Summary of the results obtained in the project entitled „Lattice defects and their influence on functional properties of nanostructured materials” (K109021)

In accordance with the proposed research plan, in the project the correlation between the processing conditions, defect structure and properties of ultrafine-grained (UFG) and nanostructured materials was studied. The investigated specimens were processed by advanced techniques such as (i) severe plastic deformation (SPD), (ii) powder metallurgy and (iii) electrodeposition. In the following, some important results are described briefly.

1. Studies of UFG and nanomaterials processed by SPD methods

Supersaturated Cu–3 at.% Ag alloy was rolled at liquid nitrogen temperature and then annealed at 623 K up to 120 min. The evolution of the ultrafine-grained (UFG) microstructure as a function of annealing time was studied. In the initial stage of the heat-treatment a heterogeneous microstructure was developed where both the dislocation density and the solute Ag concentration in the Cu matrix varied considerably. In the regions where the initial Ag particles have a very small size and/or large Cu/Ag interface energy, dissolution occurred due to the Gibbs–Thomson effect while in other volumes the solute Ag concentration decreased to the equilibrium level. In the regions where the solute Ag concentration increased due to dissolution, a considerable fraction of dislocations formed during rolling was retained in the Cu matrix after annealing. In the volumes where the solute Ag content decreased due to precipitation, significant reduction in the dislocation density was observed. The evolution and the stability of this heterogeneous microstructure were investigated experimentally and discussed using model calculations.

The mechanical properties and the microstructure of Grade 2 titanium semi-products processed by warm caliber rolling in both laboratory and industrial environments are studied. It is shown that this technology yields ultrafine-grained (UFG) microstructure with high tensile strength and good ductility at room temperature. Finite element modelling (FEM) suggests that the effectiveness of caliber rolling in grain-refinement is mainly caused by the large, homogeneous imposed strain, similar to conventional severe plastic deformation (SPD) methods. It is proved that the mechanical and microstructural properties of titanium processed by the industrial equipment are similar to the characteristics of the material manufactured in the laboratory. This observation suggests that caliber rolling carried out in industrial environments may be a candidate technology in mass-production of UFG titanium with improved mechanical properties.

An Al-1% Mg solid solution alloy with an annealed grain size of 400 micron was processed by high-pressure torsion (HPT) to produce a grain size of 200 nm with a high fraction of high-angle grain boundaries. Tensile testing at room temperature showed this material exhibited excellent strength but with little or no ductility. It is demonstrated that a combination of reasonable ductility and good strength may be achieved by subjecting samples to a short term anneal of 10 minutes following the HPT processing. Annealing at 423 K increased the average grain size to 360 nm, reduced the overall strength to a value that was 75% of the value without annealing but gave reasonable elongations of up to 0.2. Both the initial unprocessed Al-Mg alloy and the sample annealed after HPT exhibited serrated flow due to the Portevin-Le Chatelier (PLC) effect. The results suggest that the introduction of short term annealing after HPT processing may be an effective and simple procedure for achieving a reasonable level of strength together with good ductility after processing by HPT.

Ultrafine-grained (UFG) microstructures in Cu-Cr alloys were processed by high pressure torsion (HPT). HPT-processing in copper-chromium alloys leads to a significant hardening due to the formation of UFG microstructure. With increasing chromium content the microhardness rises from about 1700 to 2700 MPa due to the reduction in average grain size from 209 to 40 nm as well as the increase of the chromium content, the dislocation density and the twin-fault probability. The electrical conductivity is reduced with increasing Cr content due to the higher amount of grain boundaries and Cr alloying atoms. The heat-treatment after HPT results in a gradual decrease of the hardness and an increase in electrical conductivity. For high Cr contents (9.85 and 27%) an appropriate selection of the heat-treatment temperature enables the preservation of the high hardness while the electrical conductivity increased considerably. The significant improvement in the electrical conductivity can be explained by Cr precipitation and grain boundary relaxation. Our study demonstrates the capability of HPT-processing and subsequent heating for obtaining both high hardness and electrical conductivity in Cu-Cr alloys.

The microstructural and mechanical properties of an ultrafine-grained (UFG) Al–Zn alloy processed by high-pressure torsion (HPT) are investigated using depth-sensing indentation, focused ion beam scanning electron microscopy and scanning transmission electron microscopy. Emphasis is placed on the microstructure and the effect of grain boundaries at room temperature. The experiments show the formation of Zn-rich layers at the Al/Al grain boundaries that enhances the role of grain boundary sliding leading to unique plastic behavior in this UFG material. The occurrence of significant grain boundary sliding at room temperature is demonstrated by deforming micro-pillars. Our results illustrate a potential for using UFG materials as advanced functional materials in electronic microdevices. In addition, it was shown analytically that the corresponding indentation depth–time relationship can be described by a power-law function, suggesting a direct application of nanoindentation for the determination of the strain rate sensitivity parameter.

A 316L stainless steel was processed by high-pressure torsion (HPT) to evaluate the grain refinement and phase transformation during severe plastic deformation. The initial material was essentially a single phase gamma-austenite with a coarse-grained microstructure of ~42 μm but the grain size was reduced to ~45 nm after 10 turns of HPT. In addition, there was a phase transformation and the initial gamma-austenite transformed initially to epsilon-martensite and finally to alpha-martensite with increasing strain. The dislocation density increased to an exceptionally high value, of the order of ~10^{16} m^{-2}, in the main alpha-martensite phase after 10 HPT revolutions. The formation of the multiphase nanocrystalline microstructure yielded a four-fold increase in hardness to reach an ultimate value of ~6000 MPa. Differential scanning calorimetry (DSC) was used to study the thermal stability of the microstructure and the phase composition in nanocrystalline 316L stainless steel processed by HPT for ¼ and 10 turns. The DSC thermograms showed two characteristic peaks which were investigated by examining the dislocation densities, grain sizes and phase compositions after annealing at different temperatures. The first DSC peak was exothermic and was related to recovery of the dislocation structure without changing the phase composition and grain size. The activation energies for recovery after processing by ¼ and 10 turns were ~163 and ~106 kJ mol^{-1}, respectively, suggesting control by diffusion along grain boundaries and dislocations. The second DSC peak was endothermic and was caused by a reverse transformation of alpha-martensite to gamma-austenite. The hardness of annealed samples was determined primarily by the grain size and followed the Hall–Petch relationship. Nanocrystalline 316L steel processed by HPT exhibited good thermal stability with a grain size of ~200 nm after annealing at 1000 K and a very high hardness of ~4900 MPa.

The energy stored in severely deformed UFG 316L stainless steel was investigated by DSC. A sample was processed by HPT for N = 10 turns. In the DSC thermogram, two peaks were observed. The first peak was exothermic and related to the annihilation of vacancies and dislocations. During this recovery, the phase composition and the average grain size were practically unchanged. The energy stored in dislocations was calculated and compared with the heat released in the exothermic DSC peak. The difference was related to the annihilation of vacancy-like defects with a concentration of $\sim 5.2 \times 10^{-4}$. The second DSC peak was endothermic which was caused by a reversion of alpha-martensite into gama-austenite, however in this temperature range dislocation annihilation and a moderate grain growth also occurred. The specific energy of the reverse martensitic phase transformation was determined as about −11.7 J/g. In addition, an investigation was conducted to evaluate the effect of annealing at different temperatures on the tensile properties of UFG 316L stainless steel processed by HPT. A ‘‘moderate-temperature” annealing at 740 K resulted in reduced strength and elongation due to the annihilation of mobile dislocations. A ‘‘high-temperature” annealing at 1000 K yielded a remarkably good combination of yield strength (1330 MPa) and elongation to failure (43%) which can be attributed to the almost full reversion of alfa-martensite formed during HPT into gamma-austenite while the grain size remained very fine with a value of about 200 nm.

An investigation was conducted to examine the effect of molybdenum (Mo) content on the grain size, lattice defect structure and hardness of nickel (Ni) processed by severe plastic deformation (SPD). The SPD processing was applied to Ni samples with low (~0.3 at%) and high (~5 at%) Mo concentrations by a consecutive application of cryorolling and high-pressure torsion (HPT). The grain size and the dislocation density were determined by scanning electron microscopy and X-ray line profile analysis, respectively. In addition, the hardness values in the centers, half-radius and peripheries of the HPT-processed disks were determined after ½, 5 and 20 turns. The results show the higher Mo content yields a dislocation density about two times larger and a grain size about 30% smaller. The smallest value of the grain size was ~125 nm and the highest measured dislocation density was $\sim 60 \times 10^{14}$ m^{-2} for Ni-5% Mo. For the higher Mo concentration, the dislocation arrangement parameter was larger indicating a less clustered dislocation structure due to the hindering effect of Mo on the rearrangement of dislocations into low energy configurations. The results show there is a good correlation between the dislocation density and the yield strength using the Taylor equation. The α parameter in this equation is slightly lower for the higher Mo concentration in accordance with the less clustered dislocation structure.

A Ti-rich refractory High-Entropy Alloy (HEA) with a composition of $Ti_{35}Zr_{27.5}Hf_{27.5}Nb_5Ta_5$ was processed by 1 turn of HPT. The evolutions of the phase composition, microstructure and hardness were studied. Simultaneous phase transformation and grain refinement was observed during HPT. The initial bcc phase was transformed into a martensitic structure throughout the disk. The initial grain size (~800 µm) was refined to ~200-1000 nm irrespective of the location along the disk radius. As the imposed strain increases strongly with the distance from the disk center, the unchanged grain size along the disk radius suggests an early saturation of the microstructure during HPT. Complementary compression testing revealed that the phase transformation during deformation starts with the formation of martensitic lamellae in the initial bcc grains. This grain morphology was inherited in the elongated grain shape in the HPT-processed disk. 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 same sample due to the strong strain hardening at the beginning of compression. The small grain size resulted in a high hardness (~3500-3900 MPa) in the HPT-processed sample. There was only a slight variation in the hardness along the disk radius in accordance with the small difference between the grain sizes measured at the center, half-radius and periphery of disk processed by HPT.

An equiatomic CoCrFeMnNi High-Entropy Alloy (HEA) produced by arc melting was processed by HPT. The evolution of the microstructure during HPT was investigated after ¼, ½, 1 and 2 turns using electron backscatter diffraction and transmission electron microscopy. The spatial distribution of constituents was studied by energy-dispersive X-ray spectroscopy. The dislocation density and the twin-fault probability in the HPT-processed samples were determined by X-ray line profiles analysis. It was found that the grain size was gradually refined from ~60 mm to ~30 nm while the dislocation density and the twin-fault probability increased to very high values of about 194 × 10^14 m^−2 and 2.7%, respectively, at the periphery of the disk processed for 2 turns. The hardness evolution was measured as a function of the distance from the center of the HPT-processed disks. After 2 turns of HPT, the microhardness increased from ~1440 MPa to ~5380 MPa at the disk periphery where the highest straining is achieved. The yield strength was estimated as one-third of the hardness and correlated to the microstructure.

2. Investigation of UFG and nanomaterials processed by powder metallurgy

Ultrafine-grained Zn (UFG-Zn) with the grain size of about 200 nm was processed by Spark Plasma Sintering at 300 °C from fine Zn powder. The grain boundaries in the consolidated material were decorated by ZnO dispersoids with a mean thickness of about 20 nm. The creep behavior was studied by indentation tests in the homologous temperature range of 0.87–0.91. The activation energy of the creep for UFG-Zn was found to be much larger (211–252 kJ/mol depending on the oxide content) than the value determined previously for coarse-grained Zn (152–159 kJ/mol). The activation energy increased with increasing ZnO content in UFG-Zn. X-ray line profile analysis revealed that the population of the different dislocation slip systems changed during creep deformation, indicating a considerable dislocation activity.

Bulk polycrystalline nickel compact was processed by spark plasma sintering from heterogeneous powder consisting of a mixture of nanometer and micrometer sized particles. The consolidated samples inherited the bimodal structure of the starting powder and was composed of 55 vol.% coarse-grained (with the grain size larger than 1 micron) and 45 vol.% ultrafine-grained (with an average grain size of 550 nm) components. The deformation mechanisms were established by EBSD, X-ray line profile analysis and in-situ TEM observations. In the ultrafine-grained volume, the deformation occurred mainly through the activation of dislocation sources emitting full or partial dislocation either from grain interior or grain boundaries. Besides dislocation activity, rolling and sliding of nanograins were also observed during deformation by in-situ transmission electron microscopy, which have a considerable contribution to the observed high strain rate sensitivity of the bimodal microstructure. The cracks formed during deformation easily propagated in the nanograin regions due to the weaker particle bonding caused by the relatively high fraction of native oxide layer on the surface of the initial nanoparticles.

Coarse-grained aluminum powder with 99.5 wt.% purity was consolidated by HPT technique at room temperature using a low carbon steel powder holder. In this process, the powder experiences a semi-constrained condition because the internal wall of the powder holder can expand under the load applied during HPT. After 4 turns of HPT a relative density of 99.83% was achieved. The microstructure was characterized by EBSD and XLPA. It was found that the grain size decreased while the dislocation density increased with both increasing the distance from the disk center and the number of HPT turns. The smallest grain size and the maximum dislocation density with the values of 410 nm and 6.8×10^{14} m^{-2}, respectively, were achieved at the periphery of the disks processed for 4 turns. Tensile tests showed that the consolidation of this Al powder by 4 turns of HPT yielded a high ultimate tensile strength and a good ductility (~373 MPa and ~22%, respectively). It turned out that the yield strength versus grain size relationship obeys the Hall-Petch equation. This study demonstrates the capability of HPT technique for processing consolidated Al powder with high strength and good ductility.

An investigation was conducted to study the effect of CNT addition on the microstructure and the mechanical behavior of 316L steel. Samples with 0, 1 and 3 wt.% of CNTs were sintered by SPS method. The major phase for all samples was a γ-austenite with the fractions between 0.68 and 0.81. In the sintered CNT-free sample, beside the γ-austenite considerable amounts of bcc α-phase and Fe_3O_4 phase were detected. During sintering at high temperature, the fraction of the α-phase developed during powder milling decreased due to a reverse martensitic transformation. The Fe_3O_4 phase was also formed during the sintering process. The addition of CNTs resulted in the development of an Fe_3C phase. The fraction of this phase increased with increasing the CNT content. Sintering of the 316L powder led to a decrease in the dislocation density and a concomitant increase in the crystallite size due to the recovery and recrystallization of the severely milled microstructure. The addition of CNTs impedes these processes, therefore the dislocation density and the grain size in the 316L-CNT composites were higher and smaller, respectively, than in the CNT-free material. The increase of the CNT content from 1 to 3% did not yield a smaller grain size or a higher dislocation density. Most probably, the clustering of the CNTs in the 316L-3CNT sample decreased the hindering effect of a unit amount of CNTs on recovery and recrystallization. The CNT addition increased the hardness of the sintered 316L alloy due to the hardening effect of the CNTs, the Fe_3C phase, the smaller grain size and the higher dislocation density. At the same time, clustering of CNTs yielded a weaker bonding between the 316L grains, therefore 3% CNT addition resulted in a significant decrease in the bending strength.

3. Studies of nanomaterials processed by electrodeposition

The effect of additives (saccharin and trisodium citrate) on the microstructure of electrodeposited nanocrystalline Ni films produced from sulfate-based electrolytes was investigated. In addition, the combined effect of nickel-chloride and saccharin was also investigated for a film deposited in a Watts bath. In the films deposited without organic additives, a grain size of ~70-160 nm was observed without considerable twinning. In addition, a crystallographic texture was detected where the planes (220) were parallel to the film surface. The organic additive saccharin eliminated the texture, yielded fine-grained microstructures (~20-100 nm) and increased the density of lattice defects (dislocations and twin faults). The efficiency for grain refinement of saccharin as additive was larger for the sulfate-type bath than for the Watts electrolyte. It was found that the addition of nickel-chloride to the electrolyte (Watts bath) increased the grain size. The combined effect of nickel-chloride and saccharin led to a bimodal grain size distribution. Trisodium citrate did not result in a considerable grain refinement but increased the dislocation density. Although there was no strict correlation between the dislocation density and the grain size, the highest dislocation densities were observed for the samples having the smallest grain sizes in the studied Ni films. These specimens were processed from saccharin-containing electrolytes. It was found that in addition to the small grain size, the incorporating sulfur was also responsible for the enhanced formation of twin faults in the samples processed from saccharin-containing baths. It was proposed that the formation of twin boundaries was partly due to the sulfur codeposition on (111) planes during electrodeposition. The samples deposited from the additive-free sulfate-type and Watts-type baths exhibited similar hardness values (2000-3000 MPa). The layer grown from the trisodium-citrate based electrolyte showed higher hardness (~3800 MPa) due to the larger dislocation density. Saccharin yielded the largest hardness values due to the superimposed effect of the grain refinement and the increase of defect density (both dislocations and twin faults). The highest hardness was achieved for the sample deposited from the sulfate-type bath with saccharin additive (~5900 MPa). The combined effect of nickel chloride and saccharin yielded a smaller hardness value (4500-4600 MPa) in accordance with the bimodal nature of the microstructure.

The results of this project were published in 76 papers.