Ultrafine-Grained High Strength Cu-Ni-Si Alloys

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Abstract. Ultrafine-grained (UFG) pure copper has been in the focus of materials scientists over the last two decades, however ultrafine-grained high-strength copper alloys have scarcely been processed or characterized so far industrially.

In this contribution, UFG copper alloys, especially Cu-Ni-Si alloys, being well known as ideal materials for electromechanical connectors, springs and leadframes, are presented. 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. Yield strength and fatigue properties of metallic alloys can be significantly enhanced by severe plastic deformation methods. 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. Characterization of these materials after severe plastic deformation by swaging, wire drawing and subsequent aging was carried out using conductivity-, hardness- and tensile tests as well as highly-resolved microstructural characterization methods.

The results reveal that UFG low alloyed copper alloys exhibit impressive combinations of properties such as strength, conductivity, high ductility as well as acceptable thermal stability at low and medium temperatures. 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.

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 [1,2]. In contrast to other strengthening methods such as solid solution hardening, severe plastic deformation leads only to a weak decrease of 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 can be further enhanced and thermal stability can profit from grain-boundary pinning by precipitated nanoscale nickel silicides.

Similar to Equal Channel Angular Pressing (ECAP), swaging (or rotary swaging) and subsequent precipitation hardening is a simple method for producing ultra fine grained precipitation hardened copper alloys. Swaging is suitable for producing continuous semi-finished materials such as wires.

Fig. 1: Uncorrected EBSD-mapping (Euler angles) of ultra-fine grained CuNi₃Si₁Mg

Fig. 2: High- and low-angle grain boundaries in ultrafine-grained CuNi₃Si₁Mg (grain boundaries reconstructed)

Results and discussion

Figs. 1 and 2 exhibit the grain structure of ultra fine grained CuNi₃Si₁Mg as obtained by electron backscattering diffraction (EBSD) in the scanning electron microscope (SEM). Optimized severe plastic deformation of wires by swaging with sufficiently high cold work leads to ultra fine grained microstructures exhibiting grain sizes of 0.2 to 0.5 microns after peak aging at 450°C/1h. It can be confirmed by misorientation measurements using EBSD that the observed grain boundaries in swaged CuNi₃Si₁Mg (UNS-designation 70250) wire (diameter 2,7 mm) are in fact high-angle grain boundaries (misorientation between adjacent grains > 10°). In addition, within the ultra fine grains some low-angle grain boundaries (red colour, Fig. 2) can be detected by EBSD.

Through a combination of swaging and optimized precipitation hardening, an ultra fine grained precipitation hardened grain structure can be generated with nanoscale Ni-silicide precipitates situated predominantly at or near grain boundaries (Fig. 3), thus pinning the grain boundaries and enhancing the thermal stability at elevated temperatures. The mechanical properties of ultra-fine grained CuNi₃Si₁Mg are clearly superior to coarse-grained conditions, i.e. a significant improvement of the elongation to fracture from 7% to 14% was measured for the ultra fine grained microstructure as compared to the condition with the conventional grain size [3].

Fig. 3: Electron Channeling Contrast Imaging (ECCI)-picture of ultrafine grained CuNi₃Si₁Mg in the peak-aged condition exhibiting nanoscale Ni₂Si-precipitates at grain boundaries

Eventually, tensile strengths of 900-1000 MPa (hardness of 250-280 HV₁) are routinely possible for Cu-Ni-Si alloys, if subsequent swaging, precipitation hardening and cold work (e.g. by wire drawing) are applied (Fig. 4). For thin Cu-Ni-Si-wires, after drawing, more than 50 % of the hardening is ascribed to precipitation hardening, the remaining hardening effect is almost evenly distributed between Hall-Pech-hardening and work hardening. Compared to conventional strip material, the strength increase by ultrafine grains is only moderate (Fig. 4). This is due to the fact, that in severely cold rolled conventional strip also a high density of subgrain boundaries in addition to work hardening is created, which also leads to effective dislocation obstacles. On the other hand, the UFG structure is affiliated with superior ductility as compared to conventional strip, i.e. in 7mm swaged wires elongations to fracture of 14% at tensile strengths of 850 MPa were measured.

Higher nickel contents or the addition of chromium lead to additional hardening as demonstrated for the alloy CuNi₇Si₂Cr. In contrast to high strength single phased bronzes, the electrical conductivity of Cu-Ni-Si alloys remains attractive and typically exhibits values of 30-35% IACS after swaging. It is important to note, that every copper alloy requires specific optimized swaging conditions, i.e. CuNi₃Si₁Mg exhibits the highest hardness increase after swaging with a logarithmic strain of 2.5. In terms of hardness, increasing cold work leads to a saturated condition or even softening (Fig. 5).

Fig. 6 shows the change of electrical conductivity of the swaged and non-swaged condition during aging at 450 °C. Owing to continuous diffusion of alloying elements Ni and Si from the solid solution copper matrix into the precipitates, the scattering of electrons by the strain fields of solute atoms is diminished and the conductivity increases. It is noteworthy, that already after 10 minutes the conductivity of the swaged condition is slightly higher than the conductivity of the non-deformed condition at this temperature. Obviously, the diffusion of solute elements is significantly accelerated by fast diffusion paths such as high- and low angle boundaries which are prevalent in the swaged condition. Throughout the further aging process the electrical conductivity

of the swaged condition stays superior to the conductivity of the non-deformed condition [4,5]. This difference amounts up to 8% IACS in severely over-aged specimens, possibly being caused also by recrystallization which drastically reduces the grain boundary area in the swaged and severely over-aged condition. For comparison, standardized commercial CuNi3Si1Mg strips typically have electrical conductivities of 35-45 % IACS.

In addition to excellent quasistatic strength, optimized swaging plus consecutive aging leads to a marked increase of the 10^7 -fatigue endurance strength [4]. Moreover, if swaged and subsequently aged CuNi3Si1Mg is additionally mechanically surface treated (by shot peening, laser-shock peening or deep rolling), the fatigue endurance strength exceeds 400 MPa. The only copper alloys exhibiting higher strengths than Cu-Ni-Si alloys are high-alloyed or spray-formed copper alloys and Cu-Be alloys [6,7,8]. Minor improvements of strength in Cu-Ni-Si alloys can also be achieved by additions of Cr, Al or Ti [9,10].

Fig. 4: Tensile strength and electrical conductivity of ultra-high-strength Cu-Ni-Si alloys

Fig. 5: Effect of deformation degree on Vickers hardness of swaged CuNi3Si1Mg (prior to swaging, rods were hot extruded and solution treated at 800 °C/2 h)

Fig. 6: Conductivity vs. aging time for swaged (UFG) and coarse-grained CuNi3Si1Mg ($T = 450\text{ }^{\circ}\text{C}$)

Summary

Rotary swaging is a very efficient processes to generate high strength through ultra fine grains, especially if it is combined with precipitation hardening. Thus Cu-Ni-Si materials with very fine grain sizes in the range $0.2\text{--}2\text{ }\mu\text{m}$ can be produced. EBSD and electron channeling contrast in the SEM are very helpful tools to characterize such microstructures [11].

Swaging and accumulative roll bonding, typically lead to a maximum hardness at a logarithmic strain or deformation degree of 2.5 and 5, respectively.

Severely plastically deformed (swaged or accumulative roll bonded) and subsequently precipitation hardened Cu-Ni-Si-Mg alloys show only slightly earlier thermal softening than conventionally processed microstructures of Cu-Ni-Si alloys. The thermal stability of ultra fine grained CuNi3Si1Mg is significantly enhanced as compared to pure copper. Grain boundary pinning by nanoscopically small precipitates is suggested as the beneficial mechanism.

A crucial role is ascribed to the artificial aging treatment after the severe plastic deformation. At $300\text{ }^{\circ}\text{C}$ no over-aging was detected within 200 hours. For short time exposure (1 h) the grain structure is fairly stable up to $400\text{ }^{\circ}\text{C}$. In addition to enhanced ultimate tensile- and yield strength (with possible tensile strength $> 1000\text{ MPa}$ for CuNi7Si2Cr), also the fatigue behavior in the High Cycle Fatigue (HCF)-regime was significantly improved by the UFG-structure in the swaged plus peak-aged condition close to the surface.

It should be emphasized that Cu-Ni-Si-(Cr) alloys, whether ultrafine-grained or just fine-grained, are not genuine CuBe2-replacements, since they are unable to reach tensile strengths of $1400\text{--}1600\text{ MPa}$. The stress relaxation resistance of Cu-Ni-Si alloys is excellent and almost at the same level than Cu-Be2. However, their metal prices are significantly lower than for CuBe2 or CuBe2CoNi. In addition, in their strongest points, namely high conductivity at high strength, high ductility and bendability, as well as high fracture toughness, Cu-Be alloys have a tough stand to compete with them. Due to these properties, for many applications, Cu-Ni-Si-(Cr) alloys are the better alternative to the less ductile and less conductive CuNi15Sn8 to “replace” Cu-Be alloys.

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