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# Properties of High Performance Alloys for Electromechanical Connectors

H.-A. Kuhn, I. Altenberger,  
A. Käufler, H. Hölzl and M. Fünfer  
*Wieland-Werke AG, Ulm,  
Germany*

## 1. Introduction

Miniaturization of electronic and electromechanical components and increasing cost of materials are the driving forces for developments of high performance copper alloys for automotive and computer technologies. Electromechanical connectors are current carrying spring elements. Miniaturization requires improved mechanical strength and medium to high electrical conductivities. For automobiles this components have to operate in temperature ranges between  $-40^{\circ}\text{C}$  and  $180^{\circ}\text{C}$  under hood. For a good reliability during life-time of vehicles or multimedia devices designing engineers also expect good formability, excellent resistance against stress relaxation and fatigue behavior. The design of small box-like connectors has to overcome the contradiction between high strength and good formability. Nature of alloys also reveals reduced electrical and thermal conductivity at improved strength and vice versa reduced strength at higher conductivity. Nevertheless, development of modern copper based connector materials intends to improve strength, electrical conductivity and bending behavior simultaneously. Furthermore, a long life time of connector devices requires excellent thermal stability and resistance against fatigue damage.

In a first step the following contribution will focus on the metallurgical principles for alloy design. The role of alloying elements is described. The diverse directions of material development include optimization of standardized alloys like tin bronzes and development and processing of new alloy compositions. Beside properties of grain refined tin bronze CuSn8 with standardized chemical composition this article presents latest developments on precipitation hardened Corson-type alloys.

Corson has first described in 1927 the mechanism of precipitation of nickel silicides in copper (Corson, 1927). The successful story of CuNiSi-alloys for connector devices has started in the early 80ies (Hutchinson, 1990; Tyler, 1990; Robinson, 1990). Until today research is focused on understanding processing and optimization of standardized C70250 (UNS-designation) like CuNi2Si and related alloys of the first generation (Lockyer, 1994; Kinder, 2009). The success of an ongoing research on these alloys is due to an excellent combination of strength, conductivity, deformation behavior and thermal stability. Therefore these alloys have been applied to diverse connector and lead frame devices. In

addition, many connector devices are subjected to dynamical load (vibrations under hood) or to high numbers of repeating plug ins resulting in fatigue damage of spring elements.

Since a few years this materials are followed by more complex cobalt containing Corson-type alloys CuNi1Co1Si (C70350) which stand comparison with some copper-beryllium alloys of medium yield strength up to 850 MPa (Mandigo, 2004; Kuhn, 2007; Robinson, 2008). High strength copper nickel silicon alloys also meet requirements of high density processor sockets (Robinson, 2008). So called Hyper Corson-type alloys with more than 5 wt% of precipitates forming elements achieve 900 MPa and more (Mutschler, 2009).

This article is focused on properties of spring behavior with concern to elasticity, stress relaxation resistance and fatigue behavior with respect to microstructures of fine grained tin bronzes and precipitation hardened Corson type alloys. Deformation behavior and bendability of strip materials were already reported by (Kuhn, 2007; Bubeck, 2007).

## 2. Experimental procedure

### 2.1 Characterization of microstructure

For optical light microscopy grain boundaries, grain sizes and second phases of thermo-mechanical treated rolled strips were revealed by immersion etching in sulphuric acid solution of  $K_2Cr_2O_7$  (Hofmann, 2005).

Silicides of Corson-type alloys with diameters less than 200 nm were characterized by a Scanning Electron Microscope SEM (Zeiss Ultra). By SEM using secondary electrons as well as backscattered electrons at magnifications up to 20.000  $\times$  it was possible to image small precipitates with radii of 20 nm and dislocation induced deformation areas. Semi quantitative chemical analysis of particles was performed by Electron Dispersion X-Ray Spectroscopy EDXS (ISIS300, Oxford Instruments).

Precipitates of the Corson-type alloy C70350 were also investigated by transmission electron microscopy (JEOL 4000 FX, 400 kV). Investigations were conducted by Stuttgart Center for Electron Microscopy.

### 2.2 Mechanical properties

Strength is measured as Yield Strength  $R_{p0,2}$  and Ultimate Tensile Strength  $R_m$ . Strengths and elongations of strips were examined at room temperature by a tensile tester Z100 (Zwick).

### 2.3 Modulus of resilience

The modulus of resilience is defined by the stored energy of a spring (Fig.1):

$$\text{Resilience} = R_{p0,2}^2 / 2E \quad (1)$$

The calculation of the modulus of resilience requires exact values of the yield strength  $R_{p0,2}$  and the Young's modulus  $E$ . For a rough estimate the Young's modulus obtained from the classical tensile test is usually used. For more precise determination of the modulus of resilience the Young's modulus is preferably determined by the dynamical resonance method (Förster, 1937).

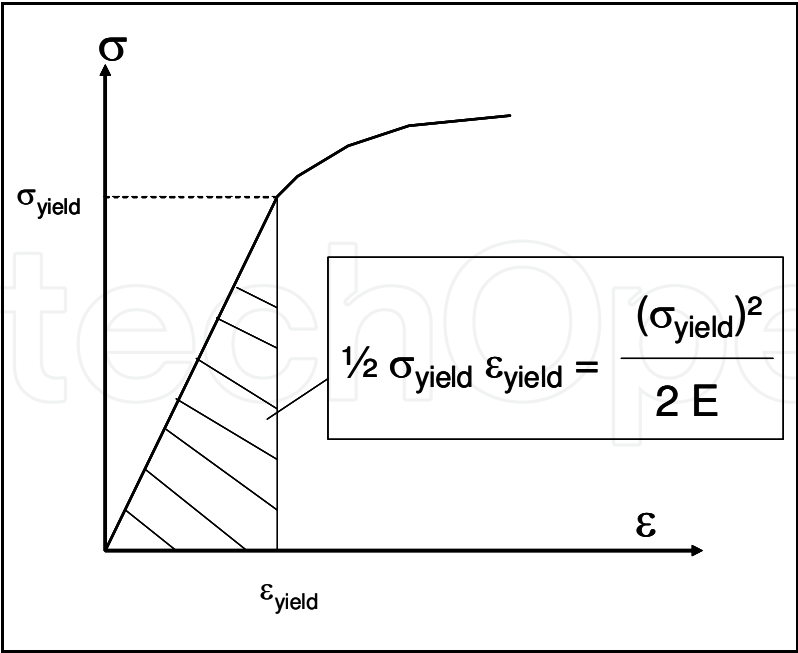


Fig. 1. Definition of the modulus of resilience of a metallic material used as a spring.

Young’s modulus  $E$  was determined by the dynamical resonance method as described in (Kuhn, 2000).  $E$  was evaluated in dependence on the resonance frequency  $f$  of the 1<sup>st</sup> transversal vibration, the specific weight  $\rho$  , length  $l$  and thickness  $t$  of the tested strip materials. The correction factor  $C$  is a function of Possion’s ratio and geometry. For resonance frequencies of 0.5 to 1 kHz specimen sizes of  $t \times 20\text{mm} \times 50\text{mm}$  were chosen. Thickness varies between 0.15 and 0.5 mm depending on the manufactured final strip gauges.

$$E = 0.94645\rho f^2 ( l^4 / t^2 ) C$$

(2)

2.4 Stress relaxation resistance

Thermal stability is expressed by the material’s resistance against stress relaxation (SRR) under a defined load at elevated temperatures between 80 and 200°C after 1000 to 3000 hours. For the tried and tested ring method (Fox, 1964) strips of 50 mm length and gauges between 0.15 and 0.5 mm were clamped on a steel ring with a defined outer radius. The applied initial stress  $\sigma_i$  in the outer surface of the strip depends on this radius and the yield strength of the copper alloy. For  $\sigma_i$  usually  $0.5$  to  $1.0 \times R_{p0.2}$  were chosen. By the time under load and temperature elastic stress changes into plastic deformation. The remaining stress is an indicator for SRR. Measured data were extrapolated to long life times by the Larson-Miller approach (Larson & Miller, 1952). Test equipment and evaluation of results is well described by (Bögel, 1994; Bohsmann, 2008).

2.5 Fatigue behavior

All fatigue tests were conducted under air atmosphere at 22°C. Specimens made from 0.3-0,6 mm strip material where cycled by alternating bending (R-ratio  $R = -1$ ) using a mechanical testing device at a frequency of 18 Hz under constant extension amplitude. The stress amplitude is calculated through the elastic properties (Young’s modulus and geometry) of the

cycled specimen with rectangular cross section. The rectangular specimens were loaded perpendicular to the rolling direction of the strip. SEM pictures were taken using a ZEISS Ultra Scanning electron microscope (equipped with a Schottky field emission cathode). Roughness values in axial direction prior to fatigue testing were  $R_a = 0,08 \mu\text{m}$  and  $R_z = 0,84 \mu\text{m}$  for the coarse grained CuSn8 and  $R_a = 0,11 \mu\text{m}$  and  $R_z = 0,78 \mu\text{m}$  for the very fine grained CuSn8.  $R_a$  and  $R_z$  of the investigated CuNi1Co1Si-Strip were 0,39 and 0,83 , respectively.

### 3. Alloys

Designer of electromechanical connectors first have to decide for high strength or high conductivity. Connectors under high current load need copper alloys with medium to high electrical conductivity. For transmission of signals copper alloys with low to medium conductivity are used. It is known that copper alloys of high strength cannot reveal high conductivities like pure or low alloyed solid solution hardened coppers. The chart of electrical conductivity versus yield strength (Fig. 2) gives a first overview about alloying systems of relevance. In case of precipitation hardened low alloyed coppers, Cu-Be-alloys and Corson-type alloys this two-dimensional interdependence is valid for good to fair bend radii  $r$  versus strip thicknesses  $t$  ratios  $r:t$  in the range of 0 to 5.

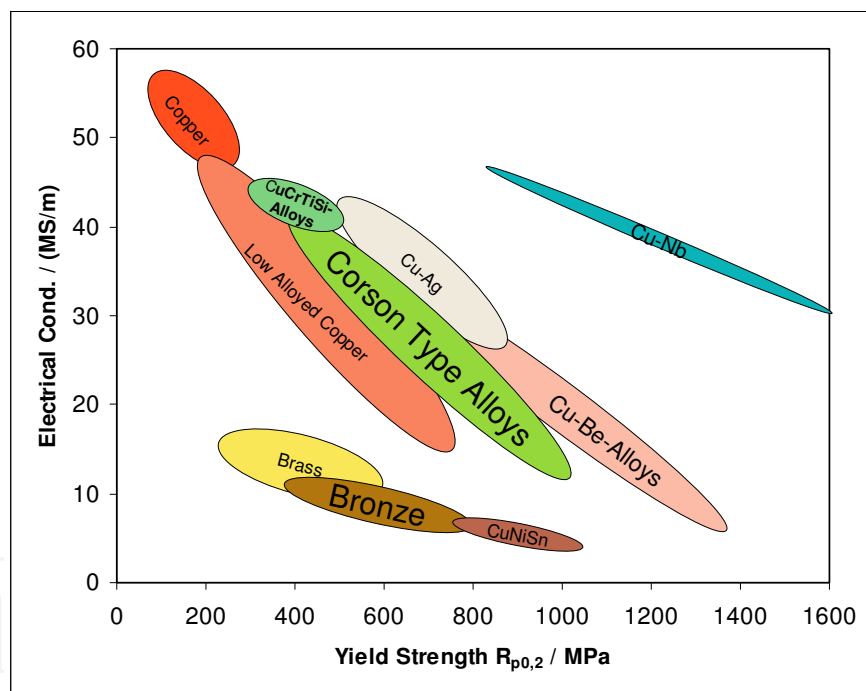


Fig. 2. Copper and Copper alloys: Electrical conductivity versus yield strength.

#### 3.1 CuSn8

In principle, the development of copper alloys for connectors is not only driven by improvement of their properties. It is also restricted by demands from connector manufacturers for standardized materials, double sourcing and materials costs. By introducing very fine grained strip materials of standardized alloys into the connector market this contradiction in customer demands can be overcome. Phosphor containing bronze CuSn8 (European Standard: CW453K; UNS-designation: C52100 ) strip materials

with an average grain size of less than 2  $\mu\text{m}$  reveal improved strength and improved formability in comparison with materials of usually medium grain sizes of 10 to 20  $\mu\text{m}$  (as shown in (Bubeck, 2007; Bubeck, 2008)). This grain refinement increases yield strength in the order of 100 to 150 MPa without any loss in formability. This is a result of optimized thermo-mechanical treatment of rolled strips. Chemical composition was not varied. Time and temperature of intermediate recrystallization annealing steps were fit to defined amounts of cold reduction in order to suppress grain growth. Grain size decreases after each cold roll and recrystallization annealing step until an average grain size of 1 to 2  $\mu\text{m}$  is achieved prior to final cold rolling. Hardening in this class of alloys is based on the Hall-Petch relation (Fig. 3) (Bubeck, 2007; Bubeck, 2008; Hall, 1951). Grain refinement leads to improved strength and ductility of strip material in comparison with conventionally processed CuSn8. This advantageous combination of mechanical properties enables manufacturers to design small box like connectors of medium to high strength with nearly sharp bend edges. Improvement of bending behavior was discussed earlier in detail (Bubeck, 2007; Bubeck, 2008). Mechanical properties of investigated strip materials are listed in Table 1.

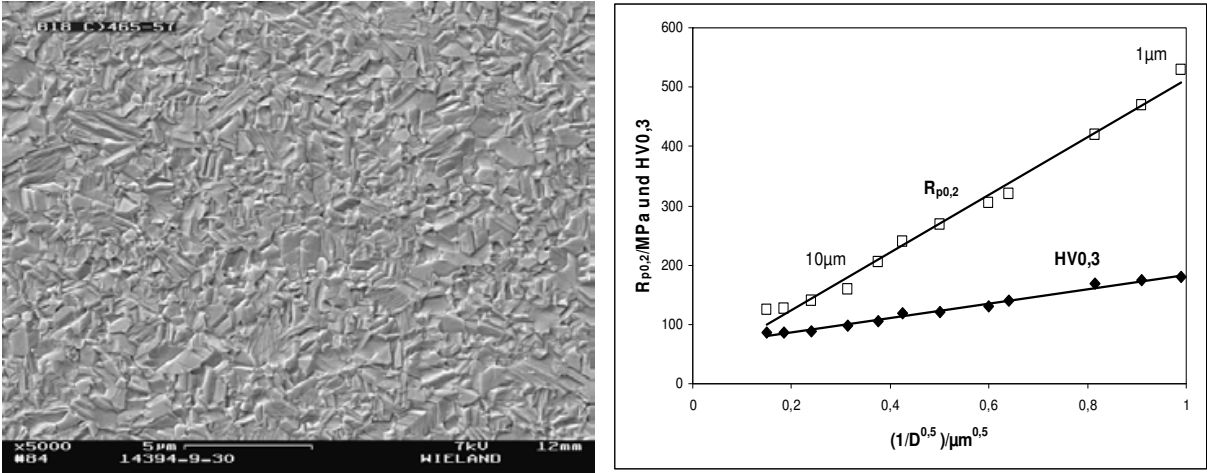


Fig. 3. CuSn8 strip with grain size 1 to 2  $\mu\text{m}$  (a), Hall-Petch-Relation: Hardness and Yield strength vs grain size (Bubeck, 2007) (b) .

Alloy	$R_{p0.2}/\text{MPa}$	$R_m/\text{MPa}$	A10 / %	Electr. Conduct. / MS/m	Minimum bend radius r:t GW/ BW*
CuSn8 Grain size 10 $\mu\text{m}$	610	665	33	8	0,5 / 1,5
CuSn8 Grain size 1..2 $\mu\text{m}$	650 ...740 780 ...830	685 ...785 800 ...925	15 ...20 5 ... 8	8 8	0 / 2 1 / 4
CuNi3Si1Mg	725	770	10,4	23,5	1,5/1,5
CuNi1Co1Si TM04	778	816	11,4	31	2,0 / 2,0
CuNi1Co1Si TM06	825	860	5,5	28	2,5 / 2,5
CoNi3,9Co0,9Si1,2Mg0,1	870 993	930 1018	2,0 2,1	18 18	2,1 / 2,1 4,4 / 7,2

\* GW: = Bend edge in good way direction (perpendicular to rolling direction), BW: = Bend edge in bad way direction (parallel to rolling direction).

Table 1. Mechanical properties, electrical conductivity and minimum 90° bend radii

### 3.2 Corson type alloys

The more traditional development approach for high strength copper alloys is focused on chemical variation of precipitation hardened alloys.

As earlier explained by (Hutchinson, 1990), silicide-containing Corson-type alloys CuNi<sub>3</sub>Si or CuNi<sub>2</sub>SiMg represent a class of materials with high strength copper materials beside the superior beryllide hardened CuBe-alloys. Processing of beryllium-containing particles during production and manufacturing of beryllium containing metals can cause lung disease (Schuler, 2005). Be-free compositions are legislatively urged in the European Union recently. Therefore many manufacturers and consumers prefer Be-free copper alloys and further developments of silicide hardened copper alloys aim at replacing copper-beryllium alloys. Targets are combinations of yield strength and electrical conductivity of 800 MPa and 50% IACS or 950 MPa and 30% IACS. For comparison the first generation of Corson alloys used for connector materials like CuNi<sub>2</sub>Si, CuNi<sub>2</sub>SiMg and CuNi<sub>3</sub>Si with volume fractions of precipitates of 2 to 3 percent is characterized by 700 MPa and 50% IACS. Beside these fundamental properties new materials have to meet requirements for excellent thermal stability with 70% remaining stress after 1000h at 150 °C and good formability.

Variations of the chemical compositions of basic Corson-alloys aim to increase the volume fraction of particles and/or improve thermal stability of precipitates. For this purpose one has to understand the role of alloying elements.

Nickel reduces the solubility of silicon in copper. This is also valid for cobalt. From the quasi binary phase diagrams, one can deduce an increase of solvus of silicides in dependence of the sum of the silicide forming elements Ni, Co and Si. The temperature of solvus line increases also with the ratio of Co versus Ni.

For example the solvus temperature of pure Ni<sub>2</sub>Si is 770 °C for 2.5 wt% of Ni plus Si and 800 °C for 3 wt%. For comparison the solution annealing temperature of pure Co<sub>2</sub>Si is approximately 1070 °C for 2.5 wt% Co plus Si. With a Ni:Co ratio of 1 at composition sum of Ni, Co and Si of 2.5 wt% the solution annealing temperature is reduced to 960 °C. These data are taken from (Mandigo, 2004). The superior hardening effect of Co-silicides was also demonstrated by (Fujiwara, 2004). The strengthening effect depends on the size, crystallographic structure and the distance between the involved particles. The radius of effective silicides is less than 100 nm.

A prerequisite for a successful solution annealing is subsequent quenching of annealed strips. For solution annealing strips, typical solution annealing treatments take place at 900 to 1000 °C. Optimized solution annealing can be verified by the minimum of electrical conductivity. For further processing of strips, grain sizes of 20 µm and less are desirable.

In the following the quenched strips are age hardened at 400 to 500 °C. With respect to isotropy of bending the amount of final cold roll prior to final age hardening is usually 25 to 50 %. An optimized combination of yield strength and electrical conductivity can be obtained when the (Ni+Co)/Si ratio is between 3.8 and 5.

Due to the enhanced solution temperature, copper alloys hardened by cobalt-silicides Co<sub>2</sub>Si reveal improved stress relaxation resistance as compared to alloys containing only Ni<sub>2</sub>Si.

Non shearable precipitates cause additional strength in dependence of their volume fraction and their radii. Strengthening of Copper-alloys hardened by silicides is based on the

Orowan-mechanism due to the semi-coherency of the orthorhombic crystal structure of  $(\text{Ni}, \text{Co})_2\text{Si}$  precipitates (Kuhn, 2007). The contribution of particle hardening  $\Delta\sigma$  to yield strength can be improved by an increase of volume fraction  $f$  and a reduction of particle radius  $r$  of precipitates:

$$\Delta\sigma \cong 6 \frac{\sqrt{f}}{r} \tag{3}$$

This formula was derived from the Orowan approach (Orowan, 1954)

$$\Delta\sigma \cong 0.8Gb\sqrt{n_A} \tag{4}$$

( $G$ : = shear modulus of copper;  $b$ : = Burgers-vector;  $n_A$ : = number of particles per unit area within the slip plane)

Fig. 4 explains the effect of particle size and volume fraction on the strengthening by non-shearable particles. For a gain of 100 MPa in yield strength a microstructure with a majority of very small precipitates with radii less than 10nm and at a volume fraction of 3 and more percent is required.

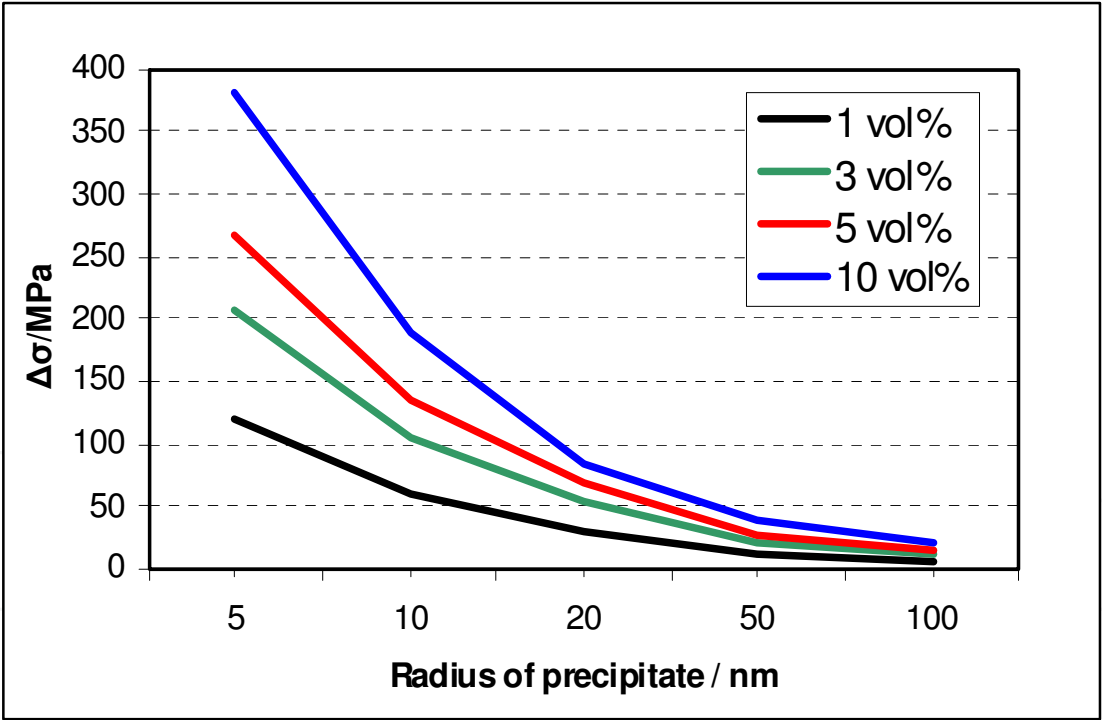


Fig. 4. Effect of particle size and volume fraction on yield strength increase according to the Orowan-mechanism.

Fig. 5 shows typical precipitate distributions of  $(\text{Ni}, \text{Co})_2\text{Si}$  in CuNi1Co1Si strip (left micrograph) and of CuNi3SiMg (right micrograph). Coherency strains as figured out by the following TEM-micrograph indicate particle diameters less than 5 nm (Fig.6) in CuNi1Co1Si. Obviously the radii of most particles vary between 2 and 100 nm.

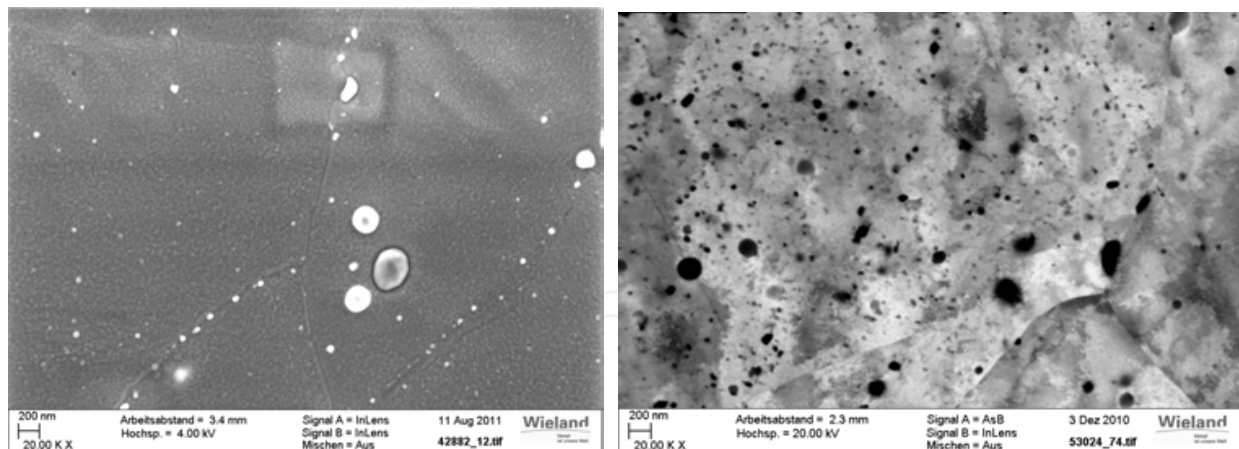


Fig. 5. SEM-micrographs: precipitates in CuNi1Co1Si, secondary electron image (left) and CuNi3SiMg, backscatter electron image (right).

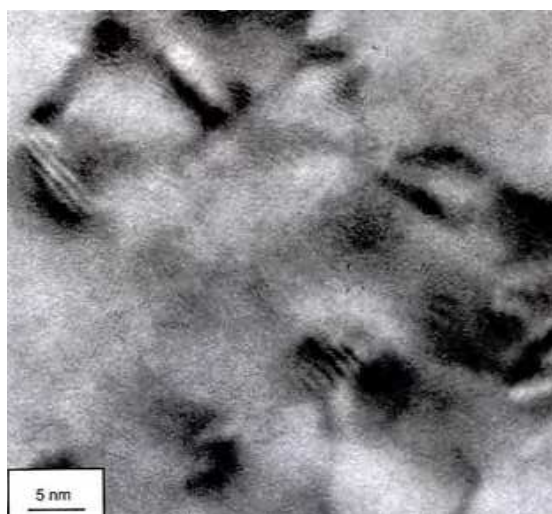


Fig. 6. TEM-micrograph of CuNi1Co1Si: Small particles and coherency strains (by courtesy of Stuttgart Center of Electron Microscopy).

Beside cobalt, nickel and silicon, other elements such as magnesium and chromium contribute to the improvement of strength and thermal stability of Corson-type alloys. Unlike in the microstructure of lower alloyed CuNi1Co1Si chromium forms coarse chromium containing silicides. One disadvantage of such coarse precipitates is the wear of stamping tools in the connector production root. Magnesium atoms improve stress relaxation resistance by solid solution hardening due to their large difference of atom radii  $r_{\text{Mg}}$  in comparison with copper  $r_{\text{Cu}}$ .  $(r_{\text{Mg}} - r_{\text{Cu}} / r_{\text{Cu}})$  is of the order of 25 %. Mg also contributes to the formation of silicides as known from the C70250 variation CuNi3SiMg.

In the following, the latest developed Corson-type alloy CuNi3,9Co0,9Si1,2Mg0,1 with yield strength beyond 900 MPa characterized by Ni and Co-containing mixed silicides and a composition of more than 5 wt % alloying elements is called Hyper Corson alloy. Unlike the microstructure of lower alloyed C70250 and C70350 some silicides of Hyper Corson alloys exhibit sizes of 5  $\mu\text{m}$ . However large silicides do not contribute significantly to strengthening, they inhibit grain growth.

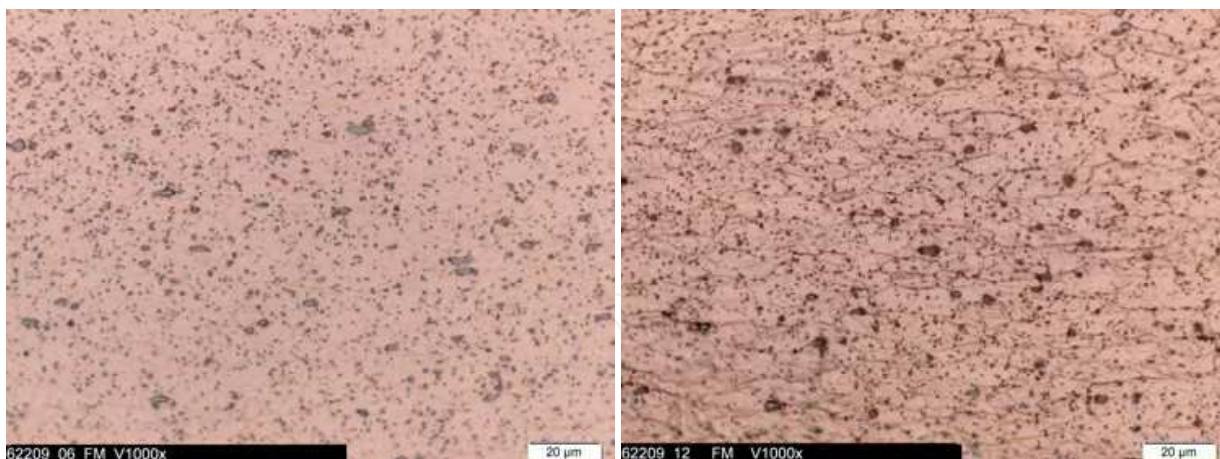


Fig. 7. Hyper Corson alloy CuNi<sub>3,9</sub>Co<sub>0,9</sub>Si<sub>1,2</sub>Mg<sub>0,1</sub>: Distribution of silicides after age hardening. Etched micrograph (right figure) indicates grain sizes of 10 to 20 μm in rolling direction.

## 4. Results

### 4.1 Stress relaxation resistance (SRR)

Mechanical properties and electrical conductivity of investigated strips of Corson type alloys are summarized in table 1.

For precipitation hardened high strength Corson type alloys used for automotive devices the acceptable SRR is at least 70% of initial stress remaining after samples are exposed for 3000 hours at 150°C. The Mg-containing alloy CuNi<sub>2</sub>SiMg (C70250) as an example for the first generation of Corson type alloys used for connector materials meets this target at an initial stress in the magnitude of the yield strength as well as the Co-containing second generation CuNi<sub>1</sub>Co<sub>1</sub>Si (C70350). The initial stresses are 738 MPa for CuNi<sub>3</sub>SiMg, 751 MPa and 739 MPa for CuNi<sub>1</sub>Co<sub>1</sub>Si TM04 and TM06, respectively, and 670 MPa for CuNi<sub>3,9</sub>Co<sub>0,9</sub>Si<sub>1,2</sub>Mg<sub>0,1</sub>. As shown in Fig. 8 for 150°C with initial stresses of 70% or equivalent to the yield strength the SRR of C70250 expressed by the remaining stress after load time is higher compared to C70350 and the Hyper Corson alloy.

Between 1000 and 3000 hours of load the average loss of stress indicates a time dependence of 12 kPa/hour for C70250 and 7 kPa/hour for both C70350 tempers. This is a first hint for an improved SRR at higher temperatures for C70350 and Hyper Corson alloy. The advantage of the Co-containing alloy becomes more obvious at 200°C. Both temper designations of C70350 and the Hyper Corson alloy exhibit a strong SRR beyond 1000 hours of load compared to R690 of CuNi<sub>3</sub>SiMg (Fig. 8). An extrapolation to 10.000 hours forecast the total loss of initial stress for CuNi<sub>3</sub>SiMg, whereas for both CuNi<sub>1</sub>Co<sub>1</sub>Mg tempers stresses of 40 to 48 % of initial strength will remain. This is also valid for the Hyper Corson alloy with a remaining stress of 55% of initial strength. For example, between 1000 and 3000 hours time of load the averaged time dependent loss of initial stress is 52 kPa/h for CuNi<sub>3</sub>SiMg and only 7 kPa/h for all Co-containing alloys.

Advantages of Co-containing Corson alloy are revealed above 150 °C. One of the reasons for this behavior is the thermal stability of Co-containing silicides as predicted by binary phase

diagrams. In relation with necessary solution anneal temperature of pure  $\text{Co}_2\text{Si}$  an elevated temperature of 473 K (200°C) is 0,37 times of  $T_{\text{sol}}$  compared to 0,42 of  $\text{Ni}_2\text{Si}$ . More decisive is the distance in temperatures between solvus line and age hardening temperature with respect to the amount of cold roll prior age hardening. In case of Co-containing Corson alloys a larger number of small silicides is expected due to a very high solution anneal temperature.

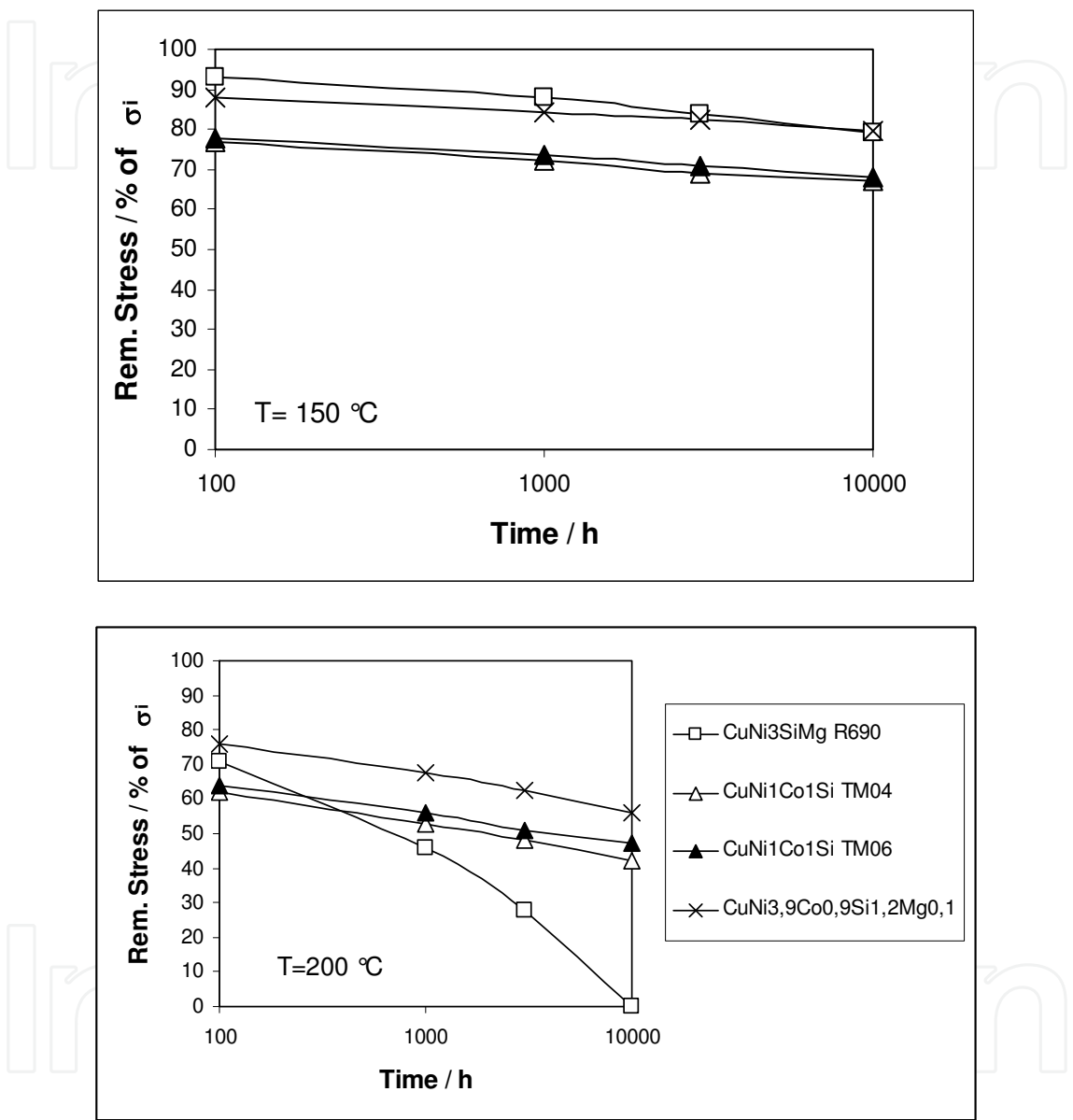


Fig. 8. Comparison of resistances against stress relaxation for temperatures 150 °C and 200 °C.

4.2 Fatigue behaviour

One of the most important properties for the functionality of copper-based connectors and springs is the ability to withstand repeated cyclic loads for many million cycles under bending-, push-pull or torsional loading conditions. The fatigue strengths of high-performance copper alloys exceed those of pure copper by up to several hundred MPa and are superior to those of non-hardened plain carbon steel, austenitic steels or at least equal

to quenched and tempered steels <sup>1</sup>. Fig. 9 gives an overview of the fatigue strength (endurance strength for 10<sup>7</sup> cycles) of several copper alloys.

Similar to other metallic materials and alloys, there is (for smooth, unnotched specimens) an empirical relationship between the fatigue strength and the tensile strength. Within the same chemical composition the fatigue strength rises with increasing tensile strength. The fatigue strength/tensile strength ratio strongly differs from alloy to alloy and is in the range of 0.25-0.55. The fatigue strengths of electromechanical connectors alloys such as CuSn8 and CuNi1Co1Si under reversed bending are in the range 300 - 450 MPa.

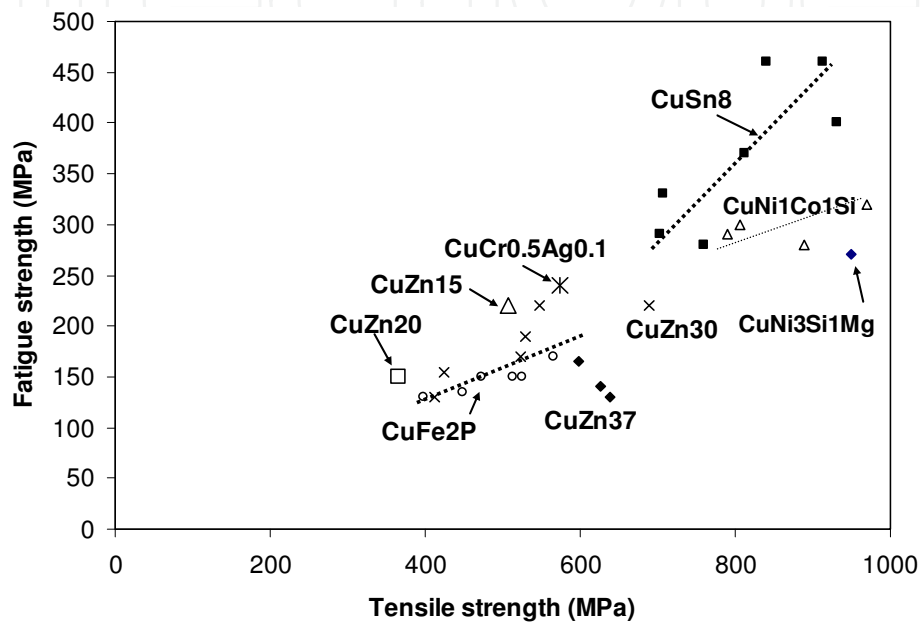


Fig. 9. Fatigue strengths of different copper-based alloys (fully reversed bending ( $R = -1$ ), samples: copper alloy strip of 0.3 to 0.6 mm thickness, loading transversal to rolling direction)

4.2.1 Fatigue of tin bronzes

Although non-precipitation hardened single phased  $\alpha$ -alloys (such as tin bronzes, e.g. CuSn8) are inferior to precipitation hardened copper alloys (such as CuNi1Co1Si) in respect to thermal stability of microstructure and stress relaxation behavior, they exhibit excellent fatigue strengths if they are sufficiently cold worked or hardened by grain refinement, (either by thermomechanical processing (Bubeck, 2007; Bubeck, 2008) or by severe plastic deformation). Fig. 10 shows the statistically evaluated stress-life (S/N) behaviour of CuSn8 in two different grain sizes, namely for average grain size of 20  $\mu\text{m}$  and for an average grain size of 1,5  $\mu\text{m}$ . It can be seen clearly, that the very-fine-grained condition shows a significantly higher fatigue life and -strength in the investigated Low Cycle Fatigue (LCF) as well as in the High Cycle Fatigue (HCF) regime.

Further fatigue strength enhancement, especially in the HCF-regime, can be achieved by ultrafine grained (UFG) or nanocrystalline material (Höppel, 2002). Grain refinement as a hardening mechanism is especially attractive in maintaining sufficient ductility for cold

<sup>1</sup> In the Very-High-Cycle (VHCF) fatigue regime (10<sup>8</sup>-10<sup>11</sup> cycles to failure ) the endurance strength of pure copper is clearly below 100 MPa (Weidner, 2010; Heikkinen, 2010)

forming processes. Very fine grained tin-bronze is thus characterized by an excellent combination of ductility and strength (Bubeck, 2007; Bubeck, 2008).

Typical crack initiation sites in high performance copper alloys are similar as in pure copper qualities, namely persistent slip bands (PSBs) at medium or high stress amplitudes, twin boundaries at low stress amplitudes [26] or grain boundaries or grain boundary triple points at high stress amplitudes. In addition, dislocation pile ups at precipitates or non-metallic inclusions may play a damaging role, especially in the VHCF-regime, below the threshold of PSB-formation.

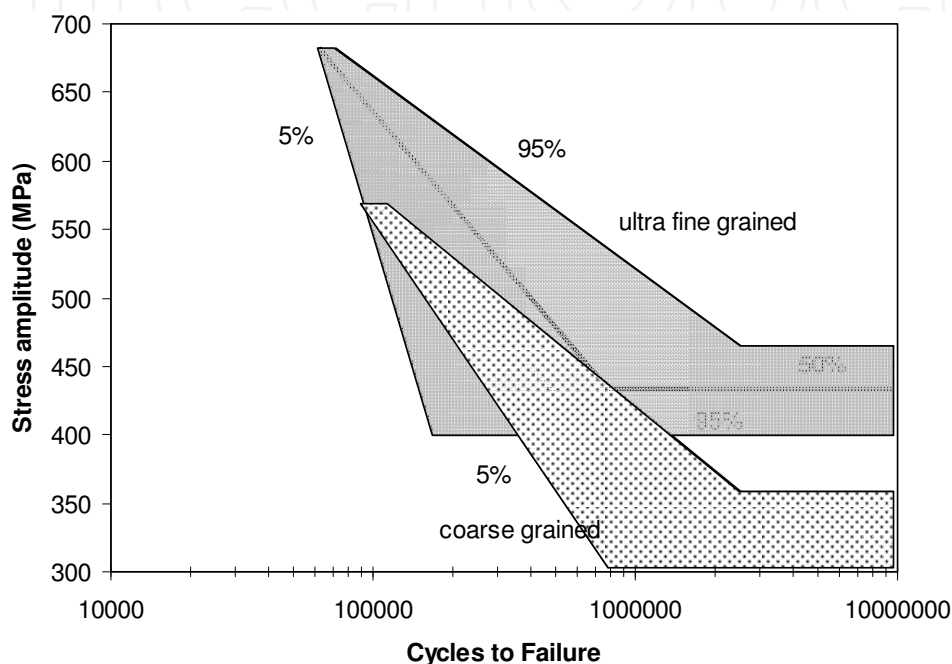


Fig. 10. Statistically evaluated S/N-curves (using arcsin $\sqrt{P}$ -method with 5%, 95% and 50% fracture probabilities) of CuSn8 for a conventional (15 microns) and a very fine grained (1-2 microns) material condition (bending fatigue,  $R = -1$ ,  $f = 18$  Hz),  $T = 22^\circ\text{C}$ .

Besides delaying the crack initiation phase, grain refinement in CuSn8 has been shown to reduce the fatigue crack propagation rate significantly for small cracks as well as for large cracks, as it was measured fractographically from spacing of striation widths on the fracture surfaces. The reduction of grain size reduces the crack growth rate for small cracks according to the slip band model (Tanaka, 2002). The reduced cyclic plasticity at the crack tip of very fine grained CuSn8 is reflected in different morphologies of the fracture surfaces of conventional and very fine grained CuSn8 (Fig. 11). The fine grained structure shows a rather smooth fracture surface with little crack tip blunting (see e.g. model by (Laird, 1962)) and less pronounced striations as in the coarser material condition.

The role of twinning for mechanical and thermal properties of high performance copper alloys remains controversial. On the one hand twin boundaries are known to be one of the preferential regions for fatigue crack initiation especially during High-Cycle-Fatigue (Bayerlein, 1991). On the other hand they can enhance the thermal stability of ultrafine grained (UFG) materials (Anderoglu, 2008) and act as weak obstacles to dislocations (Qu & Zhang, 2008). Moreover, deformation twinning can act as a supplementary mechanism to

enhance ductility, formability and bendability. The density of twins can be controlled by adjusting the grain size and the stacking fault energy of the alloy: The density of deformation twins decreases with decreasing grain size and the (largely grain-size insensitive) density of recrystallization twins increases with decreasing stacking fault energy (Vöhringer, 1972; Vöhringer, 1976).

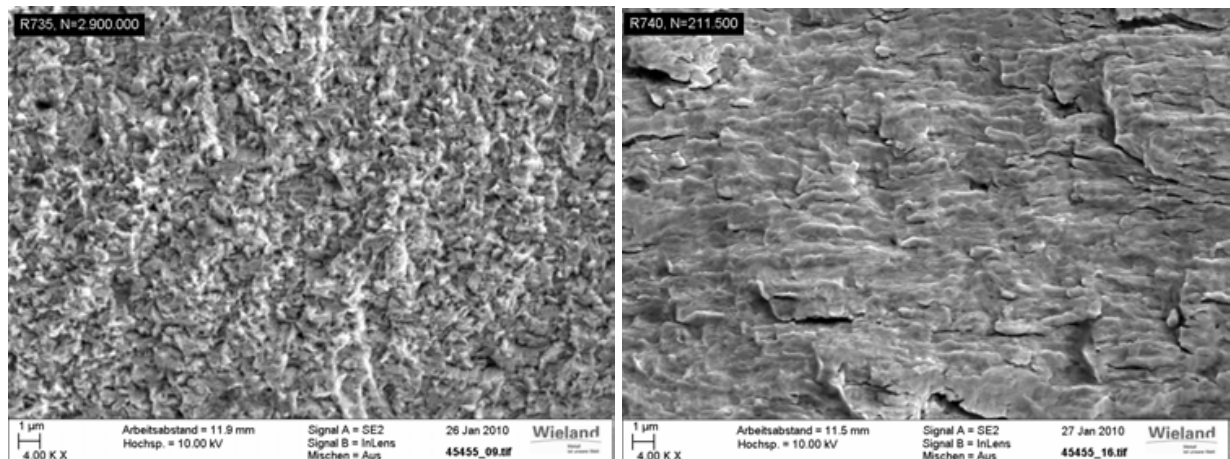


Fig. 11. SEM-micrograph of the fracture surface of fatigued CuSn8 (left: very fine-grained, right: coarse-grained condition)

Fig. 12 shows an Orientation Imaging Microscopy (OIM) picture obtained by Electron Backscatter Diffraction (EBSD) of conventional and very fine grained CuSn8. The coarse-grained CuSn8 exhibits significantly more twin boundaries (characterized by a 60°-misorientation between adjacent grains or a coincident site lattice (CSL) number of  $\Sigma = 3$ ) than the fine grained conditions (compare Figs. 13 and 2). The optimization of the nature, density and location of twins for enhanced mechanical behavior of high performance copper alloys remains a challenging task within grain boundary engineering (Randle, 1999).

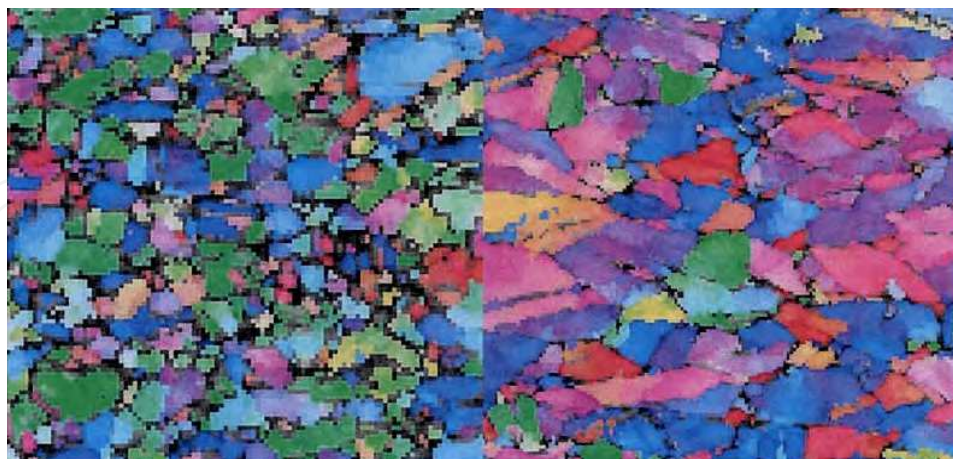


Fig. 12. OIM (Orientation Imaging Microscopy)-picture (obtained by EBSD) of coarse grained (right) and fine grained CuSn8 (left) prior to final cold rolling. Cu-type orientation is represented by blue coloured grains, Goss-type by green coloured grains<sup>2</sup>

<sup>2</sup> Calculations of Schmid- and Taylor-factors gave similar factors for both fine- and coarse-grained conditions in the order of  $\sim 2.8$

#### 4.2.2 Fatigue of precipitation hardened alloys

A combination of high fatigue strength and excellent stress relaxation stability and thermal stability can be achieved with precipitation hardened copper alloys such as CuNi1Co1Si (see also Fig. 9) or CuNi3Si1Mg. Optimized precipitation hardening promotes fatigue strength as well as high electrical conductivity. The high fatigue strength in Corson- or Corson-derived alloys is principally derived from Ni- or Co-Silicides (Lockyer, 1994) as well as Ni-Co mixed silicides which are orthorhombic and semicoherent with the  $\alpha$ -Matrix and serve as dislocation obstacles according to the well-known Orowan-mechanism (Orowan, 1933; Ardell, 1985). Fig. 13 shows precipitates in the fracture surface of fatigued CuNi1Co1Si.

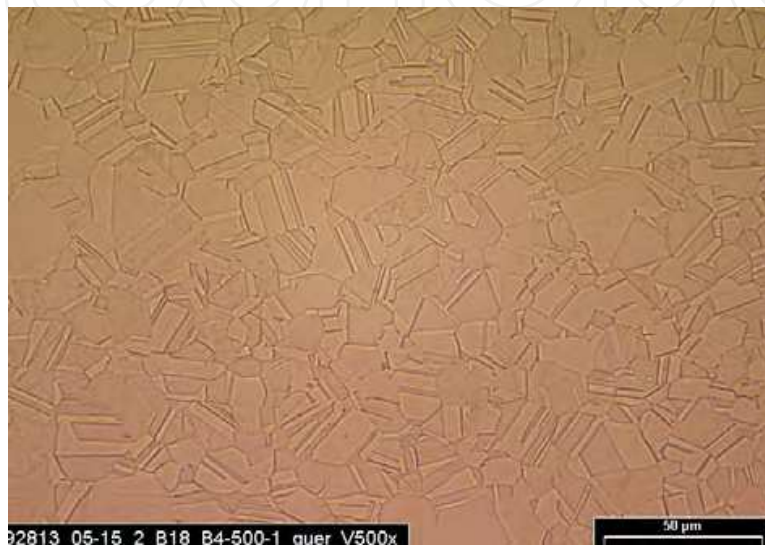


Fig. 13. Microstructure of conventionally processed CuSn8 with 2-4 twins per grain.

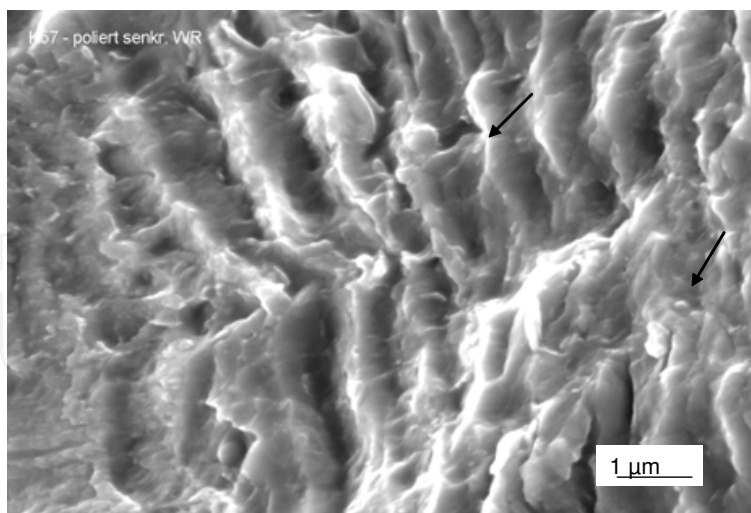


Fig. 14. Fatigue fracture surface of a spring (material: CuNi1Co1Si) exhibiting striations and precipitates (arrows).

The slopes of the fatigue strength dependence of the tensile strength as presented in Fig. 9 differ between solid solution hardened one phase CuSn8 and all precipitation hardened Corson-type alloys. The flat slope of precipitation hardened alloys can be explained by the interaction between moving dislocations and non-shearable semi coherent particles. This

mechanism may cause micro cracks around the second phases as shown in fig. 15 for CuNi1Co1Si. Due to differences in Young's modulus ( $E_{\text{Matrix}} : \sim 130 \text{ GPa}$ ,  $E_{\text{Silicide}} : \sim 160 \text{ GPa}$  (Lockyer, 1995)) additional localized strain gradients were generated. Elastically deformed particles generate residual stresses and geometrically necessary dislocations.

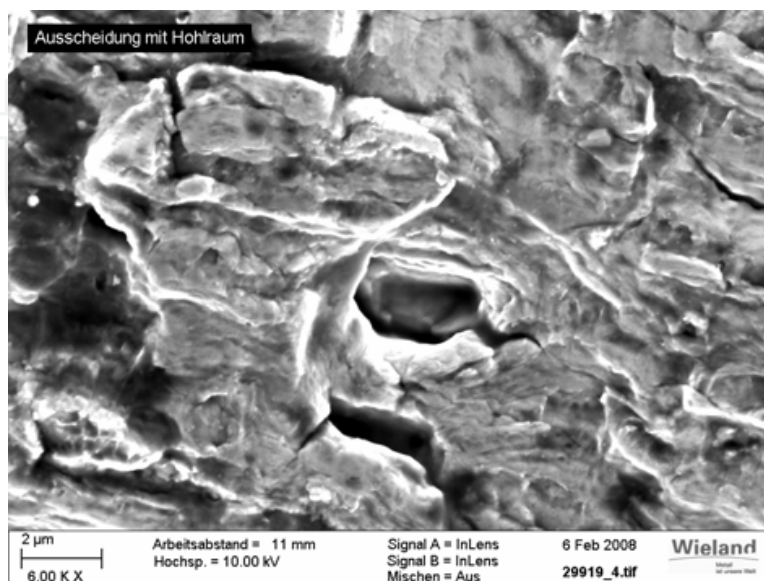


Fig. 15. Fatigued strip of CuNi1Co1Si TM04: Formation of cracks in the interface between matrix and (Ni,Co)-silicide.

#### 4.3 Modulus of resilience

The elastic behaviour of electromechanical connector materials is of utmost importance since they, besides conducting electric current, act as springs. In order to maintain their grip during service the connectors have to exert high elastic forces onto their elastic contact partner, ideally without any time- or temperature-dependent stress relaxation.

The ability of a component to store elastic energy is described by the *modulus of resilience*. Springs with a high resilience can store and release (upon unloading) a lot of elastic energy, springs with a low resilience can store and release only little elastic energy. In a stress-strain-plot the modulus of resilience of any material is defined as the area under the stress-strain curve (or *strain energy density*) up to the elastic limit (yield strength) of the material (Fig. 1). The modulus of resilience rises with increasing yield strength and with decreasing Young's modulus.

Fig.16 shows the modulus of resilience for several copper alloys including electromechanical connector alloys CuNi3SiMg and CuNi1Co1Si. The modulus of resilience of electromechanical connector alloys is in the range of 0.8-3.5 MPa (depending on the strength and temper condition, see also (Kuhn, 2007)). Finally, in respect to resilience only, a perfect copper-based spring would be made from metallic glass (such as  $\text{Cu}_{47}\text{Ti}_{34}\text{Zr}_{11}\text{Ni}_8$ ). Unfortunately, the electrical and thermal conductivity of bulk metallic glasses are rather low. Conversely, composites consisting of metallic glass and a pure copper or copper alloy with high conductivity could offer interesting solutions for high strength-high conductivity applications (Choi-Yim, 1998).

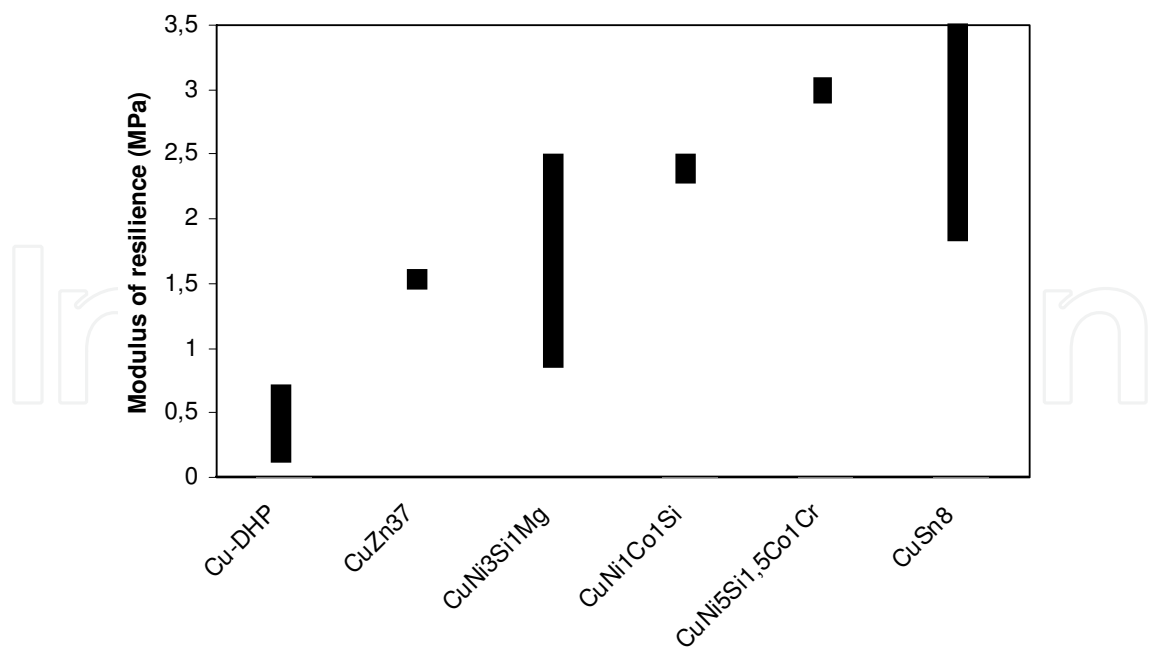


Fig. 16. Modulus of resilience for several copper alloys.

It should be noted that the modulus of resilience is temperature- and orientation- and therefore texture-dependent. In strips exhibiting a typical rolling texture, a high modulus of resilience can be found perpendicular and parallel to the rolling direction, whereas in angles in between these orientations lower values for the modulus of resilience are observed (Fig. 17).

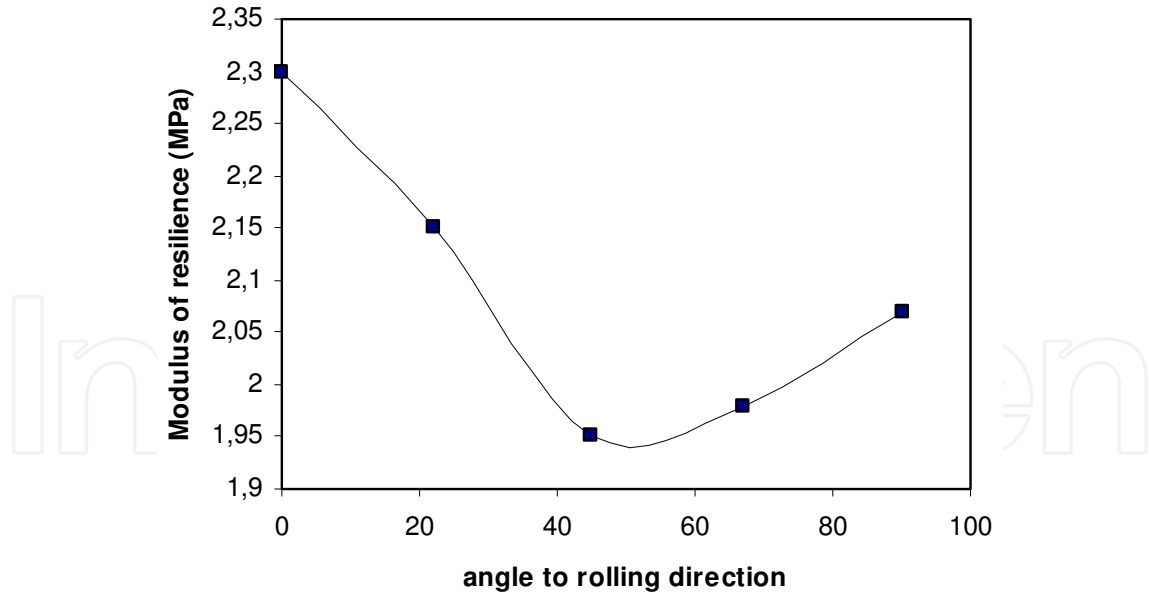


Fig. 17. Modulus of resilience of CuNi3Si1Mg in different angles to the rolling direction of a strip.

5. Conclusions

Modern Cu-based electromechanical connector alloys are characterized by a significant improvement of stress relaxation resistance in the temperature range 150°C - 200°C as

compared to classical Corson-type alloys (containing only nickel-silicides) of the first generation. The main microstructural reason for this superiority is the precipitation of finely dispersed mixed Co-Ni-silicides. Due to the high undercooling during quenching of the solution treated condition the nucleation of nanoscale (Co,Ni)<sub>2</sub>Si is enhanced. Transmission electron microscopy studies revealed precipitate diameters of < 10 nm which is assumed to be in the order of the maximum hardening contribution by precipitates. A statistical investigation of precipitate sizes and their correlation to Co-content and thermomechanical process steps therefore seem to be promising to further evaluate the potential of the Cu-Ni-Si-Co system.

High alloyed Hyper-Corson alloys containing alloying elements > 5 mass% exhibit excellent mechanical properties and therefore appear to be an attractive class of materials to replace Cu-Be alloys.

In contrast to precipitation hardened copper alloys of similar strength, single-phased fine grained and solid solution hardened tin bronzes are able to withstand higher cyclic loads in fatigue tests. It is assumed that the less pronounced strength-dependency of the fatigue strength of precipitation hardened CuNiSi alloys can be attributed to internal stress raisers in the microstructure, e.g. generation of micro cracks on the phase boundary between precipitate and matrix due to deformation incompatibilities and increased stress by pile ups of dislocations.

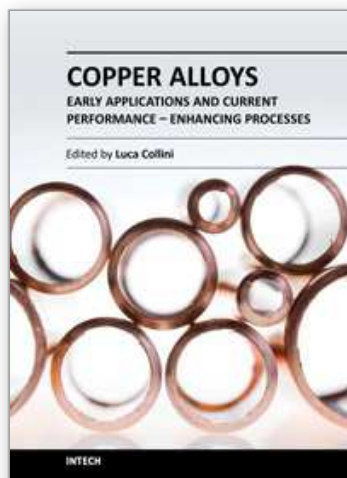
Fatigue investigations have revealed that significant grain refinement of tin bronze leads to superb fatigue strength. The grain refinement goes hand in hand with a reduction of twin density, which on the other hand reduces the number of possible crack initiation sites.

For spring applications, a high modulus of resilience is predominantly achieved by high yield strength. High strength Co-containing Corson-type alloys can therefore compete with CuSn8 inspite of lower Young's modulus.

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## **Copper Alloys - Early Applications and Current Performance - Enhancing Processes**

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Copper has been used for thousands of years. In the centuries, both handicraft and industry have taken advantage of its easy castability and remarkable ductility combined with good mechanical and corrosion resistance. Although its mechanical properties are now well known, the simple f.c.c. structure still makes copper a model material for basic studies of deformation and damage mechanism in metals. On the other hand, its increasing use in many industrial sectors stimulates the development of high-performance and high-efficiency copper-based alloys. After an introduction to classification and casting, this book presents modern techniques and trends in processing copper alloys, such as the developing of lead-free alloys and the role of severe plastic deformation in improving its tensile and fatigue strength. Finally, in a specific section, archaeometallurgy techniques are applied to ancient copper alloys. The book is addressed to engineering professionals, manufacturers and materials scientists.

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Phone: +86-21-62489820  
Fax: +86-21-62489821

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