Heating to thermal shock of Cu-based SMA using a solar concentrator

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Abstract. Solar energy represents a renewable energy which is one of the most expected to breakthrough in the next years in many application fields, as a heating source. It is expected that we can use solar energy in order to activate special materials, sensitive to heat variation, like shape memory alloys. Shape memory alloys present an increasing number of applications in the last years. Solar heat is free and endless on short time (hundreds of years) so it represents an ideal source of energy. Using a proper mirror-concentrator system, at a reduced scale for temperature lower than 500-600 °C, we can activate any type of shape memory element with different temperatures, rates of heating or maintaining periods of the heat using the shutter aperture. We analyse the behaviour of a shape memory alloy based on copper at different heating cycles in regime of shocks till 300 respectively 600 °C (with different heating rates, till 120°C/ms, excepting first cycle). The temperature variation was registered and analysed using Graphitec Corporation equipment and Origin software.

1. Introduction
Based on shape memory effect a smart material can execute work using an external source of heat. The base of special properties of shape memory alloys is the martensite transformation [1,2]. It is highly accepted that martensitic transformation can be induced by temperature variation and by stress solicitation. In the temperature variation case it is important to control with a high accuracy the transformation parameters like heating rate or upper temperature limit in order to not corrupt the shape memory effect properties [3-8].

Metallic materials processing operations (melting stage, heat treatment or surface modification of metals), are energy-intensive processes, requiring furnaces operating at high temperatures. Conventional furnaces used in the last years are electric arc furnace and induction furnace [9]. Induction furnaces are used for melting and local heat treatment and resistance furnaces with controlled atmosphere or vacuum have been the extensively used for all metals processing operations treatments ranging from 500°C to 1800°C [10]. All these variants of furnace require huge amounts of energy. Firstly, this energy was covered by fossil fuels, either directly or indirectly as electricity. Both possibilities require high environmental costs [11]. Solar energy gain space as renewable energy, with applications in different industries. At industrial level the use of non-conventional sources of energy,
notably solar energy, for metals processing applications has been minimal. Solar technology can be used as concentrated solar power (CSP) which appears to be a promising method for providing high-temperature process heat in short period of time. In this case the solar light is focussed using a system of mirrors, named also collectors, that are able to concentrate natural sunlight 40 to more than 900 times and focus it on to receivers [12]. There are many different methods to concentrate solar energy—parabolic trough, linear Fresnel, solar tower, and parabolic dish—are well known and have been employed already in the production of electricity. Of these, the parabolic trough is the most mature technology and has been operating since 1984 [13, 14].

In this article preliminary microstructural and chemical results are presented from the analyze of the surface of a Cu-based shape memory alloy subjected to thermal shocks. 10 heating/cooling cycles we applied using solar energy and a mirror-concentrator system. We follow two main ideas: first to analyse the shape memory alloy behaviour at thermal shocks (repeated heating at 300 and 600 °C) and secondly the usage of solar energy to activate shape memory alloys based on copper.

2. Experimental set-up

The solar concentrator used is part of the Promes France facility. PROMES-CNRS at Font-Romeu Odeillo host a whole range of high and very high flux solar furnaces and 10 min nearby in Targassonne the Themis solar tower [13]. Shape memory alloys samples were heated using solar light reflection from a metallic window (5x12 m) situated at the bottom of the building, through a shutters system (used to control the intensity of the light beam) and a concentrator, as presented schematically in figure 1 a). The light is forward transmitted at 1-1.5 m down to a center and spread near that. In order to locate the sample in the center of light concentration and to benefit of the biggest intensity and temperature we use an aluminium trolley, figure 1 b) that can be moved on X-Y axis. The support system is always chilled with water (the temperature can increase really fast till 3000 °C at a full opening of the shutters).

![Figure 1. Schematic view of the heating system using solar light in a) and experimental set-up in b)](image_url)

The samples, 10x10 mm, were fixed using a mechanical system and under the sample, in the middle part, a K thermocouple was used to retrieve data information connected to a Graphtec Corporation equipment type GL220. Both heating and cooling stages were registered and analysed. The shocks were performed moving the trolley from and under the sun light. The heating experimental temperatures were 300 and 600 °C ±(10-25). Before and after the thermal shocks the metallic material surface was analysed through scanning electron microscopy (SEM VegaTescan LMH II) and X-ray dispersive analyse (Bruker type).
3. Experimental results
Copper based shape memory alloy (Cu15.5Zn6.5Al) as 10x10 mm square were used for exposure to heat (10 cycles) at 300 and 600 °C. The flux was applied in the middle part of the sample by situating the sample in the middle of the solar flux. The temperature increasing and decreasing was registered using a K type thermocouple and the heat was analysed from the middle of the sample. In figure 2 a) and c) is represent the temperature variation in time for 10 heating/cooling cycles.

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

The heating process consists of a mirror that collect the sun light, a concentrator of light through a shutters system and a trolley for positioning of the sample in the middle of the concentrated light. The heat intensity is given from the shutters system opening and can be control based on the clearness of the sky. Small variations near 300 and 600°C temperatures were observed. The appearance of these variations is based on the human factor that move and sustain the trolley and can be eliminated using a motorized system. In tables 1 and 2 are presented the heating/cooling rates registered during the thermal shock experiments till 300 respectively 600 °C.
Table 1. Heating and cooling rates of shape memory alloy for thermal shocks tests till 300 °C

| Thermal shocking parameters | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 |
|-----------------------------|---------|---------|---------|---------|---------|
| Fitting rate (°C/ms)        | H       | C       | H       | C       | H       |
|                            | 10      | 3.9     | 14.8    | 5.1     | 56.3    |
| Calculated rate (°C/ms)     |            |         |         |         |         |
|                            | 12.3    | 6.1     | 17.5    | 8.2     | 56.5    |
| Thermal shocking parameters | Cycle 6 | Cycle 7 | Cycle 8 | Cycle 9 | Cycle 10 |
| Fitting rate (°C/ms)        | H       | C       | H       | C       | H       |
|                            | 26.4    | 4.7     | 42.5    | 5.4     | 61.7    |
| Calculated rate (°C/ms)     |            |         |         |         |         |
|                            | 27.9    | 9       | 41.6    | 8.4     | 59.1    |

First heating cycle, figure 2 a), present a smaller heating rate based on the behaviour of the material and the establishment of heating parameters like shutters opening value and time to reach the experimental temperature. In the other heating cycles higher heating temperatures were reached. The cooling take place at room temperature (almost 30°C) having small cooling rates. For aerospace applications the experiments must be carried out in vacuum environment where the temperature is -270.6°C and the cooling will take place much faster. We expect that local heating of the metallic material to take place in similar conditions in space environment as well as at room temperature and only the cooling to be influenced by the environment temperature.

In the second case, table 2, heating of the material till 600°C, we reached rates of 120°C/ms so the heating take place practically instant. In these conditions we can actually discuss about thermal shock of the material.

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

| Thermal shocking parameters | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Cycle 5 |
|-----------------------------|---------|---------|---------|---------|---------|
| Fitting rate (°C/ms)        | H       | C       | H       | C       | H       |
|                            | 10.7    | 10.4    | 117.5   | 3.9     | 101.5   |
| Calculated rate (°C/ms)     |            |         |         |         |         |
|                            | 11.4    | 7.5     | 116.9   | 8.5     | 97.1    |
| Thermal shocking parameters | Cycle 6 | Cycle 7 | Cycle 8 | Cycle 9 | Cycle 10 |
| Fitting rate (°C/ms)        | H       | C       | H       | C       | H       |
|                            | 90.8    | 12.9    | 94.1    | 15.5    | 92.4    |
| Calculated rate (°C/ms)     |            |         |         |         |         |
|                            | 81      | 17.9    | 81.9    | 22.1    | 81.4    |

In figure 3 is presented the surface state of the experimental alloy before, in a), and after b) and c) the thermal shocks applied to material. The surface analysed is from the middle part of the sample. The structure present primary martensitic type plates (more than 98%) with different orientations inside the grains. Structurally we don’t remark significant changes even if the plates presented in the samples after the thermal shocks are thinner in order to establish a rule of that more experiments are necessary. For third sample new compounds can be observed on the surface.
Although Cu-Zn-Al-AMF martensitic plates have an internal defect substructure created by inverse planar shear, the acoustics of the plates in the austenitic matrix are made by maceration to maintain the coherence of the crystal lattice on the austenite-martensite interface. So, the macules observed in the microstructure of these alloys are accommodating rather than transforming. In addition, it should be noted that approx. 50% of these poppies are type II, as well as AM-based Cu-Al-Ni [15]. Because of the twinning accommodation, martensite from AMF Cu-Zn-Al has a characteristic shallow relief. In the microscopic picture, figure 3 c), the intersection point of the boundaries between the 3 grains is observed. Primary martensite plates were formed on all three, growing along their length, without being able to cross the boundary between them.

The relief is also visible in the secondary plates, as shown by the electronic micrographs in Figures 3 (a) and (b), obtained on the same alloy. As a comparison between the relief characteristic of the primary plates - which crosses the whole field of micrography and that of secondary martensite plates. The latter are shorter and finer because they did not have any time or space to increase to the size of the main plates. It is also noticed that the martensite side plates have their own relief, very well emphasized. It can be seen that the thermo-elastic growth of the platiform-lenticular martensite is incoherent to the grain boundaries when they are unfavorably oriented. There are also situations when it is easiest to cross grain boundaries with favourable orientation and reduced width [16]. The growth and reversal of martensite plates is one of the most intensely studied phenomena, characteristic of thermo-elastic martensite, for which a wide variety of characterization methods were used [17].

Chemical composition of the samples was analysed in the middle part, which was also repeatedly heated. The results, table 3, present the appearance of carbon and oxygen on samples after the thermal shock. The oxygen and carbon presence are explained by the local oxidation process in the contact area of the material with the concentrated solar beam because the thermal shock was experimented in atmospheric environment.

**Table 3.** Chemical composition of the surface before and after the thermal shocks using EDAX detector

| Chemical composition | Cu wt% | Cu at% | Zn wt% | Zn at% | Al wt% | Al at% | C wt% | C at% | O wt% | O at% |
|----------------------|--------|--------|--------|--------|--------|--------|-------|-------|-------|-------|
| Initial              | 78.04  | 72.05  | 15.5   | 13.9   | 6.49   | 14.04  | -     | -     | -     | -     |
| 10 heat shocks 300°C | 73.33  | 68.01  | 14.69  | 7.93   | 5.95   | 7.87   | 1.5   | 3.07  | 8.58  | 19.13 |
| 10 heat shocks 600°C | 62.36  | 38.1   | 12.71  | 7.55   | 9.17   | 13.2   | 3.58  | 11.58 | 12.17 | 29.55 |
| EDAX error%          | 1.5    | 0.4    | 0.4    | 1      | 1.8    |        |       |       |       |       |
For both cases of thermal shock we observe a decrease of zinc content that can cause the increase of M, value [18] and modification of all other transformation points. The decrease of zinc element percentage can be a process only at the surface of the alloy and the influence of this process on the shape memory properties must be studied. A bigger decrease of zinc was registered for heating the percentage of zinc of NiTi alloy coated with various polymers, Bujoreanu at their shape. A bigger decrease of zinc was registered for heating the percentage of zinc of NiTi alloy coated with various polymers, Bujoreanu at their shape. For aerospace applications are necessary tests in vacuum conditions and the percentage of zinc analysed again.

4. Conclusions
Shape memory alloy based on copper can be easily activated using solar heat amplified by a concentrator system. The activation can be done with different heating rates till 120 °C/ms depending on the necessity of the application. A thermal shock at a temperature bigger than 300 °C lead to an oxidation of the surface and a loss of zinc element that can directly affect the transformation points of the alloy. The loss of zinc is at the surface of the shape memory element and not in depth. The influence of thermal shock on the shape memory properties must be analysed in the future.

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