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# Thermal stability of functional properties in dispersion and precipitation hardened selected copper alloys

**J.P. Stobrawa [a,b,*], Z.M. Rdzawski [a,b]**
[a] Division of, Materials Processing Technology, Management and Computer Techniques
in Materials Science, Institute of Engineering Materials and Biomaterials,
Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Non-Ferrous Metals Institute, ul. Sowińkiego 5, 44-100 Gliwice , Poland
* Corresponding author: E-mail address: jerzys@imn.gliwice.pl

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## ABSTRACT

**Purpose:** The objective of the study was to produce copper-based dispersion hardened materials of submicron grain size, determination of their basic functional properties and stability in high temperature, as well as comparison of those properties with properties of selected precipitation hardened copper alloys made by classical method of melting, casting and thermomechanical processing.

**Design/methodology/approach:** The examination was conducted on copper hardened with WC, $Y_2O_3$ and $Cr_3Si$ particles and on precipitation hardened copper alloys with addition of Cr and Ni, Si, Cr. The examination of the materials covered changes in hardness, electrical conductivity and stabilities of those properties after various heat treatment options.

**Findings:** Assuming the tendency to softening depending on annealing temperature to be as a criterion of properties stability, temperature ranges of individual alloys applications were determined

**Research limitations/implications:** The study could be supplemented with information on tendencies to high-temperature creep in the examined alloys

**Practical implications:** The materials are used for components operating in high-temperature conditions, such as components of crystallizers for continuous casting of metals, electrodes for welding, in nu clear reactors, etc.

**Originality/value:** The originality lies in examination of dispersion hardened materials (especially Cu – $Cr_3Si$) of controlled submicrometric structure obtained from initial nanocrystalline structure.

**Keywords: Nanomaterials; Functional materials; Metallography**

## MATERIALS

## 1. Introduction

The materials which are dispersion hardened with particles of metals, oxides, carbides, intermetallic compounds and others are among those of copper based materials group which are more and more widely used for applications in high-temperature conditions. They are usually produced by combination of powder metallurgy methods and controlled hot and cold deformation processes [1-4]. Those materials present good electrical and thermal conductivity, while their mechanical properties and stability in high temperature changes significantly with matrix grain size and depends on the type, volume fraction and dispersion of hardening particles. Those issues became a subject of growing number of studies in the last years [5-10]. Special interest is focused on examination of materials of nano- and ultrafine grain size. Powder metallurgy technique (using intensive milling of powders mixtures in planetary mills) is efficient method for obtaining nanometric structure in copper-based dispersion hardened materials. The studies proved that application of controlled sintering results in formation of a structure which can be stable in high-temperature [11]. The disadvantage of sintered nanocrystalline materials is their low density and tendency to form a globular structure [12 - 15]. In the result mechanical properties of sintered materials are significantly lower than theoretically expected [12, 15]. Application of [13, 14] cold or hot deformation brings significant improvement in density (up to almost 100% of theoretical density). The combined influence of deformation and temperature, however, leads to destabilization of nanostructure and formation, depending on temperature and rate of deformation, of a structure ranging from ultrafine grain to microcrystalline.

The objective of the study was to produce copper-based dispersion hardened materials of submicron grain size, determination of their basic functional properties and stability in high temperature as well as comparison of those properties with properties of selected precipitation hardened copper alloys made by classical method of melting, casting, and thermomechanical processing. For the studies, copper hardened with yttria, tungsten carbide and $Cr_3Si$ phase particles were chosen from the group of dispersion hardened materials, while from the group of precipitation hardened materials CuCr0.8 and CuNiSiCr alloys were selected.

## 2. Experimental procedure

The dispersion hardened copper based materials containing 2 wt % of strengthening phase ($Y_2O_3$, WC and $Cr_3Si$) were obtained by powder metallurgy technique, i.e. milling the input powders in the planetary ball mill, compacting and sintering. The mixtures of powders of electrolytic copper and strengthening phase were subjected to milling in a ball planetary mill (250 ml containers with 50 balls 10 mm in diameter, the weight ratio of milling media to powder was about 5:1). The optimal parameters of the process, suitable to obtain nanometric size of the powder grains, were established: rotary speed of 250 rev/min and milling time – 30 hours. Milling was performed in the atmosphere of argon and methanol. From the obtained powder mixtures samples were compacted for density, hardness and electrical conductivity measurements (Φ30x4 mm) and for extrusion (Φ10x30 mm). The green compacts were sintered at 550 – 570 $^{o}$C for 1 hour.

Precipitation hardened CuCr0.8 and CuNi3Si1Cr0.9 alloys were produced by classical method of melting, casting and plastic working. Ingots of cross-section 20x112 mm were subjected to hot deformation. Hot rolling of ingots into strips of 3 mm thickness was conducted from temperature of 950 $^{o}$C. To define optimal properties of those alloys they were subjected to quenching and ageing. The quenching was conducted from temperature of 1000 $^{o}$C (1 hr) in water, while the ageing in the wide ranges of temperature and time (450 – 600 $^{o}$C, 0.5 - 8 hours.).

For extrusion the Instron 10 T machine was adopted. After extrusion (550 $^{o}$C) the samples diameter was 3 mm. Hardness of the samples was determined by Vickers technique, and electrical conductivity with Foerster Sigmatest. Changes in hardness of the materials in the process of their annealing in the temperature range 550 – 700 $^{0}$C in the period of 1 hour were considered as a criteria of properties stability. Microstructure of sintered and extruded samples was examined using JEM 2000 FX transmission electron microscope.

## 3. Results and discussion

The microstructures of particle reinforced copper after sintering and hot extrusion are showed in Fig. 1. All the sintered materials (Fig. 1a, b, c) have fine grained matrix. The size of majority of grains is below 100 nm. Particles of the hardening phases are evenly distributed in the matrix. Their average size is between 10 and 20 nm (marked with arrows in Fig. 1).

Microstructure examinations and density measurements (table 1) showed that the materials after sintering present high porosity (density not exceed 90% theoretic ones). Using powder materials, especially nanocrystalline materials, it is very difficult to obtain samples of low porosity and strongly bound particles. As it was proved in the earlier studies, agglomeration of nanocrystalline particles which are difficult to be broken during pressing and sintering constitute a serious problem. In the result empty spaces form between agglomerates and density is low.

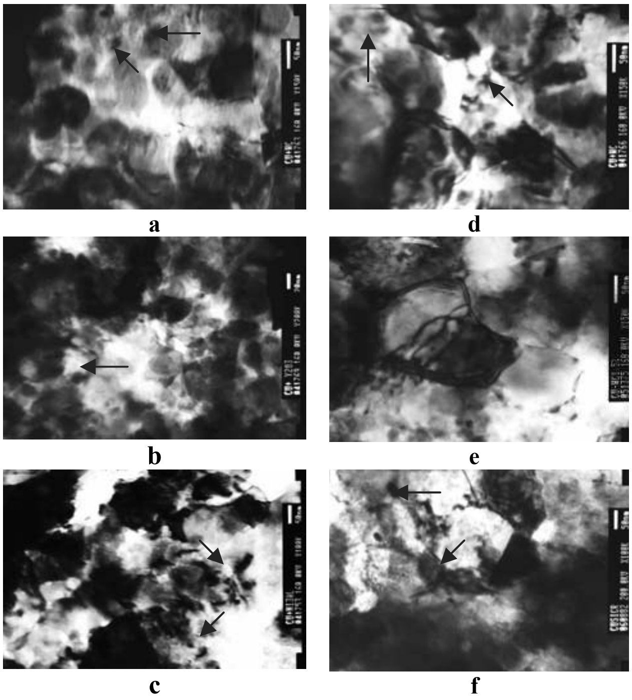

Fig. 1. Microstructure of sintered (a, b, c) and hot extruded (d, e, f) samples of dispersion hardened copper: a, d) – Cu-WC, b, e) - Cu-$Y_2O_3$, c, e - Cu-$Cr_3Si$. The arrows indicate particles of hardening phases

Basic functional properties of investigated materials are presented in Table 1. Despite nanocrystalline grain size, hardness of those materials rarely exceeds 85 HV. Such a result cannot be explained by a fact of reaching reverse Hall-Petch effect. That effect, being a consequence of a change in deformation mechanisms in nanocrystalline materials, is observed in the materials where grain size is below 20 nm. Therefore it can be assumed that relatively low hardness of nanocrystalline copper based dispersion hardened materials, as it was established in the earlier studies [12, 15], results from porosity and influence of nanometric grains agglomerates on deformation mechanism. Low electrical conductivity is also a result of high porosity [Table 1].

Table 1.
Basic functional properties of investigated materials after sintering and after hot extrusion (550 $^{o}$C)

| Material | Sintered | | | Hot deformed | | |
|---|---|---|---|---|---|---|
| | density [g/cm$^3$] | HV | γ [MS/m] | density [g/cm3] | HV | γ [MS/m] |
| Cu – WC | 7.62 | 77 | 21.16 | 8.94 | 115.3 | 42 |
| Cu -$Y_2O_3$ | 7.53 | 81 | 23.845 | 8.79 | 112.9 | 38.7 |
| Cu-$Cr_3Si$ | 7.69 | 87 | 43.5 | 8.86 | 122.2 | 46.7 |

As established in the earlier studies [11], nanometric grain size in the dispersion hardened copper based materials is rather stable in high temperature. The stability, however, can be disturbed in the hot deformation processes, so in the result of recrystallization taking place in controlled hot extrusion processes ultrafine grain size and more advantageous functional properties can be obtained. Figure 1 d, e, f presents microstructures of samples after hot extrusion in temperature of about 550 $^{o}$C. Matrix grain size is in the range 150 – 300 nm, while hardening phases particle size remains in the range of 10 to 20 nm.

Functional properties of the materials are presented in Table 1. They are much more advantageous than properties of sintered materials. Density is close to the theoretical one and the hardness is higher by 40 % in the case of Cu -$Y_2O_3$ and Cu-$Cr_3Si$ or even by almost 50 % in the case of Cu – WC. The electrical conductivity is also higher. The especially high increase of electrical conductivity was obtained for Cu – WC and Cu - $Y_2O_3$ materials. The Cu-$Cr_3Si$ material presented high electrical conductivity already after sintering so in that case the increase was considerably smaller.

The presented above results indicate the advantageous influence of the controlled hot working on properties of dispersion hardened copper alloys of initial nanocrystalline matrix and nanoscaled dispersoids. There is, however, another important issue, i.e. how stable in elevated and high temperatures are the obtained properties, especially hardness, and whether (and in what scope) the obtained materials can compete in high temperature applications with precipitation hardened copper alloys. Therefore, comparative studies of softening of those materials were conducted, in which changes of hardness after 1 hour of annealing in the temperature range 500 – 650 $^{o}$C were considered as the softening criterion. Three alloys were selected for comparison, representing groups of alloys of high, medium and low electrical conductivity and of average and high hardness, respectively. Table 2 presents the properties obtained in those alloys after ageing until the hardness peak was reached. The hardness range was 130 – 236 HV and electrical conductivity was 14 – 52 MS/m. Samples of the alloys representing those properties were used for comparison in the tests of softening.

Table 2.
Properties of precipitation hardened alloys after ageing to peak hardness

| Material | Heat treatment | HV | γ [MS/m] |
|---|---|---|---|
| CuCr0.8 | Quenching:<br>1000 $^{o}$C, 1hr, water<br>Ageing: 500 $^{o}$C / 0,5 hr | 130 | 52 |
| CuNi2Si0.3Cr0.3 | | 196 | 25 |
| CuNi3Si0.7Cr0.6 | | 236 | 14 |

Figure 2 presents results of examinations of changes in hardness of dispersion and precipitation hardened materials depending on annealing temperature. The results of electrical conductivity measurements of the samples annealed in the same conditions are also presented (Fig. 3).

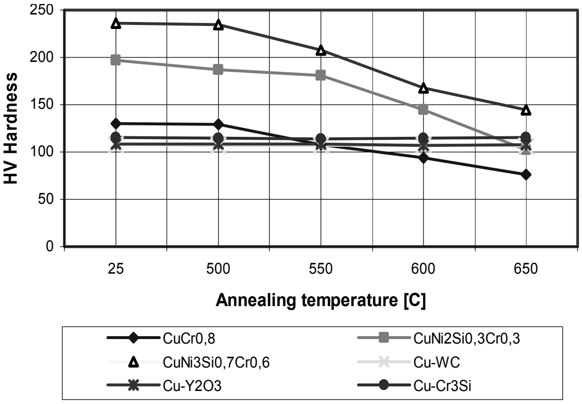

Fig. 2. Changes in hardness HV with annealing temperature; annealing time 1 hour

After comparing properties of the developed materials with comparable properties of precipitation hardened copper alloys it can be established that stability of mechanical properties in precipitation hardened materials is distinctly lower. Significant decrease in hardness is observed already after annealing in the temperature higher than 500 $^{o}$C. After annealing in the temperature of 600 $^{o}$C the decrease in hardness of CuCr0.8 alloy is about 30% and after annealing in the temperature of 650 $^{o}$C it is about 40%. In the result, after annealing in the temperature higher than 550 $^{o}$C, hardness of the dispersion hardened materials is distinctly higher than hardness of CuCr0,8 alloy, while maintaining at the same time electrical conductivity at the level of 39 – 46 MS/m (67 – 79% IACS).

CuNiSiCr alloys start softening also in the temperature higher than 500 $^{o}$C. CuNi2Si0.3Cr0.3 alloy reaches the hardness of dispersion hardened materials after annealing in the temperature range 525 – 550 $^{o}$C, however its electrical conductivity is significantly lower (about 20 MS/m). Hardness of CuNi3Si0.7Cr0.6 alloy annealed in similar conditions is significantly higher.

Further tests of hardness of that alloy proved, however, that after long-lasting annealing in the temperature of 650 $^{o}$C the hardness becomes close to the hardness of dispersion hardened materials. For example, after 8 hours of annealing the hardness of the alloy falls down to the level of 125 HV while maintaining low electrical conductivity (at the level of 14 – 16 MS/m).

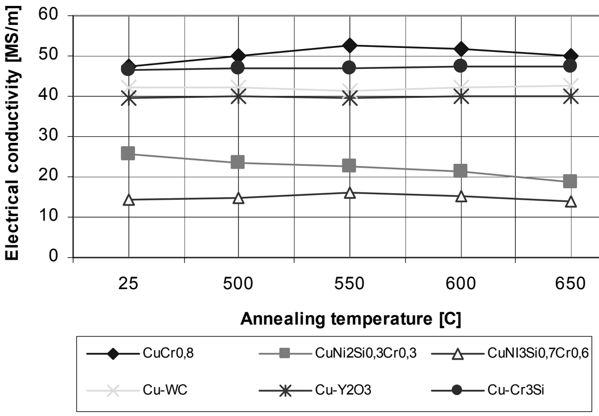

Fig. 3. Changes in electrical conductivity with annealing temperature; annealing time 1 hour

## 4. Conclusions

Basing on the obtained results the following conclusions can be drawn:

- When using controlled process of hot deformation of sintered semi-products of initial nanocrystalline structure it is possible to produce materials of submicron copper matrix dispersion hardened with nanoscaled particles WC, $Y_2O_3$ and $Cr_3Si$.
- Such materials, which contain about 2% of hardening phase, present good hardness (at the level of 115-120 HV) and electrical conductivity (at the level of 40-50 MS/m).
- The important advantage of those materials is high temperature stability of those properties in elevated and high temperatures. The conducted comparative studies of functional properties of those materials and properties of precipitation hardened alloys indicate their advantage in applications for components operating in high (550 – 650 $^{o}$C) temperature as well as in changing conditions of thermal or mechanical current load.

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