming the twin relationship between the strips and the fragmented plates. In addition, the absence of superlattice spots given by the strips indicates that they are disordered.

Figure 10(a) is a BF image of the fragmented plates in the central region of the $N = 1$ sample. In addition to the primary twins along (111) planes separating the fragments, secondary twins along (111) planes are visible which further divide each fragment plate. Figure 10(b) is a HREM image of a fragment boundary observed in the same sample. FFT images from the area delineated by the boxes A, B and C are shown as insets. A plate of about 6 nm thickness can be seen at the fragment boundary. The FFTs A and C reveal that the fragments on both sides of the thin plate have the same orientation, while the plate B is in the twin orientation with respect to A and C. It should be also noted that the superlattice spots are absent in B, which supports the probability that the thin twin plate formed at the fragment boundaries is disordered. The more details of structure and formation of the pseudo-twins are under investigation.

4. Discussion

The evolution of microstructures in Ni$_3$Al during severe plastic deformation has been investigated by various methods; the overall tendency is in general agreement with
those reported in the previous works;\textsuperscript{3,4,10,18} i.e., the formation of duplex structures composed of nanocrystalline areas of disordered fcc, and fragmented grains bounded by sharp boundaries parallel to \{111\} which maintain, at least in part, their \(\text{L}_2\) order. Further straining leads to a gradual increase in the volume fraction of the disordered nanocrystalline regions at the expense of the fragmented grains, until no trace of the latter can be found within the analyzed

![Fig. 8 TEM images of fragmented grains in Ni$_3$Al deformed by 1 turn of HPT. (a) bright-field image. (b) selected area diffraction. (c) dark-field image with fundamental reflection $g_{220}$. (d) dark-field image with superlattice reflection $g_{110}$.](image1)

![Fig. 9 TEM images of fragments boundaries. (a) bright-field image. (b) diffraction pattern showing the presence of twin spots. (c) dark-field image obtained by using the twin 200 spot marked by the dashed circle in (b).](image2)
volume. Aside from these views, the present investigation revealed the more heterogeneous nature of the deformation structures, as well as a possible mechanism of disordering by pseudo-twinning.

The panoramic images in Fig. 3 indicate not only the volume fraction evolution of the nanocrystalline region with torsional straining in a constrained HPT setup, but also the heterogeneous nature of grain refinement in the sample. The thick nanocrystalline bands form preferentially in, and extend from, the median section plane of the disc samples, parallel to the shear plane. The mechanism of the formation of this band is not clear at this point, but it may be related to a higher level of initial deformation in this middle section as a result of the HPT machine setup. The thickness of the disc sample of initial deformation in this middle section as a result of torsion straining. Hence it could be speculated that the deformation localized, at least to some extent, at the middle section near the edge, leading to the initial formation of a nanocrystalline band. Further shear straining causes a continuous increase in the volume fraction of nanocrystalline in the medium section as well as the gradual spreading of the grain-refined structure to adjacent regions. Rentenberger et al. suggested that the transition of coarse fragments to nanocrystalline occurs at their boundaries due to high stress concentration, and that the nanocrystalline structure in Ni$_3$Al accommodates larger strain than in the coarser structure. This may explain the observed heterogeneous process of nanocrystalline formation during straining. In addition, as was noted in Fig. 4(c), a network of very fine, submicron bands of disordered nanocrystalline grains is formed in the entire volume of the sample even at very low shear strains, thus explaining the rapid loss of LRO. However, the speculation cannot explain the relatively homogeneous structures in HPT-deformed pure metals. Further investigation is necessary to clarify the detailed mechanism of the heterogeneous process.

In the present study, the fragmented structures were very often found to be bounded by pseudo-twins on (111) planes. Secondary twins, which further divide the elongated fragments to equiaxed ones, were also observed, indicating a minimum of two active twinning systems. These observations are in partial agreement with a previous report of deformation twinning in HPT-deformed Ni$_3$Al. Kurznikov et al. observed twins with thicknesses of 300–400 nm on three active systems, and also much thinner twin lamellae, of ~20 nm, the latter being similar to our observations. However, the L1$_2$ long-range order was reportedly preserved. This seems to contradict the geometrical considerations of (111)(112) twinning in L1$_2$ lattice. Meanwhile, in a Ni$_3$Al alloy with a modified composition (Ni-18 mol%Al-8 mol%Cr-1 mol%Zr-0.15 mol%B), no twins were observed, although the microstructural aspect of the strained alloy was remarkably similar. The discrepancy may be due to the difference in the twin boundary energies of the investigated alloys. Rentenberger et al. attributed the disordering at the boundaries to the formation of APB tubes, which form as a result of the interaction between gliding dislocations. The present investigation revealed that the pseudo-twinning can be an additional mechanism of disordering. A possible grain-refinement mechanism is suggested which involves the formation of a fragmented structure and disordering by pseudo-twinning, and subsequently the division of elongated fragments into equiaxed fragments by secondary pseudo-twinning. As a result, a structure of equiaxed grains bounded by disordered twins forms. On further straining, these disordered boundaries can become active sources of superpartial dislocations, and they will further promote the disordering and dynamic recovery which will eventually lead to the formation of the nanocrystalline structure.

5. Conclusion

The process of disordering and grain refinement during severe plastic deformation by high pressure torsion (HPT)
was investigated for Ni$_3$Al. Even at relatively low levels of induced strain, almost complete loss of long-range order and the formation of a fully nanocrystalline band in the middle section of the disc samples were found. It is believed that this strongly heterogeneous distribution of the nanocrystalline phase in the deformed specimens is caused by the significant strain gradient occurring in the earliest stages of deformation at the sample edge, as a result of the HPT anvil geometry. Deformation twins were found at the boundaries of coarse fragmented grains and in their interiors in the sample after 1 turn of HPT deformation. The TEM analysis revealed that the twins were disordered; thus, they are pseudo-twins, never before reported in Ni$_3$Al. The observed twinning can be an important mechanism of disordering and grain refinement. More details on the structures and formation mechanisms of the pseudo-twins and their role in grain refinement are under investigation.

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