Effect of Nanocrystallization and Twinning on Hardness in Ni₃Al Deformed by High-Pressure Torsion

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Significantly larger grain size than in the case of nanostructured pure Ni. [doi:10.2320/matertrans.MRA2008485]

1. Introduction

Nanocrystalline metals have been a subject of extensive investigations for the last three decades, due to several attractive mechanical properties such as ultra-high strength and expected superplasticity at low temperatures and/or high strain rates. Severe plastic deformation (SPD) is one of the most recent process routes to obtain ultrafine-grained or nanocrystalline metallic materials in a bulk form. With such, SPD processes have been used as a tool for investigating the microstructures and properties of a wide range of pure metals and alloys. Meanwhile, the characteristics of nanostructured intermetallic compounds are at this time far less understood.

Ni₃Al is an intermetallic compound with the L1₂ ordered structure. Bulk nanostructure formation in this compound can be achieved as a result of deformation by high pressure torsion (HPT).¹⁻⁴ Plastic deformation of Ni₃Al by HPT was reported to lead to a duplex structure composed of coarse grains surrounded by regions of nano-sized grains. It has also been shown that the grain refinement is accompanied by chemical disordering to f.c.c. structure. The direct effect of such loss of long-range order is an increased mobility of dislocations and, as a result, structural softening. Thus, in the case of Ni₃Al subjected to SPD the mechanical properties would not only be affected by the activity of dislocations and the grain refinement, but also by the disordering. The purpose of the present investigation is to clarify the correlation between the evolution of hardness, such as the deviation from the Hall-Petch behavior,⁵ and the characteristic nanostructure occurring in HPT-deformed Ni₃Al.

2. Experimental Procedure

The material used in the present study was a 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. Optical microscope observations revealed columnar grains of approximately 900 × 200 μm². The discs were homogenized for 1 h at 1173 K. They were then deformed at room temperature by an HPT apparatus⁶ with a turning speed of 0.2 rpm under a nominal pressure of 5 GPa up to varying levels of strain. The imposed strain was estimated by the number of turns of the bottom anvil (N). The maximum level of plastic strain used in this study was 30 turns. The structure and mechanical properties of deformed discs were investigated by X-ray diffractometry (XRD) with Cu-Kα radiation (40 kV–250 mA), TEM (200 kV) and Vickers hardness indentation (2.942 N, 15 s). Samples for transmission electron microscopy (TEM) were cut from the edge regions of the deformed samples and electrolytically using Tenupol-5. The location of the analyzed area may roughly be estimated to a radial distance of 3.5 mm from the center of the HPT discs.

3. Results and Discussion

The XRD results are summarized in Fig. 1. The ratio between the peak intensities of the 100 superlattice reflection (I₁₀₀) and 200 fundamental reflection (I₂₀₀) is indicative of the degree of long-range order. The black solid circles show the evolution of this ratio with the number of turns in HPT deformation, N. It can be readily observed that the decrease in the I₁₀₀/I₂₀₀ is most significant during the first HPT turn, equivalent to the maximum equivalent von Mises strain of 30 (as calculated using the formula: \(\varepsilon = \frac{2\pi N r}{3t}\)), where r and t are the radial distance from the center and the thickness of the disc, respectively). The crystallite size, \(d_{XRD}\), is indicated by black solid diamonds and was estimated from...
the peak broadening of the 200 reflection in the XRD patterns using Scherrer’s equation:

\[ d = \frac{0.9 \cdot \lambda}{B \cdot \cos \theta} \]

\[ B = B_M - B_S \]

where \( \lambda \) is the wavelength of the X-ray source, \( B_M \) is the measured integral width and \( B_S \) is the standard width, measured on the diffraction pattern of the coarse-grained Ni3Al. Although included in the same plot, the average grain size value for the as-compressed \( (N = 0) \) sample, marked by \( \Phi \), was estimated from optical micrographs and included for comparison.

Fig. 1 Grain (or crystallite) size, \( d \), and XRD peak intensity ratio, \( I_{100}/I_{200} \), as a function of the number of turns, \( N \), in HPT deformation. The grain size for the as-compressed \( (N = 0) \) sample, marked by \( \Phi \), was estimated from optical micrographs and included for comparison.

The grain refinement occurs most drastically, from several hundred microns to \( \sim 100 \) nm, during the first single turn of HPT deformation. This clearly indicates that structural refinement proceeds concomitantly with disordering. An explanation for this phenomenon was suggested by Rentenberger et al.,\(^2\) based on observations made on a Ni–18 at%Al–8 at%Cr–1 at%Zr–0.15 at%B alloy. They noted that the interplay between the formation of APB tubes, which leads to local disordering, and the dynamic recovery of screw dislocations significantly promotes the grain refinement process. Since our observations of the studied Ni3Al alloy structure in the early stages of plastic deformation are remarkably similar to those of Rentenberger and coworkers,\(^2\) it is plausible that the mechanism described above applies equally well, at least qualitatively, in the case of a binary nickel aluminide.

Figure 2(a) is a dark-field TEM image of Ni3Al subjected to 30 turns of HPT deformation. A duplex structure composed of a predominant nanocrystalline (NC) area and a coarse-grained (CG) band region, running from the top to the bottom in the image, is seen. The selected-area diffraction (SAD) patterns of the NC and CG regions are shown as the insets. The almost uniform intensity of the Debye-Scherrer rings in the NC SAD pattern indicates nearly random orientations of the nanograins. No superlattice reflections can be discerned in the pattern. The CG band is fragmented into many blocks delineated by relatively sharp boundaries (marked by arrows in the image). The CG SAD pattern indicates that the sample normal is parallel to the \( h110 \) direction of the large, subdivided grain. The spreading of the fundamental reflections in the azimuth direction indicates a
maximum misorientation of the fragments of about 20 degrees. It is apparent that the boundaries between these fragments run nearly parallel to the traces of \{111\} planes, similar to what has been previously observed.\(^2\) Weak superlattice reflections, as pointed out by the white arrowheads, reveal that a low degree of long-range order is retained in the CG region. However, at this strain level the coarse-grained structure can only be found as small, isolated regions completely surrounded by the nanocrystalline structure, which explains the almost complete extinction of superlattice peaks in XRD patterns.

The grain size in the NC regions, measured from TEM dark-field images using the line intercept method, is also plotted in Fig. 1 as \(d_{\text{TEM}}\). These values are somewhat lower than those of \(d_{\text{XRD}}\). This can be explained by the fact that the \(d_{\text{TEM}}\) was measured only for the NC grains present in near-edge regions (\(r \approx 3.5\) mm), while \(d_{\text{XRD}}\) represents an average crystallite size for the whole sample. Also the heavy elastic distortion of the grain would lead to an underestimation of the grain size, since most of the grains are only partially visible under a specific diffraction condition. Nevertheless the \(d_{\text{TEM}}\) evolution exhibits a tendency very similar to that of \(d_{\text{XRD}}\). Figure 2(b) shows the bright-field image of the nanocrystalline region in the sample after 30 turns. A significant proportion of the grains exhibit striation or band-like contrast, such as those delineated in the figure. While some of these features are due to a moiré effect in regions where parts of the grains overlap, in most cases the striations are very sharp and straight throughout the grains. As Fig. 3 reveals in detail, these are in fact contrast effects due to planar defects. The grain widths are about 70 nm (grain A) and 40 nm (grain B). Despite the large imposed strain, dislocation density seems not to be very high, similar to what has been observed for nanocrystalline pure Ni.\(^8,9\) The corresponding SAD, shown as the inset, exhibits long, sharp streaks in two directions, perpendicular to the two planes of the defects in the bright-field image, indicating that the planar defects are stacking faults or twins, and the observation direction (i.e., the electron beam direction) is nearly parallel to the defect planes. It is noted that most of the faults have one end at the common grain boundary between the two grains (indicated by black arrowheads in the image), while a few of them end within the grain. This suggests that the faults are produced by the activity of the Shockley partial dislocations emitted from the grain boundaries. The details of the faults are more clearly seen in the high-resolution image presented in Fig. 3(b), which is a magnified view of the boxed area in Fig. 3(a). Several nanoscale twins (hereafter referred to as nanotwins) having widths of only a few interplanar spacings can be seen, along with several stacking faults. The single and double arrowheads denote twinning planes and stacking faults on (111), respectively. The white broken lines guide the eye to the change in direction of (111) planes caused by twinning. The widths of twin plates sometimes vary along their lengths.

In Fig. 4 the average hardness, \(H_V\), measured on the HPT-deformed samples is plotted as a function of \(d^{-1/2}\), where the values employed for \(d\) are those of \(d_{\text{XRD}}\). Some of the data from previous researches on Ni\(_3\)Al\(^1,10\) Ni-23 mass\%Cr-16 mass\%Mo-1.6 mass\%Cu alloy\(^11\) and pure Ni\(^12,13\) are also included for comparison. The data for electrodeposited\(^12\) and HPT-deformed\(^13\) pure Ni are shown by the open diamonds and circles, respectively. The white broken lines guide the eye to the change in direction of (111) planes caused by twinning. The widths of twin plates sometimes vary along their lengths.

**Fig. 3** (a) Bright-field TEM image of HPT-deformed sample (\(N = 30\)) with the corresponding diffraction pattern shown as inset. (b) High resolution image of the boxed area in (a). NTw: nanotwins.
study, marked by the black solid squares, begins to saturate at a much larger grain size of \(~100\) nm. In the case of the Ni-23 mass\%Cr-16 mass\%Mo-1.6 mass\%Cu alloy data, denoted by the open squares, the \(d\)-values used are those of the twin spacings,\(^{11}\) since it was shown that twin boundaries act as efficient barriers for dislocation movement.\(^{11,14}\) The hardness exhibits a \(d^{-1/2}\) dependence down to \(~100\) nm and then switches to an evolution which better fits a \(d^{-1}\) dependence. It can be noted that the critical grain size at which the hardness deviates from a \(d^{-1/2}\) dependence is very similar to that of the present set of data. The gray circles and diamonds indicate the data for HPT-deformed and aged Ni-Al alloys (boron-doped Ni\(_3\)Al by Languilleau et al.\(^{11}\)) and Ni-16.5 mol\%Al-8.2 mol\%Cr by Oh-ishi et al.\(^{10}\)). Both alloys were strained to a von Mises equivalent strain of \(~7\) and subsequently aged at various temperatures from 373 to 1273 K for 0.5 h\(^{11}\) or 1 h.\(^{10}\) Despite the differences in the chemical composition and aging time, the two sets of data agree quite well. Again, the maximal hardness value is recorded in the same grain size range of \(50\)–\(100\) nm. It should be noted that, in this case, the hardness peaks for these values of \(d\) and decreases at both higher and lower grain sizes. This can be accounted for by the combined effects of grain growth and re-ordering during the aging treatment. The maximum hardness of HPT-deformed and aged samples is higher by about 2 GPa than that of the disordered Ni alloys. The difference can be due to the additional hardening caused by re-ordering during the aging treatment. The hardness at the low end of the grain size range, corresponding to the as-deformed structure, roughly agrees with that of the present data.

If the hardness evolution of these alloys is compared to that of pure Ni, it readily becomes apparent that the critical grain size at which the hardness deviates from the typical \(d^{-1/2}\) dependence seems to be affected by the chemical compositions of the Ni alloys. Considering the strong influence of the chemical composition on the stacking fault energy (SFE) of alloys, insight regarding a possible effect of the SFE on the critical grain size becomes important for a clear understanding of these experimental observations. In a recent report\(^{15}\) it was shown that the compositional effect on the SFE of Cu alloys has a direct influence on the maximum grain size at which nanotwinning occurs by the grain boundary-activated mechanism described above. The compositional dependence of the stacking fault energy of Ni alloys was experimentally assessed by Beeston and France;\(^{16}\) they evaluated the effect on SFE of alloying with Cr, Fe, Ti, Al and Cu. The reduction of SFE per 1 mol\% of alloying element was determined to be 0.25\% for Cr and 0.23\% for Al. An evaluation of the SFE by the first principle calculation with the embedded-atom method (EAM) for disordered solid solutions of Ni-Cu, Ni-Co and Ni-Al by Nie et al.\(^{17}\) successfully predicted a similar tendency of SFE reduction by alloying, but the effect was less pronounced than that seen in the experimental results. Although the assessment was done for less than 10 mol\%Al, an extrapolation of the results to Ni-25 mol\%Al would lead to roughly a 6\% decrease in SFE, which amounts to about 118 mJm\(^{-2}\). Crude estimation of SFE for Ni-23 mass\%Cr-16 mass\%Mo-1.6 mass\%Cu leads to a similar value, which seems to support the similarity in the observed critical grain size for the two alloys. However, this possible explanation is only valid if the hardness of the Ni\(_3\)Al alloy evaluated in this study is considered to depend exclusively on the deformation behavior of the nanocrystalline disordered structure. In view of the evolution of the \(I_{100}/I_{200}\) ratio with induced strain and of the TEM observations of the heavily-deformed structure, as discussed above, this assumption becomes reasonable.

Deviation from the Hall-Petch relation below the critical grain size suggests a gradual change in the deformation-controlling mechanism from the conventional, intragranular type (pole mechanism) active in coarse grains to other, grain boundary-mediated mechanisms.\(^5\) Asaro et al.\(^{18}\) developed a theoretical model which indicates that, in fcc nanograined structures, the primary deformation mechanism switches from the generation and motion of perfect dislocations to the emission of partial dislocations from grain boundaries, and this new mechanism leads to a \(d^{-1}\) dependence of the hardness. This theoretical model is also confirmed by a series of MD simulations involving the accommodation of strain in nanocrystalline fcc metals.\(^{19,20}\) Thus, considering the above-mentioned compositional effect on SFE, it seems to be a natural consequence that the grain size range at which this transition occurs shifts to higher values in alloys than in pure Ni. There have been no systematic investigations of the density of deformation twins or stacking faults vs. grain size. Wu et al.\(^{5,9}\) deformed pure Ni samples with an average grain size of about 20\,nm at liquid nitrogen temperature; they observed a relatively high activity of deformation twins. This agrees with the critical grain size for pure Ni. On the contrary, twinning or stacking faults were often seen in alloys having average grain sizes as large as 75–100 nm, which also agrees with the critical grain size (as shown in Fig. 2 and 3). Hence the twins and/or stacking faults activity is closely related to the switch in the grain size dependence of the hardness.
4. Summary and Conclusions

The Ni$_3$Al intermetallic compound subjected to severe plastic deformation by high-pressure torsion had a mainly nanocrystalline structure along with a small volume fraction of coarse fragmented grains. The nanocrystalline grains contain a large number of twins and stacking faults. Most of these appeared to have one end at the grain boundaries, suggesting that grain boundaries are active sources of the Shockley-partial dislocations. The hardness reached a maximum value at a significantly larger grain size as compared to nanostructured pure Ni. The critical grain size at which the hardness saturates was found to be in the same range as those of other HPT-deformed nickel alloys with similar stacking fault energy. It is suggested that the hardness saturation reflects a change in the deformation mechanism from an intragranular process to a grain-boundary activated one, and that the stacking fault energy directly affects the critical grain size.

REFERENCES