Electron Microscopy of severely deformed L1$_2$ intermetallics

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Abstract

Severe plastic deformation (SPD) can be used to make bulk, nanostructured materials. Three L1$_2$ long-range ordered (LRO) intermetallic compounds were studied by TEM methods. The superlattice glide dislocations can dissociate according to two schemes: anti-phase boundary (APB) coupled unit dislocations or superlattice intrinsic stacking fault (SISF) coupled super Shockley partials; both of them are analysed by weak-beam TEM methods. The nanostructures resulting from SPD carried out by high pressure torsion (HPT) are strongly affected by the different dissociation schemes of the dislocations. APB-dissociated superlattice dislocations and especially the APB tubes they form lead to the destruction of the LRO by HPT deformation as observed in Cu$_3$Au and Ni$_3$Al whereas in Zr$_3$Al heavily deformed (∼ 100 000% shear strain) at low temperatures the order is not destroyed since the deformation occurs by SISF-dissociated dislocations. In addition to the effects on the LRO the different dissociation schemes of the dislocations have a strong impact on the refinement and destruction of the crystalline structure by SPD. They seem to be decisive for the dynamic recovery considered as the limiting factor for the final grain sizes and the possibility to reach amorphization. Finally, the correlation between the reduction of the LRO and the structural refinement occurring during SPD is different in the three different alloys: In Cu$_3$Au the LRO is already strongly reduced before the structural refinement reaches saturation, in Ni$_3$Al both are occurring simultaneously whereas in Zr$_3$Al the formation of the nanograins does not seem to be connected with disordering.
1 Introduction

Severe plastic deformation (SPD) is a novel tool to produce bulk nanostructured materials, i.e. materials with a typical grain size less than 100 nm [1]. By this top-down approach, bulk materials are deformed. The process of deformation introduces numerous lattice defects, which can lead to grain refinement down to grain sizes in the range of nanometers or in the case of alloys, even to amorphization [3, 4, 2]. The current interest in bulk nanocrystalline (NC) materials arises because they offer improved mechanical and other physical properties [5]. In this context long range ordered (LRO) intermetallics are of special interest because they are usually rather brittle due to their partly covalent bonding. SPD of intermetallic alloys can lead to a reduction of LRO and it has been shown that SPD-deformed Ni₃Al exhibits even superplastic behaviour [6].

In the present study, the method of high pressure torsion (HPT) is used to carry out SPD that produces bulk, non-porous specimens with a pure shear deformation up to 100 000% [7]. This large amount of shear strain requires the activation of a huge number of dislocations. In this work, we focus on L₁₂ LRO intermetallic compounds. In this case, the deformation occurs by the movement of superlattice dislocations on {111} planes having a Burgers vector: \( \mathbf{b} = a \langle 110 \rangle \) (\( a \): lattice constant). The glide dislocations can reduce their energy by dissociation. In the L₁₂ structure, there are two dissociation schemes for a \( a[\bar{1}01](111) \) glide dislocation:

\[
a[\bar{1}01] \rightarrow \frac{a}{2}[\bar{1}01] + APB + \frac{a}{2}[\bar{1}01] \tag{1}
\]

\[
a[\bar{1}01] \rightarrow \frac{a}{3}[2\bar{1}1] + SISF + \frac{a}{3}[\bar{1}12]. \tag{2}
\]

Eq. 1 shows the dissociation into unit dislocations bounding an antiphase boundary (APB) fault. The unit dislocations have the same Burgers vector as the glide dislocations in the fcc structure and they undergo a further dissociation into Shockley partials bounding a complex stacking fault in the L₁₂ structure [8]. Eq. 2 shows the dissociation into super Shockley partial dislocations bounding a superlattice intrinsic stacking fault (SISF). An important difference is that in case of Eq. 1 the chemical order is locally destroyed by the APB fault whereas in case of Eq. 2 the order is not affected by the SISF. Both dissociation schemes are observed to occur in L₁₂ intermetallics [9]. Therefore, we selected for the present study three different L₁₂ intermetallics: (i) Cu₃Au where the glide dislocations dissociate according to Eq. 1, (ii) Ni₃Al where both dissociation schemes are encountered although that of Eq. 1 is prevailing and (iii) Zr₃Al where the dissociation according to Eq. 2 is dominating at room temperature (RT) deformation.
2 Experimental Procedure

2.1 Ni$_3$Al

The Ni$_3$Al samples were grown as L1$_2$ LRO single-crystals using a modified Bridgman technique. They were homogenized at 1473 K for 120 h to reduce the grown-in dendritic structure. Samples oriented for single slip (compression axis [123]) were deformed in compression with a shear strain of 22% and cut parallel to the primary glide plane (111) to make TEM foils.

2.2 Cu$_3$Au

To get L1$_2$ ordered Cu$_3$Au samples, a special heat treatment was carried out since Cu$_3$Au has an order-disorder transition at 663 K. Samples with a grain size of about 200 µm were annealed at 623 K for 140 h and subsequently cooled by 10 K per day down to 433 K. After this treatment, the order parameter is close to 1 and the size of the grown-in domains is ~ 500 nm. For the HPT deformation, disks with a diameter of 8 mm and a thickness of 0.8 mm were made by spark cutting. The HPT deformation was conducted at a quasi-hydrostatic pressure of 4 GPa at RT.

2.3 Zr$_3$Al

The Zr$_3$Al samples were annealed at 1160 K for 24 h to facilitate the phase transformation $\alpha$-Zr + Zr$_2$Al $\rightarrow$ Zr$_3$Al since the L1$_2$ phase of Zr$_3$Al is stable only for temperatures lower than 1261 K, whereas the melting point is at 1623 K. The resulting material consisted of 80-90 % L1$_2$ ordered polycrystalline Zr$_3$Al containing residual Zr$_2$Al and $\alpha$-Zr. The HPT experiments were carried out analogous to the Cu$_3$Au ones. In addition, HPT experiments at liquid nitrogen temperature (LNT) were also conducted with the other parameters staying the same.

2.4 TEM

Out of the HPT disks of Cu$_3$Au and Zr$_3$Al, TEM disks were cut and thin foils were prepared by electropolishing using the polishing parameters described in [10] for Cu$_3$Au and 5% perchloric acid and 95% ethanol at 246 K and 11 V for Zr$_3$Al. For the Ni$_3$Al samples, 11% perchloric acid, 5% glycerin, 30% 2-butoxyethanol and 54% ethanol at 263 K and 22.5 V were used for electropolishing. The TEM studies were carried out at acceleration voltages 150 kV and 200 kV. Diffraction contrast images (bright-field (BF), dark-field (DF), weak-beam dark-field (WBDF)) were taken as well as diffraction patterns (DP) at regions of different degrees of deformation. Diffraction patterns of the Zr$_3$Al samples were recorded on a CCD and subsequently analysed using the PASAD software to get information about the state of order of the material deformed at different temperatures [11].

3
3 Results

3.1 Glide dislocations and antiphase boundary tubes in Ni$_3$Al

In Ni$_3$Al, mainly glide dislocations according to Eq. 1 are activated at room temperature; still in a few cases a transition from the dissociation scheme of Eq. 1 to that of Eq. 2 is observed. Such a transition is shown in Fig. 1 (WBDF images taken under different diffraction conditions). In Fig. 1(a) ($g = [202]$, BD $\sim [111]$) both unit dislocations and both superlattice Shockley dislocations are imaged near (1) and (2), respectively. The super Shockleys have a tendency to align along $\langle 110 \rangle$ directions (as it is seen near (2)) since in this orientation they can undergo a further dissociation leading to the formation of a locked dislocation (Giamei lock) [12]. In Fig. 1(b) ($g = [02\overline{2}]$) only one of the super Shockleys (the upper one) is in contrast since $g \cdot b \equiv [02\overline{2}] \cdot \frac{a}{2} [211] = 0$ for the lower one. In Fig. 1(c) the segment of the dislocation containing the APB fault (near (1)) is out of contrast whereas the SISF of the adjacent dislocation segment (near (2)) is in contrast. Although glide dislocations dissociate according to Eq. 1 at RT deformation, SISF are encountered in connection with dipoles since dipoles pulled out from normal glide dislocations with APB faults frequently convert into dipoles containing SISF [12]. The lines of weak contrast along $b$ visible in Fig. 1(b) and 1(c) are out of contrast in Fig. 1(a); they are identified as APB tubes built up by four intersecting APB faults. In a hard sphere model of the L1$_2$ structure the APB fault is a pure chemical fault and therefore an APB tube does not contain stair-rod dislocations at the intersection lines of the faults. APB tubes show up in superlattice reflections [13]; they should not be visible in fundamental reflections as it is the case in Fig. 1(b) and 1(c). In this context, it has to be mentioned that recent studies showed that in Ni$_3$Al the APB faults contain in addition to the chemical fault a tiny structural component giving rise to their image contrast in fundamental reflections (as imaged in Fig. 1(b) and 1(c)). In the case of intersecting APB faults this leads to very weak stair-rod dislocations ($b = \frac{a}{25} (110)$ or $b = \frac{a}{25} (200)$) [14].

In Fig. 2 APB tubes are imaged in a fundamental reflection ($g = [02\overline{2}]$). They show up as straight, weak lines. It is interesting to note that their density is at least locally quite high after only 22% of deformation. Several mechanisms have been put forward to explain the formation of APB tubes; they can be pulled out from non-aligned jogs of gliding APB-dissociated superlattice dislocations [16] and they can be formed during the cross-slip process of APB-dissociated superlattice dislocations, e.g. in the course of their annihilation [17, 18].

3.2 Antiphase boundary tubes in HPT deformed Cu$_3$Au

Fig. 3 shows a DF image and the corresponding DP of Cu$_3$Au deformed to shear strain $\gamma \sim 1000\%$ by HPT at RT. In Fig. 3(a) the APB domains are in contrast since a superlattice reflection is used as reflection vector ($g = [0\overline{1}1]$). Contrary to Ni$_3$Al, Cu$_3$Au contains grown-in APB domains. After deformation
Figure 1: WBDF images of Ni$_3$Al deformed in compression (22% shear strain) at RT. Superlattice glide dislocation showing a transition from the dissociation scheme with the APB fault to that with the SISF (marked (1) and (2), respectively). (a) $\mathbf{g} \parallel \mathbf{b}$: all dislocations in contrast. (b) One super Shockley partial out of contrast near (2). APB tubes (e.g., near (T)) in contrast. (c) Superlattice dislocation (1) out of contrast, SISF and APB tubes in contrast [15].
their density is increased as they are cut by glide dislocations. In addition to them, APB faults aligned along the traces of the \((1\overline{1}1)\) planes (which are parallel to the projection of \(b = \pm a[1\overline{1}1]\)) are visible in Fig. 3(a). They are identified as APB tubes by analysing the DP (cf. Fig. 3(b)). The DP contains the fundamental and superlattice spots corresponding to the beam direction \(BD \sim [011]\). (The fundamental spots are split since Au is redeposited epitactically on the surface during electropolishing.) In addition to the spots, streaks are observed going through superlattice spots only [19]. It is concluded that they are caused by disks in reciprocal space since their extension and intensity is relatively large near superlattice reflections (e.g. \(\pm [100]\)) that are rather weak under the given reflection condition \(g = [01\overline{1}]\). Therefore it can be followed that a high density of APB tubes is present after HPT deformation leading to a gradual reduction of the LRO.

### 3.3 SISF and amorphization in Zr\(_3\)Al

Figure 4(a) shows a DF image \((BD \sim [011])\) and the corresponding DP of a region with a high density of SISF in Zr\(_3\)Al. Due to the inhomogeneous deformation in the sample, the value of the local shear strain can only be estimated to be less than 10 000\% in the imaged region. The DF image was taken by placing the objective aperture on the streak connecting the fundamental reflection spots (cf. dashed circle in Fig. 4(b)). The streaks are caused by SISF.
Figure 3: (a) Cu₃Au deformed by HPT at RT (shear ∼1000%). (a) DF image taken with a superlattice reflection showing a high density of the grown-in APB domains cut by the glide dislocations and APB faults extended along b (dashed line, does not lie in image plane) identified as APB tubes by the DP. (b) DP showing fundamental and superlattice reflections. The APB tubes are causing the streaks going through the superlattice reflections only.
They are parallel to the (111) directions since the SISF lie on {111} planes. No streaks are observed near the superlattice spots indicating that APB faults are not occurring in a high density.

The influence of the deformation temperature on the structural changes by HPT deformation (of about the same amount) in Zr$_3$Al is shown in Fig. 5. In Fig. 5(a) the results of a sample deformed at LNT are illustrated. A band of amorphous material (labelled A) surrounded by NC regions is observed. The analysis of the DP by PASAD [11] of Fig. 5(a) reveals unambiguously that the chemical order is still present in the NC regions (grain size 10 to 20 nm) surrounding the amorphous band. Fig. 5(b) shows the results of a sample deformed at RT. The structure is NC (grain size again 10 to 20 nm), amorphous regions have not been encountered. The DP reveals that the amount of the order retained after the RT deformation is much less compared to that after LNT deformation although the amount of deformation and the grain sizes are similar in both cases.

4 Discussion

4.1 Destruction of LRO by SPD

From the experimental results shown in Chapter 3 it is concluded that the destruction of the LRO occurring during SPD is facilitated by glide dislocations containing APB faults (cf. Eq. 1).

In L1$_2$ LRO Cu$_3$Au the glide dislocations correspond to the scheme of Eq. 1 at RT deformation. SISF have not been observed. The destruction of the LRO by deformation is very effective since it occurs by both the cutting of the grown-in domains and the formation of a high density of APB tubes (cf. 3.2); the destruction seems to saturate at 5000% of deformation [20]. It should be pointed out that on a local (atomic) scale the structure will be rather inhomogeneous after the destruction of the LRO by SPD and therefore locally not equivalent to a disordered or short-range ordered (SRO) structure made by thermal treatment.

In Ni$_3$Al deformed at RT the vast majority of the glide dislocations contains APB faults; cases where a transition to a SISF-dissociated glide dislocation (as shown in Fig. 1) is observed are very rare. SISF are found to occur in Giaimei locked dipoles aligned along (110) directions. (It should be mentioned that in samples deformed at LNT a clear increase of the density of the SISF is occurring.) In Ni$_3$Al the dislocation structure observed after RT deformation contains mainly edge dislocations and only a few screws indicating that they cross-slip and annihilate thus giving rise to the formation of APB tubes [21] (This agrees with the fact that RT is below the temperature regime with an anomalous increase of the yield strength caused by screws converting to Kear-Wilsdorf locks [22]).

The destruction of the LRO starts locally in the regions of high deformation (e.g. at geometrical boundaries and slip bands); extensive disordering leading to the global loss of LRO seems to be directly associated with the process of
Figure 4: Zr$_3$Al deformed by HPT at RT (shear strain $\sim 10000\%$) (a) DF image of the SISF taken by placing the objective aperture on a streak between two fundamental reflections. The SISF are imaged as straight lines of bright contrast since BD $\sim [011]$. (b) DP with the position of the objective aperture encircled lying on a streak caused by the SISF. Streaks going through the superlattice reflections indicating APB faults have not been encountered.
Figure 5: BF images and DP of Zr$_3$Al deformed by HPT at different temperatures (shear strain $\sim$100 000%). (a) Deformed at LNT. NC phase (grain size 10 to 20 nm with an embedded amorphous band (A $\sim$50 nm wide)) lying about parallel to the shear direction (SD). The inserted diffraction pattern shows rings of superlattice reflections (marked by arrows) indicating that NC region is not disordered. (b) Deformed at RT. The size of the nanocrystals is similar to that in (a), the difference is that the DP of the NC region shows weak rings of superlattice reflections. Amorphous regions have not been encountered.
dynamic recovery followed by nanocrystallization [23]. In the nanocrystalline state, only a very small amount of residual order could be detected by high-resolution TEM [24]. It is proposed that for the process of disordering the APB tubes are more important than the stored superlattice dislocations containing APB faults. The density of APB tubes can be much higher than that of the dislocations since the long-range stress field of the tubes is very small compared to that of the dislocations (up to a factor 15). It is interesting to point out that the Ni$_3$Al samples with LRO destructed by SPD could be used to make in a bulk material tailored metastable APB domains of nanodimension that cannot be achieved by quenching.

In Zr$_3$Al the dislocation scheme of the glide dislocations is strongly dependent on the deformation temperature: Above 873 K APB-dissociated glide dislocations are prevailing; at temperatures below 673 K SISF-dissociated dislocations get more and more dominant the lower the temperature is [25, 26]. This agrees with the experimental findings of 3.3, yielding that the destruction of the LRO is more pronounced after the RT deformation than after LNT deformation. When the grain size is small, as in HPT-deformed Zr$_3$Al (10 to 20 nm), a reduction of the LRO arises together with a destruction of the structure by the atoms at the grain boundaries. This effect is even more pronounced in HPT deformed alloys since after HPT deformation, the grain boundaries are highly irregular.

4.2 Refinement and destruction of the crystalline structure by SPD

The SPD of metals and alloys leads to a reduction of the grain size by a process that is mediated by dislocations down to grain sizes of about 20 nm. At smaller grain sizes other deformation mechanisms (e.g. grain boundary mediated processes) are getting more and more important until at least in some alloys an amorphous structure is reached by destruction of the crystalline one.

In different L1$_2$ intermetallics different dissociation schemes of the glide dislocations are occurring. Superlattice glide dislocations bounding APB faults (cf. Eq. 1) are activated in Cu$_3$Au and Ni$_3$Al during RT deformation. At high densities caused by large strains they are leading to the reduction of the LRO (as discussed in 4.1). This has the important impact that after destruction of the LRO for a further deformation superlattice dislocations (a $\langle 110 \rangle$) are not necessary any more since the deformation can be carried by unit dislocations ($\frac{a}{2} \langle 110 \rangle$) like in fcc alloys. It seems safe to assume that dynamic recovery is the limiting factor for the deformation energy that can be stored by the dislocations during SPD. In Cu$_3$Au disordering takes place already in the coarse-grained material (cf. 3.2). Once the material is disordered, dynamic recovery (e.g. by cross-slip annihilation of screws) is easier than in the LRO structure.

This is used to explain the experimental result that in saturation, the grain size achieved by HPT deformation of Cu$_3$Au (100 to 500 nm) [20] is larger than that of Ni$_3$Al (4-200 nm) [27]. In Ni$_3$Al the structure stays ordered accumulating strain energy during the HPT deformation until it changes in a single step...
into a disordered NC structure. In Zr$_3$Al the dissociation of the superlattice dislocations with SISF is prevailing at RT deformation and completely dominating at LNT deformation. In this case dynamic recovery of the dislocations formed during HPT deformation is hindered since the widely dissociated super Shockley partials (cf. Fig. 1) will only partially annihilate leaving stair-rod dislocations ($\frac{a}{2} \langle 110 \rangle$) at the intersection line of the SISF behind. Therefore, a higher density of stored dislocations can be accumulated compared to the case of annihilating APB-coupled dislocations. This could explain that in Zr$_3$Al the grain size yielded in saturation by HPT at RT is small and that by deformation at LNT even amorphization can be achieved.

5 Conclusions

(i) From TEM studies it is concluded that APB-dissociated superlattice dislocations and especially the APB tubes they form lead to the destruction of the LRO by the HPT deformation as observed in Cu$_3$Au and Ni$_3$Al.

(ii) From the result of Zr$_3$Al heavily deformed at LNT ($\sim$100 000% shear strain) by HPT it is concluded that deformation by SISF-dissociated superlattice dislocations does not destroy the LRO.

(iii) It is concluded that in L1$_2$ intermetallics the two dissociation schemes of superlattice glide dislocations also have a strong impact on the refinement and destruction of the crystalline structure by SPD. The intrinsic properties of the glide dislocations (e.g. the ability of screws to cross-slip and annihilate) seem to be decisive for the dynamic recovery considered as the limiting factor for the final grain sizes and the possibility to reach amorphization.

(iv) From the results of Zr$_3$Al deformed at LNT it is concluded that the formation of nanograins is not necessarily connected with disordering.

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