EFFECT OF HEAT TREATMENT ON MICROSTRUCTURE, PROPERTIES AND THERMAL CONDUCTIVITY OF CUNI3SI ALLOY

Peter Sláma, Petr Motyčka

COMTES FHT a.s., Průmyslová 995, 334 41 Dobřany, Czech Republic, peter.slama@comtesfht.cz

Abstract
This paper deals with the influence of heat treatment (annealing, quenching, and aging) on the microstructure and mechanical properties of CuNi3Si alloy. CuNi3Si alloy is used in applications, where high electrical conductivity, thermal diffusivity and good mechanical properties are important.

Heat treatment has profound impact on mechanical properties, as well as on electrical conductivity and thermal diffusivity. For this study, specimens were subjected to various heat treatment schedules and examined in light and scanning electron microscopes. Their mechanical properties were measured by hardness testing using Vickers scale. Thermal diffusivity was measured using laser flash method in LFA 1000 instrument made by LINSEIS GmbH. Hardness of the specimens ranged from 70 to 250 HV10. Their thermal conductivity was between 72 and 162 W/m.K. The lowest thermal conductivity was found in quenched specimens with the lowest hardness.

Keywords:
High conductivity copper alloys, CuNi3Si, heat treatment, properties, thermal conductivity

1. INTRODUCTION

Cu-Ni-Si-type alloys are low-alloyed hardenable copper alloys, in which high conductivity and very high strength and hardness can be achieved. The strength of CuNi2Si alloy can be above 400 MPa and that of CuNi3Si may even exceed 600 MPa, while combined with the conductivity of more than 20 MS/m (35 % IACS). These properties make both alloys popular in electrical engineering applications as materials for integrated circuit boards, connectors, in automotive industry, as soldering iron tips and other components for resistance welding [1]. All these applications require high electrical conductivity, high strength and resistance to degradation of mechanical properties at elevated temperature.

The alloy is precipitation-hardenable with Ni2Si as the main hardening phase. Solution annealing temperature for this alloy is above 800 °C and aging temperatures (for precipitation hardening) typically range between 425 and 540 °C.

An important characteristic of the alloy is thermal conductivity \( \lambda \). In metals, where electrical and thermal conductivity result from migrating free electrons, there is a direct relationship between the thermal conductivity \( \lambda \) and electrical conductivity \( \kappa \) according to Wiedemann-Franz law [2]

\[
\lambda = L \cdot T \cdot \kappa = \text{const (T)} \times \kappa, \quad (1)
\]

where \( L \) is Lorenz number, \( L = 2.44 \times 10^{-8} \text{[W} \cdot \Omega \cdot \text{K}^2] \), \( T \) [K] denotes temperature, \( \kappa \) denotes electrical conductivity [S/m].

COMTES FHT possesses LFA 1000 apparatus by the company LINSEIS GmbH. The instrument relies on laser flash technique for direct measuring of thermal diffusivity \( \alpha \) between 0.01 and 1000 mm²/s across a range of temperatures from room temperature to 1400 °C. The measuring range for thermal conductivity \( \lambda \) is from 0.1 to 2000 W/m.K.

Thermal diffusivity is measured on the basis of temperature increase on the rear side of the specimen. It is obtained from the equation

\[
\alpha(T) = 0.1388 L^2/t_{0.5}. \quad (2)
\]
where $\alpha$ denotes thermal diffusivity [cm$^2$/s], $l$ is the specimen thickness [cm] and $t_{0.5}$ [s] is the time, in which the rear side of the specimen shows a 50% rise in temperature [3].

Thermal conductivity $\lambda$ is calculated from the formula

$$\lambda(T) = \alpha(T) \cdot C_p(T) \cdot \rho(T),$$

where $C_p$ denotes specific heat capacity [J/kg.K] and $\rho$ is the density of material.

LFA 1000 instrument also allows specific heat capacity $C_p$ to be measured through comparison with a test standard.

The purpose of experiments testing was to explore by means of the LFA 1000 instrument the effect of heat treatment of CuNi3Si alloy on its microstructure, hardness, thermal conductivity and their relationship.

2. EXPERIMENTAL

The experimental material was as-cast CuNi3Si alloy meeting the requirements of the standard ČSN EN 12163. It was produced by the company Kovohuté Rokycany. Its chemical composition is given in tab. 1:

**Tab. 1** Chemical composition of experimental material in wt. %

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ni</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN 12163</td>
<td>balance</td>
<td>2.6 – 4.5</td>
<td>0.8 – 1.3</td>
<td>max 0.2</td>
<td>max. 0.1</td>
<td>max. 0.02</td>
</tr>
<tr>
<td>specimen</td>
<td>balance</td>
<td>3.7</td>
<td>0.80</td>
<td>0.03</td>
<td>0.005</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Experimental specimens were annealed at 900 and 1000 °C and some of them quenched. Various cooling rates were employed (water quenching, air cooling, cooling in furnace). Quenched specimens were aged at temperatures ranging from 250 to 650 °C for 60 minutes and air-cooled (tab. 2).

**Tab. 2** Experimental heat treatment schedules

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Annealing and cooling</th>
<th>Specimen</th>
<th>Aging after water quench from 900 °C/2 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>1000 °C/2 hr, water</td>
<td>N2A</td>
<td>250 °C/60 min</td>
</tr>
<tr>
<td>N2</td>
<td>900 °C/2 hr, water</td>
<td>N2B</td>
<td>350 °C/60 min</td>
</tr>
<tr>
<td>N3</td>
<td>900 °C/2 hr, air</td>
<td>N2C</td>
<td>450 °C/60 min</td>
</tr>
<tr>
<td>N4</td>
<td>900 °C/2 hr, furnace</td>
<td>N2D</td>
<td>550 °C/60 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N2E</td>
<td>650 °C/60 min</td>
</tr>
</tbody>
</table>

Microstructures in specimens were examined using light and scanning electron microscopes. Their hardness was measured using Vickers hardness tester (HV10).

Specimens with a diameter of 12.7 mm and thickness of 2 mm were prepared for the purpose of thermal diffusivity measurement. Thermal diffusivity $\alpha$ was measured at a single temperature of 25 °C. Specific heat capacity $C_p$ was found by comparing with a pure Al reference standard. The result was used to calculate thermal conductivity $\lambda$.

3. RESULTS AND DISCUSSION

3.1 Properties of annealed material

Microstructures of annealed specimens are shown in Fig. 1. The material contains large blocks of primary Ni$_2$Si and small Ni$_2$Si precipitates.
Fig. 1 Microstructure upon heat treatment. Etched, 1000× magnification.

Hardness on HV10 scale, thermal diffusivity $\alpha$ and specific heat capacity $C_p$ were measured in annealed specimens. The results together and calculated values are given in table 3.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Annealing and cooling</th>
<th>HV10</th>
<th>$\alpha$ [cm$^2$/s]</th>
<th>$C_p$ [J/kg.K]</th>
<th>$\lambda$ [W/m.K]</th>
<th>$\kappa$ [MS/m] $^*$</th>
<th>% IACS</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>1000 °C/2 hr, water</td>
<td>68.5</td>
<td>0.210</td>
<td>385</td>
<td>72.1</td>
<td>9.9</td>
<td>17.1</td>
</tr>
<tr>
<td>N2</td>
<td>900 °C/2 hr, water</td>
<td>71.4</td>
<td>0.216</td>
<td>385</td>
<td>73.5</td>
<td>10.1</td>
<td>17.4</td>
</tr>
<tr>
<td>N3</td>
<td>900 °C/2 h, air</td>
<td>220.1</td>
<td>0.388</td>
<td>385</td>
<td>133</td>
<td>18.3</td>
<td>31.5</td>
</tr>
<tr>
<td>N4</td>
<td>900 °C/2 h, furnace</td>
<td>123.0</td>
<td>0.433</td>
<td>397</td>
<td>148</td>
<td>20.4</td>
<td>35.1</td>
</tr>
</tbody>
</table>

Mean value of specific heat capacity $C_p = 388$ J/kg.K and density $\rho = 8800$ kg/m$^3$ were used for calculating thermal conductivity $\lambda$.

$^*$ $\kappa$ calculated using equation 1.

The annealing dispersed the segregation that was present in the as-cast state. During heating to 900 °C, Ni$_2$Si precipitates form and coarsen (Fig. 1b). Some portion of Ni and Si dissolved into solid solution. A further temperature increase to 1000 °C caused most precipitates to dissolve and form solid solution (Fig. 1a). Values of HV10 hardness are very low, approaching those of low-alloyed copper. Thermal conductivity is the lowest among the specimens. The corresponding electrical conductivity level is 17% IASC.
The highest hardness level was found in the air-cooled specimen, where the hardening phase Ni$_2$Si precipitated in the form of clusters of small precipitates, as in Fig. 1c. In this case, hardness was 220 HV10, which is a three-fold increase. However, the values of thermal conductivity were not the highest.

Specimens that cooled down slowly in furnace contained a large number of coarse Ni$_2$Si precipitates. These precipitates were coarser and the resulting hardness was lower than in specimens cooled rapidly in air. The furnace-cooled specimens, however, showed the highest thermal conductivity of all annealed specimens.

The lowest thermal conductivity and electrical conductivity values were found in quenched specimens with the lowest hardness. Thermal conductivity and electrical conductivity are strongly affected by atoms of residual elements, namely Si, which are present in solid solution, into which they migrate upon solution annealing. The difference between amounts of undissolved Ni$_2$Si upon quenching from 1000 and 900 °C is clear to see in micrographs (Fig. 1a and 1b). Despite that, differences between hardness and conductivity values are small.

The highest thermal conductivity was found in specimen N4 that cooled down slowly in furnace. Its microstructure contained a large number of coarse particles (Fig. 1d).

### 3.2 Properties of aged (precipitation-hardened) specimens

Aging was performed on specimens that were annealed at 900 °C for 2 hours and quenched in water. When observed in optical microscope, the microstructures of specimens aged at 550 °C are very similar to those of quenched specimens (Fig. 3a). The differences can only be found by observing them in transmission electron microscope. Up to the aging temperature of 550 °C, the number of precipitates, and thus hardness as well, keep rising. At 650 °C, the material becomes overaged, the precipitates coarsen (Fig. 3b), and hardness declines.

![Fig. 3 Microstructures of aged specimens. Etched, 1000× magnification.](image)

Tab. 4 Properties of aged specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Aged</th>
<th>HV10</th>
<th>$\alpha$ [cm$^2$/s]</th>
<th>$\lambda$ [W/m.K]</th>
<th>$\kappa$ [MS/m]</th>
<th>% IACS</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2A</td>
<td>250 °C/1 hr</td>
<td>73.8</td>
<td>0.224</td>
<td>76.6</td>
<td>10.5</td>
<td>18.2</td>
</tr>
<tr>
<td>N2B</td>
<td>350 °C/1 hr</td>
<td>103.8</td>
<td>0.264</td>
<td>90.3</td>
<td>12.4</td>
<td>21.4</td>
</tr>
<tr>
<td>N2C</td>
<td>450 °C/1 hr</td>
<td>171.6</td>
<td>0.354</td>
<td>121</td>
<td>16.6</td>
<td>28.7</td>
</tr>
<tr>
<td>N2D</td>
<td>550 °C/1 hr</td>
<td>249.3</td>
<td>0.475</td>
<td>162</td>
<td>22.3</td>
<td>38.5</td>
</tr>
<tr>
<td>N2E</td>
<td>650 °C/1 hr</td>
<td>154.1</td>
<td>0.447</td>
<td>153</td>
<td>21.0</td>
<td>36.2</td>
</tr>
</tbody>
</table>
Hardness and thermal conductivity of quenched and aged specimens show similar behaviour. Up to 550 °C, both hardness and thermal conductivity increase with aging temperature, peaking at 550 °C. At 650 °C, the material is overaged and both quantities decline. The decrease in thermal conductivity is less steep.

![Graph showing dependence of HV10 hardness and thermal conductivity on aging temperature](image)

**Fig. 4** Dependence of HV10 hardness and thermal conductivity $\lambda$ on aging temperature

Microstructures of annealed and aged specimens were observed in scanning electron microscope at 10000× magnification. Densities of fine precipitates are documented in scanning electron micrographs in Fig. 5.

![Scanning electron micrographs of microstructure](image)

*Fig. 5* Scanning electron micrographs of microstructure of annealed and aged specimens. The specimens were etched.
Observation in scanning electron microscope only reveals the coarse precipitates that do not contribute to hardness but do remove dissolved elements (Si and Ni) from the solid solution, thus improving thermal conductivity. The highest value of thermal conductivity was found in N2D specimen that was aged to maximum hardness. Its scanning electron micrograph shows no coarse precipitates (Fig. 5c). The other specimens shown in Fig. 5 exhibited high thermal conductivity but their hardness was affected by their heat treatment history.

4. CONCLUSION

Effects of heat treatment (annealing, quenching, and aging) on microstructure, hardness and thermal conductivity of specimens of CuNi3Si alloy have been explored. Correlation was sought between hardness and thermal conductivity $\lambda$ (and thus also between electrical conductivity $\kappa$ calculated according to Wiedemann-Franz law).

Samples annealed (aged) after quenching exhibit similar trends of hardness and thermal conductivity. Both hardness and thermal conductivity increased with increasing ageing temperature until ageing temperature reached 550°C. Samples aged at 550°C exhibited maximal hardness and thermal conductivity (250 HV10, 162 W/m.K). Corresponding electrical conductivity was 38,5% IACS.

Over-ageing and precipitates coarsening occurs at temperature 650°C together with corresponding decrease of both values. Decrease of thermal conductivity was more significant. Hardness decreased to 62% of maximal value while thermal conductivity to 94% of maximal value.

Quenched specimens showed the lowest hardness and thermal conductivity (after quenching from 900 and 1000 °C).

In other two air-cooled and furnace cooled annealed specimens, the direct proportionality between hardness and thermal conductivity was not found. The air-cooled specimen shows notably higher hardness but lower conductivity than the one that cooled down in furnace.

These results were measured on heat-treated as-cast specimens. However, the CuNi3Si alloy is also used in wrought condition after quenching (prior to aging). Aged specimens may be expected to show similar correlations between hardness and conductivity but hardness values will be higher in such case.

ACKNOWLEDGEMENT

These results were obtained in the project no. FR-TI1/473 “Industrial research and development of technology of production of the bars made from nickel and copper alloys” funded by the Ministry of Industry of the Czech Republic.

REFERENCES