THERMOELASTIC MARTENSITIC TRANSFORMATION AND
SHAPE MEMORY EFFECT IN Cu-Zn-Al ALLOYS

Vanja D. Asanovic, Bosko F. Perovic, Zorica B. Markovic, Ana I. Kostov and Igor C. Vusanovic

The thermoelastic martensitic transformation and shape memory effect appearance in Cu-25.38Zn-3.3Al and Cu-21.6 Zn-5.64 Al alloys are studied in this paper. After performing eight various quenching procedures we realized examining of microstructure by optical microscope, X-ray examining of crystal structure, determination of martensitic and forward transformations temperatures by measuring the variation of electric resistance with temperature, tensile testing of quenched specimens at room temperature, as well as examining the martensitic substructure by transmission electron microscopy. The determination of optimal quenching procedure for examined alloys from the standpoint of relevant properties, firstly one-way shape memory effect is performed on the base of obtained results.

KEY WORDS: Cu-based shape memory alloys, thermoelastic martensitic transformation, shape memory effect

INTRODUCTION

The shape memory alloys are new special materials in which, under particular circumstances, thermoelastic martensitic transformation appears producing unusual macroscopic effects: one-way shape memory effect, two-way shape memory effect, pseudoelasticity and etc. Many alloys exhibit the shape memory effect, but only the Cu-Zn-Al, Cu-Al-Ni and Ni-Ti alloys are presently of commercial importance. Ni-Ti alloys generally exhibit better shape memory properties as well as corrosion resistance in relation to Cu-based shape memory alloys, but they are very expensive in finished form because of fabrication difficulties associated with melting and forming. Early Cu-based shape memory alloys suffered from intergranular failure due to their intrinsic coarse grain structure, but the recent development of these fine-grain alloys has significantly improved mechanical properties. So, in many cases today, Cu-based shape memory alloys provide a more economical alternative to Ni-Ti, especially in conventional thermal-mechanical actuation mechanisms (1).
The thermoelastic martensitic transformations in Cu-based shape memory alloys occur from an ordered b.c.c. \( \beta \)-phase. The high temperature \( \beta \)-phase has a disordered A2 structure, but upon cooling the structure goes through a nearest-neighbor ordering transition and develops the B2 superlattice structure. Further cooling induces next-nearest-neighbor ordering and the structure eventually becomes the DO\( _{13} \) or L2\( _{1} \) superlattice structure, depending on alloy composition and cooling rate. In order to obtain a shape memory effect in Cu-based alloys, the metastable \( \beta \)-phase must be retained for further transformation to martensite, meaning that a sufficiently rapid cooling (quenching) from the betaizing temperatures is necessary to avoid decomposition of the \( \beta \)-phase into the equilibrium phases, for example: \( \alpha \) and \( \gamma \). The transformation temperatures for these alloys are very sensitive to this quenching rate (1,2).

The thermoelastic martensitic transformation and shape memory effect appearance in Cu-25.38 Zn-3.3 Al and Cu-21.6 Zn-5.64 Al alloys after performing eight various quenching procedures are studied in this paper.

**EXPERIMENTAL**

Two shape memory alloys: Cu-25.38Zn-3.3Al and Cu-21.6Zn-5.64Al were prepared by melting oxygen-free copper and Cu-Zn and Cu-Al alloys in a graphite crucible using a resistance heated furnace. The melts were poured at 900°C into graphite molds 14x65x100 mm\(^2\) in size, which were previously heated to 120°C. Obtained ingots were machined and cut into cylindrical specimens 35 to 40 mm in diameter. Homogenization treatment was performed at 800-850°C for 2 hours followed by quenching in water at room temperature. The homogenized ingots were hot forged to plates with thickness of 3.5 - 4.5 mm after heating for 30 min at 830-850°C and then rolled, in air, to plates of 0.3 to 0.6 mm thickness. Intermediate annealing at 500°C for 60 min followed by air-cooling, was required every two or three passes. All test specimens cut from rolled plate were divided into four groups for various quenching treatments described as follows:

- **Group DQ** specimens were solution treated and directly quenched into a water bath at 17°C ± 2°C (DQ1 specimens) or into an iced-water (DQ2 specimens).
- **Specimens of group UQ** were directly quenched into a water bath at 17°C ± 2°C or into an iced-water after solution treatment, then immediately up-quenched into an oil bath at 105°C ± 5°C for 10 min and quenched again into a water bath at 17°C ± 2°C (UQ1) or an iced-water (UQ2 specimens).
- **Specimens of group SQ** were immediately quenched into boiling water (SQWB) or oil baths at 105°C ± 5°C for 10 minutes (SQOB) after solution treatment, then quenched again into water bath at 17°C ± 2°C (SQWB1 and SQOB1 specimens) or iced-water (SQWB2 and SQOB2 specimens).

Solution treating of examined alloys was performed at 890°C for 10 min in mentioned treatments. In order to investigate the influence of various quenching procedures on the appearance of thermoelastic martensitic transformation as well as shape memory effect in Cu-25.38Zn-3.3Al and Cu-21.6Zn-5.64Al alloys we realized voluminous examinations of quenched specimens:

- **Examining of microstructures using optical microscope** and X-ray diffraction examining of crystal structure. Powder X-ray diffractometry was carried out with a Phillips PW 1730 X-ray generator and vertical goniometer PW 1050/70 using a Cu target.
- **Determination of the martensitic and forward transformation temperatures** by measuring the variation of electric resistance with temperature.
- Tensile testing at room temperature using a Raunstein FPZ 100/1 machine.
- Examining of martensitic substructure by transmission electron microscope (JEOL - 2000 EX).
- Determination of shape memory recovery by direct observation of thin specimens quenched, then bent $\approx 30$ deg before heating above $A_t$ temperature.

RESULTS AND DISCUSSION

The examining of microstructure by optical microscope (Figure 1) and X-ray diffraction examining
of crystal structure (Figure 2) after performing various quenching procedures on specimens of Cu-
25.38Zn-3.3Al and Cu-21.6Zn-5.64Al alloys have shown the presence of martensite (M18R and
2H), certain quantity of $\alpha$-phase (f.c.c.) and parent phase (B2 and/or DO$_2$ superlattice). The martensite
M18R type was observed in all quenched specimens, while the martensite 2H type was not observed
only after performing step-quenching in boiling water (SQWB).

During various quenching procedures, the slowest cooling process is realized for SQWB
specimens, which is believed to be due to the rapidly formed vapor layer on the specimen surface
insulating it from the surrounding quenching medium.

The presence of DO$_2$ phase in almost all specimens indicates the appearance of the transformation
B2$\rightarrow$DO$_2$ in parent phase that could not be suppressed even with rapid quenching such as quenching
in iced-water.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figures}
  \caption{Optical microstructures of quenched specimens of Cu-25.38Zn-3.3Al (SM1) and Cu-21.6Zn-5.64Al (SM2) alloys.}
\end{figure}
Figure 2. The amount of various phases in quenched specimens of examined alloys.

The technique of measuring the variation of electric resistance with temperature was used for determining of martensitic ($M_s$, $M_f$) and forward transformation ($A_s$, $A_f$) temperatures. The experiment was carried out in domestic apparatus, which had contained all necessary devices in order to find the electric resistance drop and growth, during heating and cooling and hence determine the phase transformation temperatures. The values of $M_s$, $M_f$, $A_s$, and $A_f$ temperatures that were obtained for examined specimens are given in Table 1. These values are high but they are the results of complex influences of various factors such as: chemical composition, solution treatment temperature and duration, quenching rate, grain size and etc.
Table 1. The values of phase transformation temperatures for examined specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cu-25.38Zn-3.3Al</th>
<th>Cu-21.6Zn-5.64Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms[°C]</td>
<td>Ms[°C]</td>
</tr>
<tr>
<td>DQ1</td>
<td>257</td>
<td>202</td>
</tr>
<tr>
<td>DQ2</td>
<td>259</td>
<td>221</td>
</tr>
<tr>
<td>UQ1</td>
<td>268</td>
<td>219</td>
</tr>
<tr>
<td>UQ2</td>
<td>269</td>
<td>225</td>
</tr>
<tr>
<td>SQWB1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SQWB2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SQOB1</td>
<td>252</td>
<td>189</td>
</tr>
<tr>
<td>SQOB2</td>
<td>212</td>
<td>188</td>
</tr>
</tbody>
</table>

For the purpose of establishing the so called plateau stress on the stress-strain curve of examined alloys during deformation in quenched conditions which points the possibility of shape memory appearance, the series of tensile testing at room temperature was performed. The distinct plateau appearance was observed for DQ specimens of Cu-25.38Zn-3.3Al and also for UQ and SQOB specimens of both alloys (see Figure 3) while DQ specimens of Cu-21.6Zn-5.64Al alloy have shown poor plateau appearance. The stress-strain curves obtained for specimens step-quenched in boiling water for both alloys have not “shown” the plateau. The values of deformation which “limit” the plateau ($\varepsilon_{\text{start}}$ and $\varepsilon_{\text{finish}}$) for examined specimens are listed in Table 2. The different values for $\varepsilon_{\text{start}}$ and $\varepsilon_{\text{finish}}$ deformations for specimens that were heat treated in the same way, are probably caused by different grain orientation or grain size (3). The deformation $\varepsilon_{\text{finish}}$ is the biggest for specimens of Cu-25.38Zn-3.3Al except for step-quenched in boiling water.

**Cu-25.38Zn-3.3Al (SQOB1)**

![Stress-strain curve](image)

Figure 3. The stress-strain curve for SQOB1 specimen of Cu-25.38Zn-3.3Al alloy
Table 2. The values of deformation which “limit” the plateau for examined specimens

<table>
<thead>
<tr>
<th>Treatment</th>
<th>DQI (%)</th>
<th>DQ2 (%)</th>
<th>UQI (%)</th>
<th>UQ2 (%)</th>
<th>SQWB1 (%)</th>
<th>SQWB2 (%)</th>
<th>SQOB1 (%)</th>
<th>SQOB2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Cu-25.38Zn-3.3Al</td>
<td>0.99</td>
<td>0.95</td>
<td>1.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>Cu-21.6Zn-5.64Al</td>
<td>0.20</td>
<td>0.30</td>
<td>0.30</td>
<td>0.25</td>
<td>0.30</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In order to investigate the influences of various strains on martensitic substructure i.e., which strains could be thermal recovered, transmission electron microscopy was used for examining the martensitic substructure. In specimens deformed by strain from the plateau range, the twinnings were observed (Figure 4a), while twinnings and great dislocation density (Figure 4b) were discovered in specimens deformed by strain that exceed plateau range, which indicate the slip was activated. Since the slip is irretrievable process that could not be eliminated by heating, while the twinning is retrievable process so shape memory effect appearance might be expected in specimens in which dislocation were not observed (4).

Figure 4. TEM microphot. for DQ2 specimens of Cu-25.38Zn-3.3Al alloy (deformed by different strains)

The tensile testing of quenched specimens at room temperature indicate pseudoplasticity in the range 1.5 to 3.0% for Cu-Zn-Al alloys. The strain in plateau range is only illusive because it is not caused by slip and twinning that are mechanisms of deformation of ordinary metals, but special reorientation of twinning domains within martensitic plates. Namely, according to some investigation (5), the applied stress in shape memory alloys causes growth of martensitic domains, which are favorably oriented with respect to the stress axis at the expense of others. Consequently, the pseudoplastic deformation is realized and it appeared on stress-strain curve as plateau, which indicate that practically deformation hardening has not happened. The modified martensites of single orientation formed during pseudoplastic deformation are mainly responsible for shape recovery, since they are the only ones that are able to regain the initial configuration by retracing the transformation path
during the reverse transformation. The unfavorably oriented domain groups, however, can not possibly contribute to any shape memory recovery because of their random orientation. Since the domain group orientation in the Cu-Zn-Al system was found to be rather random, it might have so happened that the applied stress to achieve a high volume fraction of required producing the irreversible defects, such as slip, dislocations, etc. In that case shape memory recovery would not appear. The ending of the plateau stress indicate that unrecoverable deformation has realized which is followed by certain deformation hardening.

The values of shape memory recovery for examined specimens that have been obtained by direct observation of thin specimens quenched, then bent ≈ 30 deg before heating above Α₁ temperature are given in Table 3. Full shape memory recovery (100%) was not observed in examined specimens but most of quenched specimens of Cu-25.38Zn-3.3Al alloy have shown shape memory recovery greater than 90%. The absence of full memory recovery in examined specimens is probably due to great number of grains and also presence of certain amount of α-phase and/or ordered β-phase beside martensite in their structure.

<table>
<thead>
<tr>
<th>Designation of treatment</th>
<th>DQ1</th>
<th>DQ2</th>
<th>UQ1</th>
<th>UQ2</th>
<th>SQWB1</th>
<th>SQWB2</th>
<th>SOQ1</th>
<th>SOQ2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-25.38Zn-3.3Al SOO [%]</td>
<td>87-91</td>
<td>89-91</td>
<td>91-95</td>
<td>90-92</td>
<td>0</td>
<td>0</td>
<td>89-95</td>
<td>92-98</td>
</tr>
<tr>
<td>Cu-21.6Zn-5.64Al SOO [%]</td>
<td>74-79</td>
<td>72-77</td>
<td>82-85</td>
<td>85-87</td>
<td>0</td>
<td>0</td>
<td>78-88</td>
<td>73-78</td>
</tr>
</tbody>
</table>

The influence of various quenching media on shape memory recovery of specimens of Cu-25.38Zn-3.3Al alloy was not noticeable, while for specimens of Cu-21.6Zn-5.64Al were observed some memory differences. Namely, the best memory results for the latter alloy are obtained in SOQ1 specimens, somewhat lower memory values were observed for DQ specimens because of certain stabilization of martensite, while sufficient decreasing in quenched-in vacancies concentration was not obtained by UQ treatments in order to avoid martensite stabilization and show optimal shape memory effect (6). The specimens of both alloys that were step-quenched in boiling water (SQWB) have not shown memory recovery, probably due to appearance of β-phase with B2 and/or DO₃ order as well as α-phase (f.c.c.) which was confirmed by X-ray examining of crystal structure (see Fig. 2).

On the base of the obtained results, the optimal quenching procedures from the standpoint of relevant properties, firstly one-way shape memory effect are up quenching (UQ) and step-quenching in oil bath at 105°C ± 5°C (SOQ1) for Cu-25.38Zn-3.3Al alloy, while the best results for Cu-21.6Zn-5.64Al alloy are obtained by SOQ1 quenching treatment.

CONCLUSIONS

The thermoelastic martensitic transformation and shape memory effect appearance have been studied in Cu-25.38Zn-3.3Al and Cu-21.6Zn-5.64Al alloys quenched in various media. On the base of the obtained results these conclusions could be made:

- After performing various quenching procedures (direct quenching, up quenching, step-quenching) on specimens of two examined Cu-Zn-Al alloys was discovered the presence of martensite go a long period stacking order type: M18R and 2H as well as certain quantity of α-phase (f.c.c.) and parent phase (B2 or/and DO₃ superlattice). The martensite M18R type was observed in all quenched specimens, while the martensite 2H type was not observed only after performing
step-quenching in boiling water (SQWB). The presence of $\text{DO}_3$ phase in examined specimens indicates the appearance of the transformation $\text{B2} \rightarrow \text{DO}_3$ in parent phase that could not be suppressed even with rapidly quenching.

- The tensile testing of quenched specimens at room temperature was shown the distinct plateau stress appearance on stress-strain curve for DQ specimens of Cu-25.38Zn-3.3Al and also for UQ and SQOB specimens of both alloys, while DQ specimens of Cu-21.6Zn-5.64Al alloy have shown poor plateau appearance. The specimens of both alloys step-quenched in boiling water have not shown plateau stress, because of presence of certain quantity of $\alpha$-phase as well as parent phase.

- Full shape memory recovery (100%) was not observed in quenched specimens, but most of quenched specimens of Cu-25.38Zn-3.3Al have shown shape memory recovery greater than 90%. Since there are great number of grains, we could not expect full shape memory recovery. In addition, examining of microstructure and crystal structure has shown that there is certain amount of $\alpha$-phase and/or ordered $\beta$-phase beside martensite in quenched specimens.

- The tensile testing of quenched specimens and determinations of shape memory recovery have shown that for examined Cu-Zn-Al alloys the pseudoplasticity range is from 1.5 to 3.0%.

- The best shape memory behaviour of specimens of Cu-25.38Zn-3.3Al alloy is obtained by up quenching (UQ) and step-quenching in oil bath at 105°C ± 5°C (SQOB). SQOB1 quenching treatment provides the best results for Cu-21.6Zn-5.64Al alloy.

REFERENCES


ТЕРМОЕЛАСТИЧНА МАРТЕНЗИТНА ТРАНСФОРМАЦИЈА И ЕФЕКAT ПАМЋЕЊА ОБЛИКА КОД ЛЕГУРА Cu-Zn-Al

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У оквиру овог рада извршено је истраживање појаве термоеластичне мартензитне трансформације и ефекта памћења облика код легура Cu-25.38Zn-
3.3Al и Cu-21.6Zn-5.64Al. Након реализације осам различитих поступака каљења, спроведено је испитивање микроструктуре путем светлосне микроскопије, X-рај испитивање кристалне структуре, одређивање температуре мартензитне и обратне трансформације путем праћења промене електричног отпора у функцији температуре, испитивање затезањем каљених узорака на собној температури, као и испитивање субструктуре мартензита помоћу TEM-а. На основу добијених резултата извршен је избор оптималног начина каљења предметних легура са становишта једносмерног ефекта памћења облика.

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