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# High temperature Cu-Al-Nb – based shape memory alloys

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**Abstract.** New type of Cu-Al-Nb – base alloys containing nickel, cobalt and chromium with high martensitic transformation temperatures have been developed. In this paper the mechanical properties, shape memory characteristics, the temperatures of reversible martensitic transformation and thermal stability of these alloys are presented. Introducing chromium and specially nickel and cobalt to the Cu-Al-Nb alloys gives a possibility to decrease the characteristic temperatures. However, these elements create in the martensitic matrix primary particles of intermetallic phases such as AlCo and NiAl and change the chemical composition of the $Nb(,Al,Cu)_2$ – the main phase in the ternary Cu-Al-Nb alloy. Presence of precipitates results in decrease of the elongation of these alloys. Nickel and cobalt improve the thermal stability and resistance to decomposition.

## 1. INTRODUCTION

Recently a great interest is focused on Cu–based shape memory alloys for high temperature (i.e. above 200°C) applications. From the Cu–based alloys, only Cu-Al-Ni alloys can be considered as high temperature shape memory alloys (HTSMA). The main problem of polycrystalline Cu-Al-Ni alloys, however, is their brittleness. These ternary alloys are very brittle due to the large average grain size, large elastic anisotropy and segregation of impurities towards grain boundaries [1]. To improve the ductility, small addition of such elements as Ti, B, Zr can be added in combination with a proper thermo mechanical treatment, resulting in grain refinement [2]. On the other hand these alloys show presence of brittle $\gamma_2$ precipitates which lower their plasticity. Many studies have been dedicated to the influence of addition of Mn (3-5wt%) to improve the ductility and the machinobility [3]. The mostly envisaged alloy is now the alloy named CANTIM (Cu-Al-Ni-Ti-Mn).

Searching for new shape memory alloys to be applied at higher temperatures showed possibilities of using the Cu-Al-Ag alloys, in which the contents of aluminium changes in the range of 9.7 – 12.8wt% and silver – in the range of 1 – 14wt%. For these chemical compositions the alloys have $M_s > 200$°C and high spread of hysteresis of the martensitic transformation [4].

The investigations of Cu-Al-Nb show that there exists another possibility of properties' improvement of Cu–based high temperature alloys. In these alloys the aluminium content was increased up to 13.5wt% and simultaneously 0.27 – 7.86wt% of niobium was added. The alloys of such chemical composition show the $M_s$ temperature above 300°C. Small changes in niobium content in the alloy influence the martensitic transformation temperature. The addition of niobium to the Cu-Al alloy introduces large number of primary particles identified as $Nb(,Al,Cu)_2$ and Nb(,Al,Cu). High shape recovery effect at high temperature (above 350°C) is characteristic for these alloys.

Presence of niobium particles causes increase in the mechanical properties. The tensile strength is above 700MPa at elongation higher than 12% [5,6].

These results show that there exists a possibility of producing a good, new Cu-Al-Nb – base high temperature shape memory alloys.

The present work describes results obtained with the new Cu-Al-Nb high temperature shape memory alloys containing additionally Co, Ni or Cr and showing high shape memory effect, high mechanical properties and good thermal stability.

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## 2. EXPERIMENTAL PROCEDURE

Three alloys have been prepared by induction melting of pure metals under protective argon atmosphere. The alloy composition is shown in Table 1. The homogenised at 950°C ingots were hot rolled into sheets specimens of 0.7mm thickness. All specimens were solution treated at 850°C for 20min. followed by quenching to water.

**Table 1:** Chemical composition of the alloys (wt%)

| Alloy | Cu | Al | Nb | Ni | Co | Cr | Ti | B |
|---|---|---|---|---|---|---|---|---|
| A | 81,65 | 13,0 | 2,0 | 3,0 | - | - | 0,3 | 0,05 |
| B | 82,65 | 13,0 | 2,0 | - | 2,0 | - | 0,3 | 0,05 |
| C | 83,65 | 13,0 | 2,0 | - | - | 2,0 | 0,3 | 0,05 |

The martensitic transformation temperatures of the alloys were determined by using the DSC method. Experiments were carried out from 25 to 430°C at the rate of 15°C/min.. In order to analyse the alloy structure a transmission electron microscope (JEM 3010 operating at 300kV with the EDS system) was used. X-ray diffraction was also used to determine the phase composition at room temperature. In addition the shape recovery effect and mechanical properties tests were carried out.

## 3. RESULTS AND DISCUSSION

### 3.1 Martensitic transformation temperatures

The main result of adding Co, Ni, or Cr to the Cu-Al-Nb alloy is the considerable improvement of the thermal stability, resistance to the decomposition and lowering the martensitic transformation temperatures. Changes in chemical composition of the investigated alloys cause changes of temperatures of the reversible martensitic transformation. Figure 1 shows the DSC cooling and heating curves for these alloys. These results show that alloying the Cu-Al-Nb alloy with nickel, cobalt and chromium decreases the characteristic temperatures of these alloys relating to the ternary alloy [5]. From practical point of view particularly important fact is that two of these elements (i.e. nickel and cobalt) narrow the temperature hysteresis $A_f - M_f$ and $\Delta A$ (to 59°C and 16°C for nickel and to 80°C and 21°C for cobalt respectively). These hystereses are much narrower than the hystereses for ternary Cu-Al-Nb [6], Cu-Al-

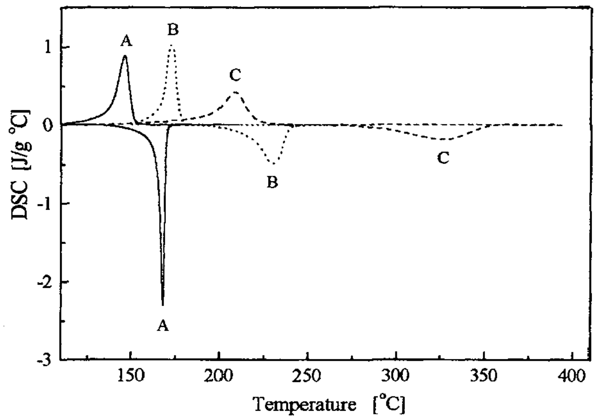



**Figure 1:** DSC cooling and heating curves for alloys A-C

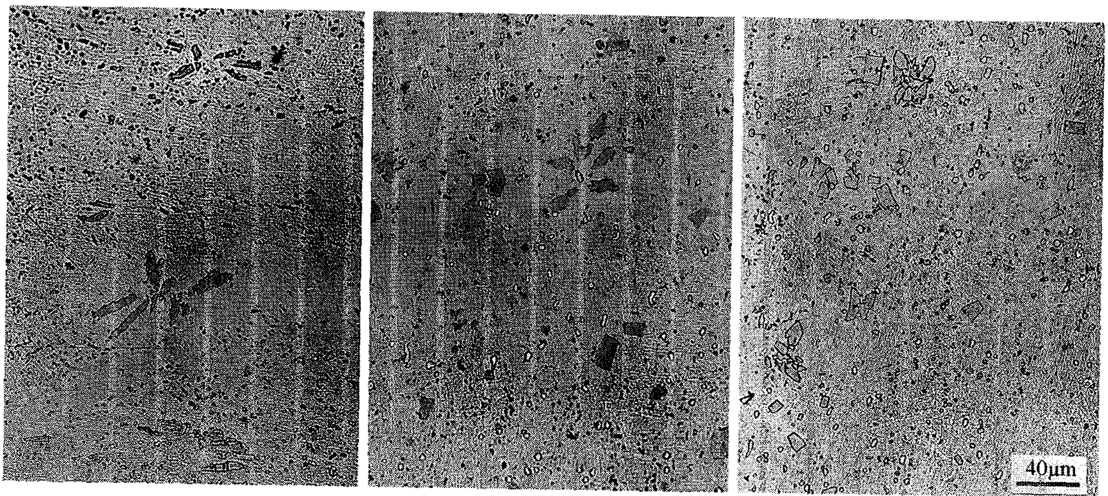
**Table 2** Martensitic transformation temperatures

| Alloy | Temperatures [°C] | | | | Hysteresis [°C] | | |
|---|---|---|---|---|---|---|---|
| | $M_s$ | $M_f$ | $A_s$ | $A_f$ | $\Delta M$ | $\Delta A$ | $A_f - M_f$ |
| A | 151 | 120 | 163 | 179 | 31 | 16 | 59 |
| B | 177 | 161 | 220 | 241 | 16 | 21 | 80 |
| C | 220 | 184 | 302 | 354 | 36 | 52 | 170 |

Ag [4] alloys. Only the alloy containing chromium has the $A_f$ - $M_f$ hysteresis wider than the ternary alloy with niobium and silver.

### 3.2 Structure at room temperature

Decreasing of the characteristic temperatures is a result of microstructure changes of the investigated alloys. Figure 2 shows the primary particles in the matrix of these alloys. It can be seen that alloy containing nickel contains lower amount and alloy which chromium contains higher amount of these precipitates (8.3% and 11.7% respectively). As can be seen, in each alloy it is possible to distinguish two kinds of precipitates. These particles differ in morphology and size.




a) b) c)

**Figure 2:** Optical micrographs of alloy doped by nickel (a), cobalt (b) and chromium (c).

The electron diffraction method and chemical nanoanalysis show that the largest particles on Figure 2 are similar to these identified in the ternary Cu-Al-Nb alloy as $Nb(Cu,Al.)_2$ [6]. For this phase the presence of stacking faults is characteristic. The density of stacking faults depends on size of these particles. Higher density was observed in smaller particles. In very large particles stacking faults can not appear (Figure 3a). Depending on the chemical composition of the alloy, this phase includes up to 7at.% of Ni and 11at.% of Co. Therefore the stoichiometric formula for these phases can be written as $Nb(Cu,Ni,Al)_2$ and $Nb(Cu,Co,Al)_2$ respectively. More complicated situation is observed in the alloy containing 2wt% of chromium. In this alloy two types of particles containing niobium were identified. These particles contain 22at.% and 10at.% of chromium respectively and about 6at.% lower content of niobium than in previously described particles. The stoichiometric formula for this phase can be written as $Nb(Cu,Cr,Al)_3$. In the new studied alloys the Nb(Cu,Al) phase [7] did not exist. Small, oval particles on Figure 2 were identified as AlNi, AlCo, Cr and also $Nb(Cu,Al)_2$ phases (Figure 3b-c).

The electron microscopic observation and X-ray analysis showed that these particles are situated mainly in the 18R type martensite matrix. Small amount of 2H type martensite was identified too. The chemical nanoanalysis shows that the martensite of the investigated alloys contains small amount of nickel, cobalt and chromium in a solid solution (~ 2,5at.% of nickel, ~1.2at.% of cobalt and ~0.3wt% of chromium). The presence of these elements in the matrix causes decrease in the characteristic temperatures of the martensitic transformation, comparing to the ternary Cu-Al-Nb alloys. On the other hand, the increase of the primary particles amount influences the widening of the $A_f$ – $M_f$ hysteresis (Table 2).

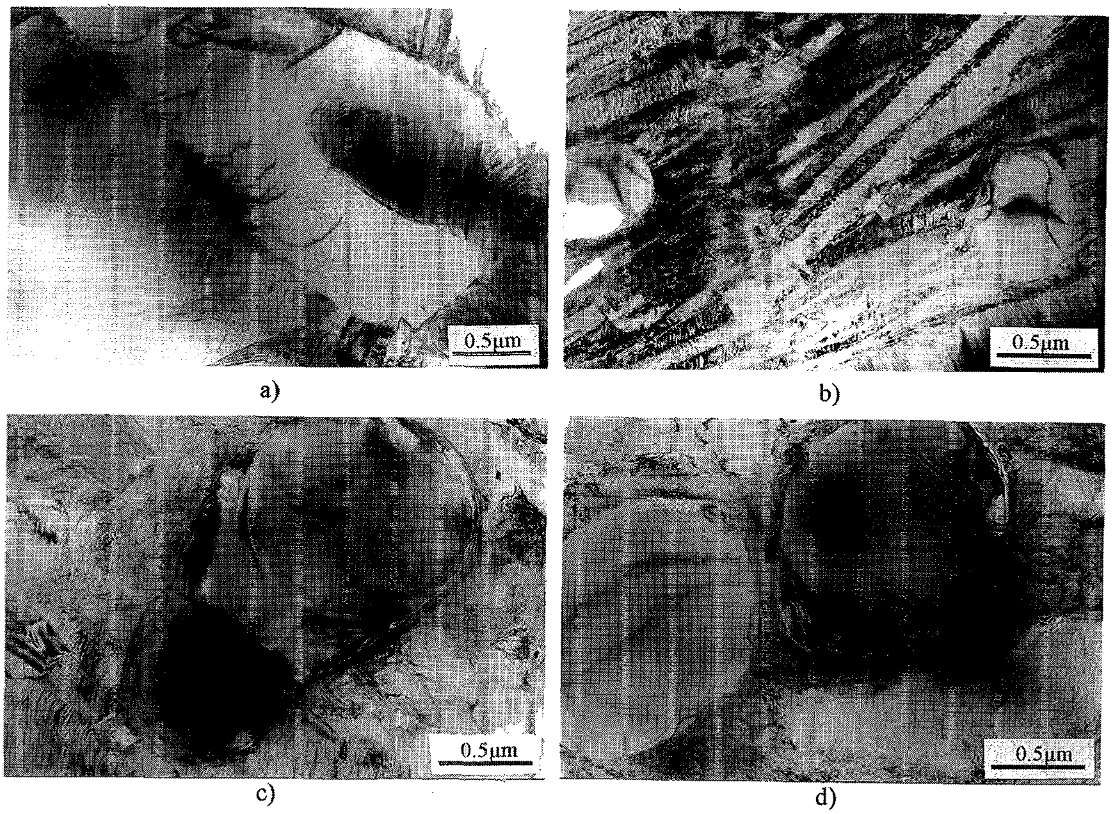



**Figure 3:** Particles of $Nb(Cu,Al)_2$ (a) and NiAl (b) phases of alloy A, AlCo of alloy B (c) and Cr of alloy C (d) in martensite matrix

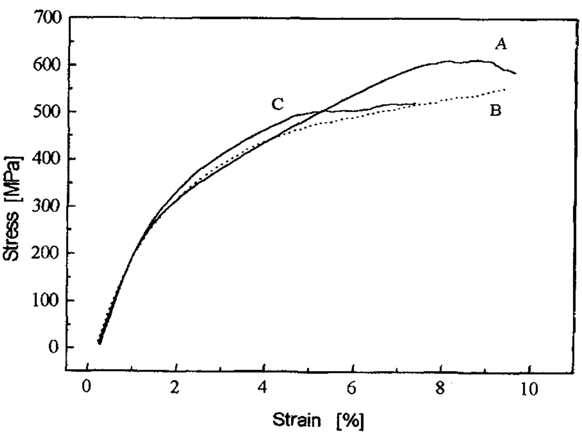



**Figure 4:** Stress – strain curves for alloys A – C

### 3.3 Mechanical properties

The presence of different kinds and sizes of particles in the martensitic matrix influences the mechanical properties of the investigated alloys. The stress-strain curve of the studied alloys is shown on Figure 4 and their mechanical properties are presented in Table 3. It can be seen that all alloys, in martensitic state, have lower strength and elongation than the basic Cu-Al-Nb alloy [6]. On the other hand, these properties are higher than for ternary Cu-Al-Ni and Cu-Al-X [8] alloys. Showing similar tensile strength and yield strength the alloys with nickel and cobalt differ from the alloy containing chromium in elongation. The Cu-Al-Nb alloy with chromium characterises with the lowest plasticity. However, this elongation is comparable to the Cu-Al-Ni alloy and is better than for Cu-Al-X alloys.

**Table 3:** Mechanical properties of alloys A – C

| Alloy | Tensile strength [MPa] | Yield stress [MPa] | Elongation [%] | Hardness [MPa] |
|---|---|---|---|---|
| 1 | 587 | 222 | 7.6 | 230 |
| 2 | 560 | 237 | 7.5 | 247 |
| 3 | 564 | 244 | 5.5 | 262 |

### 3.4 Shape memory properties

The investigated alloys show a high one way shape memory effect at temperatures above 200°C. The results of shape recovery for the initial applied strain 1.3% are presented in Figure 5. In this case the one

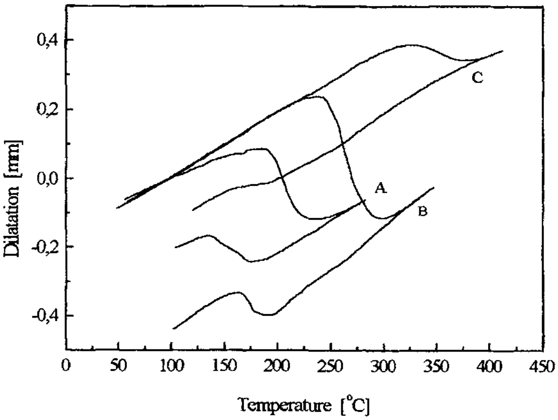



**Figure 5:** Changes of length of specimens during heating and cooling after elongation of 1.3%

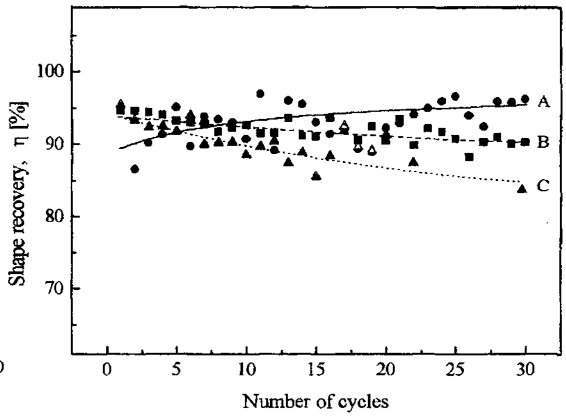



**Figure 6:** Changes of shape recovery vs number of cycles of one way effect

way shape memory effect was introduced by elongation. The specimens were heated with speed of 15°C/min. Lower shape recovery was obtained for the alloy containing chromium. This is caused by high temperature of heating - the specimens were heated up to 450 °C. The fact that specimens with higher Ms temperature exhibit lower degree of recovery was observed in [9]. The highest shape recovery of the studied alloys exhibits alloy with cobalt. After cooling, in all the alloys there occurs a noticeable two way shape memory effect. At room temperature, the alloy containing 3wt% of Ni shows about 30% of stable two way shape memory effect.

The stability of the shape memory effect was studied on strips of 0.3mm thickness by bending test. In this case the initial strain was 1.5%. Figure 6 shows the changes of shape recovery after cycling the one way shape memory effect. Multiple repetition the one way effect causes small decrease of this effect in alloys alloyed with cobalt and chromium and increase in alloy containing nickel.

### 3.5 Thermal stability

For this purpose all specimens were aged at 300°C for 30 to 3000min. To determine the thermal stability, the shape recovery, characteristic temperatures and hardness were studied. In Figure 7 the course of shape recovery of specimens after ageing is visible. Up to 1000 min. all the studied alloys show high resistance to thermal degradation. Only in the alloy containing cobalt after 3000 min. no changes of shape recovery were observed. Ageing the alloy with nickel for longer than 1000 min at 300°C causes decrease in shape recovery. Simultaneously this alloy becomes more elastic. Ageing the Cu-Al-Nb-Cr alloy for 1h cause 10% drop of the shape recovery, then the recovery is stabilised, but after 1000 min. of ageing this alloy becomes brittle. Figure 8 shows the change of hardness of the investigated alloys after ageing at

300°C.These changes in hardness are in good correlation with the changes of shape recovery. The increase of hardness of the alloy containing chromium after ageing for longer than 1000 min. shows the decomposition of matrix phase.

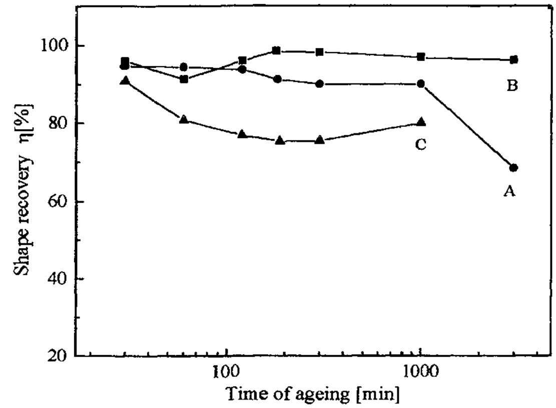



**Figure 7:** Changes of shape recovery after ageing at 300°C

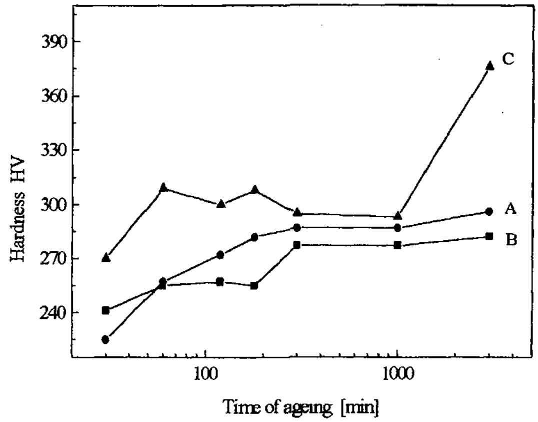



**Figure 8:** Effect of ageing time at 300°C on hardness

## 4. CONCLUSIONS

1. New kind of high temperature shape memory alloys has been achieved by addition of nickel, cobalt and chromium to the ternary Cu-Al-Nb alloy. The alloys exhibit relatively good mechanical properties, shape recovery and thermal stability.
2. The most favourable effect is achieved by cobalt addition to the ternary Cu-Al-Nb alloy causing lowering the $A_f$ to 240°C and stabilising the shape recovery by cycling and ageing at 300°C for 50 hours.
3. The properties of the studied alloys are controlled by presence of primary precipitates of different compounds into the 18R martensitic matrix.


**Acknowledgements**

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