**High-Pressure Torsion Induced Phase Transformations and Grain Refinement in Al/Ti Composites**

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**Abstract**

High-pressure torsion (HPT) deformation of multiphase metallic systems produces a high density of interfaces and leads to atomic mixing between the constituent phases. Here we present a study of the interphase boundary structure, grain size evolution and intermetallic phase formation during HPT deformation of a nano-crystalline Al/Ti composite. High-resolution transmission electron microscopy was used to study the structural features of the interphase boundaries. The Al/Ti interphase boundaries were found to significantly promote the generation of dislocations during deformation. After HPT deformation to a shear strain of 87, the average grain sizes of Al and Ti are 22 nm and 31 nm, respectively. The chemical mixing between the Al and Ti phases was enhanced by defect-mediated short circuit diffusion and dislocation-shuffle controlled plastic deformation at the interphase boundaries. The intermetallic phases formed during HPT deformation are associated with the strain energy stored by the high density of dislocations at the interphase boundaries.

**Keywords**: high pressure torsion; phase transformations; titanium aluminides; transmission electron microscopy

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**1. Introduction**

High-pressure torsion (HPT) deformation induced solid-state phase transformations have been reported in various metals matrix and composites [1-17]. Preferential phase transformations, such as formation of the super saturated solid solutions, amorphization of crystalline phases, crystallization in the amorphous matrix, and disordering of ordered phases, occur in HPT deformed composites. These transformations are influenced by several factors including: the maximum attainable strain, the solubility of the elements in each phase, the mixing enthalpy, and the atomic size difference of the constituent elements. Recently, HPT has been implemented to produce nano-crystalline intermetallic compounds (IMCs) via atomic-scale mixing of their elemental constituents. In related work with various systems such as, Cu-Al [3], Ti-Al [5,10], Ni-Al [4,5,9], Mg-Al [6,7], and Ni-Fe [8] systems, nano-crystalline IMCs generally formed prior to the saturation of the solid solutions and led to significant strength and hardness enhancement [18]. Another attractive potential application of HPT-produced nano-crystalline IMCs is in hydrogen storage [19-23]. The introduction of Mg-, Ti-, or Zr-based IMCs can reduce the enthalpy of hydride formation and the thermodynamic stability of the hydrides, and leads to a significant improvement in the hydrogen absorption and desorption kinetics.

Various mechanisms have been proposed for IMC formation driven by HPT deformation. These generally involve rapid diffusion due to the presence of high densities of vacancies, dislocations and grain boundaries [3-7]. For example, an enhancement in diffusion coefficients by a factor of 1012-1022 due to HPT processing was reported in the Cu-Al system [3]. In the Ni-Al system, the diffusion coefficients during HPT were estimated to be 1011 times higher than the lattice diffusion, and the activation energies for the diffusion at dislocations and grain boundaries were also decreased during HPT [4]. The concept of an effective temperature (*Teff*) has been adopted to explain HPT-driven phase transitions in metallic alloys. Since the atomic movements and defects generated during HPT deformation are similar to those formed during heat treatment at elevated temperatures, it is proposed that the processing of materials by HPT at ambient temperature is equivalent to heat treatment at an elevated temperature, *Teff* [24-26]. However, the *Teff* concept remains an unproven hypothesis, partly due the lack of a theoretical framework. In particular, the phase transformation mechanisms that occur during HPT are not well understood due to a lack of detailed experimental data.

Studies on HPT deformation in the Ti-Al and Ni-Al systems have suggested that a large strain and processing at elevated temperature is required for IMC formation [5,4]. In our previous study, TiAl2 and TiAl3 IMCs were produced at room temperature by using cryomilled Al/Ti nano-crystalline powder as the precursor for HPT deformation. It was demonstrated that elevated temperatures are not required for the formation of IMCs in the nano-crystalline Al/Ti system, and that dislocation- and vacancy-mediated short circuit diffusion makes a remarkable contribution to the formation of IMCs at room temperature [10]. Recently, molecular dynamics simulations were used to study the dislocation-interface interactions in metal-metal bilayer systems. It has been demonstrated that the metal-metal interfaces can act as strong barriers to dislocation propagation and can lead to considerable strain-hardening [27]. In related work on the atomic mixing in metals under shear deformation, molecular dynamics simulations revealed that atomic mixing occurs at coherent phase boundaries and involves dislocation propagation across the phase boundaries, whereas local atomic shuffling at the boundaries is the atomic mixing mechanism that occurs at incoherent phase boundaries [28]. Deformation by HPT leads to the formation of large areas of interphase boundary in metallic composite systems, however the effect of these interphase boundaries on the phase transformations and other associated phenomena have not been considered in detail. Motivated by this lack of fundamental information, we present a study on a HPT deformed nano-crystalline Al/Ti powder blend paying particular attention to the influence of interphase boundaries at different shear strains on the microstructure evolution and IMC formation. The relations between grain refinement and IMC formation during HPT deformation are also studied.

**2. Experimental**

Pure Ti powder (with 0.19% O, 0.017% N, 0.003% C and 0.013% Fe (all in wt%)) obtained from Advanced Specialty Metals (Nashua, NH) and pure Al powder (with <0.01% Cu, <0.01% Fe, <0.01% Mg, <0.01% Mn, <0.01% Si, <0.01% Zn and <0.05% O (all in wt%)) obtained from Valimet (Stockton, CA) were blended to give a mixture with an overall composition of Ti-47at.% Al. The mixture was cryomilled for 10 hours in a liquid argon environment (-181±5˚C) using a modified 1-S Szegvari attritor with a stainless steel impeller rotating at 180 rpm and 6.4 mm diameter stainless steel balls. After cryomilling, the Al and Ti particles have mean grain sizes of 42 nm and 100 nm, respectively, as measured by transmission electron microscopy (TEM). The details of the cryomilling and the microstructure of the Al/Ti powder blend are given elsewhere [29]. Briefly, the Ti particles were flattened and cold welded with Al particles; the average grain sizes of Al and Ti were almost saturated after 4 hours cryomilling; and the 10 hours cryomilled Al/Ti powder blend has average grain sizes of about 42 nm for Al and 100 nm for Ti [29]. Disks 10 mm in diameter and 0.72 mm in thickness were prepared by room temperature HPT processing of the cryomilled Al/Ti powder blend for 1, 2 and 5 revolutions under quasi-constrained conditions [30,31] at 6 GPa pressure with a rotation speed of 1 rpm. The top surfaces of the HPT processed samples were polished gently to a mirror finish using successively finer grades of SiC abrasive papers and colloidal silica suspension. The resulting disks had thicknesses of about 0.35 mm. The polished radial cross-sections of the disks were investigated by XRD using a Bruker AXS D2 Phaser diffractometer with a 30kV Cu K-α source. Vickers micro-hardness measurements were obtained from the polished disks at 0.5mm intervals along the radial direction. A minimum of 5 measurements were taken at each location using a load of 100mN with a 20 s holding time.

Due to the inhomogeneous microstructure in the center of the HPT deformed disks, no measurements were taken from the region 1mm in diameter around the central axis. TEM samples were prepared using an FEI Strata 400S Dual-Beam focused ion beam (FIB) system. FIB-cut sections were taken from the 2 revolution HPT processed disk along the shearing direction at locations 1.66 mm, 3.33 mm and 5 mm from the center of the disk. The shear strains at these three locations are 29, 58 and 87, and they are designated as Sample γ29, γ58 and γ87, respectively. A 3μm thick platinum layer was deposited onto the surface *in-situ* to protect the surface of the TEM specimen during ion milling. This deposition was performed in two steps: the first 0.5µm of Pt was deposited using the electron beam with an accelerating voltage of 2kV to crack the organometallic Pt precursor, and the remaining 2.5μm of Pt was deposited using the ion beam with an accelerating voltage of 30kV. FIB-cut lamellae 25μm x 5μm x 1μm were lifted from the disk surface, mounted onto copper Omni grids, and attached at 2 corners to limit mechanical buckling of the samples during final thinning. The lamellae were then milled to a final thickness of 50-100nm, and the ion beam currents were reduced iteratively to a value of 9.7 pA during final milling to avoid excessive Ga+ implantation and beam damage. The TEM samples were examined in a JEOL JEM-2010 FasTEM operated at an accelerating voltage of 200kV and equipped with an EDAX energy dispersive X-ray spectrometry (EDXS) system.

**3. Results**

The polished top surfaces of the HPT processed Al/Ti composite disks were examined by XRD. Examples of the indexed XRD patterns are shown in Figure 1. An XRD pattern from the cryomilled Al/Ti powder is also included in Figure 1 for comparison. The HPT deformed samples are mainly composed of crystalline hexagonal close packed (HCP) Ti and face centered cubic (FCC) Al. There is also evidence for the formation of secondary IMC phases after only 1 revolution of HPT processing. The additional peaks from these phases indicate that they are a mixture of TiAl2 and TiAl3, which is consistent with previous reports in the literature [6, 7, 11]. After further HPT processing (2 and 5 revolutions), no additional phases were identified from the XRD analysis.

The 1, 2 and 5 revolution (1R, 2R and 5R) HPT processed disks have shear strains ranging from 0-44, 0-87, and 0-244, respectively. The mean Vickers micro-hardness values as a function of the distance from the center of the disk, and as a function of the HPT shear strain, are plotted in Figures 2a and 2b, respectively. The measured micro-hardness values in the 1R HPT sample are almost even across the whole radial distance. The values increase slowly from the disk center to the edge in the 2R HPT sample. A rapid increase of micro-hardness with distance from the center is exhibited by the 5R HPT sample. In Figure 2b, it is clear that the onset of the hardness enhancement with increasing shear strain occurs at a shear strain of about 55. At lower shear strains, the Vickers micro-hardness levels off at a value of about 200 HV. At shear strains of above 55, the Vickers micro-hardness increases rapidly, reaching a value of 520 HV at a shear strain of 244. Examples of SEM micrographs from regions with shear strains (γ) of 29, 58 and 87 in the 2R HPT sample are shown in Figure 2c. The microstructure is inhomogeneous at γ=29. Only a small fraction of the Ti particles appear to have experienced severe deformation. Some Ti particles are broken into small pieces and some appear to retain their original shape. At γ=58 there is further mixing of Al and Ti, but large Ti particles remain in the mixture. At γ=87, however, the Al and Ti are mixed uniformly and their microstructures are refined significantly.

The details of the Al/Ti interphase boundary microstructures were investigated by TEM on the FIB-cut specimens from the 2R HPT γ29, γ58 and γ87 samples. Figure 3a is an example of a bright field (BF) TEM micrograph from the γ29 sample showing the inhomogeneous microstructure. The thickness of the elongated Ti and Al particles varies from 100 nm to several µm. The inset to this figure is the corresponding selected area diffraction pattern (SADP), which comprises spotty rings from the Al and Ti grains. The measured average grain sizes for Ti and Al in the γ29 sample are 85 nm and 43 nm, respectively. A phase contrast high-resolution TEM (HRTEM) micrograph from a Ti grain in this sample is shown in Figure 3b. There are low-angle grain boundaries inside the Ti grain, presumably due to dislocation rearrangement leading to the grain refinement of Ti phase. A BF image from the Al side of the Al/Ti interphase boundary is shown in Figure 3c; there are two small Al grains in the center of this area that appear to have formed at the Al/Ti interface. The HRTEM micrograph obtained from the boxed area in Figure 3c is shown in Figure 3d. The grain boundary between the two Al grains exhibits nanoscale facets. The Al grain on the right in Figure 3d is oriented along the [110] zone axis, as shown in the inset Fast-Fourier Transform (FFT) pattern. The {111} lattice fringes in the other Al grain are also indicated and in the image and the inset FFT.

Micrographs from semi-coherent Al/Ti interphase boundaries in the γ29 sample are shown in Figures 4a and 4b, respectively. Figure 4a is a BF TEM image showing an elongated Ti particle with a thickness of 50 nm along the strain direction. The HRTEM image from the boxed region at the interface is shown in Figure 4b. This shows that the (0002) planes of Ti are slightly misaligned with respect to {111} of Al. This mis-orientation of the lattices appears to be accommodated by edge dislocations in the Ti grain. Dislocation pile ups are not observed in the Ti and Al grains away from the interphase boundary. Corresponding micrographs from a typical incoherent interphase boundary are shown in Figures 4c and 4d. The BF image shows an elongated Ti particle with a thickness of about 100 nm, and an adjacent Al grain whose morphology suggests that it has sheared in conjunction with the Ti lamella (Figure 4c). The HRTEM micrograph in Figure 4d from the Al/Ti interface shows only one set of {111} lattice fringes, whereas the Ti grain is oriented along the [0001] zone axis. In the Al grain, there appears to be an accumulation of many dislocations near the incoherent interphase boundary. It is difficult to evaluate the local dislocation density accurately from such images due to the poor image quality from such strained and defective microstructures. Thus, in many areas only a single set of lattice fringes is visible. We have estimated the dislocation content by counting the numbers of terminating fringes in such regions of the HRTEM micrographs and a value of m-2 was obtained.

The γ58 sample exhibits a lamellar microstructure in which the thickness of the lamellae varies from tens to hundreds of nm, as shown in Figure 5a. The average grain sizes of Al and Ti are 44 nm and 66 nm, respectively. The SADP taken from an area which contains several Al/Ti lamellae is shown in the inset to Figure 5a. Extra diffraction spots appear inside the diffraction ring of Ti，as indicated by the arrows in the inset to Figure 5a. These diffraction spots are numbered as 1 and 2 with corresponding interplanar spacings of 0.289 nm and 0.395 nm. Since these lattice spacings do not match with any plane of Al or Ti, it indicates that the onset of phase transformation occurs in the nanocrystalline Al/Ti composite at a HPT shear strain of 58.

The detailed structure of the Al/Ti interphase boundaries were investigated in an attempt to determine the character of the phase transformation that occurs in the γ58 sample. A coherent Al/Ti interphase boundary in this sample is shown in Figure 5b. The planes in the Al grain are parallel to the (0002) planes in the Ti grain as indicated by the indexed FFT patterns. In the Al grain, there is a low angle grain boundary which appears to have formed by the rearrangement of dislocations slipping on the {111} planes. An incoherent phase boundary formed between a 30 nm thick Ti lamella and a 60 nm Al grain is shown in Figure 5c. A high-density of defects is generated in the bent Ti lamella as indicated by the arrows. The HRTEM image obtained from this boundary is shown in Figure 5d. The {111} planes in the Al lie parallel to planes in the Ti grain, and thus these grains exhibit the same orientation relationship as that found in the γ29 sample, as shown in Figure 4d. However, in this case, no dislocations are found in the Al grain. Instead, there is a third grain at the Al/Ti interface, and the lattice fringes correspond to those for the TiAl3 IMC (D022 structure) oriented along the zone axis. Thus, the extra diffraction spots 1 and 2 in the inset to Figure 5a correspond to {010} and {012} planes of TiAl3.

The BF TEM micrographs obtained from the γ87 sample revealed a further refined lamellar microstructure, as shown in Figure 6a. The Al and Ti lamellae are refined uniformly to a scale of about tens of nm. In the SADPs from these lamellae, extra diffraction rings appear around the central spots, as indicated by the arrows in the inset to Figure 6a. They are numbered as ring 1, 2, 3 and 4 with corresponding interplanar spacings of 0.285 nm, 0.391 nm, 0.508 nm, and 0.412 nm, respectively. Many IMC nano-particles were observed along the Al/Ti interphase boundaries, and they tended to be located in the Al side of these interfaces. Examples of HRTEM micrographs from the different types of IMC nano-particles and grains observed are shown in Figures 6b-d. These images show examples of h-TiAl2 (orthorhombic, ZrGa2-type, Cmmm), D022 TiAl3, and D019 Ti3Al grains, respectively. Thus, the extra diffraction rings 1, 2, 3 and 4 in the inset to Figure 6a correspond to {010} and {012} of TiAl3, of Ti3Al, and (300) of h-TiAl2, respectively.

Lastly, we note that the structural changes were accompanied by changes in the chemical compositions of the Al and Ti phases. A summary of the compositions measured from the various samples by EDXS point analyses in the TEM are listed in Table 2. The HPT deformation induced significant chemical mixing between Al and Ti, increasing the average concentration of Al in Ti grains and Ti in Al grains from 1.4 at.% and 4 at.%, respectively in the γ29 sample to 23.5 at.% and 8.8 at.%, respectively in the γ87 sample.

**4. Discussion**

The saturation of grain refinement for severe plastic deformation (SPD) processed coarse-grained single-phase metal corresponds to a dynamic balance between the formation of dislocation structures and thermally activated recovery. The phenomenon of grain size saturation in HPT-processed pure metals and single-phase alloys has been addressed in detail elsewhere [32,33]. The grain sizes observed usually range from about 100 nm to above 1 μm. In contrast, SPD processing of such materials with nano-scale grains (i.e. below the saturated grain size) usually leads to grain growth. In one example, the average grain size in cryomilled Cu powders deformed by HPT increased from 46 nm to 90 nm via grain rotation induced grain coalescence [34]. Similar grain growth phenomena were also reported in HPT-deformed nano-crystalline NiFe [35], Ni [36] and Ti [37]. In recent studies combining multiple SPD techniques on Al 7075 alloy, it was demonstrated that equal-channel angular pressing through a finer channel prior to HPT deformation led to a higher saturation hardness and a finer saturation grain size [38,39]. This suggests that the saturation grain size depends critically on the deformation history and defect content of the material prior to HPT. In the present study, the Al and Ti in the starting cryomilled nanocrystalline powder blend have average grain sizes of 42 nm and 100 nm, respectively. HPT processing further refined the average grain sizes to 22 nm and 31 nm, respectively. These values are much lower than those reported for the saturated grain size of HPT-deformed pure Al or Ti, which were 500 nm and 150 nm, respectively [40,41]. A similar pronounced grain refinement has also been reported in a HPT-deformed Cu/Cr composite [42], and this phenomenon was attributed to the effects of the heterophase boundaries introduced by SPD [42,43].

In the samples studied here, the Al/Ti interphase boundaries have a limited influence on the overall grain refinement at HPT strains below 58. The HPT-deformed nano-crystalline Al/Ti composite exhibits a morphology that is consistent with hard Ti particles embedded in a soft Al matrix. The Al matrix is thus expected to sustain the most strain, and to transfer load to the Ti particles through interphase boundary mediated plastic flow. Fragmentation of the Ti particles at a shear strain of 29 is consistent with the deformation of Ti particles being dominated by shear localization [44], as shown in Figure 2c. Consequently, a small fraction of the strain is imposed on the interphase boundaries. The grain size evolution of Al and Ti is still mediated by dislocations and their interactions with grain boundaries. Since the Al and Ti in the starting powder have different average grain sizes (42 nm and 100 nm, respectively), the Al deforms by edge dislocation emission and Ti deforms by the slip of lattice dislocations [45]. The Al grain boundaries serve as the sources and sinks of the dislocations, as shown in Figure 3d. Nanoscale facets form on the Al grain boundaries after the dislocations slip on the {111} planes, cross the grains, and annihilate in the grain boundaries. Therefore, there is also no grain refinement for Al at shear strain less than 58. In the Ti grains, dislocations are generated, rearrange to form sub-grain boundaries, and refine the grain size, as shown in Figure 3b. However, the localized shear deformation of Ti particles at a HPT strain of 29 would constrain the grain refinement so that it only occurs in the deformed area. This leads to a small reduction in the average grain size from 100 nm to 85 nm.

At a HPT strain of 58, the lamellar spacings of the Al and Ti phases were reduced to a scale of tens to a few hundred nm. This leads to a high density of interphase boundaries, which geometrically confine dislocation motion and multiplication. To accommodate the Al/Ti co-deformation, dislocations must slip across the interphase boundaries. To meet the structural requirement for slip transfer, these Al/Ti interphase boundaries have to be coherent to minimize the interface energy and misorientation between the adjacent two slip planes [46]. The coherent Al/Ti interphase boundary shown in Figure 5b has an orientation relationship of {111}Al//(0002)Ti. These parallel planes are the primary slip planes for FCC Al and HCP Ti, respectively. Therefore, slip transmission was activated and led to a considerable strain hardening, as shown in Figure 2b. Excessive dislocations could pile up at the interphase boundaries and rearrange to form subgrain boundaries leading to grain refinement, as shown in Figure 5b. Increasing the shear strain to 87 further refined the Al/Ti lamellae to a thickness of tens of nm. Interphase dislocation motion and multiplication was further promoted, and this refined the average grain sizes to 22 nm and 31 nm for Al and Ti, respectively.

The HPT deformation induced chemical mixing (see Table 2) could impede dislocation motion by solute drag [47] and may reduce the stacking fault energy (SFE) of Al and Ti. The effect of Al alloying on the SFE of Ti has been reported in several previous studies [48,49]. The measured SFEs of pure Ti and Al are 310 mJ/m2 and 166 mJ/m2, respectively. In Ti alloys with 10 at.% of Al, the SFE falls to 82 mJ/m2 [48]. The SFEs of Ti-45%Al and Ti-49%Al alloys have been estimated at 64 and 97 mJ/m2 [50],respectively. The effects of Ti on the SFE of Al have not been studied, largely due to the extremely low equilibrium solubility of Ti in Al. However, related studies in the Al-Mg and Al-Ga systems suggest that alloying of Al with Mg or Ga leads to a significant decrease in SFE [51,52]. Therefore, it is reasonable to anticipate that the mechanical alloying of Ti in Al alloy can also reduce the SFE of Al. Decreasing the minimum grain size by reducing the SFE has been reported for various SPD-processed Cu and Al alloys [51,53,54]. In this study, we infer that the chemical mixing between Ti and Al reduces the SFEs for the alloyed Ti and Al and contributes to grain refinement.

SPD-induced mechanical alloying between Al and Ti is essential for diffusion-controlled IMC formation. In several previous studies the accelerated inter-diffusion between constituent phases was attributed to an increase in the density of SPD-induced defects including dislocations and vacancies [3-7]. In cryomilled Al/Ti nano-crystalline composites it was established that the average dislocation densities of both the Al and Ti phases decrease slightly with increasing shear strain in the early stages of the HPT deformation [10]. This suggests that the microstructural refinement induced shortening of the diffusion distances and the high densities of vacancies induced by the HPT have a major effect on the chemical mixing between the Al and Ti phases at low HPT strains. At HPT shear strains larger than 58, the further refined microstructure not only reduces the diffusion distance between the Al and Ti phases to the scale of tens of nanometers, but also significantly promotes interactions between dislocations and interphase boundaries. In contrast to these diffusional mechanisms, it has also been proposed that one can have plasticity-driven chemical mixing by a dislocation shuffle mechanism [55]. This mechanism induces small compositional changes by mass-transport via slip transmission on multiple slip systems. In the case of nanoscale phases, further deformation will occur by dislocation movement until complete dissolution occurs [55,56]. In this study, multiple slip systems in the Al are activated at a shear strain of 58, with the assistance of edge dislocations in Ti slipping across the interphase boundaries, as shown in Figure 5b. Further HPT deformation can embed small Al particles into the Ti phase via the dislocations shuffle mechanism leading to a concentration of 23.7 at.% Al in the Ti grains at shear strain of 87.

In this study, the formation of IMCs was not observed around the coherent Al/Ti interphase boundaries. The intensive dislocation activities at such boundaries may lead to IMC embryos re-dissolving by the dislocation shuffle mechanism [56]. All of the IMCs that we observed lay along the incoherent interphase boundaries. A typical incoherent interphase boundary in the γ29 sample is defined by the conjunction of of a Ti grain and {111} of an Al grain, as shown in Figure 4d. The dislocation density in the Al grain was estimated at about m-2. In the γ58 sample, an incoherent interphase boundary with a similar configuration was shown in Figure 5d. A TiAl3 particle was observed at the interface, and no dislocations were observed on {111} in the Al grain. This implies that the formation of IMCs may be associated with a local decrease in the dislocation density of their parent grains. The rearrangement of dislocations to reduce strain energy could provide the free energy required for IMC formation. Moreover, the strain energy introduced by dislocation pile ups can also contribute to the growth of IMC particles. The strain energy for randomly distributed edge dislocations (*E*) is given by [57],

…………..(1)

where,is the dislocation density, is the shear modulus, is the magnitude of the Burgers vector, is Poisson’s ratio, is a constant that associates with the core energy of dislocation, and *R* is the outside radius of strain around a dislocation. An approximation of the term is 0.5 [57]. For Al, = 0.32, = 26 GPa, and *b* for ½<110>-type perfect dislocations is 0.286 nm [58]. At the incoherent interphase boundary where dislocation density is about m-2, the calculated strain energy is about 39 kJ/mol using equation (1). The activation energy of bulk diffusion controlled TiAl3 growth was reported in range of 100 - 300 kJ/mol [59,60]. However, grain boundary diffusion controlled TiAl3 growth has a much lower activation energy of about 33.8 kJ/mol [59]. The formation of IMCs may produce a coherent interphase boundary between the IMCs and the parent grains. This coherent interphase boundary may serve as a dislocation sink leading to the dislocation density decrease shown in Figure 4d. The dislocation strain energy can energetically activate the growth of IMCs. Since TiAl3 has the smallest Gibbs free energy of formation among all IMCs in the Al/Ti system [61], it is not surprising that TiAl3 was the first IMC to form under HPT deformation at a strain of 58. The IMCs having larger free energies of formation, such as TiAl2 and Ti3Al, formed at a strain of 87. This HPT-induced IMC formation sequence is consistent with the Al/Ti diffusive reaction sequence reported elsewhere in the literature [62-65].

**5. Conclusions**

We studied the effect of interphase boundaries on the microstructure evolution and IMC formation in a HPT-deformed Al/Ti nano-crystalline composite. The main conclusions drawn from this study are as follows:

1. HPT deformation refined the microstructure of the Al/Ti nano-crystalline composite, reducing the diffusion distance between the Al and Ti phases, and promoting the formation of interphase boundaries with increasing shear strain.
2. At low HPT strain, the interphase boundaries have limited influence on the grain refinement due to the inhomogeneous microstructure. At high HPT strain, the grain size of the nano-crystalline Al/Ti composite was further refined by the interactions between dislocations and interphase boundaries.
3. The chemical mixing between the Al and Ti phases was enhanced by the defect-mediated short circuit diffusion. At the coherent interphase boundaries, a dislocation shuffle mechanism may also contribute to the deformation-induced chemical mixing.
4. HPT-induced IMC formation in the nano-crystalline Al/Ti composite occurs at the incoherent interphase boundaries with the assistance of the strain energy stored by the high densities of dislocations.

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**Figure Captions**

Figure 1. XRD profiles of the 10h cryomilled Al/Ti powder and the compacts that were subsequently deformed by HPT for 1, 2 and 5 revolutions (1R, 2R and 5R, respectively).

Figure 2. Vickers micro-hardness as a function of distance from the disc center (a) and HPT deformation strain (b) for the HPT processed samples. (c) SEM micrographs from the locations with shear strains (γ) of 29, 58 and 87 in the 2R HPT sample.

Figure 3. TEM data from the γ29 sample: (a) BF image and SADP (inset) of Al/Ti interfaces. (b) HRTEM image of a low-angle grain boundary formed in the Ti. (c) BF image of Al grains along an Al/Ti interphase boundary. (d) HRTEM image of the Al grain boundary marked by the box in Fig. 3c with corresponding FFT patterns inset.

Figure 4. TEM data from the γ29 sample: (a) BF and (b) HRTEM images of a semi-coherent Al/Ti interphase boundary. (c) BF image and (d) HRTEM image with corresponding FFT patterns inset of an incoherent Al/Ti interphase boundary.

Figure 5. TEM data from the γ58 sample: (a) BF image and SADP (inset) of Al/Ti lamellae. (b) HRTEM image of a coherent Al/Ti interphase boundary with corresponding FFT patterns inset. (c) BF image and (d) HRTEM micrographs with corresponding FFT patterns inset of an incoherent Al/Ti interphase boundary.

Figure 6. TEM data from the γ87 sample: (a) BF image and SADP (inset) of the Al/Ti lamellae. (b-d) HRTEM images with corresponding FFT patterns inset of regions containing: (b) TiAl2 (c) TiAl3, and (d) Ti3Al IMCs formed in the sample.

**Table Captions**

Table 1. Average grain sizes of Al and Ti determined from TEM micrographs.

Table 2. Chemical composition of the Al(Ti) and Ti(Al) phases determined by EDXS in the TEM.

Table 1. Average grain sizes of Al and Ti determined from TEM micrographs.

|  |  |  |
| --- | --- | --- |
|  | Al (nm) | Ti (nm) |
| 10h cryomilled Al/Ti Powder blend [22] | 42 | 100 |
| γ29 FIB Sample | 43 | 85 |
| γ58 FIB Sample | 44 | 66 |
| γ87 FIB Sample | 22 | 31 |

Table 2. Chemical composition of the Al(Ti) and Ti(Al) phases determined by EDXS in the TEM.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Al (Ti) | |  | Ti (Al) | |
|  | Al / at.% | Ti / at.% |  | Ti/ at.% | Al / at.% |
| γ29 FIB Sample | 96 | 4 |  | 98.6 | 1.4 |
| γ58 FIB Sample | 91.7 | 8.3 |  | 89.2 | 10.8 |
| γ87 FIB Sample | 91.2 | 8.8 |  | 76.5 | 23.5 |