Atomistic simulation of mechanical behaviours of nanocrystalline Al alloys with grain boundary segregation

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**ATOMISTIC SIMULATION OF MECHANICAL
BEHAVIOURS OF NANOCRYSTALLINE Al ALLOYS
WITH GRAIN BOUNDARY SEGREGATION**

BABICHEVA RITA

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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ENGINEERING**

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Abstract

Bulk nanocrystalline (NC) metals and alloys demonstrating very high ultimate strength compared to conventional coarse-grained materials have a great potential for structural applications. However, their usage is limited due to low ductility and premature intergranular fracture at ambient conditions. An increase in resistance of NC metallic materials against cracking along grain boundaries (GBs) is one of the important tasks of materials science. It is believed that the possible method for their mechanical property improvement is to utilize GB segregation hardening which can be expected only for materials having very dense GB networks. Therefore, the PhD research aims to understand the mechanical behaviours of NC aluminium (Al) with GB segregation of various alloying elements through numerical simulation.

The effects of different additional elements in GBs of NC Al on the elastic-plastic, fracture and cyclic behaviours are systematically studied with the consideration of the embrittlement potency, stress-strain relation, structure evolution and deformation mechanisms of the materials via molecular statics (MS) and molecular dynamics (MD) simulations.

In order to estimate the ability of impurity elements such as Fe, Co, Cu, Ti, Mg and Pb to resist brittle GB separation in NC Al, the GB segregation energy and the embrittlement potency for the mentioned elements located at different GBs of Al bi-crystals are calculated using the MS simulation. It is shown that the Co atom in GBs of the Al bi-crystals has a noticeable positive effect on the GB strength, while Pb has a negative effect. These results are compared with those obtained by conducting the MD simulation of the stress-strain test for NC binary Al alloys with GB segregation. It is

found that GB can be strengthened (weakened) by GB segregation of Fe or Co (Cu or Pb), but is nearly not affected by those of Ti or Mg. The results of the MD simulation are in a good agreement with those obtained from the MS simulation.

Furthermore, the effect of GB segregation of Co, Fe, Ti, Mg or Pb on the elastic behaviour of NC binary Al alloys is investigated via the MD simulation. The alloying element distribution and temperature effects are considered. It is shown that alloying can significantly affect the elastic moduli of NC Al. The decrease in the atomic radii of additional elements increases rigidity of the alloys with GB segregation. It is revealed that the shear modulus of the Al-Co alloy with Co atoms in GBs does not undergo significant changes with the increase in temperature in comparison with the NC Al and the other considered alloys.

The simulation results show that GB segregation can strongly affect not only the elastic behaviour but also plastic and fracture behaviours of the NC binary Al alloys. For example, it is found that within the considered alloying elements, the GB segregation of Co, Ti or Pb atoms improve the ductility of NC Al, while its strength can be increased only by the addition of Co or Fe. The failure of the NC Al alloys with GB segregation of Fe or Mg occurs via intergranular fracture, while the other additional elements in GBs do not lead to cracking until 40% shear and tensile deformation.

The difference in deformation behaviours of the alloys is further studied via the analysis of deformation mechanisms. Two main deformation mechanisms are identified to be responsible for the plastic deformation of the NC Al having GB segregation during its shear loading along the GB plane: GB sliding (GBS) and GB motion (GBM) which normally work simultaneously during a deformation process. In comparison with these

two deformation mechanisms, a contribution from dislocation sliding is not so pronounced. A uniaxial tensile loading perpendicular to GB planes of Al promotes dislocation activity and twinning rather than GBS and GBM. It is revealed that in this case, an increased strength of the NC Al alloys with GB segregation can be explained by suppression of the perfect dislocation sliding and twinning and activation of the partial dislocation slip in a structure. It is observed that such deformation behaviour can reduce the crack propagation rate and residual strain during material cyclic loading.

This study contributes to the understanding of the deformation and damage behaviours of NC metallic materials with GB segregation, which is essential for their potential applications.

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Chapter 1 Introduction

In the past decades, nanocrystalline (NC) metallic materials having grain boundary (GB) segregation attracted great attention because of their unique properties in comparison with their counterparts without such structural elements. Promising mechanical properties of such materials have resulted in intensive interest towards the possibility of their practical applications and therefore led to an increasing demand for an understanding of the effect of GB segregation on the stress-strain behaviour and deformation mechanisms of various metals and alloys having NC structure. This chapter introduces the background of the phenomenon of GB segregation in NC materials. The motivations and objectives of the Ph.D. study are given and the organization of the dissertation is described.

1.1. Background

The existing approaches to increase the strength of bulk polycrystalline metals usually rely on the decrease of dislocation mobility and/or dislocation generation rate. This can be achieved, for instance, by severe plastic deformation (SPD) that can result in a reduction of the average grain size of metals to the nanometer scale and form the NC structure. Along with an improvement of various functional properties, such structure refinement leads to a considerable growth of yield stress of materials. A disadvantage of bulk NC metals is their highly non-equilibrium structure with large internal stresses leading to their low thermal stability and limited plasticity due to crack nucleation in GB regions.

The enhancement of mechanical properties of NC metals and alloys through the finding of methods to prevent premature crack formation in their structures is a sophisticated task of materials science. This is because the crack nucleation and propagation mechanisms depend on many factors such as the loading mode, temperature, chemical, and phase composition, stacking fault energy, grain size, texture, and impurities.

A possible way to overcome these drawbacks is to utilize the GB segregation hardening. So far, attention has been given mainly to adverse GB segregation that lead to an intergranular embrittlement and/or decrease in corrosion resistance of coarse-grained polycrystalline metallic materials. Meanwhile, it is believed that the GB segregation hardening is a new approach that could help to avoid premature crack formation and enhance ductility and thermal stability of the NC metals and alloys having, unlike their coarse-grained polycrystalline counterparts, a dense GB network.

The approach to achieve enhanced mechanical properties of bulk NC materials through an introduction of GB segregation is new because its main target is not the dislocation ensemble but the GB network. Only recently have researchers started to pay attention to the opportunity of the GB segregation hardening of NC and ultra-fine grained (UFG) alloys; however, the mechanisms of such a phenomenon are still unclear and require careful investigation. It is no doubt that in the next few years one can expect a burst of interest to the GB segregation hardening of the bulk NC metallic materials.

1.2. Motivation and objectives

Aluminum (Al) is one of the widespread metals in the world and has long been used for various applications due to its high corrosion resistance, light weight and high

deformability. Therefore, in the present work, Al has been chosen as a test metal. The formation of the NC structure in Al allows considerably increasing its strength. However, such NC Al has some limitations caused by its low ductility due to high internal stresses leading to the intergranular fracture. The possible method to enhance ductility of the NC Al could be an introduction of atoms of additional elements to its GBs that also may lead to the GB segregation strengthening.

Despite a growing number of works conducted on a topic related to the GB segregation strengthening, only some common rules for different types of metals are available so far, which are insufficient for practical applications. A systematic study of the alloying effect and, in particular, the effect of GB segregation on mechanical properties and fracture behaviour of NC alloys is important. For a clear understanding of these effects, a great variety of elements and various factors that can influence GB embrittlement (e.g., the interatomic bond energy, relative atomic radius and GB type) should be considered. Moreover, properties of NC materials can be strongly dependent on atom distribution and possible compounds of an alloying element in a structure. Experimentally, it is a great challenge to determine the location effect for certain atoms and their compounds on the properties of NC materials. However, an atomistic simulation allows tracking structure changes at the atomistic level that can help to predict and analyze experimental data.

The current PhD research would investigate the mechanical behaviour of bulk NC Al and its binary alloys with GB segregation of various alloying elements via molecular dynamics (MD) simulation. The study aims to shed light on the effect of GB segregation on mechanical properties and structure of NC Al and to predict such alloying elements

(among selected ones) that can lead to a noticeable enhancement of its mechanical characteristics and prevent premature failure. A solution of this fundamental problem could allow realizing the potential for an additional strengthening and increase in plasticity of bulk NC metallic materials. The main objectives of the Ph.D. research are set as follows.

- To evaluate the ability of various alloying elements to resist GB separation in NC Al through the calculation of the embrittlement potency of impurity atoms in GBs of Al bi-crystals;
- To study the effect of GB segregation of alloying elements on the elastic-plastic behaviour and fracture of NC binary Al alloys at different deformation conditions;
- To investigate the effect of GB segregation on structure evolution of NC binary Al alloys subjected to external loading and identify deformation mechanisms;
- To study the stress-strain behaviour and structure evolution of Al bi-crystals with GB segregation under cyclic loading at room temperature and identify deformation mechanisms;
- To define metals, within the considered additional elements, for promising mechanical properties of NC Al alloys for the possibility of their further practical applications.

1.3. Dissertation outline

This Ph.D. dissertation contains seven chapters. Following this introduction chapter, a literature review on mechanical properties, deformation and failure mechanisms of bulk

NC metallic materials, as well as on the methods for obtaining the NC structure, is provided in Chapter 2. A review of works devoted to GB segregation in various NC materials and the works on NC Al and its alloys available so far is also given. The evaluation of the ability of various impurity atoms to resist GB separation in Al is presented in Chapter 3. Chapter 4 deals with the study of the elastic behaviour of NC Al and its binary alloys, in particular, the calculation of their elastic moduli and the analysis of their thermal stability. Chapter 5 focuses on the plastic and fracture behaviour of the NC binary Al alloys with GB segregation, with the effect of such segregation on deformation mechanisms of the alloys being taken into account. Chapter 6 is concerned about the effect of GB segregation on the stress-strain behaviour and structure evolution of Al during cyclic loading. Finally, conclusions are drawn and future works are recommended in Chapter 7.

Chapter 2 Literature Review

This chapter introduces bulk metallic nanomaterials and describes briefly their fabrication and unique mechanical properties caused by structural features. In addition, it raises the issues of GB segregation in NC metals and alloys, deformation and failure mechanisms as well as applications of such materials. Afterwards, mechanical properties of coarse-grained and NC Al and its alloys are considered. Finally, MD simulation method and known theoretical studies on the effect of GB segregation on mechanical characteristics of NC materials, including Al, are briefly described.

2.1. Bulk metallic nanomaterials

Nanomaterials can be classified into zero-, one-, two-dimensional and three-dimensional ones. They are, for example, nanoparticles, nanowires, nanofilms, and bulk nanomaterials, respectively. Bulk nanomaterials have three arbitrarily dimensions above 100 nm and possess NC structure. Bulk metallic nanomaterials consist of polycrystalline metals and alloys which have nanosized grains, and therefore they can also be referred to as bulk metallic NC materials.

2.1.1. Manufacturing processes

The presence of a high hydrostatic pressure and large shear strains is typical for SPD and the main condition for producing high dislocation density and grain refinement in polycrystalline metallic materials. SPD provides a significant reduction of the average grain size and can form UFG ($d < 500$ nm) or NC structures ($d < 100$ nm). A number of experimental SPD methods have been developed to obtain bulk metallic NC materials

[1,2]. Among them, the most popular ones are the equal-channel angular pressing (ECAP) and high-pressure torsion (HPT) (Fig. 2.1).

During ECAP, a rod or bar shaped sample is pressed through a channel with an angle ϕ (Fig. 2.1(a)). This process leads to significantly high strain in a material and produces grains within the range of 100 nm to 1.0 μm . The conditions of the pressure can be modified by using different processing routes and angles ϕ . For example, it was established by Nakashima *et al.* [4] that for the formation of an equiaxed UFG structure, the angle ϕ of 90° is optimal, while the other angle can lead to non-homogeneous microstructure with elongated grains and a low fraction of high-angle GBs.

Figure 2.1. ECAP (a) and HPT (b) [3].

Unlike ECAP, HPT is a process in which a coin shape sample is subjected to a constant compressive pressure and concurrent torsion (Fig. 2.1(b)). The structure of a material formed upon such deformation can be different depending on the compressive pressure and the number of rotations. HPT can produce NC metals and alloys with grain sizes less than 100 nm and allows the realization of smaller grains than those obtained by the ECAP method. The disadvantages of the HPT approach include a small sample size and usually an inhomogeneous microstructure after deformation [5].

2.1.2. Mechanical properties

2.1.2.1. Elastic-plastic behaviour

It is well known that GBs in metals act as obstacles for a movement of glissile dislocations (the dislocation pileup mechanism) and their generation in materials with a small grain size is suppressed. The Hall-Petch law expresses a yield strength of a polycrystalline material as a function of the grain size and can be described by the following relation [6,7]:

$$\sigma_y = \sigma_0 + Kd^{-1/2}, \quad (2.1)$$

where σ_y is the true yield stress, d an average diameter of the grains, σ_0 the frictional or Peierls stress, and K a coefficient. It is seen from this equation that the yield stress of the polycrystalline material increases with a decrease in its average grain size. This principle underlies the grain size strengthening of the material. That is the reason that bulk nanomaterials demonstrate extraordinarily high strength [1,2,8-14].

The Hall-Petch law takes into account the grain size strengthening but overlooks the change of deformation mechanisms and features of GB structure of metals and alloys.

Thus, at the average grain size below ~ 100 nm, plastic deformation due to the GB sliding (GBS) mechanism that reduces the grain size strengthening may occur. As a result of this process, the mechanical properties of the materials cannot be described only by the linear Hall-Petch law. For example, despite a plastic flow, it is believed that in the nanostructured materials, a positive deviation from the Hall-Petch relationship can be observed [15]. An additional strengthening can be associated with the feature of GB structure and the dislocation, precipitation or solid solution hardening mechanisms [16-18]. However, NC materials, in particular, NC Al alloys, have a low work hardening rate and therefore a small contribution of the dislocation hardening mechanism [19].

The elastic moduli of a material depend on the nature of its interatomic bonding [20], crystallographic orientation [21], porosity [22-24] and the presence of lattice defects, such as GBs [25]. For a polycrystalline material, its bulk and interfacial elastic properties contribute to its overall elastic response. Due to an imperfection of atomic structure and the presence of many vacancies in GBs, stiffness and elastic constants of polycrystalline materials are reduced as compared to that with an ideal crystal structure of grain interior [25]. It is also observed that the decrease in grain size and hence the increase in GB density results in a great reduction of the elastic moduli of polycrystalline materials [26-29].

NC materials often exhibit low tensile ductility at room temperature, which limits their applications. The elongation to failure is typically less than a few percent. This happens because such materials have high distortions of a crystal lattice and large internal stresses that ease crack nucleation and propagation. Another weak point of bulk nanomaterials, especially for pure metals, is their low thermal stability. At elevated

temperatures, a highly non-equilibrium material with a large density of GBs transforms to a more stable one with larger grain size and hence lower strength.

2.1.2.2. Fatigue behaviour

Fatigue is a progressive structural damage of a material that can be observed when it is subjected to repeated loading and unloading. It is the most common source of material failure and therefore crucial for the application of metals and their alloys. Understanding of the fatigue behaviour of metallic materials is an important issue in material science. Investigation of structure evolution and crack growth in a material during its cyclic loading, as well as an estimation of its lifespan, are one of the main tasks scientists aim to solve in this framework.

Recent studies showed that due to a severely limited dislocation activity in NC materials [30-34] they can possess a potential for excellent fatigue resistance [35-42]. Caused by the low stability of NC structure during cyclic deformation, such materials can often demonstrate grain coarsening. For example, an abnormal grain growth right before failure was observed in NC Ni-40 wt. % Fe during stress-controlled fatigue loading [43]. Boyce *et al.* [38] suggested a model of crack initiation and its growth during cyclic loading of NC Ni alloys (Fig. 2.2). According to this model, grain stability is an important factor affecting the cracking process in the NC alloys, because first micro-cracks nucleate inside coarsened grains rather than in the NC structure. There are other factors controlling the fracture toughness and fatigue crack growth resistance in NC materials, such as specimen thickness, texture and grain morphology [44].

Intensive theoretical work was carried out in the last years to achieve a better understanding of the structural evolution and deformation mechanisms in metallic nanomaterials subjected to cyclic loading. For this, researchers usually considered NC, bi-crystalline and single-crystalline structures. Despite, in general, mechanisms of crack growth in different materials are fairly well understood, most of the works were devoted to single element materials, for example, pure Cu [45,46], Ni [46-48], Al [49], Mg [50] and Fe [51,52].

Figure 2.2. Schematic illustrating fatigue crack initiation mechanism observed in NC Ni-based alloys [38]: (a) homogeneous NC structure, (b) localized areas of coarsened grains formed at the surface of maximum stress, (c) slip processes in coarsened grains, (d) fatigue crack initiation in the coarsened grains and its propagation into the NC structure.

Results of the theoretical studies showed that the main fatigue crack propagation mechanisms are a coalescence of cracks, vacancies, and voids caused by an emission and absorption of dislocations at a crack tip or by fatigue cleavage of atomic bonds in a crack plane [45,53-56]. Due to a dislocation activity, the crack tip usually undergoes blunting

during sample loading and re-sharpening when stresses are released [45]. Nishimura and Miyazaki observed that cyclic loading of α -Fe can be accompanied with not only emission and absorption of edge dislocations and vacancy generation but also with phase transition for relaxing stress concentration around the crack tip [53]. Similar structural change near the crack tip during cyclic loading of the body-centered cubic (bcc) Fe was observed [51]. Such structural behaviour looks very close to that observed in intermetallic alloys during their uniaxial tension when domains having different elastic strains coexist in the structure [57-61]. It was found that the presence of nanoscale twins in NC metals can enhance fatigue crack growth resistance [45]. The refinement of twin thickness and the decrease in spacing between crack tip and twins resulted in fatigue crack growth resistance improvement [62]. Rupert and Schuh revealed also that cyclic loading of NC Ni leads to relaxation of non-equilibrium GB structure through dissipation of energy and reduction of the average atomic energy and additional strengthening of the material [48].

2.1.2.3. Fracture mechanisms

Metals and alloys can undergo brittle or ductile fracture or demonstrate both types. One of the main parameters which define the character of fracture in metals is temperature. The dislocation activity at low temperatures is restrained, and in this case, one can observe brittle fracture. The application of high hydrostatic pressure can reduce the growth of micro-voids and suppresses crack formation even at low temperatures. This is the reason why high hydrostatic pressure is an important component of SPD for obtaining NC materials. At moderate temperatures, fracture can occur as a result of nucleation, growth, and coalescence of micro-voids which usually form at precipitates [63] (Fig. 2.3).

The plastic flow becomes a dominant process at temperatures above $0.3 T_m$ (T_m is a melting temperature) [64], and therefore materials usually undergo ductile fracture. Such fracture normally is associated with the formation of a neck in a test sample during its loading.

For polycrystalline bcc metals and alloys, brittle fracture can be observed due to a cleavage on the $\{100\}$ planes, while those with the face-centered cubic (fcc) crystals generally undergo a plastic rupture caused by a dislocation slip on the $\{111\}$ planes [65]. Fracture of fcc metals, such as Al and Ni, does not strongly depends on the temperature.

Figure 2.3. Fracture mechanisms in metals [65].

The second important parameter which controls the type of fracture in metals is the dislocation density. Brittle fracture is typical for a material with high dislocation density because dislocations pile into one another obstructing plastic deformation as their number

increases. The presence of barriers for the dislocation movement, such as intermetallic compounds and second-phase precipitates, can also have a similar effect.

Fracture of polycrystalline metals which occurs within their grains on specific crystallographic planes and directions is called the transgranular fracture, while the crack propagation along GBs results in the intergranular fracture. The type of fracture depends on strength of interatomic bonds inside grains and in GB regions. Thus, the intergranular fracture in polycrystalline metals, unlike the transgranular cleavage, usually occurs due to the presence of free volume and the high discrepancy of atomic structure in GB regions which decrease the cohesive energy of GBs. In polycrystalline metals having grains with different crystallographic orientations, in the case of the transgranular fracture, the route of crack propagation from one crystal to another changes and corresponds to the direction of least resistance.

The third important parameter which defines the type of fracture is the average grain size. The intergranular fracture is a dominant mode of failure in the UFG and NC materials. Thus, according to results obtained by Abdollahi and Arias [66], intergranular crack propagation occurs in fine-grained microstructures, while the transgranular crack propagation is usually observed in the coarse-grained polycrystalline structure (Fig. 2.4). A similar finding was reported by Boyce *et al.* [38] (Fig. 2.2(d)). From an experimental observation, Gludovatz *et al.* [67] concluded that a fraction of the intergranular fracture decreases with an increasing average grain size. It was revealed that precipitations in GBs could also change the fracture mechanism from transgranular to intergranular [68,69] or demonstrate the opposite effect [70].

Figure 2.4. Crack path in coarse-grained (a) and fine-grained (b) polycrystalline structures [66].

2.1.3. Grain boundary segregation

In the pioneering works by Watanabe, the term ‘grain boundary engineering’ implies a control of mechanical characteristics of polycrystalline materials by affecting properties of their GB ensemble [71-73]. Until recently researchers have mostly focused on controlling the following characteristics of materials: GB density (or average grain size), texture, the percentage of special GBs and high-angle GBs. Nowadays, the study of the effect of GB segregation of different atoms and compounds on mechanical and functional characteristics of coarse-grained polycrystalline and NC materials has been gaining popularity.

Polycrystalline materials can have equilibrium and non-equilibrium segregation of solutes in GBs (Fig. 2.5). The former is associated with the lattice disorder at interfaces, and so termed because solute atoms segregate themselves to GBs in order to minimize the overall free energy of a system, while the latter is the result of an external action. Thus, it is well known that plastic deformation can create excess vacancies in metals and alloys

[74]. As a result, the supersaturated vacancies may form supersaturated vacancy-solute complexes leading to the non-equilibrium GB segregation of atoms by their complex diffusion to GBs [75,76]. Therefore, the grain refinement during HPT can be accompanied by segregation of solute atoms along GBs [77-79] as well as the dissolution of second-phase precipitates or fragmentation of intermetallic compounds [80-82].

Normally, in coarse-grained polycrystalline materials, GB segregation results in premature cracking due to intergranular fracture, but it is believed that in NC materials, they can lead to enhancement of mechanical properties [83,84]. That is why the search for alloying elements in GBs that have a positive effect on strength, ductility and fracture behaviour of an alloy is an important task of materials science. The known literature devoted to the effect of GB segregation in NC materials will be further reviewed in more details.

Figure 2.5. Schematic illustration of GB segregation of impurity atoms (shown in gray).

2.1.4. Grain boundary sliding and grain boundary motion

In UFG and NC metals and alloys, one of the possible reasons for deviation from the Hall-Petch relation is displacement of grains against each other caused by GBS. GBS and normal GB motion (or migration) (GBM), when a GB moves perpendicular to its plane, are often coupled, i.e., these mechanisms operate simultaneously (Fig. 2.6) [85-88]. Simultaneous GBS and GBM, also called the shear-coupled migration of GBs, result in a grain rotation which changes the GB misorientation angle and can be responsible for the enhancement of dislocation emission in the NC structure [89]. GBS and the shear-coupled migration reduce the energy required for deformation and increase the plasticity of polycrystalline materials [90,91].

Figure 2.6. Schematic illustration of the shear-coupled migration in a bi-crystal [85]: (a) initial bi-crystal; (b) GBM; (c) GBS. The dotted line crossing a GB represents a set of inert markers embedded in the lattice. Here, v_n and $v_{||}$ are the velocities of normal GBM and grain translation, respectively.

Plastic deformation mechanisms involving GBs have been studied extensively. The coupling effect between GBS and GBM in bi-crystals has been observed in a number of works [92-95]. The GB structure can strongly influence the coupling factor and even change its sign that affects the strength of materials [96]. The deformation temperature is another parameter determining the coupling between GBM and GBS [97].

Mompiou and Legros have observed structure evolution in fine-grained Al thin films during their tensile test *in-situ* using the transmission electron microscopy (TEM) and showed that the grain rotation results from the motion of intergranular dislocations [98]. The TEM study of the Al bi-crystal with $\Sigma 41 \{540\}$ GB helped to reveal that GBM occurs due to the decomposition of lattice dislocations interacting with GBs [99]. The analysis of the GB behaviour in Al bi-crystals by using the scanning electron microscope has revealed the shear-stress-driven GBM is accompanied by GBS and the relative grain rotation [100]. However, the migration of high-angle GBs with low Σ value can differ from that of random boundaries: their stress-driven migration is not necessarily coupled [101].

In a series of theoretical works by Wan *et al.* [102-105], atomistic simulation has revealed that kinematics of the shear-coupled GBM for the coincidence site lattice (CSL) GBs can be well explained by the GB displacement shift complete lattice (which is the reciprocal lattice of CSL) dislocation mechanism. MD simulation has been recently performed for an analysis of GBM in Al [106,107] and Ni [108]. The results have shown that GBM occurs through uncorrelated shuffling of individual atoms or, in some cases, via correlated shuffling of several atoms [108]. The effect of the free surface on the coupled GBM and GBS has been addressed in the MD study of NC Al thin films [109], while the

importance of these mechanisms in plastic deformation has been stressed, for example, in theoretical studies of the NC Al deformation behaviour [110] and Cu subject to shock loading [111].

2.1.5. Applications

Grain refinement can strongly enhance not only mechanical properties, but also various physical characteristics, such as electrical conductivity, as well as can improve corrosion resistance and functional properties of materials [9,112]. For example, it has been demonstrated that the formation of NC structure ($d \sim 20$ nm) in shape memory TiNi-based alloys used for sensors and actuators can significantly change their functional behaviours associated with the martensitic phase transformation [113].

The reduction in grain size and GBS can result in the low temperature and/or high strain rate superplasticity, that is the main reason for the ability of a material to experience a very high elongation without necking [114]. Materials with such properties are used in the commercial superplastic forming industry, when from sheets of superplastic metals and alloys, under the conditions of superplastic flow, machine parts of a complex shape are formed [115]. Materials with NC structure are attractive for such applications as pre-forms for forgings, targets for sputtering of precious metals [116]. In addition, bulk fine-grained metallic materials, for example, UFG titanium subject to ECAP, can be used for medical applications as implants [117].

2.2. Bulk nanocrystalline Al and its alloys

2.2.1. Mechanical properties of coarse-grained Al

Al has the fcc lattice (Fig. 2.7), and its stacking-fault energy is about 200 mJ/m² [118]. Dislocation slip in fcc crystals leading to their plastic deformation occurs along the close-packed plane of type {111} and the $\langle 110 \rangle$ direction. The twelve slip systems of the fcc lattice determine the high ductility of Al.

Figure 2.7. The fcc lattice.

The calculated averaged Young's modulus, shear modulus, bulk modulus and the Poisson's ratio of polycrystalline Al are 66.61, 24.64, 74.85 GPa and 0.352, respectively [119]. It is important to note that in the polycrystalline structure, the elastic moduli along various orientations can be different due to the crystallographic texture and anisotropy of single-crystalline Al, and furthermore, the elastic constants are strongly dependent on the average grain size [26-29].

Kuo and Huang [120] experimentally observed that the yield stress of the single-crystalline Al in the direction close to [001] was 76.9 MPa. Due to the presence of many defects, which promote cracking, the yield stress of the coarse-grained polycrystalline Al

could decrease down to 7–11 MPa [121]. Sil and Varma [122] showed experimentally that the strength of polycrystalline Al increased with decrease in its average grain size according to the Hall-Petch law.

For a single-crystal Al sample, the fatigue crack initiation and its propagation are related to the crystal orientation and the Schmid factor of Al slip systems [123]. In the case of the polycrystalline structure, the directions of crack propagation are always perpendicular to the direction of the maximal normal stress, while in single crystals, the fatigue cracks always tend to propagate along one or two slip planes which are close to the direction of the maximal shear stress [124] (Fig. 2.8). Videm *et al.* [125] observed using the replica technique that for the pure Al with the grain size in the range of 60–500 μm , the crack nucleation and propagation at room temperature occur along GBs at an early stage of a cyclic deformation.

Figure 2.8. Different behaviours of fatigue crack propagation between polycrystals and single crystals [124].

Due to low density, non-magnetic characteristics, high electrical conductivity and formability, as well as resistance to corrosion and relatively low cost, Al and its alloys are widely used in transportation, aerospace, electrical, construction, packaging and many other industries. That is why Al has been chosen as the material of study here.

2.2.2. Mechanical properties of nanocrystalline Al and its alloys

Improvement of mechanical and functional properties of polycrystalline Al can be achieved via SPD leading to the grain size and high dislocation density hardening mechanisms [126-128], and also it is possible through its alloying with different chemical elements which can result in the solid solution, precipitation and GB segregation strengthening [83,129,130]. Besides, alloying plays a key role in an additional microstructure refinement during SPD [131].

The effect of alloying elements on mechanical properties of a bulk NC material depends on their solubility, concentration and distribution within it [132]. During thermomechanical treatment of Al alloys, some of such elements prefer to segregate at GBs [104], some are distributed randomly in the form of a solute [133], while others form second-phase precipitates or intermetallic compounds [134]. In a coarse-grained Al alloy, SPD could redistribute its alloying elements leading to the formation of their GB segregation [16,78,79,135,136], or could result in the dissolution of second-phase precipitates or fragmentation of intermetallic compounds [81,82]. In addition, it is believed that SPD through HPT and subsequent short annealing can result not only in the bulk phase transition but also the localized GB phase transformation, e.g., in partial or complete wetting of GB [137-139]. The wetting phase can be either liquid or solid.

An in-depth analysis of existing works devoted to mechanical properties of bulk NC Al alloys was conducted by Sabirov *et al.* [16]. The total strength of nanostructured Al alloys can be estimated by taking into account that the four hardening mechanisms act independently [17,18]:

$$\sigma = \sigma_0 + \sigma_{gs} + \sigma_{ss} + \sigma_{dis} + \sigma_{or}, \quad (2.2)$$

where σ_0 is the Peierls stress; σ_{gs} represents the grain size strengthening, σ_{ss} the solid solution hardening, σ_{dis} the dislocation strengthening, and σ_{or} the precipitation or Orowan strengthening. It is believed that NC Al alloys have a low strain or work hardening and correspondingly small σ_{dis} [19].

Due to an inability to accumulate dislocations and thus the low work hardening rate, NC Al and other metals generally have a low ductility. For UFG Al alloys, a fracture strain decreases linearly with increasing the yield stress; i.e., these parameters exhibit an inverse relationship [63].

The formation of the bi-modal microstructure consisting of both nanocrystals and coarse grains allows the enhancing of ductility of nanostructured Al alloys [140-142]. Miyamoto *et al.* [143] showed that the ductility of UFG Al subjected to ECAP could be increased via testing at high strain rates and low temperatures. Such a treatment was associated with the generation of higher dislocation density and the retention of dislocation annihilation which were accompanied with increased work hardening rate and enhanced uniform elongation. Another method to increase the ductility of NC Al is to use a chemical composition modification. For example, Ye *et al.* [144] showed that the precipitate-dislocation interaction significantly increased the dislocation accumulation

capacity in the Al alloy 7075 leading to an enhancement of its plasticity. The addition of Zn to UFG Al can also be considered as the method to reach the high ductility due to the increased work hardening and formation of numerous fine slip bands [145].

Failure of UFG and NC Al samples occurred through the intergranular fracture [146]. However, it was observed experimentally that in Al alloys 5083 with the bi-modal structure, cracks were initiated on the boundaries between coarse grains and UFGs and propagated through the UFG matrix [140].

2.2.3. Grain boundary segregation in nanocrystalline Al

Due to a high vacancy concentration and non-equilibrium GBs having an increased excess energy, Al alloys subjected to SPD can have segregation of solute atoms and their clusters in GBs (Fig. 2.9). Sha *et al.* observed using the three-dimensional atom probe tomography that Mg and Cu atoms in the Al alloy after ECAP segregated strongly to its GBs [147]. It was shown that HPT could also result in the formation of GB segregation in NC Al alloys [83,131,148].

GB segregation may lead to an additional strengthening of Al alloys with small grain size. It was demonstrated experimentally that commercial NC Al alloys obtained by SPD and having the Mg GB segregation had a larger strength than that expected from the Hall-Petch law due to the grain refinement [83,84]. Anomalously high values of strength for the UFG Al alloys 7475 and 1570 deviated from the Hall-Petch dependence (Fig. 2.10), which was explained by Valiev *et al.* [148] through the formation of GB segregation that suppressed the dislocation initiation at GBs due to a solute drag [83]. The contribution of this strengthening mechanism could be up

to 40–50 % of the alloy yield stress, and it might result in the positive deviation of the Hall–Petch slope [83].

Figure 2.9. Elemental maps of the polycrystalline region of an Al–Zn–Mg–Cu alloy sample after eight passes of ECAP: (a) Mg, (b) Cu and (c) Zn [147].

Figure 2.10. The Hall–Petch dependence for Al (grade 1100) [149] and Al–3% Mg [150], and the data on the yield stresses of the coarse-grained (CG) and UFG Al alloys 1570 and 7475 obtained in [148].

Furthermore, solute atoms in GBs can detain a grain growth stabilizing a structure. Thus, GB segregation of oxygen in NC Al pins GBs, preventing the stress-assisted grain growth and resulting in increased strength and loss in ductility [151].

2.3. Theoretical studies of the grain boundary segregation effect

The approach to achieving enhanced properties of metals with nanograins via introducing GB segregation is conceptually new because it targets at affecting the GB network rather than the dislocation ensemble. Sometimes the experimental study of the NC structure with very small grain size is a great challenge, especially taking into account that it can be very costly, time-consuming and risky. Sometimes such difficulties may be overcome only through numerical methods. Therefore, in the recent years, a burst of interest has been attracted in the theoretical investigation of the GB segregation effect in various NC materials. The computational study of a material can be carried out by using the first-principles [152-154], MS and MD [12,155] simulations as well as the phenomenological approaches, such as the phase-field method [156]. From the listed computational approaches, in this Ph.D. study, MD simulation has been chosen as the main method to study deformation behaviour of NC Al alloys with GB segregation.

2.3.1. Molecular dynamics simulation

MD is a most frequently applied simulation approach to investigate structure, dynamics and thermodynamics of various metallic materials, and therefore this computational method is described in the literature quite well. Unlike experimental

methods, MD could provide a better understanding of the effect of GB segregation on the deformation behaviour of NC Al alloys because it allows the tracking of structure evolution at the atomistic level.

The atom movement and interaction in this technique is described based on the numerical integration of the Newton's equation of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i, \quad (2.3)$$

where m and $\mathbf{r}$ are the mass and position of the i -th atom, respectively. The force $\mathbf{f}_i$ acting on the atom is usually derived from the potential energy $U(\mathbf{r}^N)$ as

$$\mathbf{f}_i = -\frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}^N), \quad (2.4)$$

where $\mathbf{r}^N = (r_1, r_2, \dots, r_N)$ represents the complete set of $3N$ atomic coordinates. Eq. (2.3) is a system of N coupled second order nonlinear differential equations that cannot be solved exactly and has to be solved numerically step by step using an appropriate integration algorithm. The most common method to solve the equation and predict the position at time $(t_0 + \Delta t)$ is based on the current position of the atom $r_i(t_0)$ and the previous one $r_i(t_0 - \Delta t)$. Such integraton approach, also known as the Verlet algorithm, is based on the summation of the Taylor expansions for the time of $(t_0 + \Delta t)$ and $(t_0 - \Delta t)$. This procedure can give us the following equation:

$$r_i(t_0 + \Delta t) = -r_i(t_0 - \Delta t) + 2r_i(t_0) + a_i(t_0)\Delta t^2 + O(\Delta t^4). \quad (2.5)$$

The velocities can be obtained from

$$v_i(t_0) = \frac{1}{2\Delta t} [r_i(t_0 + \Delta t) - r_i(t_0 - \Delta t)]. \quad (2.6)$$

In Eq. (2.5), $O(\Delta t^4)$ is so called local truncation error of the Verlet algorithm which can be eliminated by using alternative versions of the Verlet integrator, such as the leap-frog algorithm and the velocity-Verlet algorithm [157].

The key factor determining the accuracy of MD simulation is to choose the available most appropriate interatomic potential of atoms' interaction that can be applied for the modeling. In order to obtain the potential function for a particular system, different approaches can be used, for example, they can involve an estimation of a fixed atom electronic wavefunction or an electronic structure calculation by using so-called *ab-initio* simulations based on the quantum mechanics. Thus, in order to define free parameters (e.g. atomic charge and radius, bond length) for empirical potentials, it is necessary to use quantum chemical simulations, or they can be reproduced from experimental physical properties, such as elastic constants, lattice and vacancy energies. In the case of the pair potentials, such as the Lennard–Jones potential, the energy can be found as a summation of the energy contributions from pairs of particles, while for the many-body potentials, the effect of three or more interacting atoms must be taken into account. In the latter case, the potential energy is defined using the density functional theory [158,159]. Based on this theory, the embedded-atom method potentials (EAM) [160] applied in the current Ph.D. research are perhaps one of the most appropriate types of the many-body interatomic potentials for MD simulation of metallic systems. For this potential, the total energy E_i of an atom i is given by

$$E_i = F_\alpha\left(\sum_{j \neq i} \rho_\beta(r_{ij})\right) + \frac{1}{2} \sum_{j \neq i} \varphi_{\alpha\beta}(r_{ij}), \quad (2.7)$$

where F is the embedding energy which is a function of the atomic electron density ρ , φ is a pair potential interaction, and α and β are the element types of atoms i and j .

In this study, all simulations were performed by involving NTU high-performance computer and using the open-source classical MD code which is called

the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [161]. LAMMPS allows modeling the time-dependent behaviour of various structural materials which consist of atoms and/or molecules. The simulation conditions, such as temperature and boundary conditions as well as pressure control parameters, strain rate and other easily can be modified through the introduction of certain commands which makes LAMMPS very efficient and flexible tool in terms of the MD simulation. Therefore nowadays, the code is widely used for investigation of deformation behaviour, atomic structure changes, cracking process and phase transformation in metallic nanomaterials.

2.3.2. Effect of grain boundary segregation in nanocrystalline materials

There have been a number of theoretical works devoted to the effect of GB segregation in NC metallic materials. By means of MD simulation, Detor *et al.* [162] demonstrated that W segregation in GBs of NC Ni could lead to a high structural stability. Frolov *et al.* [163] found via MD that the structural stability and strength of the NC Cu-6.5 at.% Ta alloy is greatly increased due to the Ta segregation in its GBs, compared with those of pure Cu and its alloys with the same amount of Ta uniformly distributed within their grains. Moreover, both theoretical and experimental studies showed that the GB segregation of Fe and especially Nb within NC Cu could significantly increase its hardness, which was explained by the reduction of the GB energy [164,165], while the GB segregation of Au in NC Pd prevented its grain growth [166,167].

An important issue that researchers focus on is the binding energy of atoms in GBs and the cohesion energy of GBs with impurities [168-170]. For instance, Rajagopalan *et al.* [155] used MS simulations to study the effect of GB segregation in tilt GBs of α -Fe. It has been revealed that impurity atoms and their arrangements in the GBs have a significant effect on the binding energies. Specifically, V impurities have a beneficial effect on the GB cohesion of the α -Fe matrix, while P impurities have the negative effect. Bentría *et al.* [171] demonstrated an enhancement of the strength of Ni with V impurity atoms in the $\Sigma 5(012)$ tilt GB as well. The effect of the impurities on the GB cohesive energy greatly depends on their atomic radii [168,172]. This effect is also determined by the GB misorientation angle. For example, it was believed that Pd, which resulted in weakening of high-angle GBs in Fe, might become a cohesion enhancer in low-angle GBs [172].

Few studies have been done on the effect of GB segregation on GBS and GBM. The competition between GBS and GBM in NC Cu with and without GB segregation was studied by Schafer and Albe via MD simulation [173]. They found that the GB segregation of Nb effectively pinned GBs suppressing GBM and allowed only GBS. Later, they addressed in more detail the contribution to plasticity from GBS and GBM for NC Cu with segregated Nb or Fe atoms [174]. It was concluded that segregating solutes and their distribution in the GBs not only altered the balance between GBM and GBS, but their precise distribution also governed the contribution of intergranular defects. The phase field method for GB solute segregation in polycrystalline binary alloys was developed by Abdeljawad

and Foiles, aiming to provide a quantitative description of the thermodynamic aspects of GB segregation [175].

2.3.3. Effect of grain boundary segregation in Al

Only few known theoretical studies have been devoted to the effect of impurity atom segregation in Al GBs. The researchers mostly focus on a bi-crystalline model. Thus, first-principles calculations have been used to study the GB segregation energy of impurity atoms in the GBs of Al bi-crystals. For example, Uesugi and Higashi suggested that Mg, Na, Ca, K and Sr in the $\Sigma 11(113)[110]$ tilt GB in the Al bi-crystal could lead to its embrittlement [152]. Razumovskiy *et al.* [154] analyzed the Ni, Zr, Mg, Si, B and P segregation in the $\Sigma 5(210)[100]$ GB of the Al bi-crystal and found that among the considered elements Ni was the best GB strengthening element. It was believed that despite the fact that Mg atoms expanded the Al GB, the strong strengthening effect due to the charge transfer mechanism overcame the size negative consequence [176], while Liu *et al.* [177] showed that Mg atom in the $\Sigma 11(113)$ Al GB with a misorientation angle of 129.52° resulted in the GB embrittlement.

There have been almost no numerical studies devoted to the effect of GB segregation on mechanical characteristics and structure of NC Al alloys. In light of this, the current work is aimed at filling this gap through exploring microstructural features and deformation behaviour of both NC and bi-crystalline Al having GB segregation of various additional atoms.

2.4. Summary

It is very important to develop approaches for improving the resistance to intergranular fracture, plasticity and thermal stability of bulk metallic nanomaterials, as well as further increasing their strength. Mechanical properties of polycrystalline Al can be heavily modified through its alloying and SPD leading to the formation of UFG or NC structures with GB segregation. Unique properties of such obtained Al alloys can be used in various applications which require enhanced mechanical characteristics.

Despite a growing number of works conducted on the GB segregation phenomena in NC metallic materials, only some common rules for different types of metals are available so far, which are insufficient for their widespread practical applications. In order to better understand the effect of such segregation on mechanical properties of nanostructured Al alloys, a great variety of elements should be tested and various factors that can influence the GB embrittlement should also be considered. Computational approaches can have certain advantages over experimental tests. Therefore, this PhD research aims to study the effect of GB segregation of different elements in NC binary Al alloys by using MS and MD simulations.

Chapter 3 Resistance of impurity elements to grain boundary separation in Al

In this chapter, in order to define the ability of alloying elements to resist GB separation in NC Al, the GB segregation energy and the embrittlement potency are calculated for them based on a bi-crystalline model by conducting MS simulation. This study aims to predict the types of elements in GBs that can lead to a noticeable strengthening of NC Al. In addition, in order to verify results of the MS simulation, the effect of GB segregation of considered additional elements on small plastic deformation of NC binary Al alloys subject to shear deformation at room temperature is analyzed using MD simulation. The results obtained from the MD simulation are compared with those from the MS simulation.

3.1. Modeling

For NC and bi-crystalline models considered in the MD and MS simulations, Al with the fcc lattice and the atomic radius of 143 pm [178] is a matrix element, while Fe, Co, Cu, Ti, Mg and Pb are additional elements with atomic radii of 124, 125, 128, 145, 160 and 175 pm, respectively [178]. Hereafter, the additional elements can be denoted as X.

As mentioned in Chapter 2, the simulation is conducted using the LAMMPS program package [161], and the inter-atomic forces are described by the many-body EAM potentials [160]. For visualization of a structure, the open source OVITO software is adopted [179,180].

The EAM potential can properly reproduce elastic properties as well as the difference between the vacancy formation and cohesive energy, which is impossible using the pair potential [181]. In the work, the same Finnis-Sinclair EAM potential is used for all the studied systems.

The EAM potential for pure Al provides a good description of solid Al properties and the melting-property data [182]. For the Al-Mg system, the potential employed in this study correctly reproduces both zero-temperature solid properties and solidus and liquid lines on the Al-rich part of the Al-Mg phase diagram [181]. In this case, the potential for Al is taken from [182], while for Mg from [183]. They correctly reproduce a number of relevant zero-temperature crystal properties including the elastic properties. The lattice parameter, elastic constants, bcc–fcc transformation energy, melting temperature and other properties for the Fe potential developed in [184] are, on average, in a better agreement with the experimental or first-principles data than other existing EAM Fe potentials. The semi-empirical interatomic potential for Al-Fe alloys yields a good description of the material structure and the diffusivity of Fe in Al [185]. In the case of the Al-Ti system [186], the Al potential is fitted to the target properties very accurately and demonstrates a good performance in tests. For Ti, the potential is fitted reasonably well to the elastic constants, thermal expansion factors and vacancy formation energy. The Al-Pb potentials reproduce well experimental data for the lattice constants and bulk moduli of Al and Pb at $T = 0$ K [187]. The elastic properties of the hexagonal close packed (hcp) and fcc Co computed with the EAM potential developed in [188] are in a good agreement with experimental data and first-principles calculations. The potential parameters for the Al-Co alloy are optimized by fitting them to several properties of the B2-Al-Co phase such as the

lattice constant, formation energy, elastic constants, as well as the formation energies of an imaginary phase Al_2Co with two different structures. The results predicted by these potential properties are in a good agreement with experimental and first-principles data [189].

From the above literature survey, it is seen that the interatomic potentials used for the simulations can reproduce elastic and plastic properties of the pure metals (Al, Fe, Co, Ti, Mg, Pb) and the studied binary systems (Al-Fe, Al-Co, Al-Ti, Al-Mg, Al-Pb) quite well. At the same time, there are some shortcomings in the considered potentials. For example, the fact that the potential for Al-Mg [181] reproduced the liquidus and solidus lines fairly well yet somewhat underestimated the liquid enthalpy of mixing suggests that there is some discrepancy in the description of the mixing entropy. The Al-Cu potential [190] demonstrated that the elastic constants for Al and Cu which were in general agreement with the experimental results; however, for the Al-Cu alloy, the agreement was worse probably due to the fact that for the cross-pair potential function, which defines the properties of the binary system, a density weighted combination of the monoatomic pair potentials without any fitting parameters was used, as explained by [191]. As for the Al-Ti system, the fitting to the elastic constants was better than with previous potentials but it was not as good as that for Al [186]. Overall, properties for the Al-Co system predicted by the potential used [189] were in good agreement with experimental and first-principles data, but there was some insignificant discrepancy in the formation energy of B2-AlCo . It was lower by 0.07 eV/atom compared to experimental data. For the Al-Pb system, the experimental solubility limits were higher, especially on the Al-rich side, than those calculated by means of the potential used in the

study [187]. The main drawback of the Al-Fe interatomic potential mentioned in the source is that the simulation results performed with a Fe concentration of 8 ppm showed the overestimated activation energy for the GB mobility [185].

According to the thermodynamic theory by Rice and Wang [192], the potency of atom X to resist brittle GB separation can be predicted by the embrittlement potency ΔE which characterizes the cohesion energy of GB with impurity atoms in it and refers to a change of its adhesion energy induced by the segregation of the impurity atom X [176,192]. If ΔE is positive, the impurity atom will lead to the GB embrittlement; otherwise, it will have the strengthening effect on GBs [152,177,192]. Through calculation of ΔE , the location effect of the substitutional impurity atoms in Al GBs on their strength can also be investigated.

The embrittlement potency ΔE is defined as the difference between the GB segregation energy ΔE_b and the corresponding surface segregation energy ΔE_s , i.e., $\Delta E = \Delta E_b - \Delta E_s$ [192]. The GB segregation energy ΔE_b of a crystalline Al system with the impurity atom X in GB is given by [152,177]

$$\Delta E_b = (E^{Al} - E^{X+Al}) - (E_G^{Al} - E_G^{X+Al}), \quad (3.1)$$

where E^{Al} and E^{X+Al} denote the total energy of a single-crystalline Al system free of any defects and that of the same system but with an impurity atom X, respectively; E_G^{Al} and E_G^{X+Al} are the total energies of a polycrystalline Al system without and with an impurity atom X in GB, respectively. A negative (positive) ΔE_b indicates that the impurity atom prefers to stay in the GB (inside grains) [152,193].

The energy of a material is the total energy of all atoms in the system. For the modelling with the use of the EAM interatomic potentials, the energy of atom i is given by

$$E_i = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (3.2)$$

where F is the embedding energy which is a function of the atomic electron density ρ ; ϕ is a pair potential interaction; α and β are the element types of atoms i and j , respectively [160]. The many-body nature of the EAM potentials is a result of the embedding energy term. Both summations in the formula are over all neighbors j of atom i within the cutoff distance.

The surface segregation energy is defined as

$$\Delta E_s = (E^{Al} - E^{X+Al}) - (E_F^{Al} - E_F^{X+Al}), \quad (3.3)$$

where E_F^{Al} is the total energy of the Al system (single-crystalline or polycrystalline) with a free surface, and E_F^{X+Al} is the total energy of the system with one matrix atom at the surface substituted with the impurity atom X [152,177].

In order to calculate the total energies E^{Al} , E^{X+Al} , E_G^{Al} , E_G^{X+Al} , E_F^{Al} and E_F^{X+Al} , the MS simulation is performed. For simplicity, a single-crystal Al is adopted to calculate E^{Al} and E^{X+Al} ; an Al bi-crystal with the impurity atom X is adopted to obtain E_G^{Al} , E_G^{X+Al} , E_F^{Al} and E_F^{X+Al} . Both symmetrical tilt and twist GBs are considered for the Al bi-crystal: $\Sigma 25(001)$, $\Sigma 13(001)$ and $\Sigma 5(001)$ twist GBs with the $\langle 001 \rangle$ axis; $\Sigma 25(710)$, $\Sigma 13(510)$, $\Sigma 5(310)$ tilt GBs with the $\langle 010 \rangle$ axis. The CSL model is used to construct the GBs.

Figures 3.1 and 3.2 show the computational cells for the energy calculations of the Al bi-crystal with the twist and tilt GBs, respectively. To obtain ΔE_b , the single-crystalline Al free of defects and that with one substitutional impurity atom X are used for the calculation of E^{Al} and E^{X+Al} , respectively, while the Al bi-crystal with one type of GBs and that with one substitutional impurity atom X in the GB are used E_G^{Al} and E_G^{X+Al} , respectively. To obtain the surface segregation energy ΔE_s , the Al bi-crystal with the free (001) surface and that with one substitutional impurity atom X at the free surface are adopted to calculate E_F^{Al} and E_F^{X+Al} .

Figure 3.1. Computational cells for (a) Al single crystal, (b) Al single crystal with the substitutional impurity atom X, (c) Al bi-crystal with the $\Sigma 25(001)\langle 001 \rangle$ twist GB and (d) Al bi-crystal with the substitutional atom X in the twist GB.

For the calculation of ΔE_b , the periodic boundary conditions are applied along three orthogonal directions of the computational cells, while for the calculation of ΔE_s , the free boundary condition is applied along the direction perpendicular to the crystallographic plane (001) to generate the free surfaces, and the periodic boundary conditions are used

along the other two directions. Before the energy calculation, all the computational cells are well relaxed to obtain the state of minimum potential energy.

Figure 3.2. Computational cells similar to those in Fig. 3.1 but for the $\Sigma 25(710)\langle 010 \rangle$ tilt GB.

Both the GB segregation energy ΔE_b and the corresponding surface segregation energy ΔE_s are examined with the impurity atoms located at different positions of the GBs. The positions of the substitutional atoms in the twist GBs are numbered as in Fig. 3.3. For the $\Sigma 25$, $\Sigma 13$ and $\Sigma 5$ twist GBs, there exist seven, four and two of such atomic positions, respectively. Taking into account the symmetry of the Al atomic structure, all the other positions in the GBs are energetically equivalent to one of the numbered positions. Figure 3.4 shows the numbered positions of the substitutional atoms in the tilt GB. For the $\Sigma 25$, $\Sigma 13$ and $\Sigma 5$ tilt GBs, there exist seven, five and three of such atomic positions, respectively.

Figure 3.3. (a) Al bi-crystal with the impurity atom X in the twist GB and the GB plane for (b) $\Sigma 25$, (c) $\Sigma 13$, and (d) $\Sigma 5$ with the positions of the substitutional atoms being numbered.

Figure 3.4. Substitution atom positions in the tilt GBs with (a) $\Sigma 25$, (b) $\Sigma 13$ and (c) $\Sigma 5$.

The MD simulation is performed for NC Al constructed in a three-dimensional cuboidal computational cell using the Voronoi procedure [24,194-196]. The cell contains about 100 randomly oriented nano-sized crystals or grains of Al, as shown in Fig. 3.5. The average size of the grains is about 10 nm. The computational cell has the edge length of 42 nm and contains almost five million atoms. Commonly, the atoms in Al GBs have a coordination number different from twelve of the ideal fcc lattice. To

create a structure with segregation in GBs, the Al atoms with the coordination number equal to eleven or ten are replaced by a type of alloying atoms, which can be Fe, Co, Cu, Ti, Mg or Pb. This procedure results in an alloying element concentration of 10.2%. The periodic boundary conditions are applied to the obtained computational cells along the three orthogonal directions to simulate bulk NC Al and its binary alloys by removing the surface effect.

Initially, the NC material computational cell is equilibrated for 50 ps at the temperature of $T = 300$ K. Then, the strain-controlled shear loading is applied to deform the cell at the constant rate of $\dot{\epsilon}_{xy} = 5 \times 10^8 \text{ s}^{-1}$ with exposure to the hydrostatic pressure of $p = 6$ GPa to prevent premature crack nucleation. During the deformation, the shear stress components τ_{xz} and τ_{yz} are controlled to be zero.

Figure 3.5. MD computational cell contains Al grains (in light gray color) and atoms of an alloying element (black) in GBs.

3.2. Embrittlement potency of impurity elements in twist grain boundaries

Figure 3.6 shows the GB segregation energies ΔE_b and the embrittlement potencies ΔE for the Al bi-crystals with the $\Sigma 25$, $\Sigma 13$ and $\Sigma 5$ twist GBs which contain different substitutional impurity atoms. The six impurity elements are sequenced in order of increasing their atomic radii along the abscissa. Note that Fe, Co and Cu, unlike Ti, Mg and Pb, have smaller atomic radii than Al, and Ti has the radius close to that of Al. The atomic positions in the GBs occupied by each impurity atom are shown on the abscissa.

It is found that for the Al bi-crystals with the Fe, Co, Cu and Ti impurity atoms, the embrittlement potencies ΔE are negative for all the atomic positions in the twist GBs. For the Al bi-crystals with the Mg atoms at most of the positions and the Pb atoms at all the positions, ΔE is positive. Hence, for the twist GBs, the impurity atoms having a smaller or nearly the same radius as Al reinforce the GBs, while those with a larger atomic radius have a weakening effect.

As mentioned earlier, the negative segregation energy ΔE_b implies that impurity atoms prefer to occupy GBs rather than grain interior, and this situation is opposite for the positive ΔE_b . For the Fe and Co impurity atoms having smaller radii than Al and the Mg and Pb impurity atoms with larger radii, ΔE_b is negative for most of their positions in the considered GBs. For the Cu and Ti impurity atoms with atomic radii close to that of Al, ΔE_b tends to be positive or nearly zero.

According to this MS study, the segregation of the Fe or Co impurity atoms in the twist GBs has a positive effect on the GB strength because both ΔE_b and ΔE are

negative for most of their positions. In contrast, the Pb impurity atoms in the twist GBs have a strong negative effect on the GB strength because ΔE is always positive although ΔE_b remains negative. The Mg impurity atoms in the twist GBs can strengthen only the $\Sigma 25$ twist GB, while the Cu and Ti impurity atoms have a negligible effect on the GB strength because ΔE_b is nearly zero or positive.

Figure 3.6. The GB segregation energies ΔE_b and the embrittlement potencies ΔE for various substitutional impurity atoms in different positions of the following twist GBs in Al bi-crystals: (a) $\Sigma 25$, (b) $\Sigma 13$ and (c) $\Sigma 5$. The positions of the impurity atom, as indicated in Fig. 3.3, as well as its atomic radius, are given along the abscissa.

3.3. Embrittlement potency of impurity elements in tilt grain boundaries

By analogy with the previous case, Fig. 3.7 shows the GB segregation energies ΔE_b and the embrittlement potencies ΔE for the Al bi-crystals with the $\Sigma 25$, $\Sigma 13$ and $\Sigma 5$ tilt GBs which contain different substitutional impurity atoms. Note that all the impurity atoms in the tilt GBs, except those in Position 1, show noticeable displacements during the energy relaxation of the bi-crystals. Therefore, for the impurity atoms in the tilt GBs, large fluctuations of ΔE_b and ΔE can be observed, compared with those for the twist GBs.

When the tilt GBs are segregated by the Fe impurity atoms in all the positions (except Position 2) of the $\Sigma 5$ tilt GB, ΔE_b is positive, indicating that these atoms generally do not remain in the GBs. Only when the Fe atoms occupy Position 7 of the $\Sigma 25$ GB, Positions 1 and 2 of the $\Sigma 13$ GB, or Positions 1-3 of the $\Sigma 5$ GB, ΔE is negative, i.e., the GB strengthening is possible.

The Co atoms tend to remain in the tilt GBs and increase their strength as both ΔE_b and ΔE are negative. For the Cu and Ti impurity atoms in the tilt GBs, ΔE_b is positive, indicating that these atoms prefer to stay inside grains rather than in the GBs. Therefore, it is expected that the segregation of these impurity atoms in the tilt GBs has a negligible GB strengthening effect, even though these atoms result in the negative ΔE for most of the considered positions.

The Mg atoms in the tilt GBs can have the strengthening effect only when they are at Position 1 in the $\Sigma 25$ GB and Positions 1 and 5 in the $\Sigma 13$ GB. The Pb impurity atoms in the tilt GBs have a strong negative effect on GB strength because they always

remain in the GBs ($\Delta E_b < 0$) and weaken them ($\Delta E > 0$), similar to those in the twist GBs.

Figure 3.7. The GB segregation energies ΔE_b and the embrittlement potencies ΔE for various substitutional impurity atoms in different atomic positions of the following tilt GBs in Al bi-crystals: (a) $\Sigma 25(710)$, (b) $\Sigma 13(510)$ and (c) $\Sigma 5(310)$. The positions of the impurity atoms, as indicated in Fig. 3.5, are given along the abscissa.

3.4. Comparison with the grain boundary segregation effect in nanocrystalline sample

In order to verify the results of the MS simulation, stress-strain curves and structures are analyzed for the NC alloys with GB segregation using the MD simulation. Figure 3.8 shows shear deformation stress-strain curves for the NC pure Al and its binary alloys with the alloying elements segregated in GBs. It is observed that GB segregation of Co and Fe in the Al alloys noticeably enhance their strengths, while those of Cu and Pb lead to the opposite effect. The Ti and Mg atoms in GBs of the Al alloys do not nearly affect their strengths. At the shear strain $\gamma_{xy} = 0.06$, the shear stresses τ_{xy} for the Al alloys with Fe, Co, Cu, Ti, Mg or Pb atoms in GBs are 1.54, 1.60, 0.73, 1.22, 1.25 and 0.78 GPa, respectively, while that of the pure Al is 1.28 GPa. It is also noticeable that when $\gamma_{xy} < 0.05$, the stress-strain curves for the Al-Co and Al-Pb alloys lie under those for the Al-Fe and Al-Cu alloys, respectively. However, when $\gamma_{xy} > 0.05$, this situation is reversed, i.e., the Al alloys with Co and Pb atoms become stronger.

In order to observe strengthening effect caused by the presence of GB segregation, the atoms of an alloying element must occupy GBs. As shown earlier, the ability of an impurity atom to occupy GB can be estimated by calculating the GB segregation energy. In the case of the MD simulation, such ability can be assessed by analyzing the material structure after small deformation because it allows tracking the position of additional atoms with respect to GBs.

Figure 3.9 shows the atomic structures of the Al alloys subject to the 6% shear deformation along the x - y plane of the computational cell. Interestingly, during the

deformation, the atoms of the alloying elements for the Al-Co, Al-Mg and Al-Pb alloys stay in GBs, but those of the other alloys do not. Since the motion of atoms due to diffusion is a slow process and cannot be tracked by the simulations, the change of positions of the alloying elements with respect to GBs has to be caused by the other mechanism, namely by GBM.

Figure 3.8. Shear deformation stress-strain curves for the NC pure Al and its binary alloys with the alloying elements segregated in GBs.

One can assume that the Al-Co alloy becomes stronger than the Al-Fe alloys at $\gamma_{xy} > 0.05$ because the GBs of the latter migrate away from the Fe atoms, thus reducing the strengthening effect due to their segregation in GBs, while Al-Co does not have such GBM.

According to the previous studies devoted to the GB behaviour in the presence of impurities [156,197-199], GBM is a very important issue in the discussion of the GB segregation strengthening effect. GBM of a material with impurity atoms is associated

with their drag force and increases as it decreases. The drag force depends on both the relative size of impurity atoms and the strength of interatomic bonds among the matrix and impurity atoms [156]. Based on the Cahn's impurity drag theory [197], it has been shown that the drag force enhances as the mismatch of the sizes of the matrix and impurity atoms increases [156]. The present work shows that the Al-Ti alloy with the GB segregation of Ti having radius close to that of Al demonstrates significant GBM due to the weak drag force. For the Al-Fe alloy with the GB segregation of Fe, although the atomic size mismatch is large, the drag force is still weak likely due to a strong contribution of the interatomic bond strengths, leading to a noticeable GBM.

Figure 3.9. Atomic structures of the NC Al alloys with the alloying elements (in blue color) at $\gamma_{xy} = 0.06$: (a) Al-Co, (b) Al-Fe, (c) Al-Ti, (d) Al-Mg, (e) Al-Cu and (f) Al-Pb.

Both the MD and MS results agree in that the GB segregation of Co atoms has a noticeable positive effect on the strength of Al GBs while that of Pb atoms has a strong

negative effect. The MD study demonstrates that the Co, Mg and Pb atoms remain in GBs of the NC Al alloys, while the Ti, Fe and Cu atoms do not, and the estimation of the GB segregation energy for these impurity elements in GB of the Al bi-crystals using the MS simulation reveals the same phenomenon. Thus, the weak strengthening effect of Ti in the case of the NC Al alloy (Fig. 3.8), which must be pronounced, according to the results of the MS simulation (see Figs. 3.6 and 3.7), can be explained by the weak drag force, which is confirmed also by mostly the positive value of the GB segregation energy for this element (Figs. 3.6 and 3.7).

It should be noted that prior to the deformation, the NC pure Al and its alloys are initially free of internal stresses. However, in practice, the structure of bulk NC metallic materials after SPD is often distorted by the internal stresses created by various defects such as dislocations, disclinations and cracks [200-206]. Therefore, the combined effect of defects and alloying elements on the mechanical properties of the bulk NC materials should also be taken into account.

Overall, the strengthening or weakening effect can be quantified theoretically through the calculation of the embrittlement potency, but this approach is used for a certain chemical element and does not take into account its concentration. There are not some common rules which could predict properties of a material with various concentrations of impurity atoms in GBs. The concentration effect on material properties could be defined as the cumulative effect, but it is necessary to take into account not only the change of the GB adhesion energy caused by the segregation of a certain element but also other factors, such as an interaction between atoms of the alloying element, their ability to form various intermetallic compounds and clusters, distribution of such

compounds along GB and their effect on GB properties. It is well accepted that first-principles simulations that take into account the electronic structure of materials could give more reliable results than the MD and MS simulations [207]. However, it is computationally infeasible to conduct the first-principles calculation of NC Al and its alloys because this approach is extremely demanding the computational resources and cannot be applied to a large number of atoms. Therefore, the MD simulation of materials with different distributions of alloying elements in GBs could give more valuable results than those obtained from the first-principles simulation and the embrittlement potency calculation.

3.5. Summary

In this chapter, the resistance of various impurity atoms in GBs of Al to their separation is analyzed using both the MS and MD simulations. The results of the MS study show that in general Co atoms increase GB adhesion, Fe and Mg have a moderate strengthening effect, while Pb has a strong embrittlement effect on GBs of Al. In order to verify the results of the MS simulation, the effect of GB segregation of the alloying elements on a stress-strain response of the NC binary Al alloys subject to small shear deformation is studied via the MD simulation. It is found that the GB segregation of Fe or Co atoms in NC Al enhances its strength. In contrast, the GB segregation of Pb in the Al-Pb alloy considerably weakens the GB adhesion resulting in a strong negative effect on the material strength, while those of Ti and Mg do not nearly have any significant effect. Overall, the results of the MD simulation are in a good agreement with those obtained from the MS study.

Chapter 4 Elastic behaviour of Al alloys with grain boundary segregation

In this chapter, the elastic behaviours, in particular, the elastic moduli of NC pure Al and NC binary Al-X alloys (X can be Fe, Co, Ti, Mg or Pb) with X atoms distributed randomly in a structure or segregated in GBs are studied by using MD simulation. The results show that the type of an alloying element and its distribution in the NC Al alloys can significantly affect their elastic moduli. In addition, the thermal stability of the shear modulus for the NC pure Al and its alloys is analyzed. According to the obtained results, only the NC Al alloy with Co atoms in GBs demonstrates the enhanced thermal stability of the shear modulus, compared to the pure Al sample.

4.1. Modeling

For the MD simulation, the three-dimensional cuboidal computational cell of Al used in the previous study is applied. A binary Al-X alloy is obtained through the addition of an alloying element X (Fe, Co, Ti, Mg or Pb) to NC Al. Two different types of X atom distributions in the NC Al-X alloys are considered in this study: segregation to GBs (Fig. 4.1(a)) and random distribution (Fig. 4.1(b)). In order to create the Al-X alloys with GB segregation of X, Al atoms with the coordination number equal to eleven or ten (coordination number of twelve corresponds to the ideal fcc lattice) are replaced by X atoms, similar to the procedure described in Chapter 3. Such a concentration of the X atoms in GBs is probably extreme but performed for computational convenience and reproducibility. Moreover, it has been shown experimentally that the concentration of

solutes in GBs could exceed their solubility in a grain interior by up to several orders of magnitude [208-210], and there is a tendency that the smaller the bulk solubility, the higher the segregation coefficient of an element at GBs would be [211].

The Al-X alloys with atoms of the alloying element X randomly distributed in the structures are obtained via replacing randomly selected Al atoms within the computational cell, including GBs, by the X atoms with a prescribed probability. Hereinafter, such alloys can also be referred to as Al-X substitutional solid solutions. The concentration of the element X for both types of distributions is 10.2 at.%, at which a pronounced effect of the element X on the elastic behaviour of the materials can be expected.

Figure 4.1. (a) NC Al-X alloy (X is one of the alloying elements considered) with GB segregation of X atoms and (b) that with X atoms distributed randomly. Al atoms are represented in light gray, while X atoms in black. The location of GBs in (b) is the same as in (a), but they cannot be seen with this type of visualization.

The MD simulation is performed using LAMMPS software. Periodic boundary conditions are applied along the three orthogonal directions of the computational cell to

simulate the bulk NC Al and its alloys by removing the surface effect. The inter-atomic forces are modelled with the EAM potentials described earlier (see Section 3.1). According to the literature survey, they can well reproduce the elastic properties of the binary Al alloys and the corresponding pure metals [181-189].

Initially, the NC Al and its alloys are relaxed at zero temperature to obtain the state of the minimum potential energy. Next, the uniaxial tensile (at 0 K) and the shear deformation (at 0, 150, 300, 450 and 600 K) at a constant strain rate of 10^8 s^{-1} in the NPT ensemble (constant number of atoms, pressure and temperature) are applied, respectively. It is verified that the reported results are not sensitive to a strain rate reduction since no defect formation is observed during small elastic deformation of the studied materials. For the simulation, the pressure and temperature damping parameters of 1000 fs and 100 fs are used, respectively. Note that prior to the shear loading at 150, 300, 450 and 600 K, the NC Al and its alloys are equilibrated for 3 ps at the corresponding deformation temperatures. During the equilibration, no noticeable diffusion of alloying element atoms or other signs of structural transformation is observed. For the uniaxial tension, the other two normal stress components and three shear components are controlled to be zero. Similarly, for the shear loading with nonzero τ_{xy} , the other five stress components are controlled to be zero.

The Young's moduli of the NC Al and its alloys are defined from the slopes of the stress-strain curves ($E_x = \sigma_{xx} / \epsilon_{xx}$, where σ_{xx} and ϵ_{xx} are the tensile stress and strain in the x direction, respectively) obtained during their uniaxial elastic deformation at 0 K up to $\epsilon_{xx} = 0.1\%$. The Poisson's ratio is calculated as $\nu_x = -(\epsilon_{yy} / \epsilon_{xx} + \epsilon_{zz} / \epsilon_{xx}) / 2$, where

ε_{xx} is the tensile strain in the x direction, and ε_{yy} and ε_{zz} are the lateral strains. NC metals and alloys can demonstrate a weak anisotropy. In order to minimize the anisotropy effect in the NC materials, E and ν are calculated for all the three orthogonal directions of the computational cell and then averaged by $E = (E_x + E_y + E_z)/3$ and $\nu = (\nu_x + \nu_y + \nu_z)/3$. The shear moduli μ of the NC Al and its alloys are computed through $\mu = E/2(1 + \nu)$. In all the cases, the degree of anisotropy of E for the NC materials is found to be within 2%.

At the finite temperatures (150, 300, 450 and 600 K), the shear moduli μ of the NC materials are found as the slopes of the shear deformation stress-strain curves ($\mu = \tau_{xy}/\gamma_{xy}$, where τ_{xy} and γ_{xy} are the shear stress and strain in the x - y plane, respectively) obtained during their elastic deformation up to $\gamma_{xy} = 0.5\%$.

4.2. Elastic moduli of nanocrystalline Al and its alloys

Figure 4.2 shows the Young's moduli E , the shear moduli μ and the Poisson's ratios ν at 0 K for the NC Al and its alloys. The moduli for the pure Al are shown by the solid horizontal lines, while those for the alloys are given by symbols. The five Al alloys are sequenced in order of increasing atomic radii of their alloying elements along the abscissa axis. The data in Fig. 4.2(a-c) is presented taking into account only the order in the atomic radius. For comparison in (d), the Young's modulus is shown as a function of an atomic radius for the considered alloying elements. Note that Fe and Co, unlike Ti, Mg and Pb, have smaller atomic radii than Al, and Ti has a radius close to that of Al [178]. All the studied NC Al alloys with different distributions of the alloying elements are

almost isotropic. The absence of anisotropy is a consequence of a random orientation of the nanograins.

For the NC binary Al alloys with the GB segregation of Fe, Co or Ti atoms, the Young's modulus E and the shear modulus μ are larger than those for the pure Al (Figs. 4.2(a) and (b)). On the contrary, E and μ of the Al alloys with Mg or Pb atoms in GBs are smaller than those of the pure Al. There exists a clear tendency that E and μ decrease with an increase in the atomic radii of the alloying elements. This principle works for both the GB segregation and the random distribution. The conclusion is made for the studied materials and should be taken with caution when applied to other systems.

The distribution of the alloying elements in the alloys has a noticeable effect on their elastic moduli. The NC Al with either the Fe or Ti atoms randomly distributed in its structure shows E of ~ 11 GPa and μ of ~ 4 GPa, which are larger than those for the case of the GB segregation of the same alloying elements. Conversely, for the Al-Co and Al-Mg solid solutions, E are ~ 7.5 and 2.5 GPa and μ are ~ 2.5 and 1.5 GPa smaller than those for the corresponding alloys with the Co and Mg atoms in GBs, respectively. At the same time, the distribution of Pb in the Al-Pb alloy does not affect E and μ . Thus, it is observed that among the considered alloys the Al-Fe solid solution has the highest E ($\sim 40\%$ larger than E of the pure Al), while the introduction of Pb to the NC Al either in a random manner or as the GB segregation reduces E by 10% .

The difference in the moduli for the case when the alloying elements are in GBs and distributed randomly is likely associated with a difference in the contributions of the Al-X and X-X interatomic bonds (X is an alloying element). The number of the X-X

interatomic bonds in the case of the alloys with GB segregation is much larger than that for the solid solutions.

Figure 4.2. Engineering elastic constants at 0 K for the NC Al (horizontal lines) and its alloys (symbols) with the alloying elements segregated to GBs (dots) or distributed randomly (triangles): (a) the Young's modulus E , (b) the shear modulus μ and (c) the Poisson's ratio ν . In (a)-(c), the alloys are ordered by increasing the atomic radii of their alloying elements. In (d), the Young's moduli of the alloys as a function of an alloying element atomic radius are given.

Pugh [212] proposed a simple empirical criterion to predict a ductile/brittle behaviour of a metallic material based on the ratio B/μ where the bulk modulus

$B = E\mu/(9\mu - 3E)$. The material behaves in a ductile manner when $B/\mu > 1.75$. Otherwise, it is brittle. In this study, calculations show that the ratio B/μ is in the range from 2.83 to 5.22 suggesting the ductile behaviour of all the considered binary Al alloys.

It is seen in Fig. 4.2(c) that the NC Al with the Fe, Co, Ti or Mg atoms in GBs has the Poisson's ratio ν close to that of the pure Al ($\nu = 0.357$), while for the Al alloy with the GB segregation of the Pb atoms, ν is considerably larger (0.386). For the Al solid solutions, the addition of the Fe, Co or Ti atoms has little effect on the Poisson's ratio ν of the NC Al, while in the case of the Mg or Pb atoms, ν of the corresponding solid solutions are considerably larger than for the pure Al.

4.3. Comparison with effective elastic constants of coarse-grained Al alloys

The free volume of GBs reduces the rigidity of polycrystals, and this effect is more pronounced for NC materials with a dense GB network [26-29]. The results presented in Section 4.2 include the effect of GB softening, and it would be interesting to estimate how strong the effect is. This can be done by calculating the elastic constants c_{11} , c_{12} and c_{44} for single crystals and evaluating the Young's modulus E and Poisson's ratio ν of polycrystalline aggregates using the Voigt-Reuss-Hill approximation [213-215], which does not take into account the effect of GBs. This approach is applied to single-crystalline Al and the Al alloys with 10.2 at.% randomly distributed X atoms at 0 K. A cuboidal computational cell containing 32000 atoms is used. The Voigt and Reuss approximations give the upper and lower bounds of the effective elastic constants, respectively, while the

Hill approximation is the arithmetic mean of the constants found from the Voigt and Reuss approaches.

Table 4.1 lists the independent elastic constants c_{ij} and elastic compliances s_{ij} for the single-crystalline Al and Al-X solid solutions calculated from the Hooke's law by using the MD simulations. Here, $c_{44} = s_{44}^{-1}$, $c_{11} - c_{12} = (s_{11} - s_{12})^{-1}$, and $c_{11} + 2c_{12} = (s_{11} + 2s_{12})^{-1}$. It is worth noting that the addition of the Fe, Co, Ti and Pb alloying elements considerably increases the elastic constants c_{11} and c_{12} , while the addition of Mg reduces them. The anisotropy factor $A = 2c_{44}/(c_{11} - c_{12})$ increases for the Al-Co, Al-Ti and Al-Mg solid solutions and decreases for the Al-Fe and Al-Pb alloys in comparison with pure Al. All calculated elastic constants c_{ij} fulfill the mechanical stability criteria for the cubic systems [216,217]: $c_{11} - c_{12} > 0$, $c_{11} + 2c_{12} > 0$ and $c_{44} > 0$.

In the Voigt average [213], it is assumed that the strain is the same in each grain, and the shear modulus μ and bulk modulus B of a cubic lattice are given by $\mu_V = [(c_{11} - c_{12}) + 3c_{44}]/5$ and $B_V = (c_{11} + 2c_{12})/3$, respectively, while in the Reuss average [208], where the stress is assumed to be the same in each grain, the moduli are found to be $\mu_R = 5/[4(s_{11} - s_{12}) + 3s_{44}]$ and $B_R = 1/(3s_{11} + 6s_{12}) = B_V$.

Based on the shear moduli μ_V and μ_R obtained from the Voigt and Reuss approaches, respectively, the average of μ can be easily found as $\mu_H = (\mu_V + \mu_R)/2$ [215], according to the Hill approximation. Then, the effective Young's modulus E and the Poisson's ratio ν of the pure Al and Al-X polycrystalline aggregates can be

calculated from the relations $E_{V,R,H} = 9B\mu_{V,R,H}/(3B + \mu_{V,R,H})$ and $\nu_{V,R,H} = (3B - 2\mu_{V,R,H})/2(3B + \mu_{V,R,H})$, where it is assumed that $B = B_V = B_R$.

Table 4.1. Elastic constants c_{ij} , elastic compliances s_{ij} and anisotropy factor A of the single-crystalline Al and Al-X alloys with randomly distributed atoms of the alloying element X (X can be Fe, Co, Ti, Mg or Pb).

$c : 10^9$ Pa	c_{11}	c_{12}	c_{44}	s_{11}	s_{12}	s_{44}	A
Al	98.52	49.55	32.52	15.3	-5.12	30.75	1.33
Al-Fe	217.16	139.32	47.34	9.24	-3.61	21.12	1.22
Al-Co	129.81	94.64	36.81	20.02	-8.43	27.17	2.09
Al-Ti	119.04	57.58	46.60	12.27	-4.02	21.46	1.52
Al-Mg	57.33	28.03	37.93	25.69	-8.44	26.36	2.59
Al-Pb	162.27	98.98	21.16	11.46	-4.34	47.25	0.67

Figure 4.3 demonstrates a comparison of the effective elastic moduli with those obtained from the deformation stress-strain curves of the NC Al and Al-X solid solutions. The upper and lower ends of the error bars in (a) and (b) correspond to the Voigt and Reuss approximations, respectively, while the Hill values are given by the dots. The triangles represent the results for the NC alloys, and take into account the contribution from GBs. It is seen that E and μ calculated for the NC materials are always lower than the corresponding values of the Hill approximation. This fact suggests a significant influence of GBs on the elastic behaviour and a reduction effect of the elastic moduli caused by a large volume fraction of GBs in NC materials [25]. E and μ for the Al-Fe,

Al-Ti and Al-Pb solid solutions are outside the range associated with the Voigt and Reuss approaches. Note that the values of E_V and E_R as well as μ_V and μ_R for these alloys are very close to each other. The opposite pattern is observed for the Al-Co and Al-Mg solid solutions, which is related with the higher anisotropy factor for these alloys.

Figure 4.3. (a) The effective Young's modulus E , (b) the effective shear modulus μ and (c) the Poisson's ratio ν of the Al polycrystalline aggregates and the NC solid solutions calculated at 0 K. The vertical bars denote the Voigt and the Reuss approximations. The solid dots correspond to the Hill approximation, while the triangles are the results obtained for the NC Al alloys. The alloys are ordered by increasing the atomic radii of their alloying elements.

The Poisson's ratio ν behaves differently from the Young's and the shear moduli as shown in Fig. 4.3(c). The values of ν calculated for the polycrystalline aggregates of the

Al-Fe and Al-Co alloys in the Voigt-Reuss-Hill approach are overestimated than those for the Al-Ti and Al-Mg systems, which are considerably underestimated. For the Al-Pb alloy, the values of ν and ν_H are almost equal. In the Hill approach, there is a clear tendency to decrease the Poisson's ratio with increasing the atomic radius of the alloying element, with the exception of the Al-Pb alloy (the pure Al should not be taken into account). Note that none of the Poisson's ratios ν calculated for the NC alloys is located in the range predicted by the Voigt and Reuss approximations.

4.4. Temperature effect on the shear moduli of nanocrystalline Al and its alloys

Since the effects of the alloying element X on E and μ are very similar (see Figs. 4.2(a,b) and 4.3(a,b)), the temperature effect is studied only for μ . In the simulation, even at a high temperature, diffusion or structure transformation cannot be observed during small elastic deformation applied to the materials. Figure 4.4 shows the temperature dependence of μ for the NC Al and its alloys. In Figs. 4.4(a) and (c), the results are presented for the alloys with GB segregation, while in Figs. 4.4(b) and (d) for the solid solutions. In Figs. 4.4(c) and (d), μ of the alloys is normalized to the corresponding μ at 0 K (denoted by μ_0).

For all the Al alloys, as expected, the shear modulus μ decreases with an increasing temperature. Such behaviour of the materials is associated with the asymmetry of the nonlinear interatomic potentials and the thermal expansion. The increase of interatomic

bond lengths results in bond softening and consequently leads to the decrease in the elastic moduli.

Figure 4.4. Temperature dependences of the shear modulus μ (a,b) and the ratio μ/μ_0 (c,d) for the NC Al, its alloys with GB segregation (a,c) and the Al solid solutions (b,d). Here, μ_0 is the shear modulus at 0 K.

The dependence for the pure Al is nonlinear, i.e., the decrease in μ at high temperatures occurs more rapidly. The curves for the Al alloys with the Co or Fe atoms in GBs lie above those for the pure Al (Fig. 4.4(a)), implying that the shear moduli μ of the alloys are higher at all the considered temperatures. Similar trends are observed for the randomly distributed Fe and Ti atoms (Fig. 4.4(b)). For the Al alloys with the Pb atoms,

regardless of the type of their distribution, the curves are significantly lower than that of the pure Al, implying that the moduli for the Al-Pb alloy are smaller. For other alloys (e.g., the NC Al with the Ti or Mg atoms segregated in GBs and the Al-Co and Al-Mg solid solutions), the temperature dependences of μ are similar to that for the pure Al. It is noticeable that μ of the Al alloys with randomly distributed Fe or Ti are larger than those for the alloys with the corresponding segregation in GBs, while this effect is opposite for the NC Al alloys with the Co or Mg atoms (Figs. 4.4(a) and (b)).

Figures 4.4(c) and (d) give an insight into how fast the shear modulus decreases with an increasing temperature. The smaller the slope of the curves and the difference between μ and μ_0 , the less the dependence of the shear modulus on temperature would be. The results demonstrate that μ of the Al alloy with segregation of Co in GBs changes insignificantly with temperature compared with those of the other considered alloys (Fig. 4.4(c)).

There are several experimental works that prove the positive effect of Co on mechanical properties of Al alloys. For example, it has been shown that Al-Co alloys obtained by the melt spinning technique with the composition range 0-12 at.% Co have very high strength and good bending ductility [218]. In another work [219], the authors showed that thermal stability and corrosion resistance of the ternary amorphous alloy Al-Ni-Y can be substantially improved with the addition of Co. They proved that the quaternary alloy $\text{Al}_{85}\text{Ni}_5\text{Y}_8\text{Co}_2$ has the best thermal stability among the considered in their work alloys. The curves for the Al alloy with the Mg atoms in GBs and the Al-Mg solid solution coincide with that for the pure Al. For all the other alloys, the μ/μ_0 curves lie below that for the pure Al implying that μ of these alloys decrease with increasing

temperature more rapidly. It should be mentioned, for the Al-Co solid solution and for the Al alloys with the Fe and Ti atoms, regardless of the type of their distribution, at high temperatures, the ratio μ/μ_0 converges to that for the pure Al. With increasing temperature, in the case of the Al alloys with the Pb atoms in GBs and especially for the Al-Pb solid solution, in all the range of temperatures, the ratio μ/μ_0 decreases more quickly than for the pure Al and the other alloys. This means that the shear modulus μ of the Al-Pb alloy, regardless of the type of Pb distribution, demonstrates the largest reduction with an increasing temperature. It should be noted that for a better understanding of the GB segregation effect on the shear modulus change with temperature, it is desirable to study the moduli of the corresponding pure metals.

4.5. Radial distribution functions

Radial distribution function (RDF) can provide certain information on the atomic structure of the studied alloys, as RDF peaks correspond to interatomic bond lengths. Therefore, it is reasonable to estimate the atomic radii from the MD simulation. Note that in a dilute random solid solution, each substitutional atom in the fcc lattice replaces twelve Al-Al bonds with Al-X bonds. Thus, RDFs calculated for the solid solutions must reflect the appearance of such bonds.

Figure 4.5 shows RDFs for the NC Al (solid line) and Al-X alloys (dashed lines): (a) Al-Fe, (b) Al-Co, (c) Al-Ti, (d) Al-Mg, and (e) Al-Pb. Only the range of distance r around the first coordination shell is shown. The use of the logarithmic scale for the ordinate axis makes it possible to reveal small peaks on the curves.

Figure 4.5. RDFs for the NC Al (solid line) and the NC binary Al alloys with the alloying elements distributed randomly (dashed lines) at 0 K: (a) Al-Fe, (b) Al-Co, (c) Al-Ti, (d) Al-Mg, and (e) Al-Pb. The arrows show additional peak representing the Al-X bond length.

RDF for the NC Al has a sharp peak at $r = 2.86$ Å corresponding to the radius of the first coordination shell of single-crystal Al. RDFs for the solid solutions have an additional peak denoted by the arrows at 2.75, 2.78, 2.86, 2.93, and 3.02 Å for the Al-Fe, Al-Co, Al-Ti, Al-Mg, and Al-Pb solid solutions, respectively. It can be seen that the

position of this peak corresponding to the Al-X bond length shifts to the right with the increasing atomic radius of the alloying elements.

The elastic moduli are dependent on the interatomic bond length: the smaller the length, the higher the stiffness would be. The RDF analysis shows that in the NC Al alloys, the position of the peak corresponding to the Al-X bond length shifts to the right with an increasing atomic radius of the alloying elements (Fig. 4.2), reflecting the correlation between the atomic radius of the alloying element and the material stiffness.

4.6. Summary

In this chapter, the elastic behaviours of the NC binary Al alloys at zero and elevated temperatures are analyzed via the MD simulation. It is shown that the atomic distribution of the alloying elements in the Al matrix can significantly affect the elastic moduli of the alloys. Another important conclusion reached is that for all the alloying elements introduced in NC Al as the GB segregation, the Young's moduli E and shear moduli μ of the alloys at 0 K increase with the decrease in the atomic radii of the alloying elements. For example, the addition of 10.2 at.% of Fe or Co atoms having smaller atomic radius than the Al atom results in an increase of E and μ of the NC Al, while Mg and Pb with a larger atomic size decrease them. It is also found that the GB segregation of Co in the NC Al decreases the shear modulus reduction rate with an increasing temperature as compared to the NC Al. All the other alloying elements considered except Mg which has no effect speed up the reduction of μ . The simulation results suggest that alloying with different elements (e.g., Co) can be an efficient way to enhance the elastic properties of bulk NC metals at ambient and elevated temperatures.

Chapter 5 Plastic and fracture behaviour of Al alloys with grain boundary segregation

This chapter considers the stress-strain and fracture behaviours of NC Al and binary Al-X alloys (X can be Fe, Co, Ti, Mg or Pb) with GB segregation during their tension and shear deformation at room temperature. The effects of alloying element distribution, temperature and hydrostatic pressure on the plastic behaviour of NC Al alloys are analyzed using the Al-Co binary system as an example. The deformation mechanisms (particularly GBM and GBS) of NC Al and Al bi-crystals in the presence or absence of the GB segregation of Co or Mg are investigated.

It is found that the NC Al and its two alloys (Al with Fe and Al with Mg) undergo the intergranular fracture, while the other alloys do not demonstrate any failure process up to 40% deformation. The deformation behaviours of the studied materials are associated not only with dislocation sliding but also with a shear-coupled migration of GBs, i.e. simultaneous GBS and GBM.

5.1. Plastic deformation and fracture

5.1.1. Modeling

For the modeling of plastic deformation of NC Al and its binary alloys, the three-dimensional cuboidal computational cell (see Fig. 3.5) and interatomic potentials previously described in Chapters 3 and 4 are used. The periodic boundary conditions are applied along three orthogonal directions of the computational cell.

The NC Al and its alloys are first relaxed at zero temperature to obtain the state of the minimum potential energy. The computational cell is then equilibrated for 50 ps at the corresponding deformation temperature. The NPT ensemble is employed for the modeling of the shear and tensile deformation with the same constant strain rate of 10^8 s^{-1} .

Uniaxial tensile and shear loading are applied to the NC materials at 300K up to 40% deformation. All the stress components except σ_{xx} (for the tension) and τ_{xy} (for the shear deformation) are fixed to be zero. Then, with the effect of alloying element distribution in the Al-Co alloys being taken into account, the simulation of shear plastic deformation (up to 20%) are performed at two different temperatures (300 and 600K) and the concurrent presence of hydrostatic pressure of 0 or 6 GPa. The shear stress components τ_{xz} and τ_{yz} are controlled to be zero, while the components $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$ are equal to 0 or 6 GPa depending on the hydrostatic pressure applied.

5.1.2. Tensile and shear deformation behaviour

5.1.2.1. Stress-strain curves

Figure 5.1 shows the stress-strain curves for the NC pure Al and its binary alloys with GB segregation of Fe, Co, Ti, Mg and Pb obtained during the uniaxial tension (a) and the shear plastic deformation (b) at 300K. It is seen that for both considered loading modes, three materials (pure Al, Al-Mg alloy and Al-Fe alloy) undergo fracture, while the other alloys do not demonstrate failure up to the 40% deformation.

Figure 5.1. Stress-strain curves of the NC Al and its binary alloys with GB segregation obtained during their tensile deformation (a) and shear deformation (b).

The stresses of the materials during their tension are always higher than the shear stresses at the corresponding deformation level. The GB segregation of Co or Fe noticeably enhances the NC Al strength, while Pb leads to the opposite effect and decreases the ultimate stresses of Al from 1.80 and 1.05 to 1.15 and 0.65 GPa during the tension and the shear deformation, respectively. The Ti and Mg atoms in GBs of the Al alloys slightly decrease the strength of Al. In case of tension, the addition of Co or Fe strengthens Al from 1.80 GPa to 2.27 GPa and 2.20 GPa, while during the shear loading, the alloying with these elements results in an increase in the strength from 1.05 GPa to 1.38 GPa and 1.30 GPa, respectively. After reaching the yield point, the stresses of the Al alloys with Co and Ti drop down to the stable plastic flow level (1.8 GPa and 1.4 GPa for the tension and 1.1 GPa and 0.85 GPa for the shear deformation, respectively) and with

further deformation, do not undergo any changes. For the alloy with GB segregation of Pb, the stresses increase gradually to reach the saturated level of the ultimate strength and then, similar to that with Co and Ti, do not demonstrate any significant changes up to the 40% deformation. The stresses of the other considered materials decrease sharply right after reaching the ultimate strength around 5% and 9% tensile and shear deformation, respectively.

Since within the studied materials only Al and the Al-Mg and Al-Fe alloys undergo failure, fracture analysis is carried out only for these three materials.

5.1.2.2. Fracture

Figure 5.2 demonstrates the structure evolution of the NC Al during the uniaxial tension and the shear deformation at room temperature. In order to make GBs more visible, the common neighbour analysis (CNA) is given in the figure. Here, the atoms of the fcc, hcp and disordered structure are shown in green, red and gray colors, respectively, while cracks forming during the deformation are given in black. A corresponding deformation level is indicated over each snapshot. The initial microcracks or voids can be seen already at the 8% tensile deformation, while upon the shear loading, they appear later (around 15 %). The cracking process is accompanied by the decrease in stresses (Fig. 5.1). The microcracks first nucleate preferably at triple junctions of GBs or close to them in GBs. An important difference between the two modes of deformation is the crack growth direction. In the case of tension, cracks propagate perpendicular to the loading direction (the x axis), while the shear deformation results in their growth at an angle of 45° to the x axis.

Figure 5.2. Fracture of the NC Al during tensile (upper snapshots) and shear deformation (lower snapshots).

The fracture processes in the Al-Mg alloy subjected to tensile and shear loading are presented in Figs. 5.3 and 5.4, respectively. Here, the upper row of snapshots is given to demonstrate the locations of Al (in light blue) and Mg atoms (in dark blue), while in the lower snapshots, similar to the pure Al case, CNA pictures are shown. The initial voids are noticeable around 6 % and 10 % of the tensile and shear deformation, respectively. Similar to the pure Al, the Al-Mg alloy demonstrates intergranular fracture upon deformation. In this case, it is clearly seen that a fracture process is accompanied with formation of multiple microvoids in GBs and later their coalescence. Such a crack growth process has been well described earlier in the literature [45,53-56].

Figures 5.5 and 5.6 present the cracking processes in the NC Al alloy with GB segregation of Fe upon the tensile and shear deformation, respectively. Similar to the previous figures, the atomic structures with Al (in light blue) and Fe atoms (in dark blue) are given in the upper row of snapshots, while in the lower snapshots, the CNA pictures are shown.

Figure 5.3. Fracture of the NC Al with GB segregation of Mg during tension. CNA snapshots are given in the lower row.

Failure occurs via intergranular fracture, which is clearly seen from the CNA snapshots. The cracks propagate inside a disordered structure of GBs, although from the upper snapshots of Figs. 5.5 and 5.6, it can be observed the cracks are away from the Fe atoms. At the same time, in the case of the Al-Mg alloy, it is noticeable that the cracks

propagate as if they split the layer of the segregated atoms in GBs into two parts (Figs. 5.3 and 5.4).

Figure 5.4. Fracture of the NC Al with GB segregation of Mg during shear deformation.

Apparently, such difference between the fracture behaviour of the studied materials can be explained by the fact that Fe has the weaker drag force compared to Mg that results in some GBM from the segregation of Fe atoms. This leads to some weakening of GBs and their separation which accompanied with the break of Al-Al interatomic bonds. In the case of the Al-Mg alloy, GBs do not migrate but, apparently, the Al-Al and Al-Mg bonds are stronger than the Mg-Mg bonds. These results are in a good agreement with those reported in Chapter 3. Thus, the estimation of the GB segregation energy and the embrittlement potency showed that generally, Mg does not strengthen GBs, while Fe

could have the GB strengthening effect but does not stay at GBs. Overall, it is revealed that in the Al-Mg alloy, the cracking process starts earlier and more intensive compared to the pure Al and Al-Fe alloy. Directions of crack growth in both the alloys are similar to that observed for the pure Al.

Figure 5.5. Fracture of the NC Al with GB segregation of Fe during tension.

Overall, it is revealed that GB segregation can significantly alter the cracking process. Thus, Mg weakens GB strength promoting cracking, and Fe does not stay in GBs during deformation, and therefore the Al-Fe alloy behaves close to the pure Al sample. In addition, the alloying elements which atomic sizes differ significantly from that of Al, such as Mg and Fe, can create high stress concentration around them that promotes void formation along GBs. GB segregation can influence the mechanisms of plastic deformation, e.g., the dislocation sliding, grain rotation etc. When such accommodation

mechanisms are active, grains deform plastically without the void nucleation otherwise a material undergoes cracking.

Figure 5.6. Fracture of the NC Al with GB segregation of Fe during tension.

5.1.3. Effect of alloying element distribution and loading conditions

The study is further focused on the effect of the deformation temperature and hydrostatic pressure on the shear deformation behaviour of the NC Al-Co alloy with GB segregation of Co atoms and the NC Al-Co solid solution having the Co atoms distributed randomly within the material.

5.1.3.1. Stress-strain curves

The shear deformation stress-strain curves $\tau_{xy}(\gamma_{xy})$ for the NC Al, Al-Co solid solution and Al-Co alloy with GB segregation of the Co atoms are presented in Fig. 5.7. Figures 5.7(a) and (b) show the results for shear loading at 300 K, and Figs. 5.7(c) and (d) are for 600 K. The curves plotted in (a) and (c) are obtained in the absence of the hydrostatic pressure, while in (b) and (d), the hydrostatic pressure is equal to 6 GPa.

Figure 5.7. Stress-strain curves for the NC pure Al (solid line), Al-Co solid solution (dotted line) and Al-Co alloy with GB segregation of Co (dashed line). For (a,b), deformation temperature is 300 K, while for (c,d), it is 600 K. Hydrostatic pressure in (a,c) is 0 GPa, while in (b,d), it is 6 GPa.

At all the considered conditions of plastic deformation, the Al-Co alloy with GB segregation of Co demonstrates a higher strength than Al, while the strength of the Al-Co solid solution is always lower. In general, the increase in temperature results in the reduction of the yield stress, while the increase in the hydrostatic pressure leads to the opposite effect. Therefore, among these deformation conditions, the highest yield stress of the pure Al and its alloys can be observed for the temperature of 300 K and the hydrostatic pressure of 6 GPa (Fig. 5.7(b)). Such a high hydrostatic pressure is typically realized during SPD through HPT [9]. As expected, the yield stress is the lowest for the Al and Al-Co alloys after the shear deformation at 600 K and the zero hydrostatic pressure (Fig. 5.7(c)). All the curves after reaching the upper limit demonstrate a slow decrease in stresses with further deformation. This can be explained by the deformation-induced grain rotation and growth due to GBM and GBS [220]. In order to analyze the stress-strain relations of the studied materials, their microstructure at $\gamma_{xy} = 0.2$ is further studied.

5.1.3.2. Microstructure analysis

The CNA snapshots of a material structure at the 20% shear strain in the x - y plane for the Al, Al-Co solid solution and Al-Co alloy with GB segregation are shown in the left, middle and right columns of Fig. 5.8, respectively.

The structure analysis of the NC Al (Fig. 5.8, left column) reveals that the fcc coordination of the atoms prevails inside the grains, especially at the deformation temperature of 300 K. At 600 K, due to large thermal fluctuations, the crystal structure in some regions inside grains is indefinite. It is noticeable that the width of GBs is larger at 600 K than 300 K. The red regions which correspond to the hcp structure reveal the

appearance of stacking faults and indicate some dislocation activities which are the highest at 300 K and the hydrostatic pressure of 6 GPa. The deformation at 600 K, regardless of the presence of the hydrostatic pressure, results in the change of positions of GBs with respect to those for the structure after the low-temperature deformation, implying that pure Al undergoes GBM and has a low thermal stability.

The Al-Co solid solution undergoes strong amorphisation during the shear plastic deformation (middle column in Fig. 5.8) [221]; a large portion of atoms is colored in gray with the indefinite crystal structure. It is noticeable that the presence of the hydrostatic pressure somewhat decreases the areas with the amorphous structure.

The Al-Co alloy with the Co atoms located in GBs (right column in Fig. 5.8) undergoes the amorphisation only in the regions close to GBs which are rich in Co. The dislocation activity inside grains can be noticed but is weaker than in the case of the pure Al. Unlike the pure Al, the Al-Co alloy with GB segregation does not undergo any GBM during the high-temperature deformation, implying that the GB segregation increases the thermal stability of the alloy. Structures presented in the right column of Fig. 5.8. confirm a possibility of the GB phase transformations discussed, e.g., in a series of works by Straumal *et al.* [137-139].

Due to the void formation (shown in black in Fig. 5.8), the NC Al has a smaller ductility than the Al-Co alloys. The voids appear only in the pure Al deformed in the absence of the hydrostatic pressure. Obviously, this process is more intensive in the case of the low deformation temperature.

Figure 5.8. CNA snapshots of the structures for Al and its alloys in the x - y plane at the 20% shear deformation. The regions with fcc, hcp, bcc and other (undetermined) areas are colored in green, red, blue and gray, respectively. The left, middle and right columns show results for the pure Al, Al-Co solid solution and Al-Co alloy with GB segregation, respectively. For each row, the deformation conditions are shown on the left of the structures. The voids are colored in black.

Figure 5.9 shows the distribution of the shear stress τ_{xy} at $\gamma_{xy} = 0.2$ in the NC Al (a), Al-Co solid solution (b) and Al-Co alloy with GB segregation of the Co atoms (c). The deformation conditions are 300 K and without the hydrostatic pressure. The voids in Fig. 5.9(a) are highlighted in black. In Figs. 5.9(a) and (c), the high shear stresses can be observed mainly along GBs, while in Fig. 5.9(b), they are scattered all over the presented cross-section area. Figure 5.9(b) also reflects that such a random distribution of high-level stresses in the Al-Co solid solution results in its amorphisation during the shear plastic deformation. Interestingly, along with the atoms having very high stresses and distributed randomly along GBs of the Al-Co alloy with GB segregation, there are regions near GBs that have very low stresses (Fig. 5.9(c)).

Figure 5.9. Shear stress distribution at $\gamma_{xy} = 0.2$ in (a) the NC Al, (b) Al-Co solid solution and (c) Al-Co alloy with GB segregation of the Co atoms. The voids in (a) are shown in black.

In the study, the shear deformation is applied to the NC structures that are free of internal stresses. In practice, however, bulk NC materials obtained by SPD and disperse metallic nanomaterials containing defects, such as dislocations and disclinations, are

characterized by the presence of high residual stresses [201-204,206]. The study of mechanical characteristics of Al alloys with the residual stresses and comparison of the results with those presented here is another interesting direction for further works.

Overall, within the considered systems, the NC alloy with Co atoms in GBs is the best material in terms of strength and ductility. Unfortunately, there is not any experimental work demonstrating the enhanced properties of NC Al alloys with GB segregation of Co atoms. However, there exists a number of works that prove the positive effect of Co on mechanical properties of Al alloys. For example, it was shown that Al-Co alloys obtained by the melt spinning technique have very high strength and good ductility [218], while an improvement in the thermal stability and corrosion resistance of the ternary amorphous Al-Ni-Y alloys after the Co addition was demonstrated in [219]. As shown in the study, Co leads to amorphisation of GB regions. Such behaviour can result in crack collapsing and inhibit the intergranular fracture increasing ductility of alloys. This process is close to the transformation-induced nano-scale plasticity that can prevent the void formation [211].

5.2. Grain boundary sliding and grain boundary motion

The existing studies are not clear enough about deformation mechanisms and mechanical behaviour of NC alloys having GB segregation. This section considers the shear deformation behaviour and deformation mechanisms of the NC Al and its binary alloys with GB segregation of the Co or Mg atoms. Such deformation mechanisms as GBM and GBS are also studied for Al bi-crystals with high-angle tilt GBs in the presence of GB segregation of the mentioned alloying elements.

5.2.1. Modeling

Five different NC materials are considered in the study: pure Al and two binary systems (Al-10.2 at.% Co and Al-10.2 at.% Mg) with the alloying atoms distributed either in GBs or randomly as a solute (see Figs. 4.1(a) and (b)). In order to obtain the GB segregation and the random distribution of the alloying elements, the same procedure described in Chapter 4 is used. Hereinafter, the NC alloys with GB segregation are termed as Al-Co(s) and Al-Mg(s), while the substitutional solid solutions with randomly distributed atoms of the alloying elements are referred to as Al-Co(r) and Al-Mg(r).

In order to make the effect of alloying element distributions more distinct, a high concentration of Co and Mg in Al is taken for the simulation (10.2 at.%). It is important to discuss whether such concentration of the alloying elements can be achieved experimentally. The solubility of Mg in Al reaches its maximum value of 18.9 at.% at 723 K, and it is equal to 1.9 at.% at room temperature [222]. It is known that the solubility level can be greatly increased in non-equilibrium alloys obtained, e.g., by quenching. Moreover, high-energy mechanical alloying at room temperature can result in the solubility of Mg in Al up to five times the equilibrium solubility limit [223]. According to the phase diagram of the Al-Co system, the solubility of Co in Al is very limited [224], but it was shown that in rapidly solidified alloy, it could be increased up to at least 1.7 at.% [225].

The atoms in GBs that have neighbours closer than 0.9 times the equilibrium interatomic distance are removed with a subsequent structure relaxation at 0 K. Prior to the deformation, all the materials are equilibrated for 20 ps at the corresponding

deformation temperature of 300 K. The periodic boundary conditions are used along the three orthogonal directions x , y and z .

The GB behaviour in polycrystals cannot be interpreted unambiguously because GBs possess curvature and their motion can be influenced by triple junctions. The relation between GBS and GBM of materials during their loading and in the presence of alloying elements is most appropriately studied for a specific GB with a exactly defined geometry. Therefore, for investigation of these deformation processes, a bi-crystalline model (see Fig. 5.10) of pure Al and corresponding Al alloys is used. The two vertical strips of tagged atoms are introduced to the structures to visualize deformation mechanisms and track the atomic motion (Fig. 5.10). The two tilt GBs existing in the computational cell are parallel to the x - z plane. One of them is exactly in the middle of the computational cell, while the other one is formed by the upper and lower faces of the cell. The GBs are introduced by rotating the fcc lattice about the z axis by the angles α_1 and α_2 in the counterclockwise direction for the upper and the lower half of the computational cell, respectively. In both grains formed in such a way, the [001] crystallographic direction is parallel to the z axis and the (001) crystallographic plane is parallel to the x - y plane.

Three sets of rotation angles are considered: $\alpha_1 = -10^\circ$, $\alpha_2 = 10^\circ$; $\alpha_1 = 12.5^\circ$, $\alpha_2 = 32.5^\circ$; $\alpha_1 = 35^\circ$, $\alpha_2 = 55^\circ$, with the same misorientation angle $\alpha_2 - \alpha_1 = 20^\circ$ being kept for all the cases. For the sake of convenience, hereinafter, such bi-crystals are denoted as I, II, and III, respectively. The choice of the rotation angles will be rationalized later. The computational cell has the dimensions of $(14+\varepsilon) \times 8 \times 1$ nm, where the value of ε , which is usually of the order of several nanometers, is chosen to achieve the absence of GBs or other lattice defects at the faces parallel to the y - z plane that normally can be

observed due to the application of the periodic boundary conditions. Similar to that of the NC Al alloys, two different types of alloying element distributions are considered: the GB segregation and the random distribution. In order to create GB segregation, Al atoms near a GB which have the coordination number of ten or eleven are replaced by Co or Mg. To create the solid solutions, 10.2 at.% of all the Al atoms are randomly substituted by Co or Mg.

Figure 5.10. Computational cell used for modeling the pure Al and Al alloy bi-crystals (shown in the x - y projection). Crystallites 1 and 2 are rotated about the z axis by the angles α_1 and α_2 , respectively, while keeping the $[001]$ crystallographic direction parallel to the z axis and the (001) crystallographic plane parallel to the x - y plane. The matrix atoms are shown in blue, additional atoms segregated at GBs in yellow and tagged atoms in red.

The strain-controlled shear loading at 300 K is applied to deform the cells at the constant strain rate of $\dot{\gamma}_{xy} = 5 \times 10^8 \text{ s}^{-1}$ with simultaneous exposure to the hydrostatic pressure of 6 GPa to suppress premature crack nucleation in the structure. During the

deformation, the shear stress components τ_{xz} and τ_{yz} are controlled to be zero, while $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 6$ GPa. The NPT ensemble is employed in the simulation.

5.2.2. Stress-strain response and structure

5.2.2.1. Stress-strain curves and structure of nanocrystalline Al

Figure 5.11 shows the stress-strain curves obtained for the NC Al and its alloys under the shear loading with the concurrent hydrostatic pressure of 6 GPa at the room temperature. In (a), the alloying elements (Co or Mg) are segregated at GBs, while in (b), they are distributed randomly in the structure. The results for the pure Al are plotted by black lines, while those for the Al-Co and Al-Mg alloys are presented by gray dashed and gray solid lines, respectively.

Figure 5.11. Stress-strain curves for the NC Al and binary Al alloys with GB segregation of the alloying elements (a) and their random distribution (b). The symbols (s) and (r) in the legends denote the type of the alloying element distribution: (s) for GB segregation and (r) for random distribution.

The effect of the Mg addition on the stress-strain responses is marginal, regardless of the type of Mg distribution in the alloy. A small strengthening effect, in comparison

with the pure Al, can only be seen for Al-Mg(s) in (a) at $\gamma_{xy} > 0.1$. The tensile strength of the pure Al and Al-Mg alloys of both the types is 1.4 GPa. On the other hand, the alloying with Co strongly influences the stress-strain behaviour, and the effect remarkably depends on the type of distribution of the Co atoms in the Al-Co alloy. The curve for the Al-Co(s) lies considerably higher than that for the pure Al, while for Al-Co(r) the stress-strain curve is significantly lower than that for the pure Al. The tensile strength of Al-Co(s) is 1.8 GPa, while that of Al-Co(r) is 1.1 GPa. Unlike the Al-Co(r) alloy, the stresses of Al-Co(s) change non-monotonically undergoing some oscillations during plastic deformation. It should be pointed out that all the curves presented in Fig. 5.11 gradually decrease after reaching the maxima.

An initial structure of Al-Co(s) is shown as an example in Fig. 5.12 (a,a'). The deformed structures of the NC pure Al, Al-Co(s), Al-Co(r), Al-Mg(s), and Al-Mg(r) at $\gamma_{xy} = 0.16$ are given in Fig. 5.12 (b,b')-(f,f'), respectively. In the panels (a)-(f), the matrix atoms are colored in blue and the additional atoms (if present) in yellow. Three vertical lines of the tagged atoms colored in red are introduced in the initial structure of the materials to visualize the atom movement during deformation, regardless of their type, and thus identify the deformation mechanisms. In the panels (a')-(f'), the CNA snapshots of the corresponding structures are presented. The atoms of the fcc lattice are shown in green, while the atoms belonging to the hcp, bcc lattices and disordered structure are given in red, blue and gray, respectively. In all the cases, the same cross-section of the computational cell parallel to the x - y plane is shown. Note that in the panels (a')-(f'), strips of the red atoms indicate stacking faults with the hcp structure produced by the

partial dislocation sliding. The gray atoms of the disordered structure can be observed at GBs and also in amorphous regions.

Figure 5.12. In (a, a'), an initial structure of NC Al-Co(s) is shown. In (b, b')-(f, f'), structures of the NC Al, Al-Co(s), Al-Co(r), Al-Mg(s) and Al-Mg(r) at $\gamma_{xy} = 0.16$ are represented, respectively. In the initial state, the tagged atoms introduced in the cell form three straight vertical lines, as shown in (a). In (a')-(f'), results of CNA are given.

5.2.2.2. Stress-strain curves and structure of Al bi-crystals

Figure 5.13 shows the stress-strain curves obtained for the bi-crystals of pure Al, Al-Co(s), Al-Co(r), Al-Mg(s) and Al-Mg(r). The results for bi-crystals I, II and III are given in Fig. 5.13 (a), (b) and (c), respectively.

Figure 5.13. Stress-strain curves of the pure Al, Al-Co(s), Al-Co(r), Al-Mg(s) and Al-Mg(r) for bi-crystals (a) I, (b) II, and (c) III.

All the curves demonstrate strong oscillation that is especially clearly seen for the cases when the additional elements are located in GBs. It is noticeable that bi-crystal I with the Co atoms in GBs and bi-crystal III with the Mg atoms in GBs have the highest strength within the considered samples which is slightly higher than 2 GPa, while the lowest shear deformation stresses are observed in the case of bi-crystal III of the pure Al and that with the Mg atoms distributed randomly. The effect of alloying element addition on the deformation behaviour of Al is the least pronounced for bi-crystal II. Unlike that in bi-crystals I and III, the GB segregation shows relatively weak strengthening effect.

Figure 5.14. Structure of (a) the pure Al, (b) Al-Co(s), (c) Al-Mg(s), (d) Al-Co(r) and (e) Al-Mg(r) for the case of bi-crystal I at $\gamma_{xy} = 0.15$.

Figure 5.15. Structures of (a) the pure Al, (b) Al-Co(s), (c) Al-Mg(s), (d) Al-Co(r) and (e) Al-Mg(r) for the case of bi-crystal II at $\gamma_{xy} = 0.15$.

Figure 5.14 presents the snapshots of the material structure for bi-crystal I at $\gamma_{xy} = 0.15$. Those for bi-crystals II and III are shown in Figs. 5.15 and 5.16, respectively. The matrix atoms, alloying elements and tagged atoms are shown in blue, yellow and red, respectively.

Figure 5.16. Structures of (a) the pure Al, (b) Al-Co(s), (c) Al-Mg(s), (d) Al-Co(r) and (e) Al-Mg(r) for the case of bi-crystal III at $\gamma_{xy} = 0.15$.

5.2.3. Driving force for grain boundary motion due to crystal elastic anisotropy

The GB network of a polycrystalline material evolves during plastic deformation due to the action of different driving forces. One of such forces stems from the difference in the elastic energy density of differently oriented anisotropic grains under shear loading [226,227]. When two grains are in contact, the crystal with a lower energy density grows at the expense of the other to reduce the total energy of the system. The driving force

calculated as the energy density difference in two elastic contacting bodies is also identical to the Eshelby force on the interface [228,229].

Therefore, the energy per atom in the ideal Al fcc lattice as the function of its orientation with respect to the homogeneous shear stress τ_{xy} is calculated. The obtained results are used for the choice of the orientation angles α_1 and α_2 of the bi-crystal grains (Fig. 5.10) and for the discussion of the deformation mechanisms.

Figure 5.17. (a) The Al fcc lattice, (b) the dependence of single-crystal Al potential energy per atom E on crystallographic orientation α at $\tau_{xy} = 2$ GPa, and (c) the difference $E_{\max} - E_{\min}$ as a function of the applied shear stresses τ_{xy} .

The computational cell of Al single-crystal is created (Fig. 5.17(a)). The cell is oriented such that the (001) plane is parallel to the x - y plane, and the angle between the $\langle 100 \rangle$ direction and the x axis equals α . The crystal is loaded by applying a homogeneous shear stress τ_{xy} with the other stress components being equal to zero.

Figure 5.17(b) shows the dependence of the potential energy per atom on α for $\tau_{xy} = 2$ GPa. Taking into account the symmetry of the lattice, it is sufficient to consider the α range from 0° to 45° . The minimal energy per atom is observed to be $E_{\min} = -3.39247$ eV at $\alpha = 0^\circ$, and the maximal energy is $E_{\max} = -3.39201$ eV at $\alpha = 45^\circ$. As seen from Fig. 5.17(c), the higher the shear stresses, the larger the $E_{\max} - E_{\min}$ value would be.

The driving force for GBM increases with an increasing difference between $E_{\max}$ and $E_{\min}$. For bi-crystal I having $\alpha_1 = -10^\circ$ and $\alpha_2 = 10^\circ$, the potential energy per atom is the same for both grains, and thus there is no driving force for GBM due to the crystal lattice anisotropy (Fig. 5.17(b)). The same can be said about bi-crystal III with $\alpha_1 = 35^\circ$ and $\alpha_2 = 55^\circ$. On the other hand, for bi-crystal II with $\alpha_1 = 12.5^\circ$ and $\alpha_2 = 32.5^\circ$, the energy difference is maximal for a given misorientation angle of 20° , and therefore in this case, the driving force for GBM is non-zero.

As can be seen from Fig. 5.11, the flow stress for all the studied NC materials is roughly between 1 and 2 GPa. For the bi-crystals (Fig. 5.13), the flow stress shows large oscillations and only for Al-Co(s) bi-crystal I and Al-Mg(s) bi-crystal III, it has a peak value slightly above 2 GPa. The calculations show that at the shear stress $\tau_{xy} = 2$ GPa, $E_{\max} - E_{\min} = 5 \times 10^{-4}$ eV/atom (Fig. 5.17(d)).

5.2.4. Grain boundary sliding and grain boundary motion in nanocrystalline Al

The partial dislocation sliding produces stacking faults with the hcp atomic order. The tracks left by partial dislocations can be observed in Figs. 5.12(b')-(f') only in a few grains of each material, which indicates that the dislocation sliding cannot give the shear strain of 16%. The structure analysis suggests that the dislocation sliding makes small contribution to the deformation of all the studied NC materials during their shear deformation. This statement is in agreement with a number of studies which have proved that the plastic deformation of NC materials is not dominated by the dislocation slip, especially at room temperature [30-34].

In order to support the discussion on contribution from GBS and GBM, an intersection of GB with the red line of the tagged atoms is schematically shown in the circled insets of Figs. 5.12(a)-(f). The GB chosen for this analysis is almost parallel to the shear plane, and normal to the red line. After the deformation up to the 16% shear strain, the red line can feature a very sharp break at the intersection with GB of Al-Mg(s) that is shown in (e). Here, GBS is the major deformation mechanism with no contribution from GBM. In the cases of the pure Al, Al-Co(s) and Al-Mg(r) shown in Figs. 5.12(b), (c), and (f), respectively, the red lines have kinks in the vicinities of GBs with the slope different from that inside the grains. This indicates the shear coupled GBM or, in other words, simultaneous GBS and GBM. For the case of Al-Co(r) presented in (d), the red lines of the tagged atoms do not have sharp breaks. From (d'), it is seen that the deformation occurs through the amorphisation of the regions surrounding GBs, and therefore the plastic flow is not localized on GBs. Further, the relation between GBS and GBM in the bi-crystals is considered.

5.2.5. Grain boundary sliding and grain boundary motion in Al bi-crystals

For the pure Al bi-crystal I, the GB located in the middle of the computational cell does not move during the deformation, but the second one moves down from the top face of the cell (Figs. 5.14(a)). As a result of such simultaneous GBM and GBS, the red lines of the tagged atoms are tilted in the upper half of the bi-crystal. In bi-crystal III (Figs. 5.16(a)), the opposite situation is observed: the GB moves up from the bottom face of the computational cell and at the 15% shear strain, it reaches the immobile GB in the middle of the cell. As a result of this, the two GBs annihilate to produce almost perfect single-crystal. The red lines of the tagged atoms are inclined in the bottom half of the cell. The coupling factor between the GBM and shear motion can be estimated to be 0.58. In bi-crystal II (Figs. 5.15(a)), both GBs move toward each other. The coupling factor for the GB initially located in the middle of the cell is roughly equal to 1, while for the other GB, it is about 2. Such cooperative GBS and GBM were described by Bobylev *et al.* [230,231] and later adopted to the fracture analysis [232-234].

The addition of the Mg atoms in the form of GB segregation (see panels (c) in Figs. 5.14-5.16) for all the bi-crystal types results in complete suppression of GBM, and the plastic deformation occurs solely through GBS. As a result, the red lines of the tagged atoms are not tilted but feature sharp breaks at the GB. In bi-crystals I and II, both GBs contribute to GBS almost equally, while in bi-crystal III, the GB in the middle of the computational cell contributes more than the GB composed by the lower and upper faces of the computational cell. A similar suppression of GBM in NC Cu with segregated Nb atoms was previously reported in [174].

In bi-crystals I and III, the Mg atoms distributed randomly in the structure reduce mobility of the GBs as compared to the pure Al bi-crystals (see panels (e) in Figs. 5.14 and 5.16). In addition, unlike the pure Al, both the GBs move in this case. For bi-crystal II (panels (e) in Fig. 5.15), Mg does not affect much the GB behaviour. Nevertheless, in all the three cases, the simultaneous GBS and GBM are observed, similar to that in the pure Al bi-crystals.

In the case of the GB segregation of Co atoms, unlike Al-Mg(s), GBM is not completely suppressed and acts simultaneously with GBS (panels (b) in Figs. 5.14-5.16).

From the panels (d) of Figs. 5.14-5.16, it is found that both GBM and GBS contribute to the plastic deformation of Al-Co(r) because the red lines of the tagged atoms are inclined in the deformed bi-crystals. In addition, it is clearly seen that the crystal structure is perturbed by the presence of a plenty of amorphous regions, which is also demonstrated in Section 5.1.3.

The deformation mechanisms revealed for the bi-crystals are in a good agreement with the results obtained for the NC materials. Particularly, the suppression of GBM can be seen in both the NC Al-Mg(s) alloy (Fig. 5.12(e)) and the Al-Mg(s) bi-crystals (panels (c) in Figs. 5.14-5.16). The simultaneous GBM and GBS take place in the NC Al-Mg(r) alloy (Fig. 5.12(f)) and in the Al-Mg(r) bi-crystals (panels (e) in Figs. 5.14-5.16). The same can be said about the NC Al-Co(s) alloy and the corresponding bi-crystals. The amorphisation during the plastic deformation can be observed for both the NC Al-Co(r) alloy and the Al-Co(r) bi-crystals. Moreover, there is a certain correlation between the strength of the NC alloys and the corresponding bi-crystals. For instance, the Al-Co(s) NC alloy and the Al-Co(s) bi-crystals demonstrate the highest strength (Figs. 5.11(a) and

5.13). On the other hand, it is quite difficult to expect a complete agreement between the stress-strain curves obtained for NC materials and those for bi-crystals with particular GBs.

5.3. Summary

The MD simulation is conducted to investigate the deformation and fracture behaviours of the NC binary Al alloys with GB segregation of different alloying elements. The results are compared to those for the NC Al. It is found that the tensile and shear loading up to 40% of the NC binary Al alloys with GB segregation of Co, Ti or Pb does not lead to any crack formation, while the NC Al and its alloys with GB segregation of Mg or Fe demonstrate intergranular fracture. The main crack initiation and propagation mechanisms are the formation of nanovoids at GBs and triple junctions followed by their growth and coalescence at higher stresses. Such void nucleation is more intensive at lower temperatures and the absence of the hydrostatic pressure.

It is revealed that the GB segregation of the Co atoms has a positive effect on both ductility and strength of NC Al, and it can improve the structure thermal stability, while the Co atoms randomly distributed within the material weaken NC Al due to the formation of a large number of amorphous regions inside grains. The segregation of Fe in GBs can lead to the strengthening of NC Al, but does not improve its ductility, while Ti demonstrates the opposite effect.

The shear deformation of NC Al is associated with the simultaneous GBS and GBM. GB segregation can significantly alter deformation mechanisms of NC Al. For instance, it is shown that the dominating mechanism of deformation for the NC Al having GB

segregation of Mg is GBS without contribution from GBM, while the high strength of the NC Al with GB segregation of Co is associated with its ability to detain both GBS and GBM.

Chapter 6 Cyclic behaviour of Al alloys with grain boundary segregation

In this chapter, the MD simulation is performed to investigate the cyclic behaviour of Al bi-crystals with GB segregation of Co or Ti atoms during cyclic tensile loading along the direction perpendicular to the GB plane. The results are given in comparison with pure Al bi-crystals. It is found that during the cyclic loading, the plastic deformation of the pure Al occurs through the perfect dislocation sliding followed by twinning. The GB segregation of Co or Ti inhibits the formation of both perfect dislocations and twins in the Al matrix, leading to decrease in the ductility of the bi-crystals and intergranular crack propagation rate. The cyclic loading of the bi-crystals with GB segregation is accompanied with the generation of the Shockley partials in GB regions.

6.1. Modeling

The computational cell in the form of a parallelepiped of $21 \times 18 \times 3$ nm is chosen for the simulation (Fig. 6.1(a)). It consists of almost 70,000 atoms of Al. The atoms form two differently oriented fcc crystals. The crystallographic orientation of the upper grain is shown in Fig 6.1(a), and the orientation of the lower grain is obtained by the clockwise rotation of the upper crystal around the [011] direction by the angle of 30° forming an asymmetrical tilt GB. The crystallographic orientations of the crystals are chosen to promote the generation of dislocations and the ease of their visualization. In both the grains, the [011] direction is parallel to the z axis. The planes of the two tilt GBs existing in the computational cell are parallel to the x - z plane. One of them is

located in the middle of the computational cell, while another one is formed by the upper and lower faces of the cell due to the use of the periodic boundary conditions along three orthogonal directions. The maximal Schmid factors m are equal to 0.408 and 0.241 for the upper and lower grains, respectively. In both the grains, there exists only one slip system with the maxima m .

Figure 6.1. (a) The MD model geometry, (b) the Al-X bi-crystal computational cell (X can be Co or Ti) after the material relaxation and equilibration at 300 K within 10 ps (Al atoms are shown in red, and X atoms segregated in GBs are in blue), and (c) the schematic illustration of the cyclic loading imposed on the bi-crystals.

In order to create GB segregation, two rows of Al atoms at the GBs are replaced by the Co or Ti atoms (Fig. 6.1(b)). The obtained high concentration of Co and Ti is far from that observed experimentally, but it can help to reveal the prominent effect of the alloying.

In order to speed up the deformation process and failure of the samples under cyclic loading, a microcrack of $2.5 \times 0.7 \times 3$ nm (the x , y and z directions) is initially introduced in the bi-crystals. For analyzing the possible GB segregation effect on structure evolution, the microcrack is created right under the interlayer of segregated atoms in the middle of the cell (Fig. 6.1(a)).

The atom interaction in the Al-Co and Al-Ti bi-crystals is described by the EAM interatomic potentials developed by Purja Pun *et al.* [189] and Zope *et al.* [186], respectively. For the simulation of the pure Al, either the interatomic potential for Al-Co or Al-Ti is used. Hereinafter, the pure Al bi-crystals are denoted as “Al_Al-Co base” and “Al_Al-Ti base” depending on the interatomic potential used. For the visualization of the atomic structure and dislocation analysis (the dislocation extraction algorithm), the OVITO software is adopted [179,180].

Before the cyclic loading, the studied materials are relaxed at zero temperature to obtain the state of the minimum potential energy and then equilibrated at 300 K for 10 ps. The NPT ensemble is employed in the simulation. During the cyclic loading of the bi-crystals, the stress-controlled tensile loading-unloading at 300 K along the y axis is applied at a constant stress rate of $d\sigma_{yy}/dt = 7 \times 10^9$ GPa/s. All the strain components except ε_{yy} are controlled to be zero in order to avoid collapsing of the microcracks due to the deformation of the computational cell along the x and z axes perpendicular to the applied loading direction.

Figure 6.1(c) illustrates the cyclic loading imposed on the bi-crystals as the dependence of the stresses, i.e. σ_{yy} versus the number of cycles N . The minimal stress $\sigma_{\min}$ corresponds to the unloaded state and is equal to 0 GPa. The initial maximal applied stress $\sigma_{\max}$ is defined as 85% of the ultimate strength obtained during the quasi-static uniaxial tension. The values of $\sigma_{\max}$ are about 3.52, 3.44, 3.57 and 3.4 GPa for the “Al_Al-Co base”, “Al_Al-Ti base”, Al-Co and Al-Ti bi-crystals, respectively. The stress ratio $R = \sigma_{\min} / \sigma_{\max}$ is equal to 0. Since the modeling of cyclic deformation is a very time-consuming process, and as a result of repeated loading and unloading, normally the material accumulates defects, leading to its hardening, in the current work, $\sigma_{\max}$ is gradually increased by 20 MPa per cycle to speed up the development of fracture.

Obviously, such characteristics as the fatigue threshold and fatigue limit cannot be defined from the simulation. However, the modeling can help to track structural changes in the bi-crystals during cyclic loading and predict the deformation mechanisms that could be observed during the stress accumulation upon the strain-controlled cyclic testing.

6.2. Cyclic stress-strain curves

Figure 6.2 shows the stress-strain curves obtained for the “Al_Al-Co base” (a), “Al_Al-Ti base” (b), Al-Co (c) and Al-Ti (d) bi-crystals during their cyclic loading. The stress-strain hysteresis loops for the “Al_Al-Co base” bi-crystal gradually shift to the right cycle-by-cycle up to its failure (Fig. 6.2(a)). A very similar behaviour for the “Al_Al-Ti base” bi-crystal is observed (Fig. 6.2(b)). It is clearly seen that the stress-strain response of the pure Al, for both the considered interatomic potentials, is quite identical in terms of

the residual strain (Figs. 6.2(a) and (b)); however, it differs noticeably from their counterparts having GB segregation. The curves for the Al-Co and Al-Ti bi-crystals are arranged more densely (Figs. 6.2(c) and (d)). In the case of Al-Co, the stress-strain loops almost merge, while the deformation of the Al-Ti bi-crystal along the y axis at the unloaded condition does not exceed 0.4%.

Figure 6.2. Stress-strain curves obtained during cyclic loading of the bi-crystals: (a) “Al_Al-Co base”, (b) “Al_Al-Ti base”, (c) Al-Co and (d) Al-Ti.

In Fig. 6.3, the time dependence of the potential energy per atom E_p is given for the considered bi-crystals. It is common for all the bi-crystals that the loading is accompanied by an increase in the energy, while the unloading leads to the decrease. From the curves,

the maximal number of cycles to failure $N_{\max}$ that the samples endure during the cyclic loading can be estimated. For the “Al_Al-Co base”, “Al_Al-Ti base”, Al-Co and Al-Ti bi-crystals, $N_{\max}$ are 25, 13, 26 and 14, respectively. It is seen that the average energy per atom for the systems having additional atoms segregated to GBs is higher than that for the pure Al. It is valid for both the interatomic potentials used for the pure Al. For the Al-Co and Al-Ti bi-crystals, E_p are about -3.40 and -3.39 eV, respectively, while for the pure Al, E_p is about -3.31 eV.

Figure 6.3. Potential energy per atom E_p as a function of time t during cyclic loading of the bi-crystals: (a) “Al_Al-Co base”, (b) “Al_Al-Ti base”, (c) Al-Co and (d) Al-Ti.

In Fig. 6.4, the dependence of the residual strain along the y axis after unloading of the bi-crystals as a function of the cycle number is presented. The change of the strain for the pure Al bi-crystals can be divided into three stages. At the first stage, the residual strain slightly increases or does not change. At the second stage, a sharp increase in strain during two loading-unloading cycles is observed. At the third stage, before sample failure, a mild increase in its size occurs. Quite different behaviours for the Al-Co and Al-Ti bi-crystals are revealed: almost no increase in the residual strain for Al-Co and only insignificant elongation after ten loading-unloading cycles for the Al-Ti bi-crystal.

Figure 6.4. Residual strain along the y axis versus cycle number after unloading of the bi-crystals.

6.3. Effect of grain boundary segregation on crack propagation

The effect of GB segregation on the crack growth during cyclic loading is analyzed. In Fig. 6.5, the dependence of the crack length and maximal opening on the cycle number N is given for the bi-crystals. The slopes of the crack length curves and

the maximal crack opening curves are different. It is seen that in the pure Al, the crack growth rate is higher than that in the Al-Co and Al-Ti bi-crystals. During the cyclic loading, before the last cycle, the crack lengths for the “Al_Al-Co base” and “Al_Al-Ti base” bi-crystals increases from ~ 27 and $30 \text{ \AA}$ to ~ 40 and $45 \text{ \AA}$, respectively, demonstrating an abrupt change in the size at $N = 10$ and $N = 4$. With further cycling up to the failure of the samples, the crack grows gradually and its size undergoes insignificant oscillation.

The crack growth rate during the cycling of the bi-crystals with GB segregation is noticeably lower than for the pure Al. Thus, for the Al-Ti bi-crystal, with the exception of the last cycle, the crack propagates gradually from ~ 27 to $35 \text{ \AA}$. In the case of the Al-Co bi-crystal, the crack size does not nearly change upon the cycling. Another important difference is that, unlike the pure Al, the bi-crystals with GB segregation do not demonstrate any abrupt changes of the crack size during the cycling.

Figure 6.5. Crack length (a) and maximal crack opening (b) versus cycle number N .

The maximal crack opening curves behave in a way similar to the crack length (Fig. 6.5(b)). With an increasing cycle number, the cracks for the “Al_Al-Co base” and “Al_Al-Ti base” bi-crystals open up to ~ 18 and $17 \text{ \AA}$ at $N = 25$ and $N = 13$, respectively. Similar to the crack propagation behavior, the bi-crystals demonstrate an abrupt increase in the crack opening at $N = 4$ and $N = 10$. In the case of the Al-Co bi-crystal, the crack size does not undergo any significant changes. For the Al-Ti bi-crystal, the maximal crack opening gradually increases (up to $\sim 13 \text{ \AA}$), but the curve slope is much lower than for the pure Al bi-crystal.

6.4. Structure evolution analysis

In order to understand the effect of the Co and Ti addition on the deformation behaviour of Al, the structure evolution analysis for the pure Al, Al-Co and Al-Ti bi-crystals during cyclic loading is carried out. In Figs. 6.6-6.9, the CNA results are presented for the “Al_Al-Co base”, “Al_Al-Ti base”, Al-Co and Al-Ti bi-crystals, respectively. Here, the single and double rows of hcp lattice atoms refer to twin boundaries and stacking faults, respectively. The atoms of bcc and disordered structures are mostly located along the microcrack surfaces or GBs or near point defects.

For all the studied materials, the atomic-scale disordered regions can be observed, especially in the loaded state. Some of such regions are encircled in Fig. 6.6 for the first cycle. These areas represent localized large-amplitude thermal fluctuations of the atoms and point defects.

Figure 6.6. Structure evolution of the “Al₂Al-Co base” bi-crystal during cyclic loading (N is the cycle number). The CNA results are given: red color represents hcp atoms, dark blue bcc atoms and light blue the atoms of the disordered lattice structure. To avoid cluttering, the atoms of the fcc structure are made invisible. The loaded and unloaded structures are indicated on the left by “ σ_{max} ” and “ σ_{min} ”, respectively.

Figure 6.7. Same as in Fig. 6.6 but for the “Al₂Al-Ti base” bi-crystal.

Figure 6.8. Same as in Fig. 6.6 but for the Al-Co bi-crystal. The arrows show the examples of Shockley partials.

Figure 6.9. Same as in Fig. 6.6 but for the Al-Ti bi-crystal.

It is seen that during cyclic loading, the pure Al samples are deformed by twinning (Figs. 6.6 and 6.7). The formation of the first twins in the “Al₂Al-Co base” bi-crystal can be observed at $N = 11$, while in the “Al₂Al-Ti base” bi-crystal this process takes place earlier, at $N = 5$. The appearance of twin plates is preceded by the formation of stacking faults crossing the grains from one GB to another, which can be seen at an early stage of the cyclic loading. The Shockley partials, which are the precursors of the formation of stacking faults, are emitted from the internal free surface of the microcrack or nearby. A similar observation [235] was reported that the free surface facilitated the nucleation of dislocations from GBs. As a consequence of such dislocation emission, the appearance of atomic steps on the microcrack surface and its growth are observed (Figs. 6.6 and 6.7). The latter finding is consistent with the models suggesting void growth by the emission of dislocations [236-239].

The first twin appears in the upper grain of the bi-crystals with the higher Schmid factor. It is noticeable that the distance between neighbouring twin boundaries increases in the loaded state and decreases after unloading. During unloading, the twins can again be transformed into stacking faults or completely disappear (Fig. 6.7), i.e. the detwinning process takes place. Twin boundary migration occurs via partial dislocation gliding along the twin boundary on the adjacent $\{111\}$ plane [240-242].

Due to very fast movement of perfect dislocations, their cores are not seen in the snapshots presented in Figs. 6.6-6.9. Normally, in conventional coarse-grained metals with high stacking fault energy such as Al, perfect dislocations do not split into partials. In the case of NC Al, the splitting distance is quite small, i.e. the emission of the trailing Shockley partial follows right after the nucleation of the leading Shockley partial, forming

a short stacking fault in between them [243-245]. Such perfect dislocations after travelling through the entire grain do not leave stacking faults and therefore cannot be detected by CNA. It is known that conventional fcc metals are normally deformed by dislocation sliding and have little contribution from twinning. Therefore, in order to evaluate a perfect and partial dislocation activity in the bi-crystals' structure subjected to cyclic loading, the dislocation extraction algorithm is used [180]. Figure 6.10 shows the dependence of a number of the $1/2\langle 110 \rangle$ perfect and the $1/6\langle 112 \rangle$ Shockley partial dislocations versus the cycle number in the loaded and unloaded states. The other type of dislocations, such as the $1/3\langle 111 \rangle$ Frank and $1/6\langle 110 \rangle$ stair-rod dislocations, are also present in the bi-crystals, but their percentage is insignificant from the total number of defects; therefore, they are not taken into consideration.

For both the pure Al bi-crystals, at an early stage of the cyclic loading, the number of perfect dislocations detected in GB regions is higher than the Shockley partials (Figs. 6.10(a) and (b)). Their number decreases with increase in the number of cycles, which can be easily seen especially in the case of the “Al₂Al-Co base” bi-crystal (Fig. 6.10(a)). It can be concluded that in the pure Al bi-crystal, at an early stage of the cycling, the main deformation mechanism is the perfect dislocation sliding. Further cyclic loading and consequently higher internal stresses lead to a reduction of the perfect dislocation activity and switching-on of the twinning mechanism when the Shockley partials emitted on an adjacent glide plane travel through an entire grain. A similar transition from one deformation mechanism to another in NC materials was revealed earlier [246]. Such tendency to twinning in NC metals can be explained by the fact that their deformation

requires considerably high stresses in comparison with conventional coarse-grained materials [247].

Figure 6.10. Dependence of the number of dislocation segments versus the cycle number for the “Al_Al-Co base” (a), “Al_Al-Ti base” (b), Al-Co (c) and Al-Ti (d) bi-crystals. The symbols “l” and “unl” denote the loaded and unloaded states, respectively.

It is noticeable that the cyclic stress-strain curves for the “Al_Al-Co base” and “Al_Al-Ti base” bi-crystals are getting denser with an increase in the number of cycles (Figs. 6.2(a) and (b)), wherein the residual strain tends to saturation (Fig. 6.4). This is presumably related to the change in deformation mechanism from the perfect dislocation sliding to twinning. Such deformation behaviour is accompanied by an abrupt increase in

the crack length and the crack opening at $N = 4$ and $N = 10$ for the “Al₂Al-Co base” and “Al₂Al-Ti” bi-crystals, respectively (Fig. 6.5(a) and (b)).

The “Al₂Al-Co base” and “Al₂Al-Ti base” bi-crystals demonstrate different maximal numbers of cycles to failure, which are 25 and 13, respectively (Fig. 6.3(a) and (b)). This difference can be explained by the fact that the Al-Ti interatomic potential gives pure Al approximately 30% lower surface energy than in the case of the Al-Co potential. The latter means that the formation of free surfaces in the “Al₂Al-Ti” bi-crystal occurs easier, which results in an earlier fracture in comparison with the “Al₂Al-Co base” bi-crystal.

The deformation behaviour of the Al bi-crystals with GB segregation significantly differs from that of the pure Al. It is revealed that the Al-Co bi-crystal does not undergo any twin formation (Fig. 6.8). Unlike the pure Al (Figs. 6.6 and 6.7), the increase in the cycle number does not lead to noticeable crack growth as well as to the rise in the residual strain up to the sample failure (Figs. 6.4 and 6.5). The dislocation analysis shows only minor perfect dislocation activity, while the number of Shockley partials is higher than that in the case of the pure Al in the whole range of cycling that is especially evident in the loaded state (Fig. 6.10(c)). Partial dislocations, as well as stacking faults, can be observed in the highly defected layer near GBs and mostly in the upper grain having the higher Schmid factor. A few examples of the Shockley dislocation locations are indicated by arrows in Fig. 6.8 for $N = 1$. Obviously, the absence of the perfect dislocation sliding and twinning results in the merging of cyclic stress-strain curves for the Al-Co bi-crystal (Fig. 6.2(c)). Apparently, the plastic deformation of the bi-crystal occurs via the sliding of partial dislocation. Such remarkable difference in deformation behaviour of the pure Al

and Al-Co bi-crystals is due to highly defected regions formed near GBs (Fig. 6.8). This is in agreement with the observation that the formation of GB segregation suppresses dislocation initiation at GBs due to a solute drag force [83].

Compared to Co, due to the weaker drag force of Ti, the GB segregation of Ti atoms cannot stop GBM during the deformation process mentioned in Chapter 3. It is clearly seen that, unlike all the other materials, after the equilibration procedure the GB plane and the microcrack of the Al-Ti bi-crystal are located on the same level (Fig. 6.9). This is explained by an insignificant migration of the GB down to the microcrack level. For the Al-Ti bi-crystal, similar to the previous case, the twinning process does not take place during the cyclic loading (Fig. 6.9). Twins can be observed only in the last cycle right before the fracture, while stacking faults appear in the structure already in the first few cycles. The number of the Shockley partials in the structure is noticeably higher than the number of the perfect dislocations (Fig. 6.10(d)). In this case, the main deformation mechanism is the partial dislocation sliding with less pronounced perfect dislocation slips. The stress-strain loops do not merge as in the case of the Al-Co bi-crystal, even though they look dense. It can be explained by the contribution of perfect dislocations into the total plastic strain (Fig. 6.2(d)) which is also reflected in a slight increase of the residual strain (Fig. 6.4). This is probably also associated with the weak drag force of Ti and some migration of GBs. In the last cycle, in the upper grain, the switching-on of additional slip systems with the lower Schmid factor can be observed (Fig. 6.9). All the studied bi-crystals undergo failure in the corresponding cycle right after reaching $\sigma_{\max}$ (see Figs. 6.6-6.9).

Another interesting effect is that the number of the Shockley partials in both the Al-Co and Al-Ti bi-crystals does not practically change with the cycle number in contrast to the number of the perfect dislocations in the pure Al structure which drastically decreases (Fig. 6.10). In the first few cycles, the release of internal stresses in the pure Al bi-crystals takes place via perfect dislocation sliding and, as a consequence, the wider stress-strain loops are observed (Fig. 6.2(a) and (b)). In further cycles, the activity of all dislocations significantly decreases and the loops become denser, i.e. high internal stresses cannot be removed via the dislocation slip, finally leading to failure. Unlike the pure Al, the bi-crystals of Al-Co and Al-Ti demonstrate high partial dislocation activity during the whole cycling. Nevertheless, the Shockley partials cannot yet provide full structure relaxation and accommodation of the plastic strain and prevent premature fracture of the samples.

Based on the above discussions, from the atomistic point of view, polycrystalline materials which are stable to cyclic loading should provide constantly high dislocation activity during cycling. The reduction of dislocation activity must be compensated by increasing the role of accommodation processes, such as GBS, GBM, and grain rotation, similar to those found in NC materials [108,246,248]. Another way to increase the partial dislocation activity is to decrease the stacking fault energy, which can be achieved by material alloying.

6.5. Summary

In this chapter, the effect of the GB segregation of Co or Ti on the cyclic stress-strain behaviour and deformation mechanisms of the Al bi-crystals during cyclic loading is considered. The results show that under the cyclic loading of the bi-crystals along the direction perpendicular to the GB plane, the pure Al undergoes plastic deformation

through the perfect dislocation sliding followed by twinning. The addition of the Co or Ti atoms in GBs inhibits the perfect dislocation slip and the twin formation, thus decreasing the plastic flow and residual strain after sample unloading. The main contribution to the deformation in the binary systems is from the slip of the Shockley partials, while the perfect dislocation activity is low.

The difference in the deformation behaviours of the pure Al and its alloys having GB segregation can be explained by the change of GB structure due to the presence of additional elements which promote splitting of perfect dislocations into the Shockley partials in NC material with the high stacking fault energy. The emission of perfect dislocations from GBs and twin formation promote crack propagation. Therefore, in the Al bi-crystals with GB segregation, cracks grow slower than in the pure Al samples.

Chapter 7 Conclusions and Recommendations

In this chapter, based on the works conducted during this PhD research, main conclusions are drawn, and future works devoted to the GB segregation effect in NC metallic materials are recommended.

7.1. Conclusions

Mechanical behaviours of NC binary Al alloys with GB segregation of different alloying elements are studied using MD and MS simulations. The GB segregation effect on the elastic-plastic deformation and fracture of the materials is explained based on the stress-strain relation, structure analysis and calculation of the change in the adhesion energy of GBs induced by the impurity atoms.

The GB segregation of Fe and Co atoms in their respective NC Al-Fe and Al-Co alloys strengthen GBs, while that of Cu and Pb atoms in their respective NC Al-Cu and Al-Pb alloys have the opposite effect. This finding is confirmed by the calculation of the embrittlement potency of the corresponding impurity elements in GBs of Al bi-crystals. It is found that GB segregation of Co increases the GB adhesion and therefore has a noticeable positive effect on the strength of Al GBs, while that of Pb has a negative effect. The estimation of the GB segregation energy and the structure analysis reveals that Co, Mg and Pb tend to occupy GBs of polycrystalline Al, while Ti, Fe and Cu demonstrate the opposite behaviour. The GBM away from the segregation of Ti, Fe or Cu is explained by the weak drag force of these elements that decreases with their atomic radii approaching that of Al.

At 0 K, the Young's and shear moduli of NC binary Al alloys with GB segregation increase with the decrease in the atomic radii of alloying elements. The addition of Fe, Co or Ti atoms into NC Al leads to the increase in its Young's and shear moduli, while the alloying with Pb decreases them. The elastic characteristics of the NC binary Al alloys are strongly dependent on the distribution of the alloying elements. Thus, the elastic moduli are larger when Fe and Ti atoms are distributed randomly within materials, while for the Al-Co alloy, the rigidity is higher for the case of GB segregation. Another finding is that Co atoms in GBs of NC Al decrease the shear modulus reduction rate with an increasing temperature, while all the other considered elements demonstrate the reduced thermal stability of rigidity as compared to the pure Al. The results suggest that alloying can be an efficient way to improve the elastic properties of NC metals at ambient and elevated temperatures.

Unlike Fe and Mg, atoms of Co, Ti and Pb in GBs of the NC binary Al alloys retard premature cracking during tensile and shear deformation of the materials at room temperature. Similar to that of the pure Al, the failure process in the Al alloys with Fe or Mg in GBs occurs through intergranular fracture. The main crack growth mechanism is the formation of nanovoids followed by their coalescence at higher applied stresses. GB segregation of Co has a positive effect on both ductility and strength of NC Al, and can also improve its structure thermal stability. GB segregation of Fe can lead to the strengthening of NC Al, but does not improve its ductility, while the addition of Ti has an opposite effect.

The shear deformation of NC Al is associated with the shear-coupled migration of GBs, i.e., with simultaneous GBS and GBM. GB segregation can significantly alter

deformation mechanisms of NC Al. Thus, the dominating mechanism of deformation for the NC Al with GB segregation of Mg is GBS with no contribution from GBM. The high strength of the NC Al with GB segregation of Co is due to its ability to detain both GBS and GBM, while the low strength of the Al-Co alloy with Co atoms distributed randomly is explained by amorphisation of its structure that leads to the ease of plastic flow.

During cyclic loading of Al bi-crystal along the direction perpendicular to the GB plane, the material undergoes plastic deformation mainly through the perfect dislocation sliding followed by twinning at higher stresses. Based on the analysis of the effect of the Co and Ti atoms in GBs, it is revealed that GB segregation inhibits both the perfect dislocation slip and the twin formation in Al, thus decreasing the plastic flow and residual strain after unloading. The main contribution to the deformation of Al binary systems is from the slip of the Shockley partials, while perfect dislocations play an insignificant role. Such difference in the deformation behaviours of Al and its alloys with GB segregation can be explained by the change in the GB structure. It is assumed that the presence of additional elements in GBs can split perfect dislocations into the Shockley partials in the NC metals with a high stacking fault energy.

The emission of perfect dislocations from GBs and twinning during cyclic loading of pure Al bi-crystals perpendicular to the GB plane promotes crack propagation. Therefore, in the Al bi-crystalline materials with GB segregation of Co or Ti atoms, when these processes are detained, cracks grow slower than in the pure Al samples. The ability of GB segregation in Al to retard the dislocation emission from GBs and twinning found in the study could be successfully used to improve strength and fatigue characteristics of NC metals.

7.2. Recommendations

Despite a large number of works that have been conducted on this topic over the past years, the effect of GB segregation on the mechanical properties, structure, stress-strain behaviour and deformation mechanisms of various NC metals cannot still be generalized. Therefore, in order to expand the knowledge on the GB segregation effect and further develop the idea of enhancement of mechanical properties of NC metallic materials through an introduction of such structural elements, the following future works are recommended.

This PhD research deals with two different types of binary Al alloys (those with GB segregation and solid solutions), but does not take into account the solubility level of the alloying elements in the Al matrix. In fact, this issue is very important and cannot be omitted for the full understanding of the GB segregation effect. As mentioned earlier, SPD can promote segregation of a certain number of additional elements to GBs. But this process cannot exclude the presence of solute atoms inside grains. Therefore, it would be interesting to study the GB segregation effect in metals with various concentration of alloying elements taking into account phase diagrams of considered systems. In addition, the effect of combined contribution from GB segregation and solute atoms in a metal matrix should also be considered.

Alloying elements, especially at low solubility, often form particles in a matrix that can be monatomic or intermetallic. They can create large stresses in materials caused by the difference in crystal lattices of the particles and matrix. For instance, the AlCo intermetallic compound has the B2 superstructure based on the bcc lattice, while pure Al and Co are the fcc and hcp metals, respectively. The particles of very small size are

typically coherent with the matrix, while the large ones often lose their coherence due to the size effect. Such structural elements can significantly change the mechanical properties of alloys. Therefore, the effect of monatomic or intermetallic particles on the deformation behaviour of NC alloys should also be studied for the cases when they are in GBs and distributed randomly in a structure.

The GB segregation effect of the same alloying element can strongly vary in different matrices. Therefore, this effect could also be studied for other metals with different crystal lattices. For example, the results obtained for the NC binary Al alloys could be compared with those for NC binary Fe alloys having the bcc matrix.

In addition, it is desirable to carry out experimental works. The mechanical properties of UFG and/or NC binary Al alloys having GB segregation should be compared with those obtained from the theoretical studies.

From an experimental point of view, the manufacturing process to achieve certain alloying element distribution is another important issue. It would be very useful to develop a thermomechanical treatment to obtain NC or UFG Al alloys with GB segregation which possess enhanced strength, plasticity and thermal stability. Such experiments could include the fabrication of materials with a desired composition, homogenization, SPD, short annealing and further mechanical testing and fracture analysis of obtained samples.

The solutions of the above-mentioned problems would help to understand the potential of GB segregation for the enhancement of mechanical properties of bulk NC metals and alloys.

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