MICROSTRUCTURAL EVOLUTION AND PHASE STABILITY OF CU/NB NANOLAMINATES SUBJECTED TO SEVERE PLASTIC DEFORMATION BY HIGH PRESSURE TORSION

BY
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DISSERTATION

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Nanostructured metals and alloys have become attractive candidates for advanced material applications due to their potential to exhibit superior material properties, honed from the existence of large density of interfaces and their interactions with dislocations and defects. Severe plastic deformation has become one of the most promising techniques for producing nanostructured materials in large amounts, and, in some cases, in the bulk shape. This dissertation focuses on providing a better understanding of deformation mechanisms imposed via severe shear deformation to Cu-Nb nanolaminates fabricated by accumulative roll bonding. Severe plastic deformation was applied in a controlled way using high pressure torsion, reaching very large strains, allowing to investigate microstructural evolutions and phase stability as a function to strain, and to reach true steady states.

The results show that the two dimensional layered microstructure was progressively replaced by a three-dimensional Cu-Nb nanocomposite. This structure remained stable with respect to grain size, morphology and crystallographic texture, and was comprised of biconnected Cu-rich and Nb-rich regions, with a remarkably small coexistence scale of 5-10 nm. In a second step, the effect of the initial layer thickness on the microstructures observed in ARB composites after HPT deformation was investigated by comparing results obtained for ARB materials with nominal layer thickness of 18 nm, 200 nm, and 2 μm. For the 200 nm ARB composites, strains exceeding 3,400 were required for destabilization of layers. At a strain of 10,000, the microstructure has fully transformed to 3-D microstructure, similar to the ones observed for 18 nm and 2 μm composites. The 2 μm ARB composites subjected to high pressure torsion showed the presence of microscopic features like folds and swirls, previously observed on the 18 nm ARB composites, and complete...
destabilization of the layered structure was observed at a shear strain of ~4,200, suggesting that in the presence of folds and swirls, the length scale dependence of the strain required to reach steady state is compatible with a super-diffusive mechanism.
Dedicated to my beloved family, and to my mother, for their unyielding support and love.
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CHAPTER 1

INTRODUCTION

Nanostructured metals and alloys have become attractive candidates for advanced material applications due to their potential to exhibit superior material properties [1]. This is especially true with respect to their mechanical properties, owing to the existence of large density of interfaces and their interactions with dislocations and defects [2–4]. While earlier synthesis of such nanostructures relied on powder processing using ball milling and inert gas condensation [2], severe plastic deformation (SPD) has become one of the most promising methods for producing nanostructured materials in bulk form [5].

Several SPD techniques are commonly employed, including equal channel angular extrusion (ECAE), accumulative roll bonding (ARB) [6], wire drawing, and high pressure torsion (HPT) [7, 8]. These processing techniques differ in terms of the strain applied to the material, e.g., nearly simple shear in ECAE and HPT but pure shear in ARB, as well as in the accessible total strain ($\gamma$), ranging from strains on the order of 1 per pass in ECAE and ARB to strains of several thousand in HPT. From a fundamental as well as practical perspective, it is therefore important and interesting to understand and control the microstructural evolution and stability of nanostructures fabricated by each of these SPD methods as well as nanostructures produced by one SPD technique and subsequently subjected to a different SPD route.

The properties of traditional materials are often optimized by the existence of second phases and inclusions, and this approach is very likely to provide similar benefits for nanostructured
materials. ARB and wire drawing techniques have been used to successfully produce bulk nanocomposites materials starting from dissimilar materials. One notable application of this approach has been the synthesis of Cu/Nb nanocomposites via ARB [9, 10], with individual layer thicknesses as small as 9 nm. Cu/Nb nanocomposites have been originally developed for high conductivity and high strength applications, and they also hold great promise for applications requiring resistance to high energy particle irradiation [11–13], to plastic deformation [14], and to exposure at elevated temperatures [15]. Cu/Nb multi-layer nanocomposites fabricated by ARB, below an individual layer thickness of ~ 1 μm, were found to have an unusual interface orientation that remains stable under further rolling deformation [14]. It is noteworthy that this interface is distinct from the one that is observed when Cu/Nb multilayers were grown by PVD. It was also shown by computer simulations that this interface stabilized under ARB may have higher shear strength [16] than those obtained by PVD. For those reasons, the stabilization of these interfaces may be useful for optimizing material properties.

This dissertation is focused on providing a better understanding on deformation mechanisms imposed via shear deformation by investigating the evolution of microstructure and phase coexistence of Cu-Nb nanolaminates fabricated by ARB when subjected to HPT. In addition to providing a change in strain path, from pure shear in rolling to simple shear, HPT makes it possible to reach very large strains, thus allowing to achieve true steady state. As detailed in the following chapters, we have characterized this steady state microstructure, namely the grain size, the scale of phase coexistence, and the crystallographic texture developed in the Cu and Nb phases, as well as the pathway that the microstructure follows to go from the nanolaminates prepared by ARB to the nanocomposites stabilized by large HPT strains.
An additional point of focus for this dissertation concerns the atomic mixing mechanisms of Cu and Nb under SPD. Moderately immiscible elements such as Cu/Ag [17], Cu/Fe [18, 19] and Cu/Co [20], are known to become chemically mixed under SPD at low temperatures. This behavior has been rationalized by the concept of relocation of atoms via ballistic mixing processes [21, 22]. Atomistic simulations [23] have suggested that the chemical mixing have a superdiffusive nature for these binary alloys, i.e. the mean square relative displacement between marker atoms increased more than linearly with time. This superdiffusive chemical mixing is forced by dislocation glide as the dislocations directly travel across interfaces; and it is consistent with recent experiments determining the critical HPT strains required to homogenize Cu/Ag composites with different initial scales of phase coexistence [24, 25]. However, the forced chemical mixing mechanisms in metal systems with high positive heats of mixing, such as Cu/Mo [26], Cu/Ta [27], Ni/Ag [28] and Cu/Nb [29] is not yet well understood. It is known that SPD can slightly increase the solubility limits of highly immiscible elements, however, no complete mixing of the system is observed. It is particularly interesting that these systems undergo self-organization under low temperature SPD, i.e., they select a steady state length-scale for phase separation that only depends on the intensity (strain) applied by SPD. Therefore, it is intriguing to investigate whether ARB processed Cu/Nb nanolayers would self-organize when subjected to high strain by HPT; and if so, to determine the length-scale and mixing mechanism of the self-organization.

In this study, ARB processed Cu/Nb multi-layered nanocomposites with different individual layer thicknesses, were subjected to various shear stains via HPT. The evolution of microstructure and mixing were characterized as a function of the applied strain, employing X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning TEM (STEM). Additionally, scanning electron microscopy (SEM) and focused ion beam (FIB) were utilized
during sample preparation. For HPT samples (on those with the initial average Cu/Nb layer thickness of \( \approx 18 \text{ nm} \)), at steady state (high strain), atom probe tomography (APT) was also performed by a project collaborator, as a complementary characterization method.

1.1. REFERENCES


CHAPTER 2

BACKGROUND

It is now well documented that most material properties depend on the microstructure of the material, and by controlling the microstructure, material properties can be altered. Nano-structured (NS) materials, defined as polycrystalline materials with average grain size at nanometer scale (less than 100 nm), have gained considerable attraction over the several decades due to their superior mechanical and physical properties in comparison to coarse-grained materials. In particular, NS materials offer substantial improvements in strength and hardness [1]. This phenomenon is a direct result from the reduction in crystal size, and largely follow extrapolations of Hall-Petch’s law to the nanometric regime. One of the main challenges to realize these improvements in engineering materials is the fabrication of NS materials, in particular bulk materials, while simultaneously controlling their nanostructuration.

Two fundamentally different processes are commonly employed to produce materials with grain sizes at nanometer length-scales [2]. The first one is the “bottom-up” approach, in which bulk NS metals are assembled from the atomic or nanoscale levels (e.g. nanoparticles). Techniques that use this approach are inert-gas condensation [3], electrodeposition [4], chemical and physical condensation [5] and high-energy ball milling followed with consolidation [6]. While these techniques can successfully produce materials with exceptionally small grain sizes down to nanometer scale, they potentially introduce contaminations and residual porosity during the fabrication process. An important concern also is that some coarsening of the nanostructures can take place during consolidation, especially when consolidation involves elevated temperatures and
high stresses. The second approach is the “top down” approach, in which starting materials with coarse grains undergo substantial grain refinement to obtain bulk NS materials. Grain refinement is often achieved through application of severe plastic deformation (SPD), by applying heavy straining or shock loading to the material without significant changes in the overall dimensions of the material. Examples of these processes are reviewed in detail in the next paragraph. Materials processed by SPD techniques have grain sizes in the range of 100 – 1000 nm, with subgrain structures, i.e. subgrains, dislocation cells and crystallites that are often smaller than 100 nm [2].

2.1. APPLICATION OF SPD FOR SYNTHESIZING NS MATERIALS

Several SPD techniques are commonly utilized, including equal-channel angular pressing (ECAP) [7], wire drawing [8], accumulative roll bonding (ARB) [9] and high pressure torsion (HPT) [10, 11]. While all these techniques are known to refine the grain sizes down to the nanometer scale, the resulting microstructure could be quite distinct, since these processing routes differ in terms of the strain path imposed on the material, e.g. nearly simple shear in ECAP and HPT but pure shear in ARB. This difference can lead to the stabilization of different crystallographic phases and possibly, different phases. Another important difference between these processing techniques is the range of accessible strain values, from strain of 1 per pass for ECAP to strains to the order of 10 for ARB and to strains of several thousand in HPT.

SPD techniques introduce the capability of producing large, bulk nano-grained materials. These techniques offer a good potential for production scale-up with the promise of producing nano-grained materials with relatively low cost. For instance, the current cost to produce a 5-20 mm diameter round nano-grained bar of titanium and titanium alloys manufactured by continuous ECAP processing was reported to range between $50 to $150/kg [2]. For HPT,
a continuous severe torsion process on Mg alloy has recently been proposed [12]. In this study, one end of an Mg-alloy rod is rotated around the longitudinal axis, while the other end is immobile. The torsion of the mobile rod end permits for a continuous production of a severely plastically deformed material. Here, local heating and cooling regions are integrated in the set-up for inhibiting localized deformation during the SPD process. The material is, however, not subjected to high hydrostatic pressure, thus, cracking of the material is inevitable. Due to necessary heating and limited amount of torsional strain caused by cracking, the refinement of microstructure is rather limited. However, this technique allowed for significant improvement on the compression formability at both room and elevated temperature, which may offer a large scale application in industry. Another attempt for continuous HPT processing included application of torsion in combination with extrusion. The container/die that holds the sample material was rotated during continuous extrusion under controlled pressure. Due to the high pressure, the sample survives mechanical failure during the process. This technique is very close to the “regular” HPT process and is very promising for a simple large scale production of SPD materials [12].

Material response to SPD has initially focused on elemental systems, but recent studies have included binary and even ternary metal systems. In systems comprised of highly immiscible elements, it is often observed that SPD cannot homogenize the material’s composition, in contrast to systems with moderately immiscible or miscible elements. It has been proposed that phase coexistence could in fact be used to optimize the microstructure and the properties of NS materials, very much in the same way as conventional materials are optimized by precipitation. Our fundamental understanding of the stabilization of nanostructures by SPD in multiphase alloys is however limited. The focus of this dissertation is thus to contribute to a development of this knowledge by focusing on Cu-Nb nanolaminates, which serves here as a model system
representative of alloy systems based on highly immiscible elements. The starting Cu-Nb nanocomposites samples were manufactured using ARB, and were then subjected to HPT. The principles of these two SPD techniques will thus be described in detail in the following section. This section will then be followed by a detailed description on material response of immiscible metals systems subjected to SPD; specifically shear deformation. Lastly, previous studies on the Cu-Nb system will be described in detail.

2.1.1. Principles of Synthesis via Accumulative Roll Bonding (ARB)

Accumulative roll bonding is a rolling deformation technique that can be used to produce nanostructured materials by accumulating plastic strain. The first application of this technique dates back many years, initially under different terminologies, i.e. cold roll bonding (CRB) or cold pressure bonding (CPB). In 1999, the first ARB process is proposed by Saito et al. [9], where bulk strips of commercial Al (1100), Al-Mg alloy (5083) and Ti-added interstitial free (IF) steel were selected to test material bonding through consecutive steps of surface treatment, stacking and roll-bonding. A representation of the ARB process is shown in Fig. 2.1.
As its name suggests, ARB is not only a deformation process but also a bonding process. In order to achieve good bonding, the material surfaces are de-greased and wire brushed before the stacking step. In some cases, ARB is carried out at elevated temperatures below the recrystallization temperature of the roll-bonded materials, to maintain a good bonding. After the sheets reach to the rolls, the wire-brushed surfaces fracture due to the sheet elongation, leading to the exposure of fresh underlying material. As the exposed surfaces from both metals come into contact, metallic bonding is accomplished. Before the bonding step, a threshold deformation must be reached [13]. However, the total amount of strain applied on the material by ARB is very limited compared to other SPD techniques such as ball milling (BM) or high pressure torsion (HPT), only reaching to a maximum plane strain on the order of 10.
2.1.2. Principles of High Pressure Torsion (HPT)

High pressure torsion is a “top-down” severe plastic deformation (SPD) process where plastic deformation is employed through compressive force and concurrent torsional straining. Even though the fundamentals of this SPD process was first proposed over 70 years ago [14], HPT gained more importance within the last 25 years, where it has been accepted as a metal forming technique, providing the opportunity to achieve exceptional mechanical strength and grain refinement down to nanometer-scale while fabricating bulk nanostructured materials. A schematic representation of the HPT process is illustrated in Fig. 2.2. Compared to other commonly employed “top-down” SPD processes, i.e. ARB, ECAP and ball milling, HPT processing gained a major interest for its capability of reaching plastic strains up to tens of thousands, without a major change in sample shape and without sample failure.

Fig. 2.2. Schematic illustration of HPT processing [15].
Samples processed under HPT are either disc or ring shaped. In HPT process, the sample is put between the anvils and compressed under a hydrostatic pressure of several GPa. Often, the bottom anvil rotates as the top anvil stays stationary, resulting in shear straining on the sample, as long as friction between the anvils and the sample surfaces is large. When deformation is uniform throughout the sample, the imposed macroscopic deformation can be directly used to calculate the resulting shear strain at any given location on the disc-sample. During HPT deformation, if sample thickness is assumed to be constant, then the total shear strain $\gamma$, at a given distance $r$ from the center of the sample of thickness $t$ is given by Eq. 2.1:

$$\gamma = \frac{2\pi r N}{t}$$

where $N$ is the number of turns applied by the anvils [18, 19]. According to this equation, the strain at the center should be zero and maximum at the edge of the disc. This allows for analysis of a spectrum of strains in one HPT processed sample.

![Fig. 2.3. Schematics of the different anvil configurations in HPT process [10].](image)

Non-constrained  Constrained  Quasi-constrained
HPT process can be applied using different anvil configurations, namely constrained, non-constrained and quasi-constrained geometries [10]. Illustrations for both anvil geometries are given in Fig. 2.3. In constrained and quasi-constrained anvil configurations, the sample is placed into a cavity in the lower anvil [20, 21], permitting zero to very limited material flow during the HPT process. These configurations are helpful in order to maintain sample thickness and shape during HPT, however, recent studies have shown that plastic deformation does not progress homogeneously through the sample thickness when these configurations were used [22, 23]. In these studies, the plastic deformation was observed to be localized near the sample surface, leading to an increase of the actual strain experienced by this area to be 1 – 2 orders of magnitude larger than calculated via Eq. 2.1.

In unconstrained geometry, the material is placed between flat anvils and is free to flow outwards under applied pressure. This configuration results in a reduction in thickness of the sample during HPT processing. A significant reduction in thickness is generally observed during the axial loading of the anvils, followed by an additional thickness reduction during torsional straining, which is smaller compared to the reduction observed at the initial stage. This phenomenon was found to be dependent on the spacing between the anvils, starting sample thickness, applied load and strength of the sample material [22]. The compression deformation applied to the sample by axial load was found to be very small, compared to large torsional straining applied on the sample, with the exception of the center of the disc. It should be noted, however, that although it is well known that HPT processing predominantly occurs by simple shear, the presence of high compressive pressure and frictional forces complicated the material flow and effect the mode of deformation.
2.2. MATERIAL RESPONSE OF IMMISCIBLE ELEMENTS UNDER SPD

In the simple case where plastic deformation is accommodated by dislocations gliding across the material’s microstructure and in particular across coherent phase boundaries, the motion of these dislocations produces a chemical mixing of the different elements present in the alloy of interest. In the case of immiscible elements, this mixing will go against thermodynamic driving forces, as long as the alloy composition and the deformation temperature are in a region of phase co-existence in the equilibrium phase diagram. In a first approximation, this forced mixing may be assumed to be independent of temperature and local concentration, in which case the mixing is said to be ballistic. Any temperature dependence is assumed to be derived from the thermally activated jumps of point defects, either by point defects produced during deformation or those on thermal equilibrium. In such immiscible alloy systems, SPD at intermediate temperature results in a competition between the chemical mixing forced by plastic deformation and the phase separation driven by thermodynamics. This competition is reminiscent of the approach introduced by Martin [23] to describe the evolution of alloys under irradiation, in which case nuclear collisions are creating the ballistic mixing. This approach can be summarized by an “effective temperature formula”, which captures the fact that by varying the temperature and the forcing rate, the system will eventually reach a steady state, ranging from random solid solution at high forcing rate and low temperature, to phase separated at low forcing rate and high temperature. While this approach has been useful to rationalize a number of experimental and computational studies on alloys subjected to irradiation and ball milling, two important modifications need to be taken into account in the context of the present study. The first point has to do with the fact that the mixing forced by dislocation glide is not diffusive, but super-diffusive. The second point is that the mixing can no
longer ballistic when considering alloy systems comprised of highly immiscible elements such as Cu and Nb. We discuss these two important points in some detail below.

The first point is best described by considering alloy systems made of miscible or moderately immiscible elements such as Cu-Ag [24] and Cu-Fe [25], which are known to become single phase alloys under SPD. In these alloys, with heats of mixing not exceeding 10 kJ/mol, atomistic simulations have suggested that dislocations can indeed directly transfer across interfaces, and that the corresponding chemical mixing forced by dislocation glide is in super-diffusive nature, that is, the mean square relative displacement between marker atoms increases more than linearly with time. This super-diffusive characteristic has been confirmed by recent experiments determining the critical HPT strains required to homogenize Cu-Ag composites with different initial scales of phase co-existence [26, 27], as we now detail.

In a binary A-B system, the rate of mixing is analogous to the rate of creating new A-B bonds per unit time (or strain). If we define here, \( N_A^B \) as the average number of B-nearest neighbors around A atoms, and \( c \) as the atomic fraction of A in A-B alloy, the chemical mixing can be characterized by a short range order \( \Omega \) defined as [34].

\[
\text{Eq.2.2} \quad \Omega = \frac{c}{1-c} \frac{N_A^B + \frac{1-c}{c}N_B^A}{N_A^A + N_B^B} - 1
\]

This parameter \( \Omega \) takes values of -1, 0 and 1 for states that are phase separated, random or fully ordered, respectively. Assuming the dislocations can easily cut through the precipitates with a probability proportional to their length-scale, the strain to reach complete homogenization (fully mixed or reach steady state) is possible with achieving the maximum number of A-B bonds.
If the evolution of \((\Omega)\) can be measured experimentally, the mixing process can be studied. The initial rate of mixing expressed in \((\Omega)\) can be expressed as [35]:

\[
\frac{d\Omega}{dt} = \frac{3g}{4} \frac{V_p}{C_B(1-C_B)} \frac{b}{R_{p,i}} \dot{\varepsilon}
\]

where \(g\) is a geometric factor, \(V_p\) is the volume fraction of the precipitates \((V_p = n_p4\pi R_{p,i}^3/3)\), \(R_{p,i}\) is the initial size of B precipitates in a binary A-B system, \(\dot{\varepsilon}\) is the strain rate, \(b\) is the Burgers vector and \(C_B\) is the molar fraction of precipitates. According to Eq. 2.3, the mixing rate for a given initial volume fraction of precipitates, is proportional to \(1/R_{p,i}\). From this relationship, the strain required to reach fully homogenization in the presence of precipitates with certain length-scale (in the absence of thermally activated diffusion) is:

\[
\Delta \varepsilon_{mix} = \frac{16 C_B (1-C_B)}{3} \frac{R_{p,i}}{V_p} \frac{b}{b}
\]

According to Eq. 2.4, if the system undergoes super-diffusive mixing, the strain required to fully homogenize the microstructure is proportional to \(R_{p,i}\). It takes the application of smaller strains to homogenize alloy systems with precipitates at smaller size. In the case of diffusive mixing, the strain required to mix (or reach steady state) would scale quadratically with the precipitate size.

In a recent study on two phase Cu_{90}Ag_{10} alloys, critical strain for complete mixing was determined as a function of the precipitate size by application of severe plastic deformation by high pressure torsion. Atom probe tomography (APT) was employed to examine the compositional homogeneity at finer length-scales. Information collected from APT experiments were used to calculate the number of nearest neighbor Cu-Ag bonds (see Fig. 2.4), normalized by the total
number of Cu-Ag bonds required for a complete solid solution. It was reported that the strain required for complete mixing scales linearly with Ag precipitate size, indicating that the forced mixing behavior is superdiffusive [27].

Fig. 2.4. Normalized number of Cu-Ag bonds as a function of strain for Cu-Ag samples with 16 nm Ag particle size subjected to 1.5 cycles (blue) and 3 cycles (green) and, 61 nm Ag particle size subjected to 6 cycles (red). The inset shows the strain to fully mix the microstructure vs the initial particle size [25].

An important consequence of this super-diffusive mixing is that these alloys can spontaneously self-organize into nanocomposites, whose length scale can be tuned by varying the temperature at which deformation takes place [24, 28–31].

Turning now to the second point, multiple studies have shown that alloy systems with high heats of mixing show different behavior. In particular, alloy systems such as Cu-Nb, Cu-Mo [32], Ni-Ag [33], remain two-phase during low-temperature SPD, even at cryogenic temperatures [34],
although they reach to homogenization over length-scales as small as ≈ 50 nm. A number of studies on alloy systems with high heats of mixing were performed to understand the extension of solid solubility. Solubility limits in these highly immiscible alloys are only slightly enhanced when subjected to SPD, even at very low temperatures, approaching 100 K. SPD experiments on Ni-Ag [33], Cu-Mo [32], Cu-Ta [35] and Cu-Nb [36] systems show that alloys with high heats of mixing do not always undergo complete homogenization under SPD, even at temperatures where vacancies are immobile. The shear induced mixing saturates at a certain phase length-scale, leading to phase co-existence, and therefore, no complete mixing of the system is observed.

While the question still remains on the failure of these binary systems to homogenize under SPD, two approaches were used to resolve this behavior. Firstly, it was suggested that the deformation is localized at the softer phase, preventing dislocation motion across interfaces. This plastic localization was indeed observed in molecular dynamics (MD) simulations of some model systems designed to be close to systems like Ag-Ni [25, 26]. The second proposed explanation is that the mechanical mixing of atoms is not truly “ballistic” and it is affected by high heat of mixing of the alloy elements. The latter explanation was investigated by Lund and Schuh [39] by employing molecular statistics on two-dimensional (2D) amorphous alloys, and it was found that at an effective temperature of 0 K, local chemical order parameter (Ω), calculated using Eq. 2.2, indicated a steady state at a certain length-scale during shear deformation.

In the case of moderately immiscible alloys, it has been proposed that selection of the final length-scale selections results from the dynamical competition between thermally activated phase separation and forced mixing. However, such a systematic understanding of mixing behavior in highly immiscible materials is still missing. In a recent study by Wang et al. [34], on phase evolution of Cu$_{80}$Nb$_{10}$Ag$_{10}$ subjected to low temperature SPD by HPT and ball milling showed
that, in the absence of thermally activated diffusion, Nb precipitates reached a well-defined steady-state size, $\approx 20$ nm, and this size results from plasticity-driven mechanisms promoting precipitate shrinkage by emission of Nb atoms from the surface as well as nucleation and growth of these new Nb precipitates due to chemically biased motion of Nb atoms during dislocation glide in Cu matrix. It was reported that the steady state microstructure length-scale relied on the competition between these two processes. It is also interesting to note that amorphous regions, a few nm wide, were noticed between Cu and Nb grains. Wire drawing experiments as well as atomic simulations also indicated that the forced mixing between Cu and Nb can lead to amorphous regions [41–44].

In addition to the effect of heat of mixing on the nature of the chemical mixing forced by SPD, it is also important to consider the effects of strain path and microstructure geometry on the mixing rate. Molecular dynamics simulations provide a convenient way of investigating these effects. Vo et. al. [40] investigated the mechanical stability of Cu-Nb systems with different microstructure (particle vs. layer) and different interface orientations ([111] Kurdjumov-Sachs (K-S), [112] K-S and Nishiyama-Wassermann (NW)) subjected to biaxial compression and biplanar shear deformation. Cu-Nb system did not show significant forced chemical mixing when subjected to biaxial compression, regardless of microstructure or interface orientation. However, particle morphology was found to be less stable compared to layers under biplanar shear deformation. It was also reported that after an equivalent strain of 10, [112] K-S orientation form diffuse interfaces, with its width ranging from 1-2 nm, see Fig 2.5 [40].
Fig. 2.5 Atomic configuration after a strain of 100 for (a) particle, (b) \{112\} K-S, (c) NW and (d) \{111\} K-S interface under biplanar shear deformation (Red: Cu, blue: Nb) [40].

An present study by Ashkenazy et al. [41] examined the mechanisms of shear mixing in highly heterogeneous systems on various two phase alloys that were subjected to cyclic shearing events at 100 K, i.e. initially spherical particles of fcc metals Ag and Ni and bcc metals Fe, Nb and V as well as mixing of a Cu particle in Cu matrix for comparison, see Fig 2.6. After a strain of 60, non-coherent bcc precipitates such as (V and Nb) in Cu matrix have been reported to retain their equiaxed morphology due to dislocation pile-up at the interfaces. The resulting deformation induced mixing in bcc precipitates was reported to be diffusive [41], i.e. the initial rates of mixing in these systems increased linearly with particle radius.
2.3. PRIOR STUDIES ON THE CU-NB SYSTEM

Initial interest in Cu-Nb system started with using Nb as one of the alloying constituents for elemental Cu, to increase the low intrinsic strength of Cu while retaining its high electrical conductivity for high field magnet applications [42–44]. Cu-Nb was reported to show the best mechanical properties among the remaining potential alloying constituents in the family of bcc elements (e.g. Cr, W, Ta, Nb, Mo, V) [42]. Cu-Nb system has negligibly small solubility in thermodynamic equilibrium. As the melting temperature for Cu and Nb differ from each other significantly ($T_m$ (Cu) = 1085°C and $T_m$ (Nb) = 2469°C) (Fig. 3.1), the synthesis of alloys from this highly immiscible system mainly relied on rolling, extrusion and mechanical alloying (MA). Due to high-energy impacts during milling, MA was reported to provide alloys with good
compositional and microstructural homogeneity and with extended solid solubility of alloy elements [43].

The interest in Cu-Nb system increased when experimental investigations showed that Cu/Nb multilayer composites (with individual layer thickness < 100 nm) manufactured by a bottom-up technique, physical vapor deposition (PVD), resulted in well-controlled lamellar structures that exhibit high thermal stability, strength, ductility, resistance to shock damage and resistance to radiation damage; significantly outperforming bulk Cu and Nb. For example, self-supported sputter deposited Cu-Nb thin films with 75 nm individual layer thickness showed stable layer structure after annealing at 800°C [45]. Moreover, when Cu/Nb multilayers were subjected to high dose implantations of 33 keV and 150 keV He⁺ at room temperature [46] and at elevated temperatures [47], these interfaces showed superior radiation resistance compared to single-crystal Cu or Nb, while no amorphization, large changes in the interface structure or atomic scale defects such as Frank loops or stacking fault tetrahedra were detected.

These desirable properties displayed by Cu/Nb nanocomposites were tied to the unusually high density of Cu/Nb interfaces that makes up a significant volume fraction of these multilayers (with layer thickness as small as 4 nm) and low density of defects accumulated at the interface when subjected to environmental conditions mentioned above. It is observed that Cu/Nb multilayer composites grown using PVD predominantly show Kurdjumov Sachs (K-S) [48] orientation, in which the Cu and Nb layers are oriented with respect to each other such that <110> direction of Cu is parallel to <111> direction in Nb in the interface plane, while close packed planes of Cu (111) and Nb (110) form an interface. Atomic simulation studies predict that this interface is atomically flat, and has a low energy configuration [49]. Additionally, it was claimed that these nanostructures have a self-healing interface, in the sense that they contain a high density of atomic
sites that can effectively promote the recombination and annihilation of point defects [45, 49–51].

The remarkable properties observed in Cu/Nb multilayers suggest that such nanocomposite materials are attractive candidates for a range of structural applications such as next generation nuclear power reactors and military applications. However, with PVD process, only thin films can be produced, and manufacturing large scale composites is prohibitively time-consuming. Several SPD techniques were used in the attempt of successfully synthesizing bulk samples. Cold drawing is employed as one of the SPD applications for producing nanocomposite Cu/Nb [52, 53]. This process stabilized highly textured Cu grains and Nb fibers and semi-coherent Cu/Nb interfaces. A slight tilt (≈ 4°) was observed between <111> Cu and <110> Nb [52, 54].

![Figure 2.7](image_url)

Fig. 2.7. Cu/Nb samples fabricated with ARB processing. The individual layer thicknesses range from 1 mm to 500 nm (upper left photo), as low as ~ 9 nm (TEM micrographs) [55].

Very recently, Cu-Nb multilayered composites were successfully synthesized from monolithic Cu and Nb metals sheets with the use of ARB [55, 56], with individual layer thicknesses
as small as 9 nm, as seen in Fig. 2.7 [55]. It was observed that under rolling strains, these Cu-Nb nanocomposites (below layer thickness ≈ 1 μm) show predominantly K-S orientation relationship between adjacent Cu and Nb grains, where \{112\}_{Cu} \parallel \{112\}_{Nb} \parallel ND, \langle 111 \rangle_{Cu} \parallel \langle 110 \rangle_{Nb} \parallel RD, and \langle 110 \rangle_{Cu} \parallel \langle 111 \rangle_{Nb} \parallel TD, with ND, RD, and TD being the direction normal to the rolling plane, the rolling direction, and the transverse direction, respectively, see Fig. 2.8 [57].

Fig. 2.8. Illustration of \{112\} K-S interface orientation [57].

The stabilization of this unusual orientation relationship, which is abbreviated as \{112\} K-S, has been rationalized by the favorable conditions for slip transfer across the Cu/Nb interfaces for these interfaces [55]. It is noteworthy that this orientation is distinct from the traditional K-S orientation relationship found when Cu/Nb multilayers are grown by PVD, in which case the habit plane of the interfaces is \{111\}_{Cu} \parallel \{110\}_{Nb}.

Since the report of \{112\} K-S orientation, several studies focused on understanding this interface at atomic and microscopic scale. Atomic simulation modeling studies indicate that
\{112\} K-S interface has an ordered but stepped atomic structure with high formation of energy (~ 820 – 886 J/m²) compared to Cu/Nb interfaces synthesized with PVD [57, 58]. Additionally while K-S interfaces obtained with PVD have low shear strength [51], computer simulations predicted that \{112\} K-S interfaces possess high shear strength [57].

In order for bulk ARB nanolayered Cu/Nb composites to be used in structural applications mentioned above, it is crucial that these materials exhibit high thermal stability as well as superior mechanical properties. Carpenter et al. [59] investigated bulk nanolamellar Cu/Nb composites with 18 nm individual layer thicknesses, processed by ARB, after annealing at temperatures up to 900°C in vacuum. It was found that Cu/Nb layer structure was maintained at least up to 700°C. At this temperature, the high energy crystal orientations was found to disappear, resulting in sharpening of the existing predominant \{112\} K-S texture [59].

In this dissertation, the behavior of Cu/Nb nanocomposites initially produced by ARB technique with material properties briefly described above, were investigated after being subjected to severe shear deformation via HPT. The principles of HPT were given in Section 2.1.2. As mentioned previously, this SPD technique introduces a different deformation mode (simple shear) than ARB (pure shear) while enabling quantification of deformation applied on the material. Large strains can be applied via HPT under high hydrostatic pressure, which prevents cracking, therefore, failure of the sample.

Prior studies of HPT mainly rely on investigating elemental metal systems. In the scope of this dissertation, we are interested in behavior of pure Cu and pure Nb under severe shear deformation, as the deformation behavior of these metals is expected to differ from the Cu-Nb nanocomposite layers studied in this research. This dissertation and the paper published on the first topic of this dissertation (Chapter 4) [60], are the first published findings on Cu-Nb system
subjected to HPT. However, effect of SPD on pure Cu by HPT has been investigated in several studies [61–64] and it is therefore useful to briefly summarize the key findings on pure Cu. Hebesberger et al. [61] ran a systematic parameter study on the resulting microstructure of pure Cu deformed by HPT with ranging hydrostatic pressures of 0.8, 2 and 8 GPa and experiment temperatures of 25°C, 120°C and 200°C. It was found that the microstructure reached to a steady state with substructures as small as 0.4 μm at strain $\gamma = 250$ at room temperature. It was reported that the length-scale of steady state microstructure decreases with applied strain but increases with increasing temperature. Later, it was suggested by Edalati et al. [62], that the grain refinement seen in pure Cu samples subjected to HPT at room temperature may be achieved by dislocation coalescence at the early stages of deformation leading to formation of subgrain boundaries. However, as deformation proceeds, competition between recrystallization and increasing dislocation density takes place, which may lead to disappearance of dislocations, until a balance between these two dynamical competition reaches to balance. Lastly, a detailed study on texture evolution of pure Cu subjected to HPT at room temperature [63] up to 10 rotations revealed an uncommon texture at strains ~ 440. It was reported that pure Cu showed strong $B/\bar{B}$ texture, which was explained by a deviation from simple shear deformation during HPT. Due to the lack of intensity in both $A/\bar{A}$ and cube texture components, one can exclude the possibility that significant dynamic crystallization took place. Mechanisms such as dynamic recovery or/and grain boundary sliding were suggested to be responsible for such uncommon texture evolution.

A number of studies focused on behavior of pure Nb when subjected to HPT [65–70]. Popova et al. [68] investigated the degree of deformation on the structure and thermal stability of pure Nb subjected to HPT. It was reported that Nb grain size (~100 nm) reached to steady state after 5 revolutions. Increased straining had not resulted in further grain refinement. These deformed
samples were found to be thermally stable up to temperatures of 600°C, and showed intense recrystallization at 700°C. It was reported that further deformation results in earlier thermal destabilization in deformed Nb, after 10 anvil rotations resulting in microstructures being destabilized at 500°C. Moreover, at steady state, the hardness of nanocrystalline Nb after HPT deformation was found to be similar to high-strength Cu/Nb composite materials. These findings on microstructural evolution of pure Nb subjected to HPT were supported by other studies [67, 69–71]. After application of HPT at cryogenic temperatures (80 K), Nb crystallite sizes as low as 75 nm and hardness of ~4800 MPa were reported [69]. Although the microstructures obtained at cryogenic temperatures were observed to be stable at room temperature, their thermal stability at high temperatures was found to be lower than that for Nb deformed at room temperature via HPT.

2.4. REFERENCES


[70] V. V. Popov, E. N. Popova, A. V. Stolbovskiy, V. P. Pilyugin, and N. K. Arkhipova, “Nanostructurization of Nb by high-pressure torsion in liquid nitrogen and the thermal stability of

CHAPTER 3

EXPERIMENTAL PROCEDURES

This chapter details the equipment and experimental methods employed in this study. During the research, sample preparation techniques, testing procedures and analysis methods were developed for achieving the most accurate and representative results.

3.1. ARB CU/NB NANOCOMPOSITES

Cu-Nb binary metal system was chosen as a model to understand the stability and evolution of microstructure when two-phase nanocomposites are subjected to severe plastic deformation. As it will be detailed in Chapter 4, we will focus on simple shear deformation, and investigate the mixing induced and the possible self-organization resulting from SPD.

Cu-Nb system can be categorized as a highly immiscible binary metal system with positive heats of solution of 98.7 kJ/mol for Nb in Cu and 46.0 kJ/mol for Cu in Nb [1]. The phase diagram of Cu/Nb system displayed in Fig. 3.1 shows no compound formation and very limited solubility in the solid state and in the liquid state below 1700 °C.
The Cu-Nb nano-laminate composites that were used in this work were fabricated by our project collaborators at Los Alamos National Laboratory (LANL) by employing accumulative roll bonding (ARB); using a combination of annealing and rolling steps, as described in detail in [2]. These samples are composed of 50/50 volume fraction, corresponding to a 51/49 weight fraction, using monolithic Cu and Nb sheets with 99.99% and 99.97% purity, respectively. With this technique, it is possible to produce multilayer nano-composites with varying layer thicknesses, as previously described in Chapter 2.

For this study, three nominal different layer thicknesses (same for both Cu and Nb layers) were studied: 18 nm, 200 nm and 2 μm. As it will further be explained in Chapter 5, that these are nominal layer thicknesses, and that the variance is quite large, e.g. between 0.718 - 2.560 for the 2 μm ARB composites. Additionally, while the 18 nm layer thickness material was fabricated with
the technique described above, the samples with 200 nm and 2 micron layer thicknesses were manufactured by employing a modified ARB method, named as “Cu Cladding” technique [3, 4]. In this method, the Nb sheet was placed between two Cu sheets during the first rolling step of ARB, rather than alternate layering of Cu and Nb sheets. As this technique was expected to be beneficial for preventing oxidation at Nb interfaces by confining Nb layer between Cu layers at every sectioning and stacking step of ARB.

3.2. APPLICATION OF SEVERE PLASTIC DEFORMATION BY HIGH PRESSURE TORSION

HPT was applied to the as-received ARB nano-laminate composites to investigate the evolution of phase co-existence and microstructural evolution under different shear strains. In order to prepare samples for HPT processing, discs with diameter d=10 mm were cut from the ARB bulk sheet using electrical discharge machining (EDM). The cutting process was carried on under continuous water stream to prevent any artifacts that might be caused from temperature increase during EDM process. During EDM, the rolling direction of the bulk material was marked on the metal discs. The ARB sample thicknesses were: ≈ 380 μm for 18 nm sample, ≈ 830 μm for 200 nm sample and ≈ 740 μm for 2 μm sample, respectively.

HPT deformation experiments were performed by our collaborators in the research group of Prof. H. Hahn at Karlsruhe Institute of Technology (KIT). HPT was carried out at room temperature, using a confining hydrostatic pressure of 4.5 GPa. The anvils were sand blasted prior to HPT to prevent slipping. The lower anvil continuously rotated at a constant rate of 1.2 rpm as the upper anvil stayed stationary. As discussed in Chapter 2, constrained anvil configuration during HPT often results in inhomogeneous deformation through thickness with most of the deformation
localized near the surface of the processed sample. This limitation was eliminated by using an unconstrained anvil geometry. The homogeneity was confirmed using a series of TEM analyses taken through the thickness of the HPT processed samples. The downside of using unconstrained geometry is that the sample thickness decreases as deformation takes place, but this effect can be accounted for in the analysis, as detailed below.

In order to investigate a wide range of shear strains, various number of rotations were processed by HPT. During HPT deformation, of the material flow is assumed to be uniform and sample thickness remains constant, the total shear strain $\gamma$ at a given distance $r$ from the center of the disc can be calculated by:

$$\gamma = \frac{2\pi r N}{t}$$

where $N$ is the number of turns applied by anvils [5, 6]. In this study, however, sample thickness was observed to decrease significantly as $N$ increased, largely due to unconstrained geometry selected for HPT processing in this study. Thus, the sample thickness evolution $t(N)$ after HPT was measured by Scanning electron microscopy (SEM) imaging on sample cross-sections, and then fitted using an exponential relaxation for selected radial distances. This fitting is shown for the 18 nm ARB sample in Fig. 3.2.
Fig. 3.2. Fitted thickness profiles for positions of HPT samples (18 nm) measured at r=1, 2, 3, and 4 mm from the center of the disc after various HPT rotations. The horizontal black dashed line corresponds to initial ARB (18 nm) sheet thickness.

The applied shear strain at selected distances of r was then deduced by using differential form of Eq. 3.3, which takes thickness evolution into consideration:

\[
d\gamma = \frac{2\pi r}{t(N)} dN
\]

The resulting shear strains for selected radial distanced used in this study are reported in Table 3.1. As seen from Table 3.1, different selected locations on samples with various HPT rotations are wide enough to cover a wide spectrum of shear strain values, from 2.0 to the order of thousands. It should be noted that the strain values calculated using Eq. 3.3 can be significantly lower than the ones obtained by the standard Eq. 3.2 when using the final thickness of the disc after subjected to HPT. This difference was calculated to be 50 % in the worst case (5 HPT turns,
at 3 mm for 18 nm ARB sample). For large strains, however, the sample thickness reduction reached near steady-state values, and difference did not exceed 20%. In practical terms, therefore, these errors have little effect on the results. In the following, the analyzed regions will be referred using strain values calculated by Eq. 3.3. This allows for a unique identification of the sample, corresponding to a unique combination of rotation (N) and radial distance (r).

For the samples with 2 μm and 200 nm nominal layer thickness, the HPT processed sample showed significant thickness reduction between the sample center and periphery, leading to a convex shape, the true relationship between the parameters in the HPT strain equation is no longer linear. Unfortunately, the number of samples used in this study was not sufficient for a calculation of strain as done for the 18 nm ARB samples, and so, despite the limitation of Eq. 3.2, we will use it as an estimate of the HPT strains. In all cases, since the thickness decreased progressively as HPT deformation was applied, the strain estimates that will be used in this chapter are thus upper bound values. We note however that for the 200 nm samples, since the thickness profile did not change much upon increasing the number of rotations from 1 to 20, the estimated strains for 20 turns should be fairly accurate. Further analysis on this subject is explained in Chapter 5.
Table 3.1. The HPT processed samples studied in this research classified in number of HPT turns, position on the sample and the corresponding applied shear strain calculated using Eq. 3.3.

<table>
<thead>
<tr>
<th>Number of HPT rotations (N)</th>
<th>Position on Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>50°</td>
<td>2.0</td>
</tr>
<tr>
<td>240°</td>
<td>8.8</td>
</tr>
<tr>
<td>5 turns</td>
<td>107</td>
</tr>
<tr>
<td>20 turns</td>
<td>960</td>
</tr>
<tr>
<td>200 nm</td>
<td>1 mm</td>
</tr>
<tr>
<td>1 turn</td>
<td>23</td>
</tr>
<tr>
<td>20 turns</td>
<td>737</td>
</tr>
<tr>
<td>2 micron</td>
<td>1 mm</td>
</tr>
<tr>
<td>1 turn</td>
<td>20</td>
</tr>
<tr>
<td>20 turns</td>
<td>1725</td>
</tr>
<tr>
<td>50 turns</td>
<td>2144</td>
</tr>
</tbody>
</table>

3.3. CHARACTERIZATION METHODS

For characterization of microstructural evolution, solid solubility and length-scale of phase co-existence, multiple characterization methods were employed. In this study, the smallest microstructural length-scale was expected to be a few tens on nanometers, making characterization challenging. A combination of characterization techniques were therefore employed for accurate analysis. These complementary techniques are described in this section.
3.3.1. X-Ray Diffraction (XRD) and Texture Analysis

The as-received ARB and HPT-deformed samples were first characterized by Panalytical/ Philips X’Pert Micro X-ray diffraction (XRD). Micro-diffraction analysis allows the measurements of very small sample volumes by using a very narrow beam through a mono-capillary system [7]. Using mono-capillary, it is possible to produce an incident X-ray beam with a diameter as small as 100 μm. This technique is essential for localized measurements on HPT-processed samples where the strain applied to the material varies significantly from the center to the edge of the sample. On several samples, macro X-ray measurements were also performed for comparison. A high magnification camera incorporated into the XRD system was used for accurate selection of area for analysis. Representative image of the micro XRD set-up and sample image from camera view are shown in Fig. 3.2 (a) and (b), respectively. The XRD system uses Cu Kα radiation, and it was operated at 45 kV and 40 mA. A Ni filter was placed in the path of the incident X-ray beam to remove Cu Kβ radiation.

The samples were first analyzed by performing 2θ-Ω scans. The 2θ-Ω measurements were commonly carried out with a 0.02° step size with 20 seconds of data collection at each step size. The offset angle between θ and Ω were defined as zero, making these scans equivalent to 2θ- θ scans. The samples were taped to aluminum sample holders, and mounted to the base plate inside the diffractometer. First, the area of interest was selected using camera view. A micrometer was then used to set the correct sample height. The top surfaces of the samples were carefully polished about 20 μm prior to XRD measurement, to remove possible surface effects introduced by HPT. The range of these surface artifacts was separately investigated by TEM analysis on cross sections, see Chapter 4.
Fig. 3.2. (a) Philips X’Pert2 XRD system with monocapillary beam set-up. (b) Camera view from X’Pert2 system positioned at the center of an HPT disc.

The axis conventions used for XRD and texture measurements are shown in Fig. 3.3. The sample directions were defined as normal direction (ND), rolling direction (RD) and transverse direction (TD), where RD and TD directions refer to the directions from the top surface of the samples during rolling. These directions become less meaningful during HPT, since they are not invariant during torsion around ND. For instance, for a given HPT rotation the RD is rotated
by an amount that increases with the depth of the analyzed region within the thickness of the sample. For XRD measurements on HPT samples, the sliding direction (SD) of the samples was always initially set parallel to rolling direction. XRD scans and texture measurements were performed at selected radial distances along the transverse direction of the sample, ranging from \( r \approx 1 \text{ mm} \) to \( r \approx 4 \text{ mm} \), unless stated otherwise.

![Diagram of axis convention and radial distances](image)

Fig. 3.3. The axis convention and radial distances used in XRD and texture measurements with respect to shear direction. The ND was common during rolling (ARB) and shearing (HPT).

Analysis of the diffraction spectra was performed using MDI Jade 9.3. Lattice constants of the phases were determined by peak fitting using a pseudo-Voigt function. Crystallite sizes were then calculated using the Scherrer formula [8] shown in Eq. 3.3:

Eq. 3.3.

\[
d = \frac{K \lambda}{\beta \cos \theta}
\]

where \( d \) is the crystallite size, \( K \) is the dimensionless shape factor (taken as 0.9), \( \beta \) is the full width at half maximum (FWHM) of the Bragg peak, and \( \theta \) is the Bragg angle of the peak.
The forced chemical mixing between Cu and Nb was analyzed using lattice parameter measurements obtained from the Cu (111) and Nb (110) reflections. Additional peaks could not be used as their intensities became very small and large HPT strains. For the as-fabricated ARB samples, however, four and five reflections could be detected for Cu and Nb phases, respectively, and the lattice parameters were taken as average over these reflections.

Since Cu-Nb system is highly immiscible, Vegard’s law cannot be directly used to calculate the chemical mixing between Cu and Nb. Instead, we employed the atomic volumes reported by Ashkenazy et al. [9] for Cu-Nb dilute solutions obtained by molecular statistics simulations. Expressions for the concentrations of Nb in Cu and Cu in Nb were obtained using the following Eq. 3.4:

\[
c_B^A = \frac{\left(\frac{a^3}{a_0^3}\right)^{-1} (\Delta V/V)_B}{(\Delta V/V)_B^A}
\]

where \(c_B^A\) is the concentration of B species in matrix A, \(a\) the corresponding lattice parameter, \(a_0\) the lattice parameter of the pure A phase, and \((\Delta V/V)_B^A\) the relative volume change resulting from the introduction of one B solute atom in a pure A crystal. These relative volume changes measured in the above atomistic simulations were 0.53 and -0.28 for Nb in Cu, and Cu in Nb, respectively [9].

For texture measurements, data was acquired for three poles for each phase: <111>, <200> and <220> for Cu, and <110>, <200> and <211> for Nb. Orientation distribution functions (ODFs) were then calculated after background subtraction by applying cubic crystal symmetry (\(\overline{m\overline{3}m}\)), and triclinic sample symmetry(\(\overline{1}\)). For texture plots and analyses, MTex 3.1 [10, 11] software was used. After ODF calculation, pole figures (PFs), inverse pole figures (IPFs) and ODF sections were
generated and plotted in shear (SD-ND) plane for detailed texture analysis. For plotting ODF sections, Bunge convention is used for the translation of crystal coordinate frame to sample coordinate frame with the use of Euler (ϕ₁, Φ, ϕ₂) angles.

3.3.2. Scanning Electron Microscopy (SEM)

Sample thickness measurements were performed using JEOL 6060 Low Vacuum SEM. For this analysis, HPT-deformed discs were carefully sectioned in half using a low speed diamond saw. The sample was then placed in SEM, and sample thickness was measured from sample cross section. One measurement was taken at every ≈ 100 μm, from one edge of the HPT-processed disc to the other edge. Approximately 90 – 100 measurements for each sample were taken to fully obtain a sample thickness profile.

High resolution SEM analysis was also performed using FEI HELIOS NanoLab™ 600i dual beam microscope as a supplementary characterization technique for length-scales larger than ≈ 25 nm. Secondary electron and backscattered electron images provided initial analyses of samples, as Cu and Nb provided good contrast.

3.3.3. Sample Preparation for Transmission Electron Microscopy (TEM)

Samples for TEM analyses were prepared the conventional lift-out method [12] using Focused Ion Beam (FIB). FEI Strata Dual Beam 235 or FEI Dual Beam HELIOS NanoLab™ 600i FIB systems were used to prepare thin foils from selected regions of HPT processed discs. Operating voltages at 30 kV and 5 kV and currents from 65 nA to 1 pA were selected to optimize sample quality while minimizing gallium implantation. The majority of these TEM samples were directly
taken from the top surface of the samples, which was polished for XRD data acquisition. The electron transparent volumes probed in these samples were therefore ≈ 20 to 30 µm below the original sample surfaces. The lift-out samples were welded on half gold mesh TEM grids using platinum source inside the FIB system. In order to evaluate the homogeneity of the samples after HPT, selected TEM samples were prepared by lifting out samples from ND-RD cross sections. The resulting TEM samples are thus ND-SD cross sections, making it possible to analyze the microstructure as a function of the distance to the HPT surface at a given radius r.

3.3.4. Transmission Electron Microscopy (TEM)

TEM was performed using two different electron microscopes. Bright field TEM images (BFTEM) and selected area electron diffraction patterns (SAED) were obtained using JEOL (Japan Electron Optics Laboratory) 2010 LaB6. High angle annular dark field imaging (Z-contrast) were carried out at JEOL 2010 F. JEOL 2010 LaB6 has a thermionic emission source whereas JEOL 2010 F has a field emission source. Both microscopes were operated using beam current of 200 kV.

Layer thickness analyses for as-received ARB samples and particle size for Nb were determined using Z-Contrast STEM imaging. These analyses were carried out using an image processing software named Gatan Inc. Digital Micrograph. Layer thicknesses and precipitate sizes were measured for a minimum of 100 measurements. Microstructural evolution was investigated using both BFTEM, SAED and Z-contrast images. For chemical mixing, SAED patterns were measured in Digital Microscope to analyze chemical mixing using Cu (111) and Nb (110) diffraction rings. Same reflections were also used for texture analysis.
3.4. REFERENCES

CHAPTER 4

PHASE AND MICROSTRUCTURAL EVOLUTION OF CU-NB NANOLAMINATES UNDER SEVERE SHEAR DEFORMATION

4.1. INTRODUCTION

As previously described in Chapter 2, this dissertation focuses on understanding the phase stability and microstructural evolution of Cu-Nb nanolaminates when subjected to severe plastic deformation (SPD) under a controlled processing condition: high pressure torsion (HPT). One of the key features that will be discussed in this chapter is the stability of Cu-Nb nanolaminates, which were initially synthesized via another SPD technique, accumulative roll bonding (ARB). ARB can produce nano-layered structures as small as 9 nm that are stable under extreme rolling strains [1, 2]. These nanostructures were reported to exhibit desirable material properties, such as superior mechanical properties and thermal resistance [3], making them excellent candidates for structural applications. Therefore, it is important to understand the material behavior when it is subjected to another deformation mode, such as shear deformation.

This chapter will start with the analysis of the starting sample: as-fabricated ARB nanocomposites with 18 nm nominal individual layer thickness was selected for this study. The effect of the layer thickness will be discussed in Chapter 5. Then, the phase and microstructural stability and evolution of Cu-Nb nanolaminates will be investigated on samples that were subjected to various shear strains under HPT. The behavior of the nanocomposites will be analyzed by several analysis techniques, namely X-ray diffraction (XRD), TEM and texture analysis. Details
on sample preparation and analyses were the same as those presented in Chapter 3, unless stated otherwise in this chapter.

4.2. INITIAL MICROSTRUCTURE OF THE ARB COMPOSITE

The microstructure of as-fabricated ARB Cu-Nb composite was examined by transmission electron microscopy. The results confirmed the previously reported nanolayered structure of ARB Cu-Nb composite, as illustrated in Fig. 4.1 (a). The average layer thickness of the nanolaminates were calculated over 100 measurements, and was found to be ~ 16.8 ± 8 nm. This value is consistent with the nominal value of 18 nm. Sharp Cu-Nb interfaces were observed in TEM micrographs. Twinning was observed in Cu layers, as seen for instance Fig. 4.1 (b). SAED patterns, see Fig. 4.1 (c), indicate a strong preferred orientation for Cu and Nb crystals with \([111]\)\(_{\text{Cu}}// [110]\)\(_{\text{Nb}}//\) RD (rolling direction). This finding is consistent with the \(\{112\}\) Kurdjumov-Sachs orientation previously reported by Carpenter \textit{et al.} [2] using precession electron diffraction and also described in detail in Chapter 2 of this dissertation.
Fig. 4.1. As-fabricated ARB Cu-Nb nanocomposites: (a), (b) bright field TEM micrographs and (c) SAED pattern corresponding to (a); the main reflections are indexed in (d). The rolling and transverse directions are shown in (a), these directions are the same for (b).

4.3. MICROSTRUCTURAL EVOLUTION WITH HPT DEFORMATION

The evolution of phases was first evaluated by XRD analysis. The 2θ-θ scans for selected HPT strains are summarized in Fig. 4.2. Bragg reflections of the bcc and fcc phases remained present even at the largest strain of 5,970, indicating the persistence of phase coexistence between Cu-rich and Nb-rich phases. The relative intensities of Cu peaks and Nb peaks, however, were significantly modified by HPT strain, pointing to the development of a preferred texture. The texture evolution observed during HPT deformation will be further discussed in detail in Section 4.4. Additionally, Bragg reflections were shifted and became broader, indicating that HPT deformation led to some amount of forced chemical mixing and to a reduction in grain size.
Fig. 4.2. XRD spectra from the ARB and 18 nm-HPT-processed samples. For clarity, only the spectra for radial distances $r=2$ and $4$ mm are displayed, and the spectra are shifted in intensity by an arbitrary amount. Corresponding strain values are indicated on the graph. Background has been removed from each spectrum. Dashed lines correspond to Bragg reflections expected for pure Nb and pure Cu.

The forced chemical mixing between Cu and Nb phases was analyzed using lattice parameter measurements obtained from the \{110\} Nb and \{111\} Cu reflections. Additional peaks could not be used as their intensities became very small at large HPT strains (Fig. 4.2). For the as-fabricated ARB material, however, four and five reflections could be detected for Cu and Nb respectively. Therefore, the lattice parameters were taken as averages over these reflections. Since Cu-Nb system is highly immiscible, with heats of solution of 98.7 kJ/mol for Nb in Cu and 46.0 kJ/mol
for Cu in Nb [4], Vegard’s law cannot be used for calculating the degree of forced chemical mixing from lattice parameters. Instead, the atomic volume measurements for Cu-Nb dilute solid solutions reported by Ashkenazy et al. [5] using molecular dynamics simulations were used. The details of these calculations were described earlier (Chapter 3). The evolution of chemical mixing with applied shear strain is plotted in Fig. 4.3, together with evolution of grain size, obtained from \{111\} Cu and \{110\} Nb peak broadening using Scherrer’s equation. It is important to note that the initial Cu grain size is very close to the nominal ARB layer thickness, indicating that layers contain one grain, or at most two, along the ND direction in agreement with the TEM observations. Once notices that the initial Nb grain size is slightly smaller than that of Cu, 13.5 nm compared to 17 nm. Similar trends have been reported for the Cu and Nb layer thickness values [1]. The solubilities reached after ARB processing are rather small, typically less than 1 at%.

Fig. 4.3. (a) Chemical mixing vs. strain and (b) grain size vs. strain for ARB 18 nm Cu/Nb nanocomposite subjected to HPT deformation.
For strains less than ~ 10, HPT deformation did not result in significant changes in either chemical composition or grain size, see Fig. 4.3. However, after further increasing the strain, the grain sizes of Cu and Nb phases were progressively reduced. At a strain of 286, the grain sizes for both Cu and Nb reached steady-state values of 6.2 and 4.7 nm, respectively. The evolution of solubility is less symmetric. Cu concentration in Nb started to increase when strain exceeded ~ 10, reaching to a steady-state value of ~ 10 at.% after applied strain exceeded 1000. In contrast, the Nb concentration in Cu started only to increase at a strain of 68.5, and reached a maximum of ~1.7 at.% for a strain of 286, before decreasing slightly to ~1.5 at.%, at larger strains.

The detailed evolution of the microstructures was investigated using TEM. For low HPT strains, γ=4.2, the microstructure was found to be very similar to that of the as-fabricated ARB sample, with well-defined layers and sharp interfaces, as seen in Fig. 4.4 (a) and (b). One noticeable difference at this low strain, however, was a slight waviness of the interfaces, which is clearly visible in HAADF-STEM images, see Fig. 4.4 (b). At a strain of γ=10.8, the interfacial waviness became more pronounced, and while the layered structure was still preserved in most regions, strain localization was observed in other areas which led to the presence of folds and vortex-like features in the microstructure, see Fig. 4.4 (c) and (d).
Further deformation by increasing the HPT strain resulted in a progressive destabilization of the nanolayered structure of the as-fabricated ARB material. At strain of $\gamma = 68.5$, a “mixed” state in microstructure was observed, in which the nanolayers coexisted with equiaxed grains, as shown in Fig. 4.5 a and b. This microstructural transformation was completed at a strain of 286, leading to complete destabilization of the initial layered structure and the formation of a 3-D
nanocomposite, with very small grain sizes. In Z-contrast STEM images, grain sizes were estimated to be ~ 5 nm (Fig. 4.5 b), in agreement with XRD measurements.

Fig. 4.5. Microstructure for an HPT strain of 68.5: (a) bright field TEM micrograph, (b) Z-contrast STEM image, (c) SAED pattern of area shown in (a and d) indexing of the main reflections in (c).

Additionally, TEM analysis performed on specimens prepared from different depths for $\gamma = 286$ confirmed that this microstructure was present throughout the thickness of the sample, as seen by comparing one specimen taken close to the disc surface (Fig. 4.6 a) and on specimen taken near the mid-plane of the disc (Fig. 4.6 b).
Fig. 4.6. Microstructure for an HPT strain of 286. Z-contrast STEM images taken from (a) \(~25\ \mu\text{m}\) below the surface, (b) \(~50\ \mu\text{m}\) below the surface. The specimen thickness after HPT was \(106\ \mu\text{m}\). The sample (b) has been obtained by FIB from a ND-RD cross-section.

The 3-D microstructure remained stable upon increasing the HPT strain to the largest value used in this study, 5970 (Fig. 4.7 a and b). It is thus concluded that this microstructure is stable under HPT deformation. In addition, selected area diffraction (Fig. 4.7 b), indicates that this 3-D steady-state microstructure had a texture quite distinct from that of the as-fabricated ARB sample, as already suggested by the XRD spectra (Fig. 4.1). The texture evolution will be discussed in Section 4.4 in detail.
Fig. 4.7. Microstructure for an HPT strain of 5970: (a) bright field TEM micrograph, (b) dark field TEM micrograph formed using a Nb (1 1 0) reflection; (c) SAED pattern of area shown in (a); (d) indexing of the main reflections visible in (c).
Fig. 4.8. APT reconstruction maps for a Cu/Nb sample deformed by HPT to a shear strain of 1990. (a) Concentration map, with color scheme varying from red (pure Cu) to blue (pure Nb). (b) Iso-concentration surfaces obtained by applying a Cu concentration threshold of 40 at. %. The green surface displayed is the largest connected set of these surfaces. Axes are in nm and apply to both figures.

The 3-D structure of the fine scale nanocomposite stabilized by large HPT strains could not be easily accessed by TEM owing to overlapping effects of the fine scale features through the thickness of the TEM foils. Thus Atom Probe Tomography (APT) was employed by one of our research collaborators, Tim Lach, to investigate this microstructure for the sample deformed by HPT to a shear strain of 1990. Reconstruction maps were built from the APT data by binning the detected atoms into contiguous 1 nm × 1 nm × 1 nm cubes, hereafter referred to as voxels, forming a simple cubic lattice. The total number of atoms detected in each voxel and the local composition were then obtained. The voxel composition is denoted in the reconstruction by its color, ranging from red (pure Cu) to blue (pure Nb) in 15 steps. The voxel concentration maps confirmed the
coexistence of Cu-rich and Nb-rich regions, as displayed in Fig. 4.8 a. However, the difference in evaporation fields between Cu and Nb [6] led to local magnification effects that resulted in inhomogeneous distributions of atoms detected in each 1 nm³ voxel. These aberrations therefore limited the chemical resolution and prevented us from determining accurately the composition of the Cu-rich and Nb-rich phases. The connectivity of these regions was nevertheless assessed by using iso-concentration surfaces defined by specified threshold values of the Cu concentration. An example is given in Fig. 4.8 b. using a Cu concentration threshold of 40 at. %. While the size of the largest connected interface varied somewhat with the threshold value, for reasonable values of the threshold, ranging from 30 to 70 at. % Cu, there always exists one interface percolating through the sample. This analysis therefore indicates that the Cu-rich and the Nb-rich regions are also percolating through the sample.

![One-dimensional composition profiles](image)

*Fig. 4.9. One-dimensional composition profiles generated from the data shown in Fig. 4.7, using a cylinder along the tip axis, (a) 5 nm and (b) 15 nm in diameter.*
The length scale of the decomposition at this high-strain sample was determined from the APT data by defining cylinders along the $z$-axis (the tip axis), and plotting the Nb and Cu concentration profiles as a function of $z$ (Fig. 4.9). This axis it is less sensitive to the local magnification aberrations [7, 8], for instance, the Cu-rich and Nb-rich regions in the $x$ and $y$ directions are considerably more extended as seen in Fig. 4.8 a. The cylinder diameter was varied from 5 to 25 nm, and for diameters between 5 and 15 nm well-defined composition modulations were observed with an average period of $\sim$10 nm, independent of the cylinder diameter. This length scale is in good agreement with the one deduced from Z-contrast TEM micrographs.

4.4. TEXTURE EVOLUTION

From XRD 2θ-θ scans (Fig. 4.2) and TEM SAED patterns (Fig. 4.7) suggested significant crystallographic texture evolution during HPT of the ARB Cu/Nb nanolayered material. To further understand the texture evolution, the XRD texture measurements were analyzed using inverse pole figures (IPFs) and orientation distribution functions (ODFs), with grain orientations represented by the three Euler angles ($\varphi_1$, $\Phi$, $\varphi_2$) in Bunge’s notation. Detailed information on texture analysis measurements can be found in Chapter 3.

Prior to HPT straining, the textures of the as-fabricated ARB were consistent with the texture measurements reported by Carpenter et al. in [2] and [9] on similarly prepared samples. HPT deformation lead to a rapid change from the initial ARB texture. For strains as small as 4.2, ODFs indicate that initial ARB texture have been largely erased, as displayed in the ODF sections $\varphi_2=0^\circ$ and $\varphi_2=45^\circ$, shown in Fig. 4.10 and Fig. 4.11 for the Cu and Nb phases, respectively. It is noteworthy that at this strain value, the layered structure was observed to be not yet destabilized, see Fig. 4.4 (a) and (b).
Fig. 4.10. $\Phi_2 = 0^\circ$ and $\Phi_2 = 45^\circ$ sections of Cu phase ODFs for selected HPT strains. Scale bar shown is in multiples of random distribution (min=0, max=4). Locations of common simple shear ideal texture components are given at the bottom.
Fig. 4.11. $\Phi_2=0^\circ$ and $\Phi_2=45^\circ$ sections of Nb phase ODFs for selected HPT strains. Scale bar shown is in multiples of random distribution (min=0, max=4). Locations of common simple shear ideal texture components are given at the bottom.
At higher HPT strains, the Cu phase shows a preferred texture that develops progressively, with a strain preference for ND // {111}, i.e. the so called A-fiber. The main ideal components present at large strains are $A/A$ corresponding to $(1\bar{1}1)[110]$ and $(\bar{1}1\bar{1})[\bar{1}10]$, and the $A_1^*/A_2^*$ components corresponding to $(111)[\bar{1}12]$ and $(111)[1\bar{1}2]$. Strains larger than $\sim 2500$ were needed for complete stabilization of this texture. The initial texture cannot be analyzed using these ideal shear texture components since it displays a rolling texture.

The texture evolution of the Nb-rich phase is more complex, as seen in Fig. 4.11. While low HPT strains greatly suppressed the initial ARB texture, transient textures developed for strains ranging from 18.8 all the way up to 1360, and at larger strains the Nb texture became nearly random. Similarly to the Cu phase, strains greater than $\sim 2500$ were necessary to fully stabilize this texture.

To investigate whether the local texture variations could account for the unusual texture development, texture analysis was performed using a larger X-ray beam, 2 mm × 2 mm, which we refer to as macro XRD, instead of the 100 $\mu$m beam size used in the results reported in the previous paragraphs. A comparison of the ODFs obtained with these two different beam sizes indicates that there is a good agreement between the textures at large strains (Fig. 4.12), with an A-fiber texture in Cu and a near random texture in Nb. In the macro XRD Cu results, the intensities of the twin-symmetric $A$ and $\bar{A}$ components are very similar, as expected from symmetry. It should be noted that comparison between micro and macro XRD results is performed here only for strains large enough for the texture be in steady state since the large X-ray beam covered regions subjected to a wide range of strain, e.g., $\sim 5100–12,550$ when the X-ray beam is centered on $r=4$ mm, four millimeters away from the center of the HPT processed sample disc.
Fig. 4.12. Comparison between the ODFs obtained from XRD data collected with a 100 μm beam size (micro XRD), and those obtained with a 2 mm beam size (macro XRD), for the ARB material and for the samples deformed to large strains by HPT. Top row for Cu, and bottom row for Nb.

4.5. DISCUSSION

HPT has been employed to evaluate the stability of ARB Cu/Nb nanolayered composites to large shear strains. We found that HPT led to profound morphological, microstructural and chemical evolutions of the Cu/Nb nanolayered material, eventually leading to the destabilization of the 2-D nanocomposite in favor of an ultrafine 3-D nanocomposite. For the as – fabricated ARB
material investigated here, with an initial nominal layer thickness of 18 nm, TEM analyses revealed that the layered structure remained largely stable for strains up to 10, although interfaces became increasingly wavy. This observation is consistent with prior reports of wavy layered patterns forming during the mechanical alloying of ductile metals [10], and during HPT deformation of two-phase materials [11].

From atomistic simulations and modeling, it is well known that the co-deformation of layered structures induces a kinetic roughening at the interfaces [12], thus resulting in wavy interfaces. It was observed at strain of 68.5 that the layered structure became severely disrupted and partially replaced by a 3-d microstructure with co-existing Cu-rich and Nb-rich phases. For a strain of 86, this morphological transformation was complete and resulted in the stabilization of a 3-D nanocomposites, which remained present at the largest shear strains (γ ≈ 6,000) used in this study. The XRD analyses indicated that the grain size of Cu and Nb phases reached a steady state at a strain of 86, whereas the chemical composition appeared to continue the evolution slightly, reaching a steady state for strains exceeding ~ 3500. In contrast to moderately immiscible alloys such as Cu-Ag [12]–[14] or Cu-Fe [15], a large HPT strain could thus not force the highly immiscible Cu and Nb elements into a solid solution. This result is consistent with the stabilization of the nanocomposites in Cu-Nb mixtures subjected to other SPD techniques such as ball milling [16] and wire drawing [17, 18], as well as in other highly immiscible alloy systems such as Ni-Ag [19], Fe-Ag [20], Cu-Mo [21] and Cu-W. It should be noted here that previous reports on complete alloying of Cu_{90}Nb_{10} mixtures by ball milling [22, 23] are questionable since the Cu lattice parameter measured never exceeded 0.364 nm (indicating a Nb solubility of 1.6 at%); however, ball milling was performed at liquid N\textsubscript{2} temperatures, and partial amorphization at the interfaces is a possibility. Analysis of atomic mixing explained in Section 4.3 suggests that the maximum
solubility observed in this study was ~ 2 at.%. Such a low solubility is consistent with APT data obtained from wire drawing alloys [18], HPT of Cu-Nb-Ag alloys [24] and indeed the ball milling results reported in Refs. [21] and [22]. Excess Nb atoms can form very small precipitates, which would then be very difficult to detect by XRD. It is interesting to note that the solubility of Cu in Nb was significantly larger, saturating at ~10 at.% at large strains, as shown in Fig. 4.3. Similar values of ~10–15 at.% have in fact been measured by APT in wire-drawn Cu/Nb composites [17]. This larger non-equilibrium solubility of Cu in Nb compared to Nb in Cu can be rationalized by the lower heat of solution of Cu in Nb, 0.6 eV, compared to 1.3 eV for Nb in Cu [5].

The evolution of textures in the Cu and Nb phases with strain also revealed new insights about SPD in strongly immiscible alloys. First, the ARB texture was already largely destabilized after a strain of ~4.2 (Fig. 4.10 and 4.11). This result is consistent with MD simulations indicating that {111} K-S orientation relationship is not stable under simple shear deformation [25, 26]. Secondly, the preferred textures stabilized at very large strains, an A-fiber texture for Cu and a nearly random texture for Nb, appear to be quite distinct from the textures reported for nominally pure Cu deformed by HPT [27, 28] and the ones expected for bcc elements, such as Fe [29] deformed in simple shear. In the case of pure Cu, the dominant texture components identified by Enikeev et. al. [27] were $B/\overline{B}$ with some significant C component. In my study, none of these texture components was present in Cu/Nb nanolayers subjected to large HPT strains, as displayed in Fig. 4.10. However, since those findings came from monolithic Cu that had been HPT processed using quasi-constrained HPT for strains not exceeding ~ 300, and therefore one should be careful in comparing these results. Thirdly, preferred orientations of Cu and Nb phases required unusually large strains to reach steady state, and furthermore, Nb phase presented transient textures between strains ranging from ~ 18.8 to ~ 1360. These results suggest that the texture evolution and
stabilization in these Cu/Nb nanocomposites is strongly influenced by the constraints imposed by 3-D nanoscale phase co-existence. In that context, it should be noted that the transient textures in Nb started to develop at a strain of \(\sim 18.8 \text{–} 68.5\), which coincides with the destabilization of the layered morphology. Moreover, the same large strains required for the stabilization of textures are also the ones required for the Cu and Nb solubilities to reach steady state, as seen in Fig. 4.3. It is remarkable that at large strains the Cu phase developed a fairly strong texture, with maximum intensities in the ODFs of approximately four times that of a random distribution, while the Nb phase reached a near random texture. This result suggests possibly that, at steady state, plastic deformation is mainly accommodated by deformation of the Cu phase.

One intriguing aspect of the transformation of the ARB nanolayered structure to a 3-D nanocomposite structure pertains to the mechanisms driving this morphological evolution. It is often observed that layered structures can unravel by a pinch-off mechanism. The kinetic roughening of interfaces imposed by plastic deformation could certainly lead to the pinching off of layers, especially considering the small initial layer thickness used in the present study. On the other hand, the presence of S-shape or Z-shape folds and vortex-like features were observed, see Fig. 4.13. These features suggest that another plastic instability might also be taking place. Macroscopic swirls and vortex-like features have been reported for duplex stainless steels [30] processed by HPT, and was described by the development of a Kelvin-Helmholtz instability. The scale of the swirls in those studies, however, were typically hundreds of microns, and thus much larger than the folds observed here, and the geometry of those swirls seems to be directly derived from the geometry of the torsion test. The folds that we observed are, in fact, more similar to those recently reported in hypoeutectic Cu–Ag alloys subjected to HPT [14].
Fig. 4.13. TEM micrographs displaying the presence of folds and vortex-like features. (a), (b) Low magnification Z-contrast STEM image for a strain of 10.8 and 4.2, respectively. The near-vertical dark bands result from foil thickness variations introduced by FIB sample preparation. Nb-rich layers appear brighter than Cu-rich ones. (c) BRTEM image for a strain of 4.2 showing detail in micrograph shown in (b).

These Cu–Ag folds have been linked to shear banding, which does not appear to be present in our Cu/Nb samples. It is also possible that the folds in Cu/Nb are related to the folds forming in layered geological materials subjected to shear deformation by plate tectonics [31–33]. Despite the
vast difference in length scale, the physical processes involved in both cases appear to share similarities. Further analyses on the origin of these folds will be provided in Chapter 5.

The 3-D nanocomposites stabilized at large HPT strains possess remarkable features. First the scale of phase co-existence is very small. Z-contrast STEM imaging indicates that this scale is ~5–10 nm (Fig. 4.6). A complete characterization of this structure is very challenging because the scale is finer than the typical TEM sample thickness, leading to significant superposition for the near equiatomic composition of the ARB samples. APT was thus used to further evaluate these nanostructures. Although APT lacks atomic resolution because of the large difference in evaporation fields for Cu and Nb, atom reconstruction maps confirmed the 3-D coexistence of Cu-rich and Nb-rich phases, with a characteristic length scale of ~10 nm, as illustrated in Fig. 4.9. It should be noted also that iso-concentration surfaces generated in this study establish that both phases are connected, which is not surprising for mixtures with nearly equiatomic compositions. Moreover, TEM dark field imaging and XRD peak broadening showed that the Cu and Nb grain sizes are also of the order of 5 nm. It is therefore concluded that each Cu-rich or Nb-rich ligament comprises 1–2 grains. As it is indicated in Chapter 2, one of the interests in developing Cu/Nb nanolaminates and nanocomposites resides in their potential for absorbing point defects and dislocations, owing to their high interfacial area. In that respect, the 3-D nanocomposites stabilized by large HPT strains offer a high potential. The specific interfacial area is estimated from APT iso-concentration surfaces to be ~0.30 nm⁻¹, compared to 0.056 nm⁻¹ for the as-fabricated ARB material. Prior studies on Cu/Nb and Cu/V layered structures have indicated, however, that the efficiency for absorbing point defects or He atoms is also a function of the crystallographic orientation of the interfaces [34, 35]. It would therefore be interesting to determine the He storage
capacity of these 3-D nanocomposites, and to compare it with that measured on Cu/Nb nanolayers with well-defined interfaces [35].

The steady-state grain size of the 3-D Cu/Nb nanocomposites is much smaller than the ones obtained after room temperature HPT deformation of the pure metals, typically 150 nm for pure Cu [36], [37] and 100-150 nm for pure Nb [38]. In the pure Cu samples deformed by HPT, however, grain size distribution and microtexture developments provided clear evidence for recrystallization [28]. In contrast, Lim and Rollett [39] showed that, in Cu–Nb layered composites, recrystallization in the Cu layer was suppressed during rolling when the layer thickness was below ~1 μm. Our analysis of the microstructure and texture of 3-D nanocomposites stabilized by HPT is consistent with this result, leading to very small grain sizes. It should also be noted that the steady-state grain size stabilized by ball milling is also quite small, typically 5 nm [22], probably for similar reasons. One interesting fundamental question raised by the stabilization of these 3-D nanocomposites concerns the selection of the length scale of phase coexistence. As described in Chapter 2 previously, it has been proposed that nanoscale phase separation results from the competition between thermally activated phase separation and forced mixing moderately immiscible alloys [12, 13, 40]. Recent atomistic simulations support this simple picture and the corresponding analysis of the length scale selection resulting from this dynamical competition [41]. In a recent investigation of phase evolution in Cu$_{80}$Nb$_{10}$Ag$_{10}$ subjected to low temperature SPD by HPT and ball milling, Wang et al. [24] showed that, in the absence of thermally activated diffusion, Nb precipitates reached a well-defined steady-state size, ~20 nm, and that this size results from plasticity-driven mechanisms promoting precipitate shrinkage as well as re-precipitation. More work is needed to determine whether a similar rationalization could also apply to the bi-connected Cu–Nb 3-D composites stabilized by HPT. The starting material for the present
investigation was an ARB Cu/Nb nanolaminate with (112) K-S orientation, thus with high shear strength interfaces. It would be interesting to investigate the evolution of Cu/Nb nanolaminates with low interface shear strength, such as PVD Cu/Nb nanolayers where interfaces are predominantly (111) K-S. Hoagland et al. [42] calculated that dislocations would be attracted by these weak interfaces, and these authors predicted that “weaker boundaries afford a greater barrier to the transport of slip across the boundary than very strong boundaries”. This prediction was in fact recently confirmed by MD simulations [25, 26], showing that, in simple shear deformation, (111) K-S and NW Cu/Nb interfaces are much more resistant to chemical mixing than (112) K-S interfaces. At large enough shear strains, however, the activation of multiple slip systems should eventually lead to the formation of interface steps, leading to interface roughening, and to the progressive destabilization of the initial layered structure. It is thus anticipated that the threshold strain required for destabilizing layered structures with low shear strength interfaces would be larger than the one reported here for (112) K-S interfaces, but, in the limit of very large strains, a 3-D nanocomposite would nevertheless be stabilized.

Lastly, it is interesting to note that wire drawing experiments and atomistic simulations indicated that the forced mixing of Cu and Nb could lead to the formation of an amorphous phase [5, 17, 43]. No amorphous phase was identified in the present work by either selected area diffraction patterns in TEM analyses or XRD, but we note that the detection of such a phase in the 3-D nanocomposites stabilized at large HPT strains would be very difficult owing to the fine scale of phase coexistence compared to typical TEM foil thickness.
4.6. CONCLUSION

In this work, nanolayered Cu/Nb composites fabricated by ARB, with a nominal layer thickness of 18 nm, were subjected to large shear strains using HPT at room temperature to investigate the phase and microstructural stability of the nano-layers under severe shear strains. It was observed that the evolution of the microstructure proceeded in successive steps. First, at strains of $\gamma=4.2$ and beyond, XRD characterization indicated that the $\{112\}$ K-S orientation relationship and texture stabilized by ARB were destabilized. TEM showed that the layered morphology resisted HPT deformation to strains up to $\sim10.8$. As the HPT strain was further increased, a 3-D microstructure replaced the initial ARB layered structure, with a reduction in the length scale of phase coexistence. The average grain size of both Cu and Nb was also reduced, down to $\sim5$ nm at a strain of 286, while strains as large as $\sim3500$ were required for the chemical composition of these phases to reach steady state. The steady-state solubility of Nb in Cu and Cu in Nb were found to reach $\sim1.5$ at.% and $\sim10$ at.%, respectively. This significant difference in solubility was assigned to the large asymmetry of the thermal solubility between the Cu-rich side and the Nb-rich side of the equilibrium Cu–Nb phase diagram. At large strains, the textures of the Cu and Nb phases stabilized around an A-fiber texture and a near random texture, respectively. These textures appear thus to be distinct from those reported in monolithic Cu and Nb subjected to HPT, suggesting a significant effect of the 3-D Cu–Nb nanoscale phase coexistence on texture. The length scale of these 3-D nanocomposites was very fine, and determined by TEM and APT to be $\sim5–10$ nm. The present findings suggest that HPT can be used to stabilize interconnected nanocomposites at very small scales and with a very high density of interfaces. In addition to its stability under HPT deformation, this morphology thus offers attractive features for trapping point defects and rare gas
atoms under irradiation, which makes this microstructure worth investigating in the context of designing radiation-resistant materials.

4.7. REFERENCES


CHAPTER 5

DEPENDENCE OF DEFORMATION BEHAVIOR ON THE LENGTH-SCALE OF ARB COMPOSITES

5.1. INTRODUCTION

Building on the results described in Chapter 4, this chapter will be focused on investigating three important questions in order to further our understanding of the evolution of highly immiscible elements subjected to severe plastic deformation:

1. What is the shear strain required to destabilize the layered structure and form a 3-D steady state microstructure?
2. What is the morphological pathway followed by Cu-Nb nanolaminates as they evolve from 2-D layered microstructure to a 3-D microstructure?
3. Is the final 3-D microstructure a unique steady state?

These three questions are related with one another, and we will be addressing them by investigating Cu-Nb layered composites with larger nominal layer thicknesses, 2 μm and 200 nm. The evolution of these samples after various HPT strains will be compared with those described previously in Chapter 4 for ARB composites with 18 nm nominal layer thickness. We first discuss briefly the details specific to each question, and how we will proceed to address them.
5.1.1. Strain Required to Reach Steady State for Different Layer Thicknesses

The strain required for destabilization of Cu-Nb nanolayers should provide important information regarding the plastic deformation in these composites. In the case of moderately immiscible systems, the dependence of the strain required for homogenization as a function of the initial decomposition scale was used to provide direct experimental evidence of the super-diffusive character of the chemical mixing forced by SPD [1, 2]. In contrast, for the highly immiscible Cu-Nb system, atomic simulations indicate that the forced mixing should be diffusive [3, 4]. Although we know that HPT will not homogenize Cu-Nb, we showed in Chapter 4 using XRD that significant chemical mixing takes place at large strains, especially for Cu in Nb. Following that same approach, we will study the dependence of this partial mixing with the initial ARB layer thickness, in an attempt to determine whether the mixing is indeed diffusive. Another phenomenon that takes place concurrently with the chemical mixing is the morphological transformation of the microstructure, from 2-D to 3-D. We note however that, for highly immiscible systems, the dependence of the rate of this morphological evolution with the initial layer thickness may be distinct from that of the forced chemical mixing, as the former evolution is greatly influenced by kinetic roughening of interfaces and other interface instability, in contrast to the latter. For both properties, forced mixing and nanocomposite morphology, we will thus attempt to determine the strain required for reaching steady state for various initial thickness of the Cu and Nb nanolayers. Specifically, if the strain-dependence is controlled by diffusive processes, it is expected that the critical strain required to reach steady state will scale with the square of the initial layer thickness, in contrast to a linear scaling in the case of super-diffusive mixing. The results presented in Chapter 4 showed that, for Cu-Nb nanolayers with the nominal ARB layer thickness of 18 nm, the strain required to stabilize the 3-D nanocomposite structure was bounded by values of 70 and 300. If the
hypothesis of super-diffusive mixing is correct, then the strain required for reaching steady state should not exceed 3,000 and 30,000 for nominal Cu-Nb nanolayer thicknesses of 200 nm and 2 microns, respectively. On the other hand, in the case of diffusive processes, the corresponding strains would be 30,000 and 3,000,000, respectively. These strains are obviously very large, but since values $\approx 10,000$ can be reached by HPT, it seems possible to distinguish the two mechanisms by focusing on the sample with a nominal layer thickness of 200 nm. We will show later that, owing to the initial layer reduction imposed by compression during HPT, the ARB sample with a 2 µm initial layer thickness can also provide useful information.

5.1.2 Morphological Pathway to Layer Destabilization and 3-D Steady State

The second question addresses the morphological pathway followed by Cu-Nb composites when subjected to shear strain via HPT, which is important to understand the deformation mechanisms in this system. So far, the results presented and discussed in Chapter 4 on the 18 nm Cu-Nb nanocomposites demonstrated that at low strains ($\gamma<10$), interface roughening was accompanied by macroscopic layer folds and swirls. This evolution was followed by layer destabilization observed at $\gamma=68.5$, resulting in equiaxed 3-D microstructure for strains exceeding 286. However that at lower strains, formation folds and swirls with high local plastic strains were observed. These structures are reminiscent of similar formations observed in geological materials, albeit over much larger length and time scales. In this case shear deformation resulted from plate tectonics [5]. Despite the large differences in scale, the physical process behind both cases may be similar. These features have also been observed in duplex stainless steels subjected to HPT [6], and attributed to the development of Kelvin-Helmholtz instability. However, a quantitative study
testing this hypothesis had not yet been reported. The scale of these features in these studies, however, are typically hundreds of microns, and they may be related to the macroscopic constraints of the HPT test. Swirls at smaller scales were reported by Tian et al. [7] on hypo-eutectic Cu-Ag alloys subjected to HPT and by Ren et al. [8] on Cu-Nb nanocomposites fabricated by ARB and then subjected to wear. These reported length-scales are more consistent with my results. However, the occurrence of folds in these studies has been linked to shear banding, which was not observed in my study.

An intriguing question here are the conditions required for the formation of these folds and swirls. Two possible reasons can be proposed for the formations of such unusual microstructural features. The first explanation is that these structures are triggered the presence of perturbations (inclusions, roughness of layers after ARB) in the microstructure, causing disruption of the strain deformation path, leading to deformation localization around the existing perturbation. A second reason concerns the differences in deformation behavior of Cu and Nb layers under severe shear deformation. Since Cu and Nb grains in the 18 nm sample extend over the thickness of the layers, the deformation and rotation of each grain is severely constrained by the presence of Cu/Nb interfaces, which are strong obstacle for dislocation motion. It has been proposed that in ARB materials with layers containing many grains, this constraint would be sufficiently relaxed to suppress the formation of folds and swirls. In order to investigate this question, we will focus on the 2 µm ARB samples, since it has been reported that each layer contains multiple grains, typically 5 to 10. It is important to note that these 2 µm ARB samples had the same chemical composition and similar Cu/Nb interface orientation relationship as the 18 nm samples.
5.1.3 Uniqueness of the Steady State 3-D Microstructure

The final question focuses on the steady state microstructure after HPT deformation. The experiments described above will make it possible to investigate whether Cu$_{50}$Nb$_{50}$ composites with different starting layer thicknesses reach the same steady state at large HPT strains. As reported in Chapter 4, Cu-Nb nano layers with initial average layer thickness of 18 nm self-organized into a 3-D nanostructure with steady-state length scale between 5-10 nm after being subjected to high strain at room temperature. A well-defined microstructure and crystallographic texture was reached, and it was found to be stable for strains up to 6,000, the highest strain studied in that work. Experimental studies on different Cu-Nb systems subjected to deformation via different techniques (ball milling, HPT, etc.), reported similar final length scales, from 5 to 20 nm [9, 10]. A recent experimental study on Cu-Nb-Ag systems subjected to HPT at room temperature, reported that Nb precipitates reached a steady state size of ≈20 nm, which seemed to be independent of the initial microstructure, and weakly dependent on the composition. This nanoscale self-organization was rationalized as resulting from a competition between plasticity-driven mechanisms promoting precipitate shrinkage as well as re-precipitation [10]. In order to determine whether the initial layer thickness had an influence on the steady state reached at large strains, ARB composites with nominal layer thicknesses of 200 nm and 2 μm were subjected to various shear strains via HPT, and characterized by BFTEM, DFTEM, and HAADF-STEM analysis.
5.2. INITIAL MICROSTRUCTURE OF THE ARB COMPOSITES

As discussed in the previous section, two new Cu-Nb ARB composites were used to investigate the evolution of microstructure when they were subjected to shear strain via HPT. The Cu-Nb multilayer composites were fabricated using processing steps similar to those used for 18 nm ARB samples. However, there are a few important differences in the processing and experimental procedures which should be noted. The first difference between samples analyzed in Chapter 4 versus Chapter 5 was that the ARB samples used in Chapter 5 were stacked such that new Cu-Nb interphases were only created during the first roll bonding step. Further roll bonding only created bonding between Cu/Cu interfaces. This method, named as Cu cladding (CC) [11, 12] enabled two advantages on sample synthesis. Firstly, it allowed for Cu/Nb interfaces to be subjected to the same amount of strain throughout the ARB process, regardless of the position of the interface in the stack. Secondly, the surface layers of the multilayer nanocomposites were always Cu surfaces, therefore, suppressing any oxidation of Nb surfaces. Additionally, any oxidation or impurities that were present on the Cu and Nb surfaces during the initial roll bonding were spread, limiting the effect of these impurities on the interfacial structure [11].
The microstructure of the 2 μm-ARB composite is displayed in Fig. 5.1. The SEM image reveals that Cu/Nb layers had wavy interfaces rather than the straight interfaces seen in 18 nm – ARB nanocomposites. TEM micrographs showed that there are multiple grains through the thickness of each layer, confirming results reported earlier [11, 13]. The layers were chemically sharp. The actual layer thickness was determined by Carpenter et al. [11] by averaging over 900 measurements. It is reported as a function of the rolling reduction and strain in Table 5.1 [11, 13, 14]. The hardness measurements were performed using nanoindentation. As the 2 μm ARB composite have Cu/Nb layers that were too thick for the nanoindentation measurements, the hardness values for these samples could not be obtained. However, one expects smaller hardness values for the 2 μm - ARB composites as they have a coarser microstructure than the 200 nm - ARB composites.
<table>
<thead>
<tr>
<th>Nominal Layer Thickness</th>
<th>Average Measured Layer thickness (μm) / Variance</th>
<th>Rolling Reduction (%)</th>
<th>Rolling Strain</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Nb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 μm</td>
<td>2.029 / 0.718</td>
<td>1.999 / 2.560</td>
<td>98.9</td>
<td>4.58</td>
</tr>
<tr>
<td>200 nm</td>
<td>0.198 / 0.0173</td>
<td>0.172 / 0.0419</td>
<td>99.99</td>
<td>9.23</td>
</tr>
</tbody>
</table>

Table 5.1. Properties of as-fabricated ARB materials analyzed in this study [11, 13, 14].

It is noteworthy that the variance of layer thickness is significantly higher when the material is coarser. The spread of the average layer thickness reduces as the layer thickness gets smaller. Nb layers showed a broader range in thickness for both ARB samples compared to Cu layers. While the questions investigated studied in this chapter employs the nominal layer thickness as a parameter for understanding the forced chemical mixing mechanism, it is thus important to keep in mind that the local layer thickness may depart significantly from the nominal value.

We complemented this information by determining the grain sizes for Cu and Nb in the 2 μm samples using XRD. The Cu and Nb grain size was measured to be 35.7 ± 0.8 nm and 25.1 ± 0.5 nm, respectively. As stated in the previous section, and unlike in the 18 nm ARB samples, the grain sizes are much smaller than the average layer thicknesses, indicating that the layers contain multiple grains along the ND direction, in agreement with our TEM observations and previous reports [11, 13].
We now turn to some general information about the evolution of the samples, so as to be able to estimate the shear strain at a given distance from the center of the samples, for a given number of HPT turns. As the samples used in this chapter were fairly thick, \( \simeq 700 \) to \( 850 \) \( \mu\text{m} \), they underwent significant reductions in thickness. The local thickness values taken from the center, and from 1, 2, 3 and 4 \( \text{mm} \) positions away from the disc center were measured from the sample cross section observed in an SEM and were plotted for various HPT turns, see Fig. 5.2.

Fig. 5.2. The evolution of bulk sample thicknesses under various HPT turns for the 2 \( \mu\text{m} \) and 200 \( \text{nm} \) ARB composites.
Firstly, the ARB composites with 200 nm nominal layer thickness showed an expected trend for bulk thickness reduction under HPT. The starting sample thickness of ~ 750 μm decreased down to ~ 250 μm (at the center of the disc) after 1 rotation. After 20 rotations, some additional but smaller reduction in thickness was observed, resulting in thicknesses of ~ 220 μm and ~ 66 μm at the center and periphery, respectively. ARB composites with 2 μm nominal thickness, however, experienced significant amount of thickness reduction during HPT processing. The initial sample thickness of ~ 800 μm decreased to less than ~ 250 μm at the center of the sample just after 0.5 turns. An intriguing point here is the curve for 1 HPT turn on the 2 μm-ARB composite, where the sample behaved unexpectedly, as the thickness at the center gets larger than what was measured for the 0.5 turns. This unusual behavior can possibly result from a combination of reasons including: the compression applied during HPT as well as material properties (see Table 5.1) for the 2 μm ARB composites. A high confining pressure of 4.5 GPa was applied in our experiments to prevent any slippage and fracture of the sample during the anvil rotations. However, due to this large compression, the anvils may deform elastically. This allows for the confinement of the material at the inner part of the anvils, while the outer part is free to flow outward as burr when non-constrained anvil geometry is selected. Additionally, the back-pressure affecting the outer part of the sample hinders the outflow of the material close to the center due to very small clearance between the anvils. These events result in a convex shaped HPT processed disc, just like observed in our experiments, in which there is a significant difference between the thicknesses of the center and the periphery of the sample, especially at the initial stages of HPT processing.

As described in Chapter 3, the common strain calculation for samples subjected to HPT is based on a linear relationship between the number of rotations applied, the position on sample and the inverse of the sample thickness. As our HPT processed sample showed significant thickness
reduction between the sample center and periphery, leading to a convex shape, the true relationship between the parameters in the HPT strain equation is no longer linear. Unfortunately, the number of samples used in this study was not sufficient for a calculation of strain as done for the 18 nm ARB samples in Chapter 4, and so, despite the limitation of Eq. 3.1, we will use it as an estimate of the HPT strains. In all cases, since the thickness decreased progressively as HPT deformation was applied, the strain estimates that will be used in this Chapter are thus upper bound values. We note however that for the 200 nm samples, since the thickness profile did not change much upon increasing the number of rotations from 1 to 20, the estimated strains for 20 turns should be fairly accurate.

Fig. 5.3. Microstructure of the as-fabricated 2 μm - ARB nanocomposite taken from the center of the HPT disc after 0.5 turn: (a) bright field TEM micrograph and (b) corresponding SAED pattern; the main reflections are indexed in (c). The shear and normal directions are shown in (a).

It can be anticipated that the initial compression of the samples during the beginning of HPT deformation resulted in a reduction of the layer thickness, as for instance reported by Pouryazdan et al. [2]. For that purpose, we determined the actual layer thickness in the 2 μm-ARB sample,
from a TEM sample prepared via FIB at the center of the ARB sample subjected to 0.5 HPT turns. This sample should not be have been subjected to any shear deformation, as the center of an HPT deformed disc undergoes zero shear strain theoretically. The average layer thickness was measured over 50 layers and calculated to be ~ 214 nm (standard deviation: 133.7), see Fig. 5.3. Based on the reduction in sample thickness, assuming to be accommodated by homogeneous radial flow, one would have expected that the layer thickness be reduced by 850/250 ≈ 3.5. So the reduction factor measured by TEM is quite larger, 2/0.214 ≈ 9.3. It should be however kept in mind that the 2 µm sample has large layer thickness variance, and since the TEM analysis was applied to one small region, it is more reasonable to use the sample thickness reduction than the TEM-measured layer thickness reduction to evaluate the effective layer thickness in the 2 µm samples. The strains estimated for reaching the steady state 3-D microstructure in these samples should then be less than the previous estimations, making them accessible with the HPT conditions we used.

In the case of the 200 nm samples, no TEM analysis at low HPT turns was performed near the center of the specimens, and we will thus use the overall sample thickness reduction after 1 turn, 750/250 ≈ 3, to estimate the effective layer thickness in these samples. We note that although there is a significant layer thickness reduction in the 2 µm ARB samples, Cu and Nb layers were observed to still contain multiple grains as seen in Fig. 5.1. These samples are therefore still suitable for testing the hypothesis that folds and swirls should be suppressed in the case where layers contained many grains. It is also interesting to note that in the 200 nm ARB samples, each layer contained only one grain, so the comparison between these two samples should be informative.
5.3. SHEAR STRAIN REQUIRED TO REACH STEADY STATE

In order to determine the shear strain required to reach 3-D steady state, as-fabricated ARB samples with 200 nm and 2 μm nominal thicknesses that were subsequently subjected to large shear strains, and were compared to the previously analyzed 18 nm –ARB samples. As described in the introduction section of this chapter, the shear strain required to reach steady state were estimated to be in the range of ~ 700 - 3,000 and ~7,000 - 30,000 for 200 nm and 2 μm, respectively, if the system experiences forced mixing through a super-diffusive process. However, due the reduction of sample thickness due to compressive force applied during HPT the estimated critical strains to reach steady state 3-D microstructure should be expected to be less. The analysis of the results will be given in Section 5.4.

The evolution of microstructure for 2 μm – ARB samples were first analyzed by XRD. After strain of γ ≈ 10, the grain sizes were progressively reduced. At strain γ ≈ 120, the grain sizes for Cu and Nb both reached a steady state value of 7.0 and 4.7 nm, respectively. We can already note that these steady state sizes are very similar to the ones determined for the 18 nm ARB sample, 6.2 nm and 4.7 nm, respectively. Furthermore the strain required for reaching the steady state values is ≈ 100, compared to ≈ 50 for the 18 nm ARB samples. The chemical mixing measured from XRD displayed a more complex evolution. For strains up to ≈ 200, the solubilities increase in a manner that is similar to what we observed for the 18 nm sample, with a slight increase of Nb solubility in Cu, ≈ 1-2 at.%, and a much larger increase for the solubility of Cu in Nb, approaching 10 at.%. At larger strains, the Nb solubility in Cu remains small and fairly constant. The Cu solubility in Nb however displays an unexpected behavior, with a significant decrease of this solubility, reaching ≈ 5 at. % at the largest available strains. The reason for this evolution is unknown and should probably warrant repeating the measurements, since, all three values at large
strains come from the 50 turn sample, and had to be taken closer to the periphery of the discs, in particular for the last two data points. Nevertheless, the data indicates that the strain at the sharp rise of the solubility is ≈ 30, compared to ≈ 10 for the 18 nm ARB samples.

Fig. 5.4. (a) Grain size and (b) chemical solubility in 2 μm-ARB composites subjected to HPT
Fig. 5.5. Microstructure of the 2 μm-ARB nanocomposites after an HPT strain of 4188: (a) bright field TEM micrograph, (b) dark field TEM micrograph formed using a Nb (110) reflection, (c) SAED pattern of the area shown in (a), (d) indexing of the main reflections in (c), and (e) Z-contrast STEM micrograph. (a) and (b) are prepared from the HPT disc surface, (e) is prepared from disc cross section.
The microstructure at high HPT strains was investigated using TEM. As indicated in Fig. 5.5 caption, samples from multiple positions on the sample were prepared, corresponding to the sample applied strain, i.e. ND-SD lift-outs were prepared from the HPT disc surface after fine surface polish and SD-ND lift outs from the disc cross section, after cutting the HPT disc in half and lightly polishing the cut surface. This second procedure made it possible to take samples near the middle of the thickness of the original discs, while the first procedure resulted in samples taken about 20-40 microns below the surface of the discs. The similarities between these different types of samples indicate that these microstructures were representative of the discs. This allowed for the confirmation of the homogeneity of the samples. At a strain of $\gamma \approx 4188$, the microstructure showed a complete destabilization of the layers and the formation of a fine scale 3-D microstructure, see Fig. 5.5. The SAED micrograph in Fig. 5.5 (c), confirms a similar preferred orientation compared to the steady state microstructure observed in 18 nm – ARB composites after a strain of 5970. This texture is quite different from that of as-fabricated ARB samples. Average Nb grain size were measured over 50 grains and calculated to be $\sim 4.2$ nm by dark field TEM micrographs, in agreement with XRD results as well as Z-Contrast STEM images see Fig. 5.5. (b) and (c).
Fig. 5.6. Microstructure of the as-fabricated 200 nm - ARB nanocomposite at a strain of ~ 3421: (a) bright field TEM micrograph and (b) corresponding SAED pattern; the main reflections are indexed in (c). The shear and normal directions are shown in (a).

In the case of 200 nm-ARB composites, the microstructural evolution showed layered structure after a HPT strain of ~ 3421, see Fig. 5.6. The layers appear heavily distorted, and it is not clear on this bright field image whether these layers fully correspond to alternating Cu and Nb layers. The corresponding SAED pattern displayed in Fig. 5.6. (b) shows some residual texture from the as-received ARB sample as both Cu and Nb phases show preferred orientations. It is therefore clear that at this strain, the microstructure had not yet reached the expected 3-D steady state microstructure.
At larger HPT, i.e. ~10,000, the microstructural evolution was completed, see Fig. 5.7. At this strain, the 200 nm-ARB nanocomposites went through complete destabilization of the layer structure, transforming to a 3-D microstructure. The apparent grain size measured from the bright field images, \( \approx 5-10 \) nm, is close to what had been observed in the 18 nm and 2 \( \mu m \) ARB composites.

**5.4. MORPHOLOGICAL PATHWAY TO LAYER DESTABILIZATION AND 3-D STEADY STATE**

Previous results on the 18 nm ARB nanocomposites demonstrated that at low strains (\( \gamma<10 \)), interface roughening was accompanied by large layer folds and swirls. This was followed by the destabilization of the layers at strain of 68.5, and complete transformation from 2-D layers to 3-D
equiaxed grains after a strain of 286. We investigate here whether folds and swirls were also present in thicker ARB samples after HPT deformation.

For this study, FIB lift-out samples were prepared from the cross section of HPT discs of 2 μm and 200 nm ARB composites that underwent low HPT strains. As indicated in the introduction section of this chapter, the formation of swirls can be caused by two possible reasons, one intrinsic, via an instability induced by plastic deformation of Cu/Nb interfaces, and a second one, extrinsic, due to the presence of inclusions and impurities.

SEM images of 2 μm samples subjected to different HPT strains are displayed in Fig. 5.8 and Fig. 5.9. At strain of ~ 20, some waviness at the interfaces was observed, however, no significant evidence for fold and swirl formation was found.

![SEM images for 2 μm – ARB composites subjected to; (a) γ ~ 20 and, (b) γ ~ 60. The sample directions are as marked.](image)

Upon further straining, i.e. at a strain of ~ 60, folds and vortex-like features were observed in the microstructure. Fig. 5.9 (a) and (b) shows these features at higher magnification. As seen in Fig. 5.9 (a), taken with SEM at a higher magnification of image displayed in Fig. 5.8 (b), a linear
feature running diagonally through the image presents similarity with what would be expected for a shear band. More remarkably, multiple folds and swirls were observed throughout this cross section.

Fig. 5.9. SEM images of 2 μm – ARB composites subjected to γ ~ 60, at higher magnifications of Fig. 5.8 (b). The sample directions are as marked.

The microstructure of the 200 nm ARB nanocomposites at strain of γ ~ 103 is shown in Fig. 5.10. No clear evidence of folds and swirls was found for γ ~ 55 and γ ~ 103. This is surprising since these samples accommodated only one grain through the layer thickness, as in the case of the 18 nm samples. The SAED pattern displayed in Fig. 5.10 (b) reveals the existence of nanocrystalline microstructure.
Fig. 5.10. Microstructure of the 200 nm ARB composite after an HPT strain of ~ 103: (a) SEM image, (b) bright field TEM, (c) corresponding SAED pattern. The main reflections are indexed in (d). Note that the vertical lines at the bottom of the image in (a) are caused by ion beam milling.
5.5. DISCUSSION

The deformation behavior of ARB nanocomposites with two different nominal layer thicknesses, 2 μm and 200 nm, were investigated after subjected to HPT deformation. Three related questions were addressed, pertaining to the strain required to reach steady state microstructure, the morphological evolution during deformation, and the final 3-D microstructure for samples with different initial layer thicknesses.

Starting with that third question, we observed that, regardless of the initial microstructure or length-scale, the system reaches to a unique 3-D steady state with grain size values for Cu and Nb of ≈ 7 nm and 5 nm, respectively, determined by XRD. TEM analysis indicated that the 3-D structures had typical length-scales of 5-10 nm, thus indicating that the 3-D nanocomposite structure contained nearly individual Cu and Nb grains. This steady state microstructure is very similar to the ones observed in Cu-Nb system subjected to ball milling, however, a direct comparison is not possible since ball-milled Cu-Nb alloys were dilute in Nb.

We turn now to the question on the dependence of the strain to reach steady state with the initial length scale of the nanolaminates. As stated in Section 5.1, a significant reduction in sample thickness was observed for the thicker ARB composites used in this study, and therefore the nominal layer thickness is not a good measure of the characteristic length scale of the layered microstructure at the beginning of the HPT deformation. The sample thickness measured at the center of the discs and after 0.5 or 1 turn was found to be 3.5 and 3 times less than the initial value before HPT processing, for the 2 μm and 200 nm ARB samples respectively. One important consequence for this work is that sample thickness led to a reduction of Cu and Nb layer thicknesses. TEM results obtained from the center of discs confirmed this layer thickness reduction. While the reduction factor measured by TEM, ≈ 9, is larger than the one predicted by
sample thickness reduction, owing to the large variance in layer thicknesses in the 2 µm ARB samples, in the following we will use the sample thickness reduction to estimate the effective layer thickness at the start of the HPT deformation. This approach leads us to use the following effective layer thicknesses: 65 nm for the nominally 200 nm layer thickness samples, and 570 nm for the nominally 2 µm layer thickness samples. These samples have therefore effective layer thicknesses ≈ 3.6 times and ≈ 32 times larger than the 18 nm ARB samples.

For the 2 µm ARB composites, at the high HPT strain of γ ~ 4200, the layered structure is replaced by a 3-D microstructure with co-existing Cu-rich and Nb-rich phases. Recalling that the strain required to reach steady state was between 70 and 300 for the 18 nm samples, and noting that $32^2 \approx 1,000$, the strain for reaching steady state should be between 70,000 and 300,000 if diffusive mixing were to be controlling the refinement of the microstructure. We can thus safely exclude this hypothesis. The strain interval for superdiffusive mixing is ≈ 2,200 to 9,000, and thus is compatible with the observation of a 3D equiaxed structure at a strain of 4,200. Further measurements, in particular at lower strains, would be necessary to confirm this conclusion.

In the case of 200 nm – ARB samples, but with an effective layer thickness of 65 nm, noting that $3.6^2 \approx 13$, the expected strains intervals for reaching steady state should be 250 to 1,100 for superdiffusive mixing and 910 to 3,300 for diffusive mixing. It is therefore very surprising to see the persistence of the layered structure at a strain of ≈ 3,400, although it is encouraging to see that at a strain of ~ 10,000 the 2-D layered microstructure eventually transformed to 3-D equiaxed microstructure. There is no simple explanation to this surprising observation, and it suggests that it would be necessary to repeat this set of experiments.

Lastly, we investigated the question of the morphological pathways of the evolution of the microstructures by subjecting the 2 µm and 200 nm ARB composites to low shear strains.
Previously, the existence of unusual and intriguing microstructural features, such as folds and vortex-like structures were observed for the 18 nm sample when the strains were less than ~10. In the case of 2 μm samples, these features were observed at strain of ~ 60, in addition to some layer surface roughness. Two hypotheses had been proposed to account for the formation of these folds and swirls. The first one is that they are triggered by defects or inclusions. The samples used in this study were however obtained by Cu-cladding method, which prevents surface oxidation of Cu-Nb interfaces during rolling process. Furthermore no inclusion was ever observed near the center of the swirls. We thus conclude that this hypothesis should be discarded. The second hypothesis suggested that the constraints imposed by Cu/Nb interfaces could prevent the deformation and rotation of grains, leading to a plastic instability. As reported above, the 2 μm-ARB composites contained multiple grains through the ND direction of the layers, which should have relieved these constraints at most of the interfaces, now between Cu/Cu and Nb/Nb grains. Nevertheless abundant folds and swirls were observed in 2 μm-ARB deformed to a strain of ≈ 60. This observation suggests at first that this mechanism may also be excluded. One should however be more cautious since in these 2 μm ARB samples a non-negligible fraction of the interfaces are still Cu/Nb interfaces, and, under large enough driving force, a plastic instability could still be triggered at those interfaces, progressively invading the whole microstructure. This suggests that in order to gain firmer ground on this question, it would be interesting in the future to characterize samples at the onset of the appearance of swirls, although this would clearly be a delicate task.
5.6. CONCLUSION

Cu/Nb composites fabricated via ARB and consisting of different layer thicknesses were subjected to HPT to provide further understanding of the deformation and mixing mechanisms active in these highly immiscible nanolaminates. First, it was found that the steady states reached for widely different initial layer thickness were very similar in term of grain sizes, resulting in the formation of 5-10 nm equiaxed nanocomposites. The steady-state solubility of Nb in Cu was also independent of the initial state. One set of samples suggested that the solubility of Cu in Nb could be different, or alternatively suggesting that, for that solubility, the true steady state had not been reached for the 18 nm ARB samples in Chapter 4. It would however be necessary to repeat the experiments on the 2 µm samples to reach a firm conclusion.

In the case of the 2 µm ARB samples, after correction from the initial sample an layer thickness reduction, the strain necessary to transform the initial 2-D structure into a 3-D structure appears to be compatible with a superdiffusive mixing, and certainly incompatible with a diffusive process. Quite surprisingly, in the case of 200 nm samples, the strains required to stabilize the 3-D microstructures are larger than those expected for either super-diffusive or diffusive mixing. It seems however that this sample behaved differently, in particular folds and swirls were absent from their microstructures. This is likely to explain why a much larger strain was required to stabilize the 3-D microstructure. This analysis suggests that, when folds and swirls form, the strain required to stabilize the 3-D microstructure is compatible with a super-diffusive process.

Lastly, unusual microstructural features such as layer folds, swirls and vortex-like structures were observed in the 2 µm-ARB samples at a strain of ~60, with features very similar to those reported in Chapter 4 for the 18 nm ARB samples for strains of ~ 10. The proposed
explanation is that these features result from an instability starting at the Cu/Nb interfaces present in the 2 µm ARB samples.

5.7. REFERENCES

[8] F. Ren, “Private communication.”


CHAPTER 6
CONCLUSIONS

This dissertation is focused on providing a better understanding of deformation mechanisms imposed via shear deformation in highly immiscible alloy systems by investigating the evolution of microstructure and phase co-existence of Cu-Nb nanolaminates fabricated by accumulative roll bonding (ARB) when subjected to large shear strains by HPT. These ARB composites were reported to show improved material properties due to the high number and distinct properties of interfaces introduced and stabilized by the ARB process [1–3]. The as-fabricated samples were subjected to deformation by HPT, as a controlled application of shear strain. In addition to providing a change in strain path, from pure shear in rolling to simple shear, HPT makes it possible to reach very large strains, thus allowing to achieve true steady state [4, 5]. This steady state microstructure, namely the grain size, the scale of phase coexistence, and the crystallographic texture developed in the Cu and Nb phases, as well as the pathway that the microstructure follows to go from the nanolaminates prepared by ARB to the nanocomposites stabilized by large HPT strains were investigated by combining XRD and TEM characterization.

A detailed and systematic study was first carried out on Cu-Nb ARB composites with 18 nm nominal layer thickness. It was found that the evolution of microstructure proceeded in successive steps. Applied shear strains exceeding 4.2 resulted in the destabilization of KS {112} orientation relationship observed in the as-fabricated 18 nm samples, while the layered microstructure resisted destabilization until strains up to 10.8 were reached. As the HPT strain was further increased, a 3-D microstructure replaced the initial ARB layered structure, with a reduction in the length scale.
of phase coexistence. The average grain size of both Cu and Nb was also reduced, down to \(\sim 5\) nm at a strain of 286, while strains as large as \(\sim 3500\) were required for the chemical composition of these phases to reach steady state. The steady-state solubilities of Nb in Cu and Cu in Nb were found to reach \(\sim 1.5\) at.\% and \(\sim 10\) at.\%, respectively. This significant difference in solubility was assigned to the large asymmetry of the thermal solubility between the Cu-rich side and the Nb-rich side of the equilibrium Cu–Nb phase diagram. At large strains, the textures of the Cu and Nb phases stabilized around an A-fiber texture and a near random texture, respectively. These textures appear thus to be distinct from those reported in monolithic Cu and Nb subjected to HPT, suggesting a significant effect of the 3-D Cu–Nb nanoscale phase coexistence on texture. The length scale of these 3-D nanocomposites was very fine, and determined by TEM and APT to be \(\sim 5–10\) nm.

In a second step, the dependence of some key points of these evolutions were investigated by analyzing ARB composites with different nominal layer thicknesses, i.e. 2 \(\mu m\) and 200 nm. Samples were found to undergo thickness reduction during HPT deformation, for instance, in composites with 2 \(\mu m\) nominal layer thickness, bulk thickness reduction had led to a decrease in the average Cu/Nb layer thickness by a factor 3.5 to 9. At shear strain of \(\sim 4200\), the 2 \(\mu m\) ARB composite showed a complete destabilization of the layered microstructure, as well as the presence of folds and swirls, as in the 18 nm ARB samples. These observations suggest that, in the presence of these swirls, the length scale dependence of the strain required to reach steady state is compatible with a super-diffusive mechanism [6]. For the 200 nm ARB composites, surprisingly, no folds or swirls were observed, and much larger strains, exceeding \(\sim 3400\) were required to reach steady state. At a strain of \(\sim 10,000\) the microstructure had fully transformed from the 2-D layered microstructure to 3-D phase with a reduction of the length-scale of phase coexistence. The average
grain sizes of Cu and Nb were also reduced, and measured ~ 5 nm for strains exceeding ~ 120 for the 2 μm-ARB composites. The steady-state solubility of Nb in Cu and Cu in Nb were found to reach ~2 at.% and ~8 at.%, respectively, which is consistent with the results from 18 nm ARB composites. A reduction in Cu content in Nb-rich phase was observed after strains exceeding ~4200. It is possible that it can be resulted from surface effects during sample preparation for XRD, and thus it needs to be further investigated.

The present findings suggest that HPT can be used to stabilize interconnected nanocomposites at very small scales and with a very high density of interfaces. In addition to its stability under HPT deformation, this morphology thus offers attractive features for trapping point defects and rare gas atoms under irradiation, which makes these microstructures worth investigating in the context of designing radiation-resistant materials. The information provided in this dissertation has illuminated the complexities of material response under severe plastic deformation and introduced an extensive knowledge on stability and evolution of the highly immiscible Cu-Nb system at various shear strains.

6.1. REFERENCES


