Activation of CuAlNi SMAs Using Solar Energy

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Abstract: Shape memory alloys are special materials that can perform mechanical work during martensitic transformation. CuAlNi shape memory alloys have gained attention based on their high transformation temperatures domain and can be considered as HTSMAs (high-temperature shape memory alloys). The thermal component in order to achieve martensitic transformation can be obtained from sun using a solar concentrator. The heating/cooling process was registered and analyzed during the experiments. The material surface was investigated by microstructure point of view using scanning electron microscopy (SEM VegaTescan LMH II, SE detector) and atomic force microscopy (AFM EasyScan II, non-contact mode). The experiments follow the material behavior during fast heating and propose the possibility of activating smart materials using the sun heat for aerospace applications.

Keywords: shape memory alloy; solar energy; SEM; AFM; martensite.

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1. Introduction

Cu-Al-Ni type alloys have been developed, due to the martensite thermo-elasticity, in the commercial forms Cu-Al-Ni-X or Cu-Al-Ni-Mn-X, where X is an alloying element, with the role of finishing the structure which may be missing for certain Al/Ni reports [1, 2]. It can be seen that the values of Ms (martensite start) are very high, the (hyper) eutectoid alloys having interest having transformation points between 100-400 °C with interest for high-temperature applications (HTSMs) [3-6]. In addition, precipitation of the extremely hard γ2 phase cannot be suppressed even by a fast cooling stage. In order to eliminate the above disadvantages, the alliance with Ni was used. Following the introduction of nickel, the eutectoid moves to approx. 14% Al, concentration corresponding to a critical temperature Ms in the vicinity of the ambient temperature if the application requires [7]. If more than 5% Ni is added, γ2 precipitation is suppressed, but NiAl precipitates may occur, which are almost as fragile. For these reasons, the usual concentration of alloys with the shape memory based on Cu-Al-Ni is Cu-(10-14)% Al–(2-4)% Ni [8]. The typical structure of

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these alloys may contain: equilibrium phases: a solid solution \( \alpha \) (cfc), isomorphic with copper, with the lattice parameter increasing with Al and Ni concentrations \( (a = 0.3658 \text{ nm for Cu-13\% Al-4\% Ni}) \) [8, 9]; monoclinic NiAl intermetallic compound, with 3R structure and lattice parameters: \( a = 0.418 \) nm, \( b = 0.271 \) nm, \( c = 0.628 \) nm and \( \beta = 800 \); solid solution \( \gamma_2 \), based on the electronic compound \( \text{Cu}_9\text{Al}_4 \), with complex cubic crystalline lattice with 52 atoms per elementary cell and the parameter \( a = 0.868 \) nm [8]. The metastable phases: austenite \( \beta_1 \), not transformed, based on the electronic intermetallic compound \( \text{CuAl}_3 \), with structure \( \text{D0}_3 \) and the network parameter \( a = 0.5836 \) nm [9, 10]; tension-induced monoclinic martensite, with 18R2 packing order and lattice parameters \( a = 0.443 \) nm, \( b = 0.533 \) nm, \( c = 3.819 \) nm and \( \beta = 890 \) [9]; thermally induced orthorhombic martensite, with the 2H packing order and the network parameters \( a = 0.439 \) nm, \( b = 0.5342 \) nm, \( c = 0.4224 \) nm; tension-induced monoclinic martensite \( \alpha_1 \), with 6R packing order and lattice parameters \( a = 0.4503 \) nm, \( b = 0.5239 \) nm, \( c = 1.277 \) nm and \( \beta = 89.30 \).

In this article, the activation of CuAlNi shape memory alloy using solar energy is analyzed by means of the behavior of the alloy at 10 thermal shocks cycles till 300, respectively 600 °C with high heating/cooling rates.

2. Materials and Methods

The heating experiments were realized on a solar concentrator, part of the Promes - France laboratories. PROMES - CNRS at Font-Romeu Odeillo has a whole range of systems based on solar flux that can be used as experimental furnaces or heating systems, figure 1. Intelligent materials like SMAs (shape memory alloys) were activated with help from solar beam reflected by a mechanized metallic window (5 x 12m) situated at the bottom of the building, through a shutter system (used to control the intensity of the light beam) and a concave concentrator, as presented schematically in figure 1. The beam is transmitted at a focus point 1-1.5 m down to a center.

In order to locate the sample in the center of light concentration and to the benefit of the biggest intensity and temperature, we use an aluminum trolley, top figure 1) that can be translated on X-Y axis [4, 11]. The sustaining aluminum system is continuously cooled with water in order to avoid accidents. The metallic experimental probes, squares of 10x10 mm with a K thermocouple, used to retrieve data about the temperature evolution in time, connected to a Graphite Corporation equipment type GL220 [3, 12]. Both heating and cooling stages were registered and analyzed, figure 2 a)-d). The thermal shocks were performed, moving the trolley from and under the sunlight [13-15]. The experimental heating temperatures were 300 and 600°C ± (10, respectively 25 °C because of the thermal inertia of the metallic samples). The appearances of these variations are based on the human factor that moves and sustains the trolley and can be eliminated using a motorized system.

First heating cycle, in both cases, figure 2 a) and c), present small variations and larger time, based on the human skill usage but after the time period to reach the proposed temperature (is a factor of the sun power) all the other heatings (thermal shocks) present a smaller time period to be applied. Besides the actual analysis of the heating/cooling rate from registered data, we obtain a fitting rate from the experimental curves.

In tables 1 and 2 are presented the heating/cooling rates registered during the thermal shock experiments till 300 respectively 600 °C. The heating rates are between 10 to 80 ºC/ms and the cooling rates between 12 and 70 ºC/ms. Using a shutters system, we can control the intensity of the light beam and a trolley for positioning the sample in the middle of the fascicule.

The advantages of solar heating for shape memory alloys used for space applications are given
Activation of CuAlNi SMAs using solar energy

by constant light intensity in space comparing with applications of SMAs on earth were clouds can affect the solar intensity. Using a proper controlling system of sun intensity, we can obtain a perfectly repeatable intensity for certain time periods in order to stimulate a shape memory element as many times is necessary.

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**Figure 2.** Temperature variations on CuAlNi sample in time a) and c) during the solar heating and room cooling and linear fit of heating in b) and cooling in c) of the curves.

**Table 1.** Heating and cooling rates of shape memory alloy for thermal shocks tests till 300 °C.

<table>
<thead>
<tr>
<th>Thermal shocking parameters</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
<th>Cycle 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting rate (°C/ms)</td>
<td>9.4</td>
<td>16.9</td>
<td>24.6</td>
<td>22.9</td>
<td>59.4</td>
</tr>
<tr>
<td>Calculated rate (°C/ms)</td>
<td>12.1</td>
<td>24.7</td>
<td>33.2</td>
<td>29.5</td>
<td>51.6</td>
</tr>
<tr>
<td>Thermal shocking parameters</td>
<td>Cycle 6</td>
<td>Cycle 7</td>
<td>Cycle 8</td>
<td>Cycle 9</td>
<td>Cycle 10</td>
</tr>
<tr>
<td>Fitting rate (°C/ms)</td>
<td>56.2</td>
<td>37.7</td>
<td>53.7</td>
<td>30.4</td>
<td>67.1</td>
</tr>
<tr>
<td>Calculated rate (°C/ms)</td>
<td>50.5</td>
<td>39.3</td>
<td>46.6</td>
<td>36.8</td>
<td>67.2</td>
</tr>
</tbody>
</table>

**Table 2.** Heating and cooling rates of shape memory alloy for thermal shocks tests till 600 °C.

<table>
<thead>
<tr>
<th>Thermal shocking parameters</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
<th>Cycle 5</th>
</tr>
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</tr>
<tr>
<td>Thermal shocking parameters</td>
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<td>Cycle 7</td>
<td>Cycle 8</td>
<td>Cycle 9</td>
<td>Cycle 10</td>
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<tr>
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</tr>
</tbody>
</table>
3. Results and Discussion

After the 10 heating/cooling cycles at 300 or 600 °C, the surface of the experimental samples was investigated through SEM and AFM techniques. In figure 3, SEM images of CuAlNi alloy are presented as a) initial state, b) after 10 heating/cooling cycles to 300 °C and c) after 10 heating/cooling cycles to 600 °C.

Figure 3. SEM images of CuAlNi alloy a) initial state; b) after 10 heating/cooling cycles to 300 °C and c) after 10 heating/cooling cycles to 600 °C.

Phase β, based on the Cu$_3$Al intermetallic compound, represents austenite which, at very slow cooling, decays eutectoid at 570°C [16-19] resulting in a solid isomorphic solution with copper (α, cfc) and a solid solution based on the intermetallic compound of Cu$_9$Al$_4$ type (γ2, a complex cube with 52 atoms per elementary cell), figure 3 c) [20]. When cooling at normal speeds, the austenite β (A$_3$) is ordered to become β1 (D0$_3$), at approx. 525 °C. The same thing happens with the solid solution α, which is ordered at short distances and becomes α2 [21, 22].

The microstructure profile at the surface was analyzed, at a smaller scale, using the AFM technique. In figure 4 are presented AFM images of CuAlNi surface a), d) initial state; b), e) after 10 cycles at 300 °C and c), f) after 10 cycles at 600 °C.

The results don’t present modifications in case of thermal solicitation till 300 °C (10 cycles), figure 4 comparison between a) and b), in 2D and d), and e) for 3D images. In the case of heating to 600 °C a modification of the microstructure relief can be observed, comparison between a) and c), confirming the observations from SEM analyze, figure 3 a) and c).
Activation of CuAlNi SMAs using solar energy

As the heat-induced martensite plates, from Cu-Al-Ni alloys, continuously increase upon cooling and continuously shorten upon heating [20] can conclude that there is a balance or exchange between chemical free energy and free energy; elastic deformation at transformation [21]. This martensitic transformation, with thermal hysteresis of the order of 30K [23], corresponds to a simple memory effect of the shape of approx. 4% and a two way shape memory effect of approx. 2% [24].

4. Conclusions

Thermal activation of metallic elements made of CuAlNi – SMAs is easily done by sun energy. Different temperatures can be reached with different heating rates based on the application needs. Solar concentrators (with different dimensions) can be considered a cheap, inexpensive, and proper solution for shape memory alloy functionalization in inaccessible spaces or for aerospace applications. Heating the surface of CuAlNi till 300 and 600 °C produces a modification of the chemical composition by forming oxides (copper-based most of them) identified through SEM and AFM analyses. SEM and AFM results present no modification at the primary plates dimensions and orientation also after the thermal shocks no secondary plates formation was observed in case of heating the material till 300 °C but when we analyze the sample heated to 600 °C no more martensite plates appear based on a high heating stage and also a relatively high cooling rate, further investigation on the relief modification must be realized by means of the depth of the modification. New experiments with thermal shocks are necessary in a vacuum state in order to analyze the material behavior in aerospace conditions.

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Conflicts of Interest

The authors declare no conflict of interest.

References