Microstructure and Mechanical Behavior of Ultrafine-grained Ni-Mo Alloys Processed by Top-Down and Bottom-Up Methods

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Ph.D. Thesis Booklet

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Introduction

The production of ultrafine-grained (UFG) or nanostructured materials either by top-down or bottom-up route is usually accompanied by lattice defect formation, such as stacking faults, grain boundaries (GBs), dislocations and vacancies. The type and density of lattice defects can have significant impact on the properties of nanomaterials. Therefore, it is important to deepen our understanding about the relationship between lattice defects and properties of nanomaterials. Over the years, there is an increasing interest in employing severe plastic deformation (SPD) techniques for production of UFG materials. High-pressure torsion (HPT) is considered as the most effective SPD method in grain refinement and improvement of the strength of metallic materials. Moreover, the experiments showed that a combination of HPT with other SPD and non-SPD processing routes (such as rolling) gives the potential for achieving a greater grain refinement in bulk metallic materials. In the case of bottom-up techniques, the processing by electrodeposition is a conventional yet one of the most effective and low-cost methods. Further improvement in the properties of UFG and nanomaterials can be achieved by the addition of alloying elements which influence the microstructure as well as its thermal stability. Similar effect is expected when organic additives are added to the electrodeposited materials.

Ni-Mo alloys exhibit high hardness, wear, thermal and corrosion resistance, and have several important practical applications. However, the effect of Mo atoms on the microstructure and defect structure of UFG Ni prepared by different processing techniques has never been investigated yet. For this purpose, Ni-Mo alloy specimens were processed by both bottom-up (electrodeposition) and top-down (severe plastic deformation) routes with similar chemical compositions. My PhD research incorporated the influence of processing route on the microstructure, defect structure and mechanical properties of UFG and nanocrystalline Ni-Mo alloys. It also takes into account the influence of Mo alloying and saccharin addition on the characteristics of Ni alloy thin films processed by electrodeposition. In addition to the study of the thermal stability of the microstructure and defect structure during annealing, the correlation between the lattice defects and the mechanical properties was also investigated.

In my PhD research work, I performed the X-ray experiments for the characterization of all the samples investigated within the scope of this thesis to determine various microstructural parameters. For this purpose, after measuring the X-ray diffraction (XRD) patterns, I conducted the evaluation using the X-ray line profile analysis (XLPA) method. I carried out the sample surface preparation for X-ray and scanning electron microscopy (SEM) investigations. I evaluated the electron backscatter diffraction (EBSD) images to obtain grain size and grain boundary fractions using OIM software. Additionally, I calculated the grain sizes using transmission electron microscopy (TEM) images for those thin film samples which were beyond the detection limit of EBSD. I evaluated the differential scanning calorimetry (DSC) thermograms and calculated the stored energies for SPD processed and electrodeposited samples. I also performed the microhardness tests to determine the mechanical properties of the samples and then correlated the mechanical properties to the microstructure and defect structure.

Layout of the Thesis

This thesis is divided into five chapters as follows:

In Chapter 1, I include a brief description about the properties and applications of Ni-Mo systems. Additionally, this chapter summarizes the processing of UFG and nanocrystalline (NC) materials by top down and bottom up methods. The effect of processing techniques and their conditions on the microstructure, defect structure, thermal stability and mechanical properties of the as-processed materials is also discussed.

In chapter 2, I present the details of the material processing and the experimental techniques used in this research. XRD technique was extensively used in this study, therefore the detailed description of XLPA method is included along with brief details of other characterization techniques such as SEM and TEM, DSC, microhardness and uniaxial tensile tests.

In chapter 3, I show the influence of Mo addition on the microstructure, thermal stability and hardness of Ni alloy processed by a combination of cryorolling and HPT. The evolution of microstructure, defect structure and mechanical properties of UFG Ni alloys processed by SPD with increasing SPD straining is presented. Additionally, the evolution of grain size and dislocation density were also investigated as a function of the annealing temperature and then correlated to the evolved DSC peaks. The results obtained within the scope of this chapter have been published in three journal papers [P1-P3].

In chapter 4, I present the evolution of the microstructure, defect structure as well as mechanical properties of thin films of Ni alloys with low and high Mo concentrations, which were processed by electrodeposition with and without saccharin addition. The calculation of the change of stored energy during annealing is also included. The scientific results shown in this chapter were published in journal and conference papers [P4-P7].

In chapter 5, I discuss the influence of processing route on the microstructure, defect structure, thermal stability and stored energy. For this purpose, I compared the results obtained by the investigation of Ni-Mo bulk nanomaterials processed by HPT with that of Ni-Mo layers with very similar compositions but processed by electrodeposition. The results presented in this chapter were published in two journal papers [P6, P7].

New Scientific Results

The new scientific results of my PhD research can be summarized as follows:

1. Both Ni alloys with low (0.3%) and high (5%) Mo contents remain in solid solution state even after cryorolling and HPT. Although the grain size was not refined into the UFG regime during cryorolling, there were very high dislocation densities (~15-35 × 10^{14} m^{-2}) in both alloys. HPT at RT led to further enhancement in the dislocation density up to ~30-60 × 10^{14} m^{-2} and a concomitant gradual grain refinement below 200 nm. Irrespective of the Mo content, the saturation of the dislocation density occurred earlier (after 5 turns) than for the grain size (only after 20 turns) during combined cryorolling and HPT. The minimum grain size and the maximum dislocation density values are, respectively, smaller and higher in the alloy with high Mo content than in the material with low Mo concentration due to the pinning effect of Mo atoms on the lattice defects. This effect also hinders the clustering of dislocations within the grains as indicated by the higher value of the dislocation arrangement parameter.

2. The hardness for both alloys saturated and became homogeneous along the disk radii after 5 turns of HPT. The maximum hardness values achieved for 0.3% and 5% Mo concentrations were ~3200 and ~4300 MPa, respectively. The higher saturation hardness with 5% Mo is in accordance with the microstructural observations. It is demonstrated that the hardening caused by the combined process of cryorolling and HPT may be related to the increase of the dislocation density using the Taylor equation. The α parameter in this equation has a lower value for the higher Mo content due to the less clustered dislocation structure.

3. For the HPT-processed samples, the recovery of the UFG microstructures started at ~400 K irrespective of the Mo content but recrystallization occurred at a much higher temperature for the Ni alloy with higher Mo content. During recovery, the low-angle grain boundary fraction increased due to the arrangement of dislocations into low energy configurations, such as low-angle grain boundaries. In the recrystallization process, the fraction of low-angle grain boundaries decreased. The temperature range of the recovery is much larger for the alloy with higher Mo content (~515 K) than that for the sample with lower Mo content (~280 K). After annealing up to ~1000 K, the grain size remained much smaller for the sample with higher Mo concentration. Moreover, the larger Mo content yielded a separation of recovery and recrystallization processes in the DSC thermogram. In comparison to the sample with lower Mo content, there is a much higher onset temperature of recrystallization for the alloy with higher Mo concentration due to the segregation of solute Mo atoms at the grain boundaries which may reduce the grain boundary energy and additionally hinders the motion of the grain boundaries. The higher Mo concentration has a more pronounced hindering effect on recrystallization than on recovery. It is concluded that the higher Mo content significantly increases the stability of the SPD-processed UFG microstructure in Ni.

4. Annealing to ~600 K resulted in a considerable hardening for the sample with lower Mo content while the ductility remained unchanged. This annealing-induced hardening was explained by the annihilation of mobile dislocations and the clustering of the remaining dislocations into subgrain boundaries. An increase of the Mo concentration in UFG Ni led to a much lower annealing-induced hardening which was explained by the hindering effect of Mo atoms on the annihilation and clustering of dislocations. Therefore, the influence of Mo content on the annealing-induced hardening in UFG Ni-Mo alloys is

opposite to the trend observed formerly for their nanocrystalline counterparts processed by bottom-up methods due to the different strengthening mechanisms. Annealing to high temperatures resulted in a simultaneous reduction in the strength and an improvement in the ductility in UFG Ni-Mo alloys. The softening and the increase of ductility were lower for the alloy with higher Mo concentration, indicating a better thermal stability of this sample compared to the sample with lower Mo content.

5. In the electrodeposited Ni-Mo layers, the increase of Mo content resulted in a smaller grain size as well as a higher dislocation density and twin fault probability in the Ni layers. This effect is more pronounced for the electrodeposited films than for the UFG Ni-Mo alloys with similar compositions but processed by SPD. This difference can be attributed to the different formation mechanisms of lattice defects: during SPD-processing and electrodeposition deformation-induced and grown-in defects were formed, respectively. The addition of saccharin to the electrolyte bath also yielded an increase of the lattice defect density in Ni-Mo layers for both low and high Mo contents. This effect can be explained by the co-deposition of sulfur together with Ni. The increase of the defect density due to saccharin addition is more pronounced for Ni film with low Mo concentration.

6. The increase of Mo concentration in Ni films resulted in a considerable improvement of the thermal stability of the nanocrystalline microstructure. The improved stability due to Mo alloying can be attributed to the pinning effect of Mo on the lattice defects such as dislocations and grain boundaries, thereby retarding recovery and recrystallization of the nanocrystalline microstructure. The electrodeposited film with higher Mo concentration exhibited a better stability than the SPD-processed counterpart with the same Mo content. Although both Mo alloying and saccharin addition resulted in a strong

increase of the lattice defect density in electrodeposited Ni layers, their effects on the thermal stability were significantly different. Namely, saccharin yielded a significant reduction of the thermal stability of the nanocrystalline Ni microstructure because this additive increased the defect density during deposition, thereby enhancing the thermodynamic driving force for recovery and recrystallization. At the same time, the impurity elements (e.g., sulfur) deposited from saccharin cannot hinder effectively the recovery and recrystallization of the nanocrystalline microstructure in Ni films, causing a reduced thermal stability.

7. The stored energy investigation for the electroplated Ni films with both low and high Mo contents revealed that the majority of the released heat (~77%) can be attributed to the contribution of grain boundaries while the rest was caused by the annihilation of dislocations and twin faults. From the equality between the measured and calculated released heats, the grain boundary energy was estimated as ~0.5 and ~0.7 J/m^2 for low and high Mo concentrations, respectively. These values are in the lower part of the possible grain boundary energy range (0.4 - 1.4 J/m^2), suggesting a low excess volume in the grain boundaries of the present electroplated films. The grain boundary fraction in the released heat was significantly smaller (less than 55%) for UFG Ni-Mo samples with similar compositions but processed by HPT. For these specimens, the sum of the heat contributions of grain boundaries, dislocations and twin faults was much smaller than the released heat obtained by DSC. The difference was attributed to vacancies and vacancy clusters. The estimated vacancy concentration was about 10^{-3}. The higher Mo content yielded a two times larger vacancy concentration. The electroplated layers contain less vacancies than the HPT-processed samples, especially for low Mo content. The increase of Mo concentration in the electrodeposited films from ~0.4 at.% to ~5.3

at.% resulted in an enhancement of the stored energy with a factor of about two. This change is caused by the larger defect density and the smaller grain size. The influence of Mo content on the stored energy is less pronounced in the samples processed by HPT.

8. The investigation of the hardness of the electrodeposited Ni-Mo films showed that before annealing the saccharin-free layer with low Mo content has lowest hardness value in comparison with the other investigated Ni-Mo layers. This can be explained by the much higher grain size and lower dislocation density for this film compared to the other three electrodeposited samples. For other investigated layers, the hardness values were very close, despite the very different dislocation densities and twin fault probabilities. The grain size values for these three samples were very small (between 20 and 30 nm), which can cause change of the main deformation mechanism from dislocation glide to grain boundary sliding. Among all the layers, the minimum variation in the hardness during annealing was observed in the saccharin-free layer with high Mo content in accordance with the best thermal stability of the microstructure of this film. Furthermore, the addition of saccharin reduced the temperature of the large hardness reduction. At the same time, the increase of Mo content increased the thermal stability of the layers. Unlike HPT processed samples, no annealing-induced hardening was observed in the studied electrodeposited Ni-Mo layers.

Research Achievements

The results obtained during my PhD research were published in 8 papers (7 publications are related to the dissertation). Additionally, these results were presented at 5 international conferences and seminars.

Publications related to this Thesis

P1. **Kapoor G**, Huang Y, Sarma VS, Langdon TG, Gubicza J, Effect of Mo addition on the microstructure and hardness of ultrafine-grained Ni alloys processed by a combination of cryorolling and high-pressure torsion, Materials Science and Engineering A 688: 92-100 (2017).

P2. **Kapoor G,** Huang Y, Sarma VS, Langdon TG, Gubicza J, Evolution of the microstructure during annealing of ultrafine-grained Ni with different Mo contents, Materials Characterization 130: 56-63 (2017).

P3. **Kapoor G,** Huang Y, Sarma VS, Langdon TG, Gubicza J, Influence of Mo alloying on the thermal stability and hardness of ultrafine-grained Ni processed by high-pressure torsion, Journal of Materials Research and Technology 6:(4) 361-368 (2017).

P4. Gubicza J, Pereira PHR, **Kapoor G**, Huang Y, Sarma VS, Langdon TG, Annealing-induced Hardening in Ultrafine-grained Ni-Mo Alloys, Advanced Engineering Materials 20:(9) 1800184 (1-4) (2018).

P5. **Kapoor G**, Péter L, Fekete E, Gubicza J, Defect structure in electrodeposited nanocrystalline Ni layers with different Mo concentrations, AIP Conference Proceedings 1953, 030047 (2018).

P6. **Kapoor G**, Péter L, Fekete E, Lábár JL, Gubicza J, The influence of Mo addition on the microstructure and its thermal stability for electrodeposited Ni films, Materials Characterization 145: 563-572 (2018).

P7. **Kapoor G**, Péter L, Fekete E, Lábár JL, Gubicza J, Stored energy in nanocrystalline Ni-Mo films processed by electrodeposition, Journal of Alloys and Compounds 796: 307-313 (2019).

Other publication

P8. Athreya CN, **Kapoor G,** Gubicza J and Sarma VS, Influence of mode of plastic straining on the microstructure of Ni and Ti deformed through rolling and torsion, Materials Characterization 132: 205-214 (2017).