Characterization of ultrafine grained Cu-Ni-Si alloys by electron backscatter diffraction

I Altenberger¹, H A Kuhn¹, M Gholami², M Mhaede², L Wagner²
¹ Wieland Werke AG, Central Laboratory, Ulm, Germany
² Institute of Materials Science and Engineering, Clausthal University of Technology, Clausthal-Zellerfeld, Germany
E-mail: igor.altenberger@wieland.de

Abstract. A combination of rotary swaging and optimized precipitation hardening was applied to generate ultra fine grained (UFG) microstructures in low alloyed high performance Cu-based alloy CuNi3Si1Mg. As a result, ultrafine grained (UFG) microstructures with nanoscopy small Ni2Si-precipitates exhibiting high strength, ductility and electrical conductivity can be obtained. Grain boundary pinning by nano-precipitates enhances the thermal stability. Electron channeling contrast imaging (ECCI) and especially electron backscattering diffraction (EBSD) are predestined to characterize the evolving microstructures due to excellent resolution and vast crystallographic information. The following study summarizes the microstructure after different processing steps and points out the consequences for the most important mechanical and physical properties such as strength, ductility and conductivity.

1. Introduction
Precipitation hardened Cu-Ni-Si alloys are a well established and technologically important class of materials for a wide range of applications where high strength and good conductivity are required [1]. Yield strength and fatigue properties of metallic alloys can be significantly enhanced by severe plastic deformation methods [2,3,4]. In contrast to other strengthening methods such as solid solution hardening, severe plastic deformation leads to a weaker decrease of electrical conductivity and is therefore a means of enhancing strength while maintaining acceptable conductivity for current bearing parts and components. By a subsequent aging treatment the severely plastically deformed microstructure of Cu-Ni-Si alloys can be further enhanced and thermal stability can profit from grain-boundary pinning by precipitated nanoscale nickel silicides.

2. Experimental procedures
The investigated copper alloy is the Corson-type alloy [5] CuNi3Si1Mg, which has experienced wide-spread use as connector-, leadframe- and high-strength wire material. The material condition in our present study was hot extruded, homogenized (solution annealed), rotary swaged and subsequently precipitation hardened. Typical solution treatment temperatures are 800-950 °C. The precipitation hardening was carried out at 450 °C. According to [6] a full solution anneal in Corson-type alloys is difficult due to required solution anneal temperatures of around 1000 °C, which is industrially unrealistic. Backscatter (electron channeling contrast imaging = ECCI) electron microscopy [7,8] was carried out using an AsB (Angle Selective Detector) [9] in a Zeiss ULTRA scanning electron microscope equipped with a thermal field emission cathode. Typically, an aperture lens of 120 µm and acceleration voltages of 10-20 kV at a working distance of 2-6 mm were used (preferably at an acceleration voltage of 15-20 kV to allow for sufficient probe current). Theoretically, under optimized beam conditions, it is possible to visualize single dislocations by the ECCI technique [10], however, this is focus of some future investigations. Instead, in this paper, we will confine to investigate the high- and low angle boundary structure. Except for the working distance, these adjustment were also used for electron backscattering diffraction (EBSD) investigations. Here, an EBSD-unit by Oxford was used. The EBSD patterns were recorded using a 4x4 binning, data acquisition and calculation of the patterns were performed by a Nordlys camera and AZTEC software by Oxford, respectively.
addition to orientation mappings, band contrast mappings were generated. The band contrast (or image quality or pattern quality) which represents the contrast of the EBSD kikuchi pattern from each point in the EBSD mapping, describes the perfection of the crystal lattice at that point. The band contrast map is usually illustrated in a gray scale and it produces the real microstructure (with local deformation and subgrains or increased dislocation density), similarly as in a backscatter or electron channeling SEM picture [11]. Prior to EBSD and ECCI-characterization in the SEM, the samples were carefully mechanically ground up to 2400 grid (SiC paper), then polished up to 1 µm and finally vibration polished for 3 hours with dispersed Mg-Oxide to aim for a sample surface with as little preparational cold work as possible. Two sets of experiments were carried out: swaging (which was carried out at TU Clausthal) of solution annealed bars from an initial diameter of 24 mm to a diameter of 7 mm (phi = -2,4) as well as swaging of a solution annealed wire with a diameter of 5,3 mm to a diameter of 2,7 mm (phi = -1,39). In both cases, precipitation annealing after swaging was done at 450 °C at different aging times. In the following elaborations we will use the terminology “peak-aged” for samples which were precipitation hardened at 450 °C for 1-6 hours and “over-aged” for conditions which were precipitation hardened for >16 h. Further details concerning the aging kinetics for the 2,7 mm wire are given in [12]. Finally, the swaged and subsequently precipitation hardened samples were mechanically characterized by tensile- and hardness tests. Moreover, the electrical conductivity of the different tempers before and after artificial aging was measured.

3. Results and discussion
CuNi3Si1Mg was hot worked (extruded) at 800-900 °C, then solution treated at 800 °C/2 h (or alternatively at 950 °C/10 min) and subsequently water-quenched. The microstructure after this treatment exhibits a recrystallized coarse grain structure with twins within the grains. Coarse Ni-silicides (diameter > 200 nm) were not dissolved at this homogenization temperature (Fig. 1).

![Fig. 1](image1.jpg)

Fig. 1: Microstructure of CuNi3Si1Mg after solution annealing at 800 °C/2 h and water quenching.
The solution annealed condition was swaged from a diameter of 5.3 mm to a diameter of 2.7 mm. As a consequence of the swaging process the dislocation densities and thus the hardness of the samples were increased (from 60 HV1 to 160 HV1). In addition, many subgrains as well as some high angle boundaries were generated. This condition was then artificially aged at 450 °C/1h which corresponds to the peak-aging state for this diameter. The artificial aging step leads to a further hardness increase of 218 HV1 by the formation of very small Nickel-silicides which are the strengthening phase in the Cu-Ni-Si system [13,14]. The microstructure after the aging process is exhibited in Figs. 2 and 3 as a ECCI (electron channeling contrast imaging [7,8]) SEM micrograph and as a orientation mapping from EBSD, respectively. The ECCI pictures show very strong orientation contrast (Fig. 2), but without quantitative grain orientation measurements it is not possible to tell whether the obtained structure is a true high angle grain boundary structure or merely an arrangement of many subgrains within larger grains. In order to differentiate between high- and low-angle grain boundaries EBSD measurements of the aged condition were carried out. Fig. 3 shows an orientation map of the swaged and peak-aged condition (For a successful misorientation profile measurement a reconstruction of the grains can be necessary due to the poor detectability or non-detectability of grain boundaries and directly adjacent regions).
**Fig. 3:** EBSD orientation map (Euler angles) and high- (misorientation > 10°) and low angle boundaries (misorientation < 10°) of the center region of the swaged and peak aged condition (sample diameter 2.7 mm), cross-section

Better detection for ultra fine grained structures in Cu-Ni-Si alloys can also be achieved by lowering the acceleration voltage of the SEM from 20kV to 15 kV, however at lower incident electron beam energies the backscatter contrast will be affected negatively. Obviously, a high content of high angle grain boundaries (misorientation > 10°) occurs with some low angle grain boundary substructures within the grains (marked red in Fig. 3). Low angle grain boundaries with misorientations <2° were disregarded in the mappings. The majority of grains have grain diameters < 1 µm and thus it is justified to classify this condition as ultra fine grained (UFG).

In a second set of experiments bars of 24 mm diameter were swaged down to a diameter of 7 mm and then artificially aged at 450 °C for different aging times. Fig. 4 shows the deformation structure in the center of the specimen after swaging in a ECCI micrograph. The observed grain structure can be described as a precursor to a fully ultra fine grained microstructure with many low angle sub-grain boundaries. Due to the local material flow during swaging, twisting and elongation of whole grain areas may occur. In contrast to Fig. 4, Fig. 5 shows the near-surface regions (distance to surface: 50-100 µm) of the swaged condition. Here, the grain- or sub-grain size is significantly smaller and typically in the range of 200-800 nm. Furthermore, a striking feature of this regions is certainly the pronounced elongation of the grains.

**Fig. 4:** ECCI backscatter micrograph of the center after swaging (sample diameter: 7 mm)

This difference between center and near-surface regions in the 7 mm thick samples was also observed after aging, as illustrated in the EBSD band contrast pictures (Figs. 6 and 7). In contrast to the as-swaged condition, the ultra fine grains in near-surface regions have become less elongated and more equiaxed (Fig. 7, band contrast). Also, within these ultra fine grains less strain than in the grains of the center regions is observed. Figs. 7 and 8 show orientation maps of the center- and near-surface regions of the swaged and peak aged sample. It is assumed that in spite of the relatively high temperature of 450 °C during aging, significant grain coarsening in the course of recrystallization is strongly suppressed due to the preferential formation of Ni-silicides in sub-grain and grain boundaries (Fig. 9). These silicides act to decrease the mobility of the grain boundaries and play a key role in the good thermal stability of ultra fine grained precipitation hardened copper alloys (For comparison:
recrystallization of severely plastically deformed pure copper subjected to accumulative roll bonding [15] already starts at 200 °C, whereas no significant hardness decrease occurs at 350-400 °C after 1h in fully aged CuNi3Si1Mg which was severely plastically deformed by swaging or accumulative roll bonding (ARB) [16].

**Fig. 5:** ECCI backscatter micrograph of near-surface regions after swaging (sample: bar with 7 mm diameter)

![ECCI backscatter micrograph](image)

**Fig. 6:** EBSD band contrast picture of the center regions of the swaged and peak-aged condition (sample: bar with 7 mm diameter)

![EBSD band contrast picture](image)

However, extended exposure to a temperature of 450 °C for at least 30 hours leads to pronounced over-aging where recrystallization of the grain structure as well as coarsening of Ni-silicides are clearly visible (Figs. 10-11). On the other hand, a relatively fine grain size (though not ultra fine grained) prevails even in the over-aged condition, and extended temperatures of 450 °C in typical applications of Cu-Ni-Si alloys such as connector pins are not realistic or typical. Table 1 and Fig. 12 summarize the mechanical properties and electrical conductivities of severe plastically deformed CuNi3Si1Mg1. Although a through-thickness ultra fine grained microstructure was not achieved in the 7 mm bars, the resulting properties are nonetheless impressive. Complementary studies on the higher alloyed spray
formed Cu-Ni-Si alloy Cu$_7$Ni$_2$Si$_1$Cr [17] demonstrated that via severe plastic deformation such as swaging even strength-conductivity combinations equal to Cu-Be-alloys are possible. Certainly, in the wake of the current REACH legislation, the motivation to replace Cu-Be alloys by less hazardous (and cheaper) Cu-alloys should be justified.

**Fig. 7:** EBSD band contrast picture and orientation map (colouring: Euler angles) of near-surface regions of the swaged and peak-aged condition (sample: bar with 7 mm diameter)

**Fig. 8:** EBSD Orientation map of the center regions of the swaged and peak-aged condition (colouring: Euler angles), same area as shown in Figs. 6 and 9
**Fig. 9:** EBSD phase map of the swaged and peak-aged condition (red: fcc copper, bright or coloured dots: Ni-silicides (orthorhombic as well as hexagonal))

**Fig. 10:** EBSD band contrast picture and high- and low-angle boundaries (bold lines: high angle grain boundaries, faint lines: low angle grain boundaries) of the center regions of the over-aged condition (sample: bar with 7 mm diameter) (Compare to Fig. 6, however, note different magnifications)
Fig. 11: Band contrast picture of the near-surface regions of the over-aged condition (sample: bar with 7 mm diameter)

|                     | Yield strength (MPa) | Ultimate tensile strength (MPa) |
|---------------------|-----------------------|---------------------------------|
| after hot extrusion | 267                   | 483                             |
| after solution annealing (800°C) | 153                 | 331                             |
| after swaging (phi = -2.4) | 587                   | 588                             |
| after aging at 450°C/6 h | 810                   | 865                             |
| after aging at 450°C/12 h | 768                   | 826                             |

Table 1: Mechanical properties of CuNi3Si1Mg after swaging and different aging times (T_aging = 450 °C) (swaged from 24 to 7 mm)
Fig. 12: Properties of swaged and precipitation hardened CuNi3Si1Mg as well as of related alloys [16]

4. Summary
The current results indicate that swaging and subsequent optimized precipitation hardening is a suitable process route to produce Cu-Ni-Si materials with very fine grain size in the range 0.2-2 µm. Whereas swaging of wires (diameter 5.3 mm) was able to generate a through thickness ultra fine grained structure (with grain diameters of 300-500 nm), thicker bars (diameter 24 mm) exhibited only an ultra fine grained near-surface zone while the center of the specimen remained largely non-UFG (with grain sizes >1 µm) in spite of severe plastic deformation, however with a large content of subgrains and low-angle boundaries. This can be ascribed most likely to the different deformation gradients across the bar in thin and thick samples.

EBSD is an excellent method for characterizing ultra fine grained Cu-Ni-Si alloys due to the vast and valuable amount of quantitative information regarding the nature of the involved grain boundaries and precipitates. Principally, EBSD has also qualified as a tool to qualitatively characterize nanoscale Ni-silicide precipitate arrangements, although further work is needed here to assess whether a quantitative agreement with other methods (such as TEM) is possible.

In all cases, a good agreement between ECCI (Electron Channeling Contrast Imaging) methods and band contrast mapping derived from EBSD was found. It is assumed that the nanoscale precipitates play a key role for the thermal stabilization of the partially ultra fine grained microstructure by pinning grain boundaries. Therefore, ultra fine grained precipitation hardened Cu-Ni-Si alloys are possible candidates for a new generation of high strength connector pins at service temperatures > 250 °C. The tensile strength of the swaged and precipitation hardened material is excellent and may reach values up to 850-900 MPa at elongations to fracture of 16 % and electrical conductivities of 35% IACS or higher. Cu-Ni-Si alloys with strengths exceeding 1000 MPa (and thus potentially able to replace Cu-Be alloys) are possible if alloys with higher Ni-contents such as spray formed CuNi7Si2Cr [17,18] are used (Fig. 12).

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References
[1] Kuhn HA, Altenberger I, Käufler A, Hözl H, Fünfer M, Properties of High Performance Alloys for Electromechanical Connectors, In: Copper Alloys (Ed. L. Collini), INTECH, 2012.
[2] Valiev RZ, Islamgaliev RK, Alexandrov IV 2000 Progress in Materials Science 45 103.
[3] Höppel HW, May J, Göken M 2004 Adv. Eng. Mater. 6 781.
[4] Mughrabi H, Höppel HW, Kautz M 2004 Scripta Mater. 51 807.
[5] Corson MG, Z. Metallkunde 1927 19 370.
[6] Kinder J, Huter D 2009 METALL 63 298.
[7] Zauter R, Petry F, Bayerlein M, Sommer C, Christ HJ, Mughrabi H 1992 Phil. Mag. A 66 425.
[8] Altenberger I, Kuhn HA, Hözl H 2012 Prakt. Metall. Sonderband 44 79
[9] Jaksch H 2007 Proc. 18th National Electron Microscopy Congr., Eskisehir, Turkey, p. 29.
[10] Picard YN, Kamaladasa R, De Graef M, Nuhfer NT, Mershon WJ, Owens T, Sedlacek L, Lopour F 2012 Microscopy Today 20 12.
[11] Zhilyaev AP, Kim BK, Nurislamova GV, Baro MD, Szpunar JA, Langdon TG 2002 Scripta Mater 46 575.
[12] Altenberger I, Kuhn HA, Mhaede M, Gholami M, Wagner L 2012 METALL 66 500.
[13] Lockyer SA, Noble FW 1994 J. Mater. Sci. 29 218.
[14] Wang C, Zhu J, Lu Y, Guo Y, Liu X 2014 J. Phase Equilibra and Diffusion 35 93.
[15] Blum W, Li Y, Breutinger F 2004 Acta Mat. 52 5009.
[16] Kuhn HA, Altenberger I, Riedle J, Hölzl H 2013 Proc. Copper 2013 –vol VI Downstream Fabrication, Santiago, Chile, p 129
[17] Altenberger I, Müller HR, Zauter R 2010 Proc. Copper 2010, GDMB, Clausthal-Zellerfeld, p. 3.
[18] Altenberger I, Kuhn HA, Müller HR, Gholami M, Mhaede M, Wagner L, Int. J. Mat. Product Technology, 2014, in print.