# Defect Structure in Ultrafine-grained Silver and a Copper-Silver Alloy Processed by Severe Plastic Deformation

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– PhD Thesis –

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# Introduction

Ultrafine-grained (UFG) materials are currently a major focus in materials science due to their unique properties in comparison to their coarse-grained counterparts. Specifically, an important feature of UFG materials is their high strength at ambient temperatures. Severe plastic deformation (SPD) methods, such as equal channel angular pressing (ECAP), high-pressure torsion (HPT) and rolling at liquid nitrogen temperature are effective tools for producing bulk UFG metals. The mechanical properties, such as the strength and ductility, are strongly affected by the lattice defect structure of UFG metallic materials. For instance, it has been shown that a combination of large strength and good ductility could be achieved in nanocrystalline metallic materials containing high density of twin boundaries. The evolution of the microstructure during SPD have been studied extensively for face-centered cubic (fcc) metals with medium or high stacking fault energies (SFEs). At the same time, a very little information is available on the defect structure in UFG fcc metals with low SFE. In these materials besides dislocations a considerable density of twin boundaries is expected to form during SPD which may influence their mechanical performance.

The main goal of my PhD work was to study the effect of low SFE on the evolution of lattice defects (e.g. dislocations and planar faults) during processing of the UFG microstructure by different SPD methods. The majority of the results presented in my thesis were obtained on silver as this material has the lowest SFE in pure fcc metals. The evolution of the defect structure as a function of strain applied in SPD was investigated for two impurity levels. The influence of impurities and the method of SPD (ECAP or HPT) on the room and high temperature thermal stability of the UFG microstructures were also studied. Additionally, the effect of the combination of cryogenic rolling and subsequent annealing on the microstructure and mechanical properties of a copper-silver alloy was studied.

## Experimental Methods

In this thesis silver samples with two different impurity concentration and a copper-silver alloy were investigated. The UFG microstructure was achieved by ECAP and HPT for the silver and by cold rolling for the copper-silver samples. The microstructure of the samples was characterized mainly by x-ray line profile analysis. This non-destructive method provides information from a relatively large volume, hereby giving the characteristic parameters of the defect structure with good statistics. From the broadening of the Bragg-peaks the crystallite size distribution, the dislocation density, the edge-screw character of dislocations and the planar fault probability can be determined. There are numoerous methods to obtain these information from the x-ray line profiles. In this study the convolutional multiple whole profile fitting method was applied. For direct observations of the microstructure transmisson electron microscopy, scanning electron microscopy and electron backscatter diffraction were applied. The mechanical properties of the samples were characterized by uniaxial compression and tensile tests and microhardness measurements. The high temperature thermal stability of the samples was investigated by differential scanning calorimetry. Additionally the point defect structure in the silver samples was studied by positron annihilation lifetime spectroscopy.

## New Scientific Results

1. The influence of impurities on the evolution of microstructure in Ag during ECAP-processing was investigated. The type and density of lattice defects were determined in 99.99 at.% (4N) and 99.995 at.% (4N5) purity silver. The minimum grain size achieved by ECAP in pure Ag was about 200 nm irrespective of the impurity atom concentration. The dislocation density also showed similar evolution for both 4N5 and 4N impurity levels: first it increased and saturated after 8 passes at similar values and then decreased. The saturation dislocation density was very large compared to other fcc metals due to the high degree of dislocation dissociation caused by the low SFE which hindered the annihilation of dislocations during SPD. The evolution of twin boundary frequency was very different for the two impurity concentrations: it increased monotonously up to 16 passes in the case of 4N5 purity samples while for 4N purity specimens it saturated after 4 passes and then decreased with increasing number of passes. The impurity atoms were most probably concentrated preferentially at the grain boundaries with decreasing grain size thereby hindering the emission of twinning partials from boundaries that led to a decrease of the twinning activity in the less pure material after 4 passes [1–4].

2. The samples processed for $4-16$ passes showed self-annealing (softening without heat-treatment) during storage at room temperature. Despite the small difference in purity, the 4N samples exhibited a much lower degree of softening than 4N5 specimens as

impurity atoms pinned dislocations and grain boundaries thereby hindering both recovery and recrystallization. In the case of the 4N5 purity samples, an increasing number of ECAP passes led to a more rapid self-annealing due to the increase of the fraction of the twinned volumes that can act as nuclei for recrystallization. At the same time, the 4N purity specimen processed through 16 passes exhibited lower degree of softening than the samples processed through 4 or 8 passes, and this is due to the lower level of twinning [2, 3, 5–7].

3. The high temperature thermal stability of ECAP-processed 4N5 and 4N purity UFG silver were compared according to DSC experiments. The results showed that the activation energies for recovery and recrystallization were similar for both materials but the temperature of the exothermic DSC peak maximum was higher and the heat released was lower for the 4N purity sample. The primary contributions to the stored energy before recovery and recrystallization were given by the grain boundaries and the dislocations. A significant fraction of stored energy ($15 - 20\,\%$) was retained in the samples after the exothermic DSC peak due to the remaining UFG regions and the high density of small dislocation loops. The reduced heat released for the 4N purity sample is primarily due to the lower vacancy concentration before the DSC peak, as compared to the 4N5 purity specimen. This phenomenon is attributed to a reduction of free volumes by segregation of dopants at the grain interfaces [8, 9].

4. The minimum grain size achieved by SPD in 4N purity Ag was about 200 nm for both ECAP and HPT, i.e. its value is not very sensitive to the method of SPD. However, the retarding effect of the high pressure in HPT on the dislocation annihilation resulted in a $2-3$ times larger dislocation density than in ECAP-processing. The samples processed by HPT exhibited an inhomogeneous microstructure in the axial direction of the disk which resulted in spatially heterogeneous thermal stability of the UFG microstructure. During annealing in the middle of the HPT-processed disk the recrystallizaton occurred earlier than in the surface layers, which yielded a double exothermic peak in the DSC thermogram. [4, 10, 11].

5. The defect structure in Cu−3 at.% Ag alloy processed by cold rolling at room and cryogenic temperatures and subsequently annealed at high temperature was studied. After annealing, an inhomogeneous solute atom distribution developed in the Cu matrix due to the heterogeneous dissolution of nanosized Ag particles, resulting in regions with varying Ag content in the matrix. In the region where the solute concentration increased, the dislocation density developed during rolling was retained in the Cu matrix even after annealing, while in the region where the Ag solute content did not increase, significant decrease in dislocation density was observed. Therefore, in the rolled and annealed samples, bimodal microstructures were developed where both the dislocation density and the solute concentration vary considerably. The as-rolled samples exhibited high strength with negligible uniform elongation. After short-time annealing the strength decreased marginally with

significant improvement in the uniform elongation. This is attributed to the bimodal microstructure in the Cu matrix since the reduction of the dislocation density in some regions increased the strain-hardening capacity of the material [12].

## Conclusions

In this thesis the evolution and the stability of the defect structure in UFG silver and copper-silver alloy were studied. It was obtained that in silver due to the low SFE the saturation dislocation density is extremely high compared to other pure fcc metals, while the minimum grain size was roughly the same (about 200 nm). The dislocation density and the twin boundary probability are not monotonous functions of the strain applied during SPD. The type and density of lattice defects were strongly affected by the impurity level of silver and the method of SPD-processing (ECAP or HPT). It was shown that the low SFE facilitates self-annealing in silver after SPD-processing, but this can be considerably hindered by a slight increment in the impurity level. This has a large significance in the application of UFG materials, since the annihilation of lattice defects implies the decrease of strength which may affect the viability of UFG materials for use as structural components. It was revealed that the thermal stability of the UFG microstructure in the surface regions of the HPT-processed silver disks was better than the stability of the internal region due to the axial inhomogeniety of the lattice defect structure. It was also established that in supersaturated Cu-Ag solid solution rolling and subsequent heat treatment caused a heterogeneous solute atom and lattice defect distributions, which yielded a good combination of strength and ductility.

In summary, this study contributes to a better understanding of the influence of SFE, impurities and alloying elements on the properties of SPD-processed UFG materials. Therefore, my results have an indirect effect on the development of UFG materials with improved mechanical performance and better thermal stability.

# List of Publications Related to the Thesis

[1] J. Gubicza, N. Q. Chinh, J. L. Lábár, Z. Hegedűs, and T. G. Langdon, "Twinning and dislocation activity in silver processed by severe plastic deformation," *Journal of Materials Science*, vol. 44, pp. 1656–1660, Feb. 2009.

[2] J. Gubicza, N. Q. Chinh, J. L. Lábár, Z. Hegedűs, and T. G. Langdon, "Unique Features of Ultrafine-Grained Microstructures in Materials Having Low Stacking Fault Energy," *Materials Science Forum*, vol. 659, pp. 171–176, Sept. 2010.

[3] Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, Z. Fogarassy, and T. G. Langdon, "The effect of impurity level on ultrafine-grained microstructures and their stability in low stacking fault energy silver," *Materials Science and Engineering: A*, vol. 528, pp. 8694–8699, Nov. 2011.

[4] Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, Z. Fogarassy, and T. G. Langdon, "Microstructure of low stacking fault energy silver processed by different routes of severe plastic deformation," *Journal of Alloys and Compounds*, vol. 536, pp. S190–S193, Sept. 2012.

[5] J. Gubicza, N. Q. Chinh, J. L. Lábár, Z. Hegedűs, P. Szommer, G. Tichy, and T. G. Langdon, "Delayed microstructural recovery in silver processed by equal-channel angular pressing," *Journal of Materials Science*, vol. 43, pp. 5672–5676, July 2008.

[6] J. Gubicza, N. Q. Chinh, J. L. Lábár, G. Tichy, Z. Hegedűs, C. Xu, and T. G. Langdon, "Stability of microstructure in silver processed by severe plastic deformation," *International Journal of Materials Research (formerly Zeitschrift für Metallkunde)*, vol. 100, no. 06, pp. 884–887, 2009.

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[8] Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, Z. Fogarassy, and T. G. Langdon, "The Influence of Impurity Content on Thermal Stability of Low

Stacking Fault Energy Silver Processed by Severe Plastic Deformation," *Materials Science Forum*, vol. 729, pp. 222–227, Nov. 2012.

[9] Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, Z. Fogarassy, K. Süvegh, and T. G. Langdon, "High temperature thermal stability of ultrafine-grained silver processed by equal-channel angular pressing," *Journal of Materials Science*, vol. 48, pp. 1675–1684, Oct. 2012.

[10] Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, J. L. Lábár, and T. G. Langdon, "Stability of the ultrafine-grained microstructure in silver processed by ECAP and HPT," *Journal of Materials Science*, vol. 48, pp. 12–19, Jan. 2013.

[11] Z. Hegedűs, J. Gubicza, P. Szommer, N. Q. Chinh, Y. Huang, and T. G. Langdon, "Inhomogeneous softening during annealing of ultrafine-grained silver processed by HPT," *Journal of Materials Science*, vol. 48, pp. 7384–7391, July 2013.

[12] K. Sitarama Raju, V. Subramanya Sarma, a. Kauffmann, Z. Hegedűs, J. Gubicza, M. Peterlechner, J. Freudenberger, and G. Wilde, "High strength and ductile ultrafine-grained Cu–Ag alloy through bimodal grain size, dislocation density and solute distribution," *Acta Materialia*, vol. 61, pp. 228–238, Jan. 2013.