Defect Structure in Plastically Deformed High-Entropy Alloys

Anita Heczel

Ph.D. Thesis

Supervisor: Prof. Jenő Gubicza, DSc

Eötvös Loránd University, Department of Materials Physics

Doctoral School of Physics, Materials Science and Condensed Matter Physics program

Head of doctoral school: Prof. Tamás Tél
Head of doctoral program: Prof. István Groma

Budapest
2018

Introduction

Conventional solid solutions are generally based on one principle element, and other alloying atoms are added only in small concentrations for the improvement of properties. In the last decade, a new type of alloy concept, known as high-entropy alloys (HEAs), was proposed. HEAs are disordered solid solutions, containing five or more principal elements with atomic concentrations between 5% and 35%. These alloys are currently in the focus of materials science because they have desirable properties, such as high hardness and strength, good resistance to thermal softening, oxidation, wear and corrosion. The yield strength of these alloys can be further increased by refining the grain size and increasing the dislocation density.

The study of the plastic properties in HEAs is of great importance from the point of view of their practical applications. For the study of the plastic behavior of HEAs at high strains, severe plastic deformation (SPD) techniques must be applied. SPD is an effective tool for increasing the strength of materials. During SPD processing both the grain refinement and the increase in the dislocation density may contribute to hardening. SPD processing is expected to yield an additional improvement in hardness of HEAs. However, the evolution of the lattice defects, such as dislocations or twin-faults, during SPD and their influence on the mechanical behavior have not been deeply understood yet.

The goal of my PhD work was to study the defect structure and the mechanical properties of HEAs with different chemical compositions and crystal structures. The following alloys were investigated: $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$, $Ti_{35}Zr_{27.5}Hf_{27.5}Nb_5Ta_5$ and $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$ HEAs. I hope that my results will contribute to a deeper understanding of the relationship between lattice defects and mechanical properties of HEAs.

Experimental Methods

The studied materials were prepared by vacuum arc melting technology. The samples were plastically deformed by quasi-static and dynamic compression tests, and by high-pressure torsion. The defect structure was studied mainly by X-ray line profile analysis (XLPA) which method yields a good statistics of the results due to the relatively large studied volume. The average lattice constant and other important parameters of the microstructure such as the diffraction domain size, the twin-fault probability, the dislocation density and the edge/screw character of dislocations were determined by XLPA. The elastic anisotropy factor required for XLPA procedure was determined by nanoindentation. For direct observation of the microstructure, transmisson electron microscopy, scanning electron microscopy and electron backscatter diffraction were applied. The spatial distribution of constituents was studied by energy-dispersive X-ray spectroscopy. The mechanical properties of the samples were characterized by uniaxial compression and microhardness test, as well as by compression of micropillars.

New Scientific Results

The goal of my PhD work was to study the defect structure in plastically deformed HEAs with different chemical compositions and crystal structures, such as the equimolar $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ with bcc structure, the Ti-rich $Ti_{35}Zr_{27.5}Hf_{27.5}Nb_{5}Ta_{5}$, which exhibited a martensitic phase transition from bcc to orthorhombic structure, and the equimolar $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$ with fcc structure. The research results are summarized in the following 8 thesis points which are listed in three groups in accordance with the three different materials.

1. $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ HEA was compressed at room temperature to the plastic strains of 3, 10 and 20%. Additionally, two samples were impacted using a Hopkinson pressure bar at the initial impact velocities of 10 and 20 m/s up to the equivalent strains of 50 % and 130 %, respectively. The following results were obtained:

1.1. The elastic anisotropy factor of $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ HEA was determined by an indentation method as 2.3 ± 0.2 which was required for the determination of the edge/screw character and the density of dislocations by XLPA. Using the obtained elastic anisotropy factor, the theoretical values of the parameter describing the dislocation character were determined for pure edge and screw dislocations. Comparing these values with the experimentally determined parameters, it was found that the screw character of dislocations became stronger with increasing strain during compression of $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ HEA. This can be explained by the reduced mobility of screw dislocations compared to edge dislocations in bcc structures [1].

1.2. A high density of dislocations (10-15 × 10^{14} m^{-2}) was developed during compression even at moderate plastic strains (10-20%). In the impacted samples, the dislocation density was even higher with the values of about 47 × 10^{14} m^{-2} and 32 × 10^{14} m^{-2} for the velocities of 10 and 20 m/s, respectively. This can be attributed to the higher strain and strain rate applied during the impact test. The smaller dislocation density for the sample impacted at 20 m/s compared to that for 10 m/s can be explained by a possible recovery of the microstructure due to the annealing of the material at high strain rates. The dislocation density obtained by XLPA was in accordance with the dislocation spacing observed in the TEM images [1,2].

1.3. The present HEA material has a high yield strength of about 890 MPa. The strain hardening during compression was caused by the increase of the dislocation density. The dislocation hardening parameter (α) has a relatively low value (~0.16) but it is still in the range determined for other bcc non-HEA metallic materials. It was found that the Peierls stress has the main component in the flow stress, and dislocation hardening has a lower contribution even for high dislocation densities [1].

2. The evolution of the phase composition, microstructure and hardness during plastic deformation of a Ti-rich HEA with the composition of $Ti_{35}Zr_{27.5}Hf_{27.5}Nb_{5}Ta_{5}$ was studied. The following results were obtained:

2.1. Due to processing by 1 turn of HPT, the initial grain size (~800 μm) was refined to ~200-1000 nm, irrespective of the location along the disk radius. In this Ti-rich HEA material, besides the refinement of the microstructure, a phase transition also occurred during HPT. The initial bcc phase was transformed into an orthorhombic structure throughout the disk. Very high dislocation densities were observed in both the center

(~43 × 10^{14} m^{-2}) and the periphery (~103 × 10^{14} m^{-2}) of the HPT-processed disk. A very high hardness with the values between 3500-3900 MPa was measured on the HPT-processed sample, which changed only slightly along the disk radius in accordance with the microstructure observations. These results indicate a very early saturation of the microstructure and the hardness with increasing strain imposed in HPT-processing [3,4].

2.2. Complementary compression test revealed that the phase transformation during deformation starts with the formation of orthorhombic lamellae in the initial bcc grains. This grain morphology was inherited in the elongated grain shape in the HPT-processed disk. The phase transformation was nearly completed even at a strain of about 11.5%. The yield strength of the initial material was ~277 MPa, which is much smaller than one-third of the hardness (~1000 MPa) measured on the initial sample due to the strong strain hardening in the beginning of compression. The yield strength and the strain hardening were lower and higher, respectively, for the Ti-rich HEA than in the case of the equimolar $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ material [3,4].

3. The evolution of the defect structure, grain size and hardness during HPT processing of an equiatomic CoCrFeMnNi HEA was studied. The following results were obtained:

3.1. In the initial sample, the average grain size was determined as ~60 μm. After 2 turns of HPT, the grain size was refined to ~30 nm at the periphery of the disk. At the same time, in the disk center the grain size was reduced only to ~4 μm after 2 turns, indicating a high sensitivity of grain refinement on the gradient in shear strain along the disk radius. It has been shown that the dislocation density increased rapidly with increasing numbers of turns in HPT processing. After 1/4 turn, high dislocation densities with the values of ~43 and ~91 × 10^{14} m^{-2} were detected in the center and the periphery of the HPT disk, respectively. Further straining up to 2 turns increased the dislocation density to ~126 and ~194 × 10^{14} m^{-2} in the center and the periphery, respectively. The high shear strains at the edge of the disks processed by 1 and 2 turns of HPT yielded large twin fault probabilities of ~2.2-2.7%. It was revealed that the low SFE of the equiatomic CoCrFeMnNi HEA is a deterministic factor in the development of the very high defect density (dislocations and twin faults) during HPT. At the same time, the minimum grain size in the HPT-processed CoCrFeMnNi HEA was much smaller than in Ag with very similar SFE, due to the significantly higher melting point of the HEA material [5].

3.2. Similar to the microstructure, there was a large gradient in the hardness along the disk radius. The maximum hardness value at the periphery of the disk processed by 2 HPT turns was measured as ~5380 MPa. A good correlation between the yield strength estimated as one-third of the hardness and the calculated values was achieved using α = 0.16 and k = 21 MPa·μm$^{1/2}$ in the Taylor and Hall-Petch terms of yield strength, respectively. The relatively small value of α was attributed to the low SFE of the CoCrFeMnNi HEA since the clustering of highly dissociated dislocations in low SFE materials is hindered and the less clustered dislocation structure usually yields a small value of α in the Taylor equation [5].

3.3. The local mechanical behavior in the Co/Cr/Fe-rich and Mn/Ni-rich regions was studied by micropillar compression. Only slight differences were found between the stress-strain curves recorded in the Co/Cr/Fe-rich and Mn/Ni-rich volumes, suggesting that the chemical heterogeneities in the $Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$ HEA have only a negligible effect on the local mechanical behavior. The average saturation flow stress obtained by pillar compression was 1535 ± 68 MPa which is only slightly smaller than the value determined as one third of the macrohardness (1758 ± 100 MPa). This observation suggests a negligible size effect in the present micropillar compression experiments [6].

Conclusions

In this thesis, the relationship between the lattice defects and the mechanical properties of HEAs was studied. This study contributes to a better understanding of the relationship between the lattice defects and mechanical properties of HEAs. Some of my results fill the gaps in the literature, because the evolution of the lattice defects, such as dislocations or twin-faults, during SPD and their influence on the mechanical behavior have not been deeply understood yet.

Publications of the Author Related to This Thesis

[1] G. Dirras, J. Gubicza, A. Heczel, L. Lilensten, J.-P. Couzinie, L. Perriere, Y. Guillot, A. Hocini, Microstructural investigation of plastically deformed Ti20Zr20Hf20Nb20Ta20 high entropy alloy by X-ray diffraction and transmission electron microscopy, Materials Characterization 108 (2015), 1-7.

[2] G. Dirras, H. Couque, L. Lilensten, A. Heczel, D. Tingaud, J.-P. Couzinie, L. Perriere, J. Gubicza, I. Guillot, Mechanical behavior and microstructure of Ti20Hf20Zr20Ta20Nb20 high-entropy alloy loaded under quasi-static and dynamic compression conditions, Materials Characterization 111 (2016), 106-113.

[3] A. Heczel, L. Lilensten, J. Bourgon, L. Perrière, J.P. Couzinié, I. Guillot, G. Dirras, Y. Huang; T.G. Langdon, J. Gubicza, Influence of High-Pressure Torsion on the Microstructure and the Hardness of a Ti-Rich High-Entropy Alloy, Materials Science Forum 879 (2017), 732-737.

[4] A. Heczel, Y. Huang, T.G. Langdon, J. Gubicza, Investigation of Lattice Defects in a Plastically Deformed High-Entropy Alloy, Materials Science Forum 885 (2017), 74-79.

[5] A. Heczel, M. Kawasaki, J.L. Lábár, J. Jang, T.G. Langdon, J. Gubicza, Defect structure and hardness in nanocrystalline CoCrFeMnNi High-Entropy Alloy processed by High-Pressure Torsion, Journal of Alloys and Compounds 711 (2017), 143-154.

[6] A. Heczel, M. Kawasaki, D. Ugi, J. Jang, T.G. Langdon, J. Gubicza, The influence of chemical heterogeneities on the local mechanical behavior of a high-entropy alloy: A micropillar compression study, Materials Science and Engineering: A 721 (2018), 165-167.