Thermomechanical treatment of low-alloy copper alloys of the kind CuCo2Be and CuCo1NiBe

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ABSTRACT

Purpose: The aim of the investigations is to test the influence of the complex thermomechanical treatment on the structure and mechanical properties of low-alloy copper alloys with cobalt, beryllium and nickel of the kind CuCo2Be (CB4) and CuCo1NiBe (CCNB).
Design/methodology/approach: The range of investigations comprises an analysis of the complex technique of thermomechanical treatment of the investigated alloys and the conventional thermal treatment of these alloys, the analysis of their chemical composition, a static tensile test, measurement of their hardness, observations of their structure on a light microscope and a fractographic analysis on an electron scanning microscope.
Findings: The analysis of the results of investigations concerning the mechanical effect properties permitted to determine the effect of the combined thermomechanical treatment and the comparatively performed precipitation hardening on the structure and mechanical properties of the investigated low-alloy kinds of copper. The character of cracking in the course of stretching were determined basing on fractographic tests.
Practical implications: The investigated copper alloys subjected to a complex thermomechanical treatment display a higher strength and lower plastic properties in comparison with these properties achieved by means of the conventional heat treatment.
Originality/value: Complex thermomechanical treatment ensures an optimal strength of the investigated alloys as well as satisfying plastic properties.
Keywords: Metals; Copper alloys; Thermomechanical treatment; Structure; Mechanical properties

Reference to this paper should be given in the following way:

1. Introduction

The dynamic development of the electrical and electronic industry requires the application of materials characterized by a considerable plasticity and electrical conduction good thermal conductivity and, some chemical affinity with oxygen. Copper and its alloys are characterized by all these properties. Copper is used both in the form of pure metal and in the form of alloys, the group of which comprises brass, bronze, copper-nickel and low-alloy copper alloys.
Next to ferrous alloys and aluminum, copper alloys are nowadays the most industrially applied structural materials. Aluminum bronze, for instance, displays, after quenching and tempering a strength comparable with steel, tin bronze is elastic, plastic and resistant to corrosion; beryllium bronze does not scintillate and is, therefore, applied in electrical contacts in the production of explosives and in mines exposed to methane hazard [1-9].

Low-alloy kinds of copper belong to a group of copper alloys which are expected to display not only high physical, but also mechanical properties. The latter can be achieved by the choice of an optimal chemical composition and an adequate technique of thermomechanical treatment.

In order to improve the strength of alloys which do not undergo polymorphous changes the widely combined (complex) thermomechanical treatment (CTMT) is applied, comprising hot plastic deformation, solution heat treatment, cold plastic deformation and ageing. It may be realized in various variants, depending on the sequence of the operations of saturation, ageing and plastic deformation [10-13].

The character and kinetics of the precipitation processes and the degree of strain hardening of alloys subjected to a combined thermomechanical treatment change considerably depending on the conditions of plastic deformation and ageing, and also on the sequence in which these operations are carried out. In result of strain hardening of the structure of alloys subjected to such a treatment a high strength and hardness can be achieved, depending mainly on the density of vacancies and dislocations, and also on the parameters of cold plastic deformation and the amount, dispersion and distributions of precipitations arising in the course of ageing. An increased condensation of vacancies and density of dislocations facilitates the nucleation of precipitations in the course of ageing. An increased density of dislocations at higher levels of plastic deformation leads to an increased dispersion of precipitations in the course of ageing, thus influencing essentially the strain hardening of the alloys.

The aim of the investigations was to study the influence of complex thermomechanical treatment and precipitation hardening by means of the conventional heat treatment (CHT) on the structure and mechanical properties of selected copper alloys of the kinds CuCo2Be and CuCo1NiBe with the symbols CB4 and CCNB complying with the standard PN-EN 12163 [16].

2. Experimental procedure

The investigations concerned two kinds of low-alloy copper alloys with the chemical composition and denotations presented in Table 1. The applied materials were ingots of alloys of the type CB4 and CCNB after vacuum casting. Ingots obtained in the process of producing rods were subjected to a complex thermomechanical treatment (Fig. 1), comprising the following operations:

- solution heat treatment of the rods in water from the temperature of extrusion
- heating the rods up to the temperature of solution heat treatment 965°C for 30 minutes and soaking them for 60 minutes,
- solution heat treatment in water,
- cold broach of the saturated alloys with an overall rolling reduction of 90% to rods with a diameter 20×10 mm,
- ageing for 5 hours at a temperature of 460°C connected with air cooling.

<table>
<thead>
<tr>
<th>No</th>
<th>Kind of the alloy</th>
<th>Kind of analysis</th>
<th>Chemical composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CuCo2Be CB4</td>
<td>control</td>
<td>Co  2.14  Ni  0.33  Be  0.5  Fe  Rest  Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wg.</td>
<td>Co  2.8  Ni  0.3  Be  0.7  Fe  Rest  Cu</td>
</tr>
<tr>
<td>2.</td>
<td>CuCo1NiBe CCNB</td>
<td>control</td>
<td>Co  1.13  Ni  1.20  Be  0.4  Fe  Rest  Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wg.</td>
<td>Co  0.8  Ni  0.8  Be  0.7  Fe  Rest  Cu</td>
</tr>
</tbody>
</table>

For the sake of comparison the investigated alloys were also subjected to the conventional heat treatment and precipitation hardening, applying varying temperatures of solution heat treatment and ageing (Fig. 2). Solution heat treatment was employed from the temperature of 850°C, 950°C and 1000°C for 60 minutes with simultaneous cooling in water. The alloys were heated up to 850°C and 950°C in an electrical chamber furnace produced by the firm THERMOLYNE with a power rating of 4,4 kW, equipped with a control unit warranting measurements of the temperature with an accuracy of ±1°C. For heating to a temperature of 1000°C a silit chamber furnace of the type PSK with a thermocouple Pt-RhPt was applied. The alloy copper supersaturated from the temperature 950°C was aged for 4 hours within the temperature range from 200°C to 450°C connected with air cooling. For this purpose an electrical chamber furnace PEK2 was used, warranting an accuracy of measurements amounting to ±5°C.
2. Experimental procedure

CCNB complying with the standard PN-EN 12163 [16].

The investigations concerned two kinds of low-alloy copper alloys with the chemical composition and denotations presented in Table 1.

The chemical composition of the investigated alloys was analyzed making use of the spectrographic method. The mechanical properties of the alloys CB4 and CCNB after CTMT and CHT were tested on the universal testing machine INSTRON 1195 applying a gauge head which permits to record forces in the range up to 100 kN and the rate of stretching up to 20 mm/min. The static tensile test was performed on samples with threaded grabbing tail-pieces 6 mm in diameter, their gauge length amounting to 26 mm. The hardness was measured making use of Vickers's method and metallographic observations were carried out on longitudinal microsections of the investigated alloys after their thermomechanical treatment and also after precipitation hardening. The structures of the investigated alloys were observed on a light microscope type Leica MEF 4A with a magnification of 100 to 1000 times. Fractographic investigations were realized after decohesion in the tensile test, applying a scanning electron microscope SUPRA from the firm Zeiss with a resolution of 2 µm at an accelerating voltage of 20 kV. The fractures were observed at a magnification from 10^3 to 10^5 times. In the microanalysis of precipitations revealed on the fractures of the tested samples an X-ray microanalysis EDX was used, with the scanning microscope is equipped.

3. Experimental results

The results of the static tensile test permitted to determine the mechanical properties of the alloys CB4 and CCNB after their complex thermomechanical treatment and CHT. The mechanical properties of the investigated alloys after their CTMT may be gathered from Table 2, and those after precipitation hardening by means of the conventional heat treatment from Tables 3 and 4 as well as from Fig. 3.

### Table 2.
Mechanical properties of the investigated alloys after their complex thermomechanical treatment

<table>
<thead>
<tr>
<th>No.</th>
<th>Kind of the alloy</th>
<th>Rm [MPa]</th>
<th>Rm0.2 [MPa]</th>
<th>A [%]</th>
<th>Z [%]</th>
<th>HV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CB4</td>
<td>889</td>
<td>843</td>
<td>12</td>
<td>19</td>
<td>451</td>
</tr>
<tr>
<td>2.</td>
<td>CCNB</td>
<td>1046</td>
<td>936</td>
<td>14</td>
<td>20</td>
<td>461</td>
</tr>
</tbody>
</table>

Copper alloys are after their complex thermomechanical treatment characterized by a better strength and lower plastic properties, if compared with their state previous to precipitation hardening (Tables 2 and 4, Fig. 3).

### Table 3.
Mechanical properties of the investigated alloys after solution heat treatment in the CHT

<table>
<thead>
<tr>
<th>No.</th>
<th>Kind of the alloy</th>
<th>Temperature of solution heat treatment [°C]</th>
<th>Rm [MPa]</th>
<th>Rm0.2 [MPa]</th>
<th>A [%]</th>
<th>Z [%]</th>
<th>HV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CB4</td>
<td>850</td>
<td>329</td>
<td>136</td>
<td>44</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>307</td>
<td>114</td>
<td>43</td>
<td>67</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>302</td>
<td>107</td>
<td>41</td>
<td>49</td>
<td>64</td>
</tr>
<tr>
<td>2.</td>
<td>CCNB</td>
<td>850</td>
<td>344</td>
<td>124</td>
<td>45</td>
<td>70</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>319</td>
<td>113</td>
<td>44</td>
<td>65</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>309</td>
<td>106</td>
<td>42</td>
<td>54</td>
<td>66</td>
</tr>
</tbody>
</table>

### Table 4.
Mechanical properties of the investigated alloys after ageing in the CHT

<table>
<thead>
<tr>
<th>No.</th>
<th>Kind of the alloy</th>
<th>Temperature of ageing [°C]</th>
<th>Rm [MPa]</th>
<th>Rm0.2 [MPa]</th>
<th>A [%]</th>
<th>Z [%]</th>
<th>HV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CB4</td>
<td>200</td>
<td>319</td>
<td>127</td>
<td>41</td>
<td>52</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
<td>658</td>
<td>529</td>
<td>25</td>
<td>42</td>
<td>227</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>757</td>
<td>598</td>
<td>19</td>
<td>32</td>
<td>378</td>
</tr>
<tr>
<td>2.</td>
<td>CCNB</td>
<td>200</td>
<td>325</td>
<td>113</td>
<td>40</td>
<td>54</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
<td>768</td>
<td>565</td>
<td>23</td>
<td>36</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>785</td>
<td>568</td>
<td>21</td>
<td>31</td>
<td>345</td>
</tr>
</tbody>
</table>

* Ageing after solution heat treatment from the temperature of 950°C.
The highest strength after (CTMT) was found in the alloy CCNB (Table 2). After such a treatment the alloy displays a high tensile strength $R_m$ about 1046 MPa, a yield strength $R_{p0.2}$ of about 936 MPa, an elongation $A$ of about 14 % and a reduction of area $Z$ of about 20%. The high strength properties of the investigated alloys are the result of the use of the large rolling reduction (Z>90%) during CHT, it lead probably to enlarged thickness of dislocation in structure and the intensifying the precipitation processes during aging. This leads to secretion the of particles strengthening about large thickness dispersion [1,5,12]. The phenomenon of the precipitation processes require the spacious investigations from utilization the modern techniques in this the mainly transmission electron microscope.

The alloy CB4 displays after the same treatment lower mechanical properties: $R_m$ about 889 MPa, $R_{p0.2}$ about 843 MPa, $A$ about 12%, $Z$ about 19%. After solution heat treatment in the process of conventional precipitation hardening the tensile strength $R_m$ and yield point $R_{p0.2}$ of the alloys CB4 and CCNB decreases with growing temperature of solution heat treatment. The strength of the supersaturated alloy CCNB is in the temperature range of 850°C to 950°C higher than that of the alloy CB4, the plastic properties being comparable - Table 3. Elongation after solution heat treatment from this range of temperature amounts in the case of the investigated alloys A about 44 %, reduction of area $Z$ about 67%. At a maximum temperature of solution heat treatment the strength of the alloy CB4 is about 30 MPa higher than that of the alloy CCNB, the plastic properties of both being comparable: $A$ about 42%, $Z$ about 52%.

The increase of the temperature of ageing of the investigated alloy copper in the course of conventional heat treatment involves also an increase of the strength accompanied by a decrease of the plastic properties (Table 4). After ageing at 450°C the alloys CB4 and CCNB attain a twofold increase of $R_m$ and a fivefold increase of $R_{p0.2}$ in comparison with the supersaturated state (Table 2.) The tensile strength of the alloy CB4 reaches after ageing at a temperature of 450°C the value of about 760 MPa, and the alloy CCNB even 785 MPa. The plastic properties of both these alloys are after their ageing comparable. A rise of the temperature of ageing from 200-450°C leads to smaller elongations of their investigated alloys from about 40 % to about 20 % and to a drop of reduction of area from about 53 % to about 32 %. The results of changes of the mechanical properties generally confirm the course of changes of the measured hardness. Copper alloys of the type CB4 and CCNB display after their CTMT a higher hardness than after precipitation hardening by means of the CHT. After complex thermomechanical treatment the hardness of the alloys CB4 and CCNB amounts, respectively, to 451 HV and 461 HV, and after precipitation hardening in the course of CHT to 378 HV and 345 HV, respectively (Fig. 3).

Metallographic tests have made it possible to determine the effect of the complex thermomechanical treatment and the conventional heat treatment within the range of precipitation hardening on the structure of copper alloys of the types CB4 and CCNB. The results of metallographic observations are to be seen in the microphotos presented in Figs. 4-12. The structures of the investigated alloys subjected to CTMT are characterized by elongated grains of the solution – $\alpha$, with precipitations of various sizes and shapes (Figs. 4-6). Single large precipitations in the shape of irregular polygons, arranged in bands or series, are frequently fragmented or cracked (Figs. 5, 6). Cracks appear mainly during the process of plastic deformation in CTMT deformation. Besides single precipitations in the grains of the matrix-$\alpha$ also numerous minute dense spheroidal precipitations do occur (Figs. 5, 6).

Figs. 7-12 illustrate the observations of the structure of the investigated alloys subjected to conventional precipitation hardening. In the structure of the alloys CB4 and CCNB after solution heat treatment within the temperature range from 850°C to 1000°C grains of the solution-$\alpha$ are to be observed of various sizes with precipitations (Figs. 7 and 9). In comparison with the alloy CCNB, the structure of the alloy CB4 displays smaller grains (Figs. 7, 8 and 9, 10). After solution heat treatment from 950°C in this alloy there are grains of the solution-$\alpha$, sized 5-10 $\mu$m, and in the alloy CCNB grains 10-50 $\mu$m in size (Figs. 7, 8).
An increase of the temperature of solution heat treatment involves an increase of the grains in the matrix-α. After precipitation hardening connected with ageing at a temperature of 200 to 450°C in the structure of the alloys in the grains of the matrix-α precipitation have been observed in the shape of dispersive spheroidites and irregulars polygons (Figs. 11, 12). Spheroidal precipitations are probably the phase CuBe [14,15], and if shaped like polygons, they are probably a variant of pure cobalt-α or the phase abundant with Co. The occurrence of this latter phase was confirmed by the results of X-ray microanalysis (Fig. 13). In the chemical composition of the precipitation occurring on the fracture of the alloy CB4 after solution heat treatment from 950°C the presence of cobalt and nickel was detected with a concentration of 51 % and 10.2 % by weight, respectively (Fig. 13).

The results of fractographic investigations of the samples after decohesion in the tensile test, concerning the alloys CB4 and CCNB permitted to assess the character of fractures after their CTMT and CHT. The investigated alloys are characterized by a ductile crystalline fractures (Figs. 14a, 15a). On the surface of the fractures numerous cut wells have been detected, resulting from the plastic deformation of the material, as well as craters of various sizes, containing precipitations varying in their concentration by weight; cobalt about 75%, nickel about 10%. Hollow craters are caused, among others, by the extraction of precipitations during the tensile test.

The chemical composition of the precipitations was, determined by means of X-ray microanalysis EDX - Figs. 14b and 15b. After solution heat treatment from the temperature 950°C and ageing at 200°C alloy copper of the type CB4 and CCNB displays ductile transcryalline fractures, and after ageing at 450°C mixed fractures with a dominating share of plastically deformed areas (Figs. 16, 17). On the surface of the fractures numerous microcracks and areas with smooth walls and visible jogs could be detected (Fig. 17).
Fig. 10. Large grains in the matrix-$\alpha$ with precipitations in the alloy CCNB after solution heat treatment from 1000°C

Fig. 11. Microstructure of the alloy CB4 after CHT: solution heat treatment 950°C; ageing 450°C

Fig. 12. Microstructure of the alloy CCNB after CHT: solution heat treatment 950°C; ageing 450°C

Fig. 13. Results of the microanalysis of the chemical composition of precipitations in the alloy CB4 after solution heat treatment from 950°C during the CHT

Fig. 14. Ductile transcry stalline fracture of the alloy CB4 after its complex thermomechanical treatment (a) and X-ray analysis of the precipitation from Fig. a (b)

Fig. 15. Ductile transcry stalline fracture of the alloy CCNB after its complex thermomechanical treatment (a) and X-ray analysis of the precipitation from Fig. a (b)

Fig. 16. Mixed fracture of the alloy CB4 after solution heat treatment from the temperature 950°C and ageing at 450°C

Fig. 17. Mixed fracture of the alloy CCNB after solution heat treatment from 950°C and ageing at 450°C

4. Conclusions

Basing on the performed analysis of the results of investigations the following conclusions may be drawn:

1. Copper alloys of the type CuCo$_2$Be (CB4) and CuCo$_1$NiBe (CCNB), subjected to complex thermomechanical treatment are characterized by a better strength and a lower plasticity than when they are subjected to the conventional heat treatment in the range of precipitation hardening.

2. Complex thermomechanical treatment warrants a high strength $R_m$ of about 1046 MPa in the case of the alloy CCNB at a value of the index $R_{p0.2}/R_m$ amounting to 0.89. In the case of the alloy CB4 these values amount to 890 MPa and 0.89, respectively.

3. After the complex thermomechanical treatment the structure of the investigated alloys is characterized by elongated grains in the matrix-$\alpha$ with precipitations of the primary phase, rich in cobalt and nickel (Co about 75%, Ni about 10%) varying in size and shape.

4. Thermomechanical treatment of the investigated alloys warrants a better refinement in the solution-$\alpha$ than the conventional heat treatment.

5. The investigated types of alloy copper display after their conventional heat treatment in the range of precipitation hardening a similar structure and state of precipitation.

6. After the complex thermomechanical treatment the alloys CB4 and CCNB are characterized by ductile transcry stalline fractures, whereas after the conventional heat treatment there are mixed fractures with a dominating share of plastically deformed areas.

Acknowledgements

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References

[16] PN-EN 12163