THERMODYNAMIC MODELLING OF Cu-Al-Mn-Ag ALLOYS

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ABSTRACT

Shape memory alloys (SMA) are highly interested functional materials which have the ability to recover their previous form when subjected to thermal or mechanical variations. SMA alloys exhibit unique properties like the shape memory effect, the superelastic effect, damping, corrosion, and extraordinary fatigue resistance. Shape memory effect is based on martensitic transformation which represents a diffusionless and reversible solid state phase transformation which occurs between the high-temperature austenite phase and the low-temperature martensite phase. The transformation temperature is crucial for area of SMA alloy application. Cu-Al-Mn alloys under equilibrium conditions, undergoes to decomposition of β phase to α and γ′ phase. The fast quenching decomposition could be suppressed and metastable martensite phase formed, with orthorhombic and tetragonal crystal structure, depending on δα and δ1 parent phase. Ternary Cu-Al-Mn alloys and Cu-Al-Mn-Ag were prepared by melting of pure metals in the electric arc furnace, in argon atmosphere, and casted in a cylindrical mould. Specimens were thermal treated at 900 °C and quenched in water. Calculation of phase diagram was performed by the Thermo-Calc program, by minimization of Gibbs free energy of system and CALPHAD method using parameters of pure elements according to SGTE database and optimized thermodynamic parameters for binary and ternary system. Microstructure was determined by Field emission scanning electron microscope (FE-SEM) and phase elemental analysis was performed by energy dispersive X-ray spectroscopy (EDS). Martensite and austenite transformation temperatures were followed by Differential thermal analysis (DSC). Results showed two-phase morphology in the as-cast state and completely formed martensite structure, with different types of martensite, in quenched Cu-Al-Mn alloys.

MATERIALS AND CHARACTERIZATION

The raw materials used for alloys preparation were pure elements of copper, Cu, purity of 99.9%, aluminium, Al purity of 99.5%, manganese, Mn, purity of 99.8% and silver, Ag, purity of 99.99%. Cu-Al-Mn with 7-11 wt.% of aluminium, 9 wt.% of manganese were prepared by melting of pure metals in the electric arc furnace, and vacuum for 2 times. Alloys were re-melted for 5 times for better homogenization and casted in the mould dimensions t = 8 mm and length of 12 mm. Cu-Al-Mn-Ag alloy was prepared by melting in the induction furnace. Specimens were investigated in the as-cast and thermal treated state. Thermal treatment was performed at 900 °C for 30 min followed by quenching in water. Ternary specimens were also subjected to homogenization at 300 °C for 14 days, aimed to detect "l" phase. For microstructure investigations samples were prepared by grinding at grades 120, 240, 400, 600, 800, 1200, x-ray polishing and etching with solution of 2.5% FeCl₃+8%HCl+7%H₂O. Microstructure analysis was carried out by Optical microscope Olympus GX 71 and Scanning Electron Microscope Tescan Vega, equipped by Energy dispersive spectroscopy (EDS), Bruker, with acceleration voltage of 20 kV. Thermodynamic modelling of Cu-based alloys was performed by Thermo-Calc. Transformation temperatures were determined by Differential Scanning Calorimeter NETZSCH STA Jupiter 449 as well as by Modulated Differential Scanning Calorimeter MDSC Mettler-Toledo 822e for low temperature range. Dynamic measurements were performed through a heating/cooling measurements, in inert atmosphere and with heating/cooling rate of 10 K/min.

CONCLUSION

Thermodynamic calculation was done for Cu-Al-Mn alloy in the Cu-rich corner. The area of stability of the β-phase, crucial for the formation of a metastable phase β′, responsible for shape memory effect was determined. Invariant eutectoid reaction \( \beta \rightarrow \alpha + \gamma' \) occurs at 393 °C during equilibrium cooling. It can also be noticed that under equilibrium conditions \( \gamma' \) (Cu,Mn)Al ternary phase is stable under 500 °C. What is confirmed by SEM analysis of Cu-Al-Mn-Ag alloys after homogenization at 300 °C for 14 days. Results showed intensive formation of martensitic structure in Cu-Al-Mn-Ag alloy after heat treatment at 900 °C, with Mn=28wt% and Mn=10wt%. In both, Cu-Al-Mn and Cu-Al-Mn-Ag alloys, the zigzag martensitic groups, characteristic for \( \beta' \) type of martensite, and coarse variants which are characteristic for \( \gamma' \) martensite were observed.

Table 1. Phases in Cu-Al-Mn system taken in calculation

<table>
<thead>
<tr>
<th>Phase/ Temperature range</th>
<th>TD database name</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>Lattice Parameters [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>L</td>
<td>cF4</td>
<td>Pm3m</td>
<td>a = 361.48</td>
</tr>
<tr>
<td>β, 1099–761</td>
<td>FCC_M</td>
<td>cF4</td>
<td>Im3m</td>
<td>a = 294.6</td>
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<tr>
<td>γ, 873</td>
<td>GAMMA</td>
<td>cF4</td>
<td>Fm3m</td>
<td>a = 871.32</td>
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<tr>
<td>cbcc (AlMn) &lt; 710</td>
<td>CBCC_A12</td>
<td>cF4</td>
<td>Lm3m</td>
<td>a = 891.39</td>
</tr>
<tr>
<td>( \gamma' ) &lt; 559</td>
<td>Cu,Mn, Al</td>
<td>cF24</td>
<td>Fd3m</td>
<td>a = 690.46</td>
</tr>
</tbody>
</table>

Figure 1. Calculated vertical \( Cu_{x}A_{3}Mn_{y}Ag \) phase diagram

Figure 2. Liquidus projection

Figure 3. Isothermal section at 400°C

Figure 4. DSC cooling curve of Cu-7.4Al-9Mn alloy after homogenization at 300°C

Figure 5. SEM of Cu-7.4Al-9Mn alloy after homogenization at 300°C

Figure 6. DSC curve of heat-treated Cu-8Al-9Mn SMA alloy

Figure 7. SEM of Cu-Al-Mn SMA alloy with 4 wt.% of added Ag