Structural study and phase transformation of Cu-Al-Ni shape memory alloy produced by severe plastic deformation

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Martensitic transformation and mechanical behavior are investigated on extremely brittle Cu-13Al-4Ni shape memory alloy subjected to severe plastic deformation (SPD) by high speed high pressure torsion (HSHPT). The HSHPT process involves high pressure coupled with torsional deformation of the alloy, at which large rotation speed (1795 rpm) of the upper punch generates heat by friction. The experiments are carried out in a Bridgman cell right from room temperature. The disc-shaped Cu-Al-Ni samples produced by this technique have diameter between 20 and 29 mm and thickness until 0.16 mm, depending on the extent of deformation. Microstructural analyses are performed on the alloy that had undergone processing by optical, scanning electron as well as transmission electron microscopy. The microstructural investigations show that increasing the degree of deformation leads to gradual grain refinement. The microstructural changes are correlated with the Vickers hardness of the alloy. The alloy processed by HSHPT shows reversible martensitic transformation without the necessity for post-deformation annealing and phase transformation stability after 10 thermal cycles, too.

Keywords: Shape memory alloys, Cu-Al-Ni alloys, SPD, HSHPT, DSC, TEM

Research into Cu-13Al-4Ni shape memory alloy (SMA) was initiated within the past couple of decades owing to its ease of production and processing, lower cost, and attractive functional properties, such as superelasticity, one- and two-way shape memory effect. This SMA undergoes a diffusionless martensitic transformation between a high temperature metastable beta phase (austenite) and two coexisting low-temperature phases, namely orthorhombic and monoclinic martensite. Copper-based shape memory alloys are easier to produce and process. But conventional polycrystalline Cu-Al-Ni shape memory alloys are brittle due to their high elastic anisotropy and the presence of coarse grains. For the brittleness reason they have some limitations for industrial applications. Grain refinement reduces stress concentration in the grain boundaries and has been used to improve the mechanical properties of polycrystalline Cu-Al-Ni alloys. Attempts to improve the ductility of these polycrystalline copper-based shape memory alloys by grain refinement have only resulted in limited success. Many studies have been carried out so as to enhance it, such as the use of alloying elements, formation of single crystals, adoption of appropriate thermomechanical treatments, etc.

Processing by severe plastic deformation (SPD) produces considerable reduction in the grain size of bulk alloys. The classic high pressure method (HPT) enables production of ultrafine, nanocrystalline or amorphous microstructure in easy-to-deform metallic materials. In the present study we used the standard HSHPT technology to fabricate disc springs with ultrafine and nanocrystalline microstructure in difficult-to-deform alloys. The new technology helps obtain active elements with diameters of up to 40 mm, which is larger than that can be obtained from classic HPT. In specific case of SMAs the amorphization that appears on HPT is avoided. The discs have shape memory properties immediately after severe plastic deformation, without the need for the additional post-deformation annealing.

The driving force to study an alloy that has undergone processing by HSHPT stems from the need to produce less expensive smart materials for industrial applications with specific functional properties in nano- and micro-scale systems. The structural applications of concrete require improving mechanical properties, especially improvements in...
strength, which is correlated with microstructure. The application of SMAs as sensors and actuators also requires precise transformation temperatures and good thermal stability. But these properties are greatly influenced by microstructural features, chiefly grain size. The alloys with grain sizes in a submicron (100-1000 nm) or nanocrystalline (≤100 nm) range, processed by severe plastic deformation (SPD), exhibit novel and improved properties. The behavior of shape memory alloys, which exhibit unique functional properties, is evaluated by the structural changes on a submicron scale.

Materials and Methods

Cast Cu-13Al-4Ni (all concentrations given in wt%) alloy ingots were obtained by induction melting using high purity elements, whose purity was in excess of 99 wt%, in a crucible. The as-cast conical ingots (diameter between 25-40 mm and 150 mm in thickness) were extruded at 900°C. The HSHPT research studies were initiated on air cooled extruded wires (4 mm thickness and 14.92 mm in diameter). Billets were cut from the extruded rods and subjected to strain levels of 1.71, 2.62, 2.89, 3.35, 3.59 and 3.62 by HSHPT. The SPD discs were obtained after giving different amounts/degrees of deformation achieving up to 29 mm in diameter and between 0.29 mm and 0.16 mm in thickness. The extent of deformation/plastic strain was estimated using the following relationship:

\[ \varepsilon = \ln \left( \frac{h_i}{h_f} \right) \]  

where \( h_i \) and \( h_f \) indicate the initial and final thickness of the sample, respectively. This equation is most accurate for the value of true strain in HSHPT process, because in this process the torsion of the sample could not be appreciate using the rotation angle of the mobile anvil like in traditional HPT were the slippage is very limited.

The HSHPT parameters were selected using an EATON SVX024A1-4A1B1 frequency converter via PLC XC 200. The rotational speed of the upper punch was selected at 1795 rpm. The maximum torsional moment was 41.88 Nm. Pressure variation was recorded with a Hottinger Spider 8 equipment. Because of the extreme brittleness of this alloy the pressure levels were kept subsequently at 0.01 GPa, 0.06 GPa 0.12 GPa, and 0.68 GPa, as is shown in Fig. 1.

Specimens were prepared for microstructural examinations by optical (OM) as well as transmission electron microscopy (TEM). The discs were diametrically cut and embedded into decreasing grain/size (of up to 2000 mesh), subjected to disc polishing using alumina powder with a particle size of 0.04 µm followed by etching with a solution of FeCl₃ in distilled water. Microstructural examinations were first carried out on hot extruded alloy specimens and on billets subjected to HSHPT processing to varied levels of deformation. This was done so as to reveal the influence of processing on microstructure and properties. An OLIMPUS BX51 microscope, equipped with a video camera and QCapture software, was used for the optical microscopic examinations.

The microstructural examinations were intended to throw light on the changes brought about by the compressive and torsional forces introduced during processing by HSHPT. For a much deeper examination of the microstructure the specimen that was subjected to a deformation level of 1.71 was analysed by transmission electron microscopy (TEM). The microstructural analysis of the samples by TEM was carried out using a Tecnai 20G2 TEM equipped with EDX facility operating at a voltage of 200 kV. Thin foils from extruded and HSHPT processed billets were prepared using an electrolyte with 90% by volume of methanol and 10% by volume of nitric acid. The transformation temperatures of the specimens processed to contain different degrees of deformation were determined by differential scanning calorimetry (DSC TA Q20). A heating/cooling rate of 50°C /min in the range of 0 to 250°C was adopted for the experiments.

The samples for microhardness were extracted from both the extruded initial samples and discs from HSHPT processed alloy. Room temperature Vickers...
microhardness values were determined using an indenter under a load of 0.98067 N (HV0.1) applied for 10 s.

**Results and Discussion**

**Parameters of HSHPT process**

The HSHPT process, which was derived from the traditional HPT, affords the advantage of reducing the crystallite size to submicroscopic levels even in alloys that are difficult workability. The HSHPT facility and technology on different system alloys are described elsewhere.\(^{11,6,17}\)

The fundamental difference between classic HPT and high speed HPT lies in setting an elevated rotational speed of superior anvil, which causes slippage between the sample and the anvil. In the case of brittle alloys, the HPT method that involves high initial strength by compression are not reliable.\(^{18}\) The new HSHPT technology, which causes intense friction between the anvil and billet through implementation of an elevated rotational speed of the superior anvil (1795 rpm), leads to refinement of grains size down to nanocrystalline range even in brittle and hardly deformed materials.\(^{16,17}\) The temperature in the sample, experimentally measured, rises from room temperature up to the temperature at which threshold of plasticity is attained (~800°C). Severe plastic deformation occurs quickly under in less than 20 s. By monitoring deformation and by controlling process parameters the results are reproducible. The HSHPT technique enables fabrication of disc whose diameter was up to 29 mm, a noteworthy feature for Cu-13Al-4Ni SMAs that suffer from the problem of severe brittleness. It is important to note that during manipulation of the HSHPT discs no brittle fracture was observed. The Cu-13Al-4Ni discs became more flexible as the thickness decrease.

Results from the earlier studies showed significant improvement in the functional properties of the submicrometric, ultrafine grained or nanostructured alloys processed by severe plastic deformation techniques.\(^{11,19-22}\)

**Microstructures**

Figure 2a shows the micrograph of Cu-13Al-4Ni SMA in the initial extruded state. In SMAs either austenite or martensite or a mixture of austenite and martensite may be present depending upon their thermomechanical history. It can be observed from the micrograph that the original coarse β grains (with diameter between 200-300 μm) are preserved and homogeneously distributed. Martensite with plate-like and needle-like morphologies is present within these polygonal grains. These morphologies are referred to as twin type martensite: β₁’ (18R) monoclinic and γ₁’ (2H) orthorhombic.\(^{23}\) As shown in Fig. 2b, subjecting the alloy to HSHPT processing to a logarithmic strain of 2.62 leads to complete modification of the microstructure. It is obvious from the micrograph that the coarse grains have completely been replaced by flowlines.

The bright field (BF) TEM images (Fig. 3) of the extruded alloy at room temperature show martensite plates and stress fields. Figure 3a reveals a large martensite plate (ML) and a thin plate (MT). Within the large martensite plate are present parallel dislocation lines (DL) as well as dislocation tangles (DT).\(^{24,25}\)

The room temperature TEM micrographs show a heavily deformed microstructure of the HSHPT
processed alloy incorporating a logarithmic strain of 1.71. The images were taken from the flow plane, which is parallel to the surface area of HSHPT. In Fig. 4a, a representative martensitic morphology is clearly visible. The finer twins and needles and variant structure are accompanied by Ni$_3$Al precipitate particles (dark contrast) of 30-60 nm in size (P).

Most grain boundaries are curved (GBc) and some are faceted (GB$_F$)$^{26,27}$. The specimens subjected to HSHPT contain martensitic plates, which resemble to severe plastic deformation processes followed by post deformation annealing (PDA)$^{28,29}$. As can be seen in Fig. 4a, the original coarse β grains in range of 200-300 μm were refined to about 1 μm, in case of 1.71 logarithmic strain achieved by HSHPT. It should be noted that at room temperature, the alloy is in the martensitic state under $M_F$, as can be seen from DSC curves (Fig. 5).

In Fig. 4 (b,c) the presence of a high density of dislocations can be observed on boundaries that act as obstacles for dislocation slip, leading to their accumulation. The martensite plates are much finer on the order 50 to 90 nm (Fig. 4d). Simultaneous application of compression and rotation leads to large grain refinement. The amorphization that is specific to HPT no longer appears after this type of severe plastic deformation.

Fig. 3 — Bright field TEM images of hot extruded Cu-13Al-4Ni alloy (a) martensite morphology and (b) stress fields

Fig. 4 — Bright field TEM images of Cu-13Al-4Ni alloy after HSHPT processing to a logarithmic strain of 1.71 (a) and (b) central area of disc; (c) and (d) peripheral area of disc
Phase transformation temperatures

It is common practice to apply post deformation annealing (PDA) treatments to severely plastic deformed alloys to regain reversible martensitic transformation inhibited by internal stresses and accumulation of dislocations. The novel HSHPT technique enables obtaining sub-micrometric grain size discs from Cu-Al-Ni with forward and reverse martensitic transformation, without the necessity for PDA.

As far as the Cu-Al-Ni SMA that is being studied a complete and reproducible superelastic behavior has been reported in bulk to micro-nano scale alloys based on the stability of the phase transformation temperature. DSC is a useful technique to investigate phase transformation stability during heating and cooling cycles.

Figure 5 shows the DSC plot for the forward and reverse martensite transformations in Cu-13Al-4Ni alloy after severe plastic deformation by HSHPT with a logarithmic strain of 2.32. The heating/cooling rate was kept at 50°C/min. The first 10 cycles involving heating up to 250°C and cooling to 0°C confirm repeatability of martensitic transformation.

Table 1 shows the transformation temperatures after HSHPT process. The $M_s$ temperature changed from 105.78°C to 115.32°C, while the $A_s$ temperature changed from 71.6°C to 78.54°C. The enthalpy changes ($\Delta H$) for direct transformations remain almost constant and tend to stabilize. A similar tendency is exhibited by enthalpy changes in the case of reverse transformations, as can be seen in Table 1. We can conclude that after severe plastic deformation via HSHPT Cu-13Al-4Ni alloy exhibits good stability to phase transformation.

Microhardness

Figure 6 shows a non-linear increase in hardness with increasing logarithmic strain. The hardness change is significant and is correlated to the corresponding microstructure with the lowest degree

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$M_s$ (°C)</th>
<th>$A_s$ (°C)</th>
<th>$\Delta H^{M \rightarrow A}$ (kJ/kg)</th>
<th>$\Delta H^{A \rightarrow M}$ (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>105.78</td>
<td>71.60</td>
<td>6.950</td>
<td>4.532</td>
</tr>
<tr>
<td>2</td>
<td>106.51</td>
<td>72.73</td>
<td>6.667</td>
<td>4.326</td>
</tr>
<tr>
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<td>107.61</td>
<td>73.29</td>
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</tr>
<tr>
<td>4</td>
<td>109.73</td>
<td>74.98</td>
<td>6.635</td>
<td>4.561</td>
</tr>
<tr>
<td>5</td>
<td>110.71</td>
<td>75.84</td>
<td>6.652</td>
<td>4.647</td>
</tr>
<tr>
<td>6</td>
<td>112.35</td>
<td>75.55</td>
<td>6.309</td>
<td>4.816</td>
</tr>
<tr>
<td>7</td>
<td>112.93</td>
<td>76.11</td>
<td>6.128</td>
<td>4.860</td>
</tr>
<tr>
<td>8</td>
<td>114.19</td>
<td>77.20</td>
<td>6.031</td>
<td>4.886</td>
</tr>
<tr>
<td>9</td>
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<td>78.23</td>
<td>6.338</td>
<td>4.884</td>
</tr>
<tr>
<td>10</td>
<td>115.32</td>
<td>78.54</td>
<td>6.470</td>
<td>4.660</td>
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</table>
of deformation applied by HSHPT process. A considerable increase in hardness (4141 MPa) due to HSHPT can be seen after a logarithmic strain of 3.62 as against 2803 MPa for the hot extruded sample.

Conclusions

Based on the results obtained from the OM, TEM, DSC and hardness studies conducted on the disc samples of Cu-13Al-4Ni (wt%) SMA processed by HSHPT the following conclusions can be drawn:

(i) Cu-13Al-4Ni, a brittle SMA, subjected to severe plastic deformation by HSHPT, a new and reliable method, helped achieve fine-grained discs of up to 29 mm diameter.

(ii) Unlike in classic HPT considerably larger discs can be achieved by HSHPT within a matter of a few seconds.

(iii) Deformation applied to bulk coarse grained hot-extruded samples lead to a change of structure to nanocrystalline size martensitic plates.

(iv) Grain refinement is not accompanied by a high density of lattice defects as in conventional cold working.

(v) The alloy processed by HSHPT shows reversible martensitic transformation without the necessity for post-deformation annealing. The severely plastic deformed alloy highlighted phase transformation stability after 10 thermal cycles between 0°C and 250°C.

(vi) HSHPT leads to an overall increase in the strength of the copper-based SMA. Due to microstructural refinement the microhardness increases from 2800 MPa to 4140 MPa. (48% increase)

(vii) Cu-13Al-4Ni alloy processed by HSHPT and possessing refined grains and phase transformation stability can be a good candidate for actuator applications.

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