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Investigations of Solid Phase Processes in CuAlNi Base Shape Memory Alloys

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Abstract. Cu based Shape Memory Alloys are favored because of their high transformation temperatures and low price. However, their brittle behavior and the ageing processes due to cycle heating limit the alloys' practicability. To extend their suitability, Mn and Fe were added to the base CuAlNi alloy in order to increase ductility. The ageing processes and the effect of the Mn and Fe addition were examined using differential scanning calorimetry, optical microscopy, scanning electron microscopy, transmission electron microscopy and in-situ optical microscopy.
Transformation temperatures shifted to higher temperatures in the CuAlNi alloy as the ageing time was increased. In CuAlNiMn and CuAlNiMnFe alloys the thermoelastic martensitic transformation disappeared in the aged samples. The cause of this effect turned out to be an exothermic process starting at around 300°C, which was previously not known. The examinations were focused to characterize and identify this exothermic process.

1. Introduction

The main advantages of the CuAlNi shape memory alloys (SMAs) are their high transformation temperatures (~50°C-150°C) and low price compared to other SMAs [1, 2, 3]. However, their brittle behaviour and the ageing processes limit their applications [1, 2, 3, 4]. To improve their ductility, Mn and Fe were added to the base Cu-13.4Al-5Ni alloy. The required section of the Cu-Al phase diagram is shown in Fig. 1. The ageing processes were examined in the base CuAlNi and the modified CuAlNiMn and CuAlNiMnFe alloys. The results of the CuAlNi alloy were reported elsewhere [5]. In the case of the CuAlNiMn and CuAlNiMnFe alloys, the thermoelastic martensitic transformation (TMT) was destroyed by an exothermic process that started at around 300°C. Because of its strong effect on the suitability of the alloys, our aim was to examine this exothermic process. The intention of the present paper is to characterize qualitatively this exothermic process. The process will be examined quantitatively later.

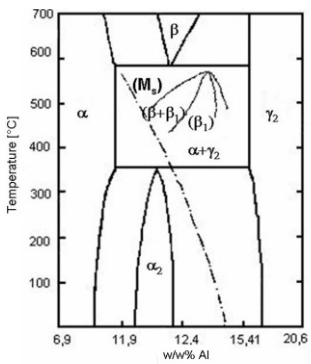

Fig. 1. The specified Cu-Al phase diagram

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2. Experimental

The alloys were produced as 3 mm diameter single crystal rods by Bridgeman method at the University of Leuven. Samples were spark cut with a thickness of 1-1,5 mm at the University of Debrecen. The composition of the samples was examined by ICP (Inductive Coupled Plasma) method at the Metalcontrol Ltd., Miskolc. The compositions are shown in Table 1.

Table 1. The compositions of the alloys

Nominal composition	Al	Ni	Mn	Fe
Cu-13,4Al-5Ni-4Mn-2Fe	9,9	4,85	4,16	1,92
Cu-3,4Al-5Ni-4Mn	10,2	4,92	4,12	0,01

The samples were homogenized first in a salt bath, later in an air furnace at 900°C for 60 minutes, than quenched in room temperature water. Ageing heat treatments were performed in a salt bath at 300°C for 1, 2, 4, 8, 16 minutes, than quenched in room temperature water. DSC examinations were first carried out by a TA Instruments DSC 2920 Modulated device at the University of Leuven, later with a Netzsch 204 heat flux DSC. Heating/cooling rates were 10°C/min. Differences between the two devices are not relevant, since there were no comparison between their results. The samples were polished and etched with $FeCl_3$-HCl solution for optical microscopic examinations. Optical microscope examinations were carried on a Zeiss AX10 microscope. A Hitachi 4800 device with EDAX was used for the SEM examinations. Samples for the TEM examinations were prepared by ion beam milling method. The TEM examinations were performed using a JEOL JEM 3010 equipment at the University of Debrecen. The samples were polished (but not etched) and covered with vapoured Au (just as used by non-conductive sample preparation for SEM) for the in-situ microscopic investigation (voltage: 2,2 kV, acceleration voltage: 2,2 kV, ionisation current: 10 mA, time: 2X45 sec.). In-situ optical microscopic examinations were performed using a Reichert Vacutherm sample heating unit and a Reichert optical microscope. Heating was not controlled, the temperature was set using a transformator connected to the Vacutherm. Image recording was carried out by a Moticam 1000 PC camera and a personal image capture software. All of the not labelled examinations were performed at the University of Miskolc.

3. Results and discussion

The first and second DSC cycles of the CuAlNiMn sample aged for 1 minute in the salt bath are shown in Fig. 2.

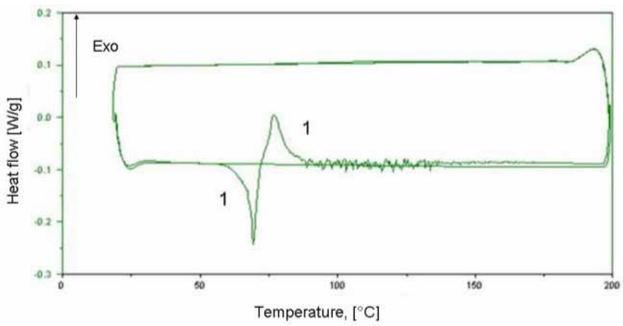


Fig. 2. The first and second DSC cycles of the 1 minute aged CuAlNiMn alloy

The endothermal peak of the thermoelastic martensite→austenite transformation can be seen during the first heating which is followed by an exothermic peak with roughly the same latent heat. The peaks are followed by some fluctuation. There are no peaks during cooling and in the second cycle. The lack of any processes during cooling and in the second cycle yields that the structure formed by the exothermic process is stable on this temperature range. The same peaks could been observed on the DSC cycles of the samples aged for 2, 4 and 8 minutes, but both peaks became smaller with increasing ageing time. After 8 minutes ageing the peaks totally disappeared and there were no processes during the DSC examinations at all.

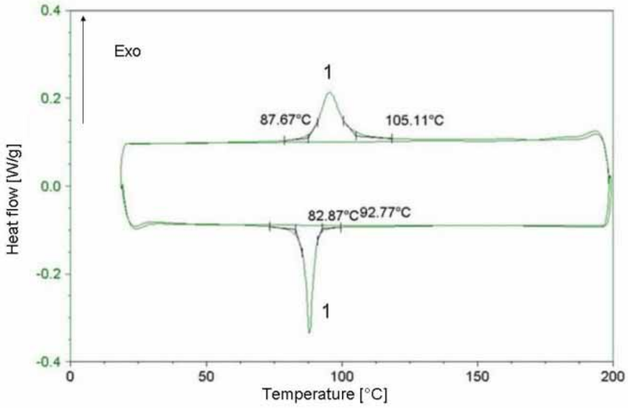


Fig. 3. The first and second DSC cycles of the 1 minute aged CuAlNiMnFe alloy

The first and second DSC cycles of the CuAlNiMnFe alloy aged for 1 minute in the salt bath can be seen in Fig. 3. The thermoelastic martensite→austenite transformation can be seen during the first heating cycle. There is an exothermic peak during cooling. There are no peaks during the second cycle, which suggests that the exothermic peak in the first cooling cycle is not the peak of the thermoelastic austenite→martensite transformation. This yields again that the structure produced by the exothermic process during the first cooling is stable on this temperature range. The same peaks could been observed on the DSC cycles of the samples aged for 2, 4, 8 and 16 minutes, but both peaks became smaller with increasing ageing time. After 8 minutes ageing the peaks totally disappeared and there were no processes during the DSC examinations at all.

It is seen that ageing at 300°C causes drastic changes in the processes in both alloys. The facts that the exothermic processes produced a stable structure in both CuAlNiMn and CuAlNiMnFe alloys and the peaks became smaller with increasing ageing time suggests that the same process occurred in both alloys.

We suppose that the exothermic processes seen on the DSC cycles are the same processes that started during the ageing heat treatments. This is confirmed by the fact that as the ageing time is increased, i.e. the exothermic process evolutes during heat treatment, the smaller peaks appear on the DSC curves. We suppose that the exothermic process during ageing heat treatment starts to transform the austenite into a stable phase, which does not transform to martensite during the quenching after the ageing heat treatment. If the ageing time is not enough to transform the whole sample to this stable phase, some austenite remains to transform to thermoelastic martensite during the quenching. When this sample is subjected to DSC examination, the remaining thermoelastic martensite transforms to austenite, than the exothermic process carries on to transform it to the stable phase. As the ageing time is increased, the fraction of the remaining austenite decreases, decreasing the heat effects during DSC examination. If the ageing heat treatment is long enough, the whole austenite transforms to the stable phase and no heat effect is seen on the DSC curves.

The main difference between the two alloys is that the exothermic process continues right as the martensite transforms to austenite in the CuAlNiMn alloy and during cooling in the CuAlNiMnFe alloy. Because the exothermic processes seem to be the same, only the results of the CuAlNiMnFe alloy will be presented. If there is a difference between in any of the results of the two alloys, it will be noted.

To see the heat effect of the exothermic process that started during heat treatment, a not aged sample was heated up to 400°C in the DSC. The cycle is shown in Fig. 4. It is seen that the exothermic process starts roughly at around 300°C and finishes upon heating. There were no processes during the cooling stage.

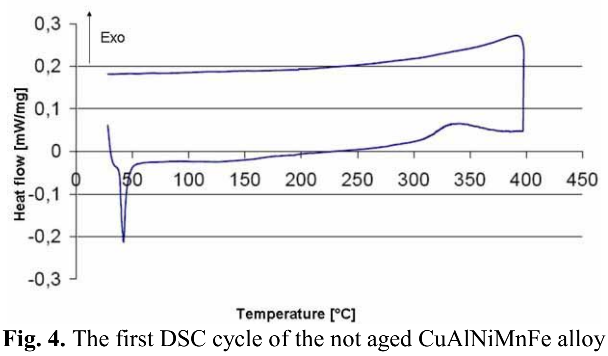
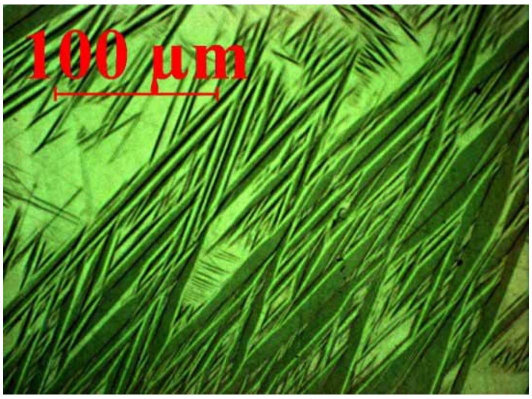


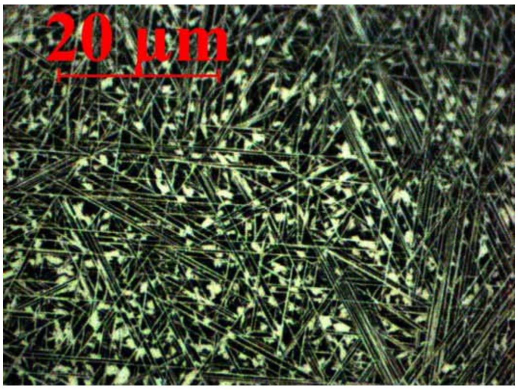
Fig. 4. The first DSC cycle of the not aged CuAlNiMnFe alloy

To see what structure does the exothermic process produce, different structure examinations were carried out on not aged samples and on samples heated to 400°C in the DSC. This way it is possible to compare the structure of the thermoelastic martensite to the stable phase produced by the exothermic process. Fig. 5 a. shows the optical microscopic image of the not aged sample. The thermoelastic martensitic structure can be clearly observed. The structure of the aged sample can be seen in Fig. 5. b The structure contained needles/plates which are much smaller compared to the plates of the thermoelastic martensite. The fine structure can also be seen in Fig. 5. c at larger magnification.



a)

b)



c) Fe 100X

Fig. 5. Optical microscope images of the CuAlNiMnFe alloy. a) structure of the not aged sample M=20X, b) structure of the aged sample, M=20X, c) structure of the aged sample, M=100X

The structure of the aged sample was examined by SEM and EDAX as well. Figs. 6, 7 and 8. show the SEM images of the aged sample. In Fig. 6. it can be observed that the sides of the plates are not flat as in the case of martensite, but they are rough.

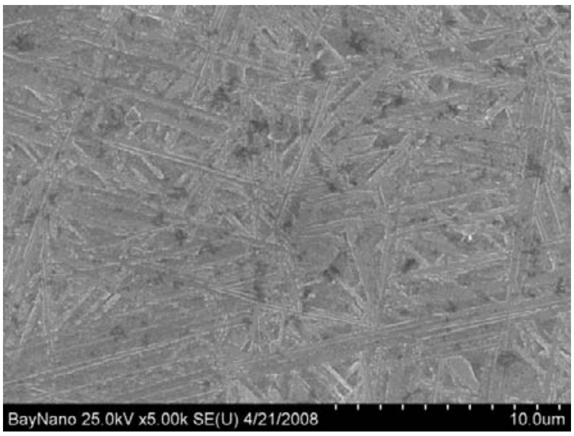


Fig. 6. SEM image of the aged CuAlNiMnFe alloy, M=5kX

At larger magnification it can be seen that the rough sides of the plates are caused by precipitations on the sides of the plates (Fig. 7.). The precipitations can be found all over the structure. The precipitations are so fine that no compositional differences could be detected by EDAX method.

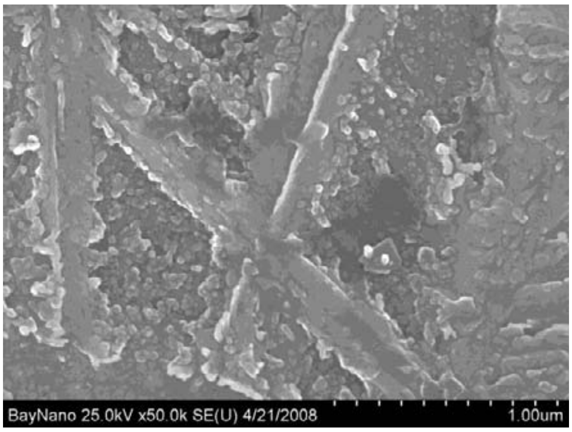


Fig. 7. SEM image of the aged CuAlNiMnFe alloy, M=50kX

The precipitations can be seen in Fig. 8. at larger magnification. Precipitations can also been observed inside the plates. The ones inside the plates are lengthwise, while the ones outside the plates are quasi spherical. The precipitations are in the range of ~50 nm of magnitude.

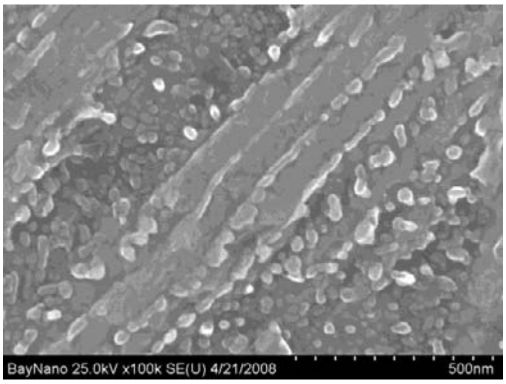
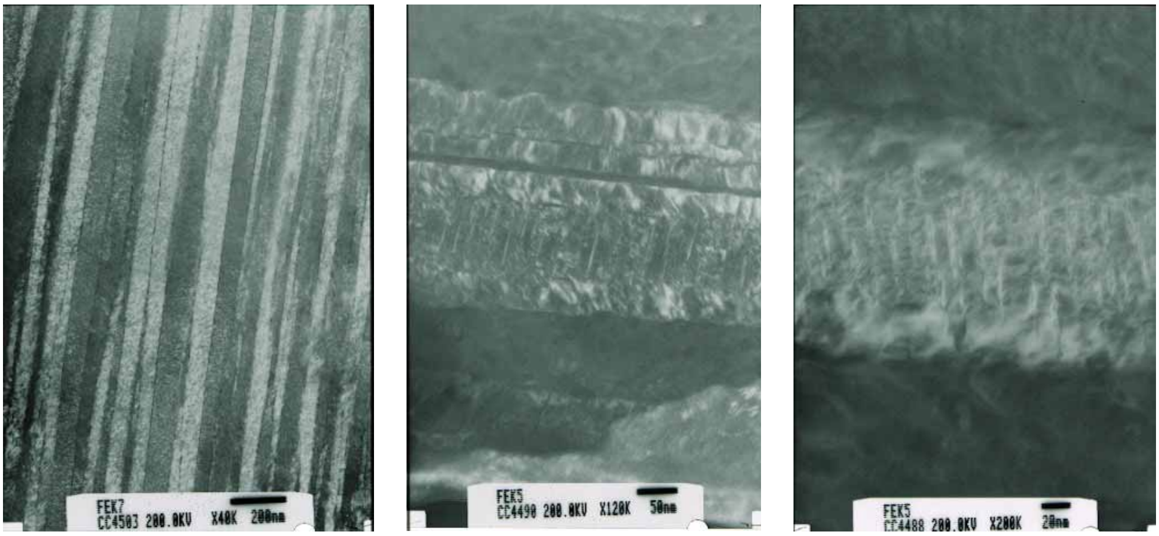


Fig. 8. SEM image of the aged CuAlNiMnFe alloy, M=100kX

TEM examinations were also carried out on the not aged and aged samples. The TEM image of the not aged sample can be seen in Fig. 9. a. The fine plates of the martensite can clearly observed. The structure of the aged samples is shown in Fig. 9. b and c. It can be seen that the structure of the plates differ on the sides and in the middle. The precipitations can be observed on the sides of the plates, while very fine lamellar structure can be seen in the middle of the plates perpendicular to the length of the plates.
In the case of the CuAlNiMn alloy, the precitipiations could be observed in the middle of the plates as well.
Although the structure of the aged sample is too fine to detect compositional differences between the plates and the precipitations, the presence of a second phase is evident. This plate-like structure that contains precipitations of a second phase is some kind of bainite.
However, according to the DSC examinations, this bainite forms upon heating. This anomalous phenomena can be confirmed if the evolution of the bainite is observed by an in-situ technique. Since both the martensite→austenite and the autenite→bainite transformations are followed by the vanishing and evolution of a surface relief, in-situ optical microscopic examination can be a proper method to monitor these processes. In-situ optical microscopic examination was frequently used in the 60's. Because of the difficulty (or lack) of continuous etching upon heating, the application of this technique fell back. The advantage of transformations followed by surface relief variation is that samples do not need etching.
To prevent the samples from oxidation, they were vapour covered with Au with the technique used for SEM sample preparation. The surface evolution of the martensite→austenite and the austenite→bainite transformations could be seen as the sample was heated up to ~400°C. The heating system was set to 400°C and

it was simply turned on. This way the sample was subjected to a quick heating. In Fig. 10. a The initial martensitic structure can be seen. In Fig. 10. b the relief of the martensite vanished upon heating and the smooth surface of the austenite can be observed (with some scratches). In Figs 10. c-f the relief evolution by the austenite→bainite transformation can be seen. The scratches also became sharper in Figs 10. c-f. because a very small oxidation/vapourisation occurred during the experiment. (This was confirmed by the fact that the Au layer was darker after the examination.) In Fig. 10. f the evoluted relief of the bainite can be observed. The relief was visible if the focus was somewhat above or below the original surface of the austenite.



a) b) c)

Fig. 9. a) TEM image of the not aged CualNiMnfe alloy, M=40kX, b) TEM image of the aged CuAlNiMnFe alloy, M=120kX, c) TEM image of the aged CuAlNiMnFe alloy, M=200kX

With this in-situ examination the austenite→bainite transformation is confirmed to occur upon heating. This unique behaviour seems to be anomalous at first, but it can be explained if we consider the behaviour of the CuAlNi based system and the results of the experiments. Previously it was revealed that the diffusion in the base CuAlNi alloy is slow enough to retard the formation of equilibrium (α and γ_2) phases during a DSC examination with a general (10 °C/min) scanning rate [5, 6]. In that system this slow diffusion involves the diffusion Al. However, the diffusion of Mn and Fe are not known so far in these systems. As the results revealed, precipitations in the range of ~50 nm formed during the DSC experiments with 10°C/min scanning rate. The compositions of these precipitations are not known, but they must consist of Mn and/or Fe since they were not observed in the base CuAlNi system. This yields that the addition of Mn and Fe results somehow to form precipitations at scanning rates where the equilibrium Cu-Al phases (α and γ_2) do not form. Since the martensitic state is a metastable state of the alloy, it can be understood why the precipitations formed upon heating. It is also likely that these precipitations contain some amount of Al and/or Cu. As these precipitations formed, the composition of the alloy suffered changes in the vicinity of the precipitates. It was revealed that precipitations formed all over the sample, meaning that the composition of the whole sample changed due to the precipitation process upon heating. According to the Cu-Al phase diagram (Fig. 1.) the M_s temperature can be risen above 500°C if the Al content decreases. If the Al content decreased notably due to the precipitation process, it can be understood why the austenite transformed to a martensite again. This structure consists of some kind of martensite and precipitations. A structure like this is called bainite. The bainite is stable on the examined temperature range due to the concentration change. Furthermore, the precipitations can act as inhibitors for further transformation. The above mentioned theory is only a proposal. It is not proven, but according to the results it can be the mechanism of the exothermic process. The exothermal process will be examined with other methods as well to confirm or confute this proposal.

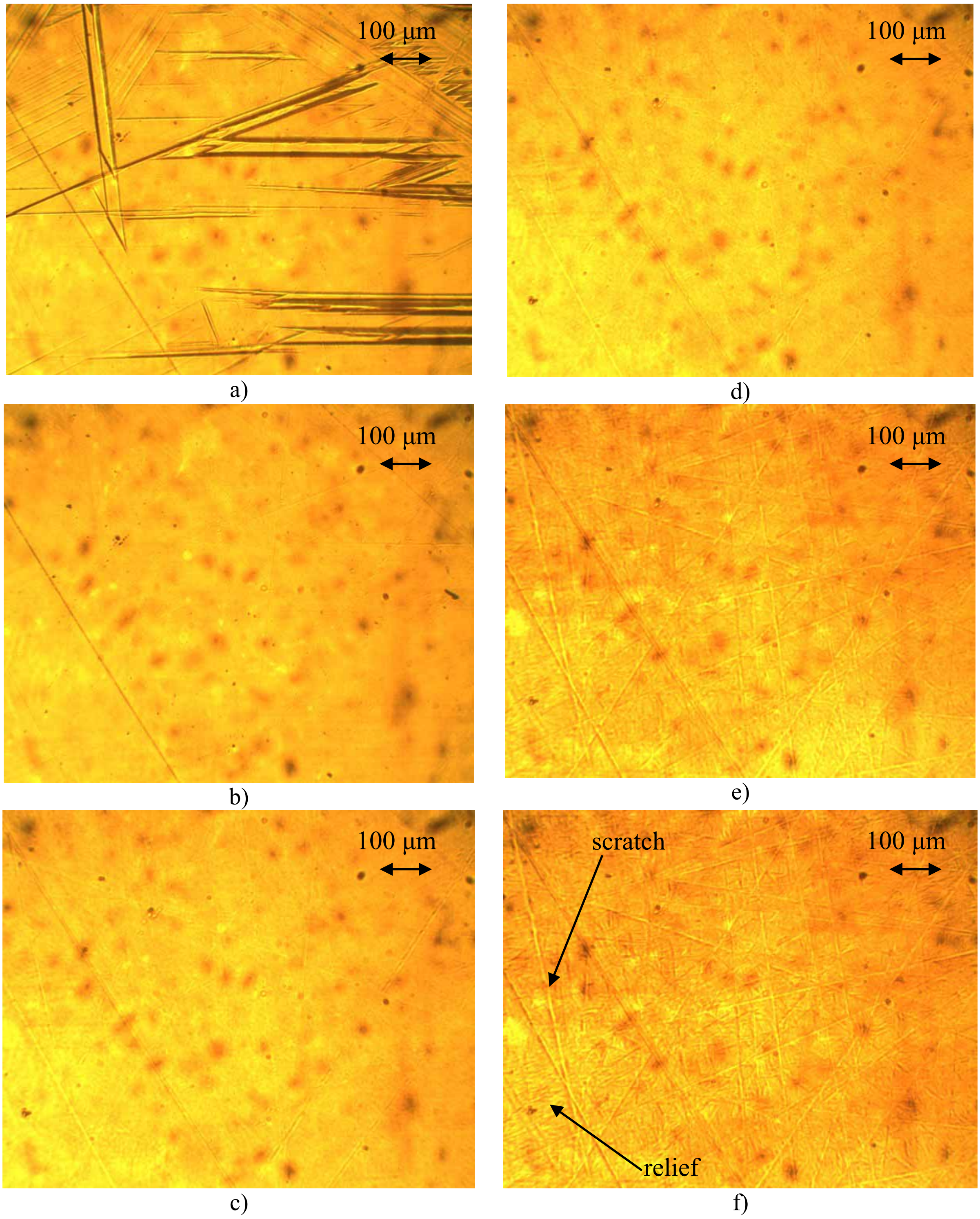


Fig. 10. a)-f) Optical microscope images of the not aged CuAlNiMnFe alloy upon heating. a) initial martensitic structure, b) austenite, c)-f) evolution of surface relief of the austenite→bainite transformation

4. Summary

The effect of ageing was examined using DSC, optical microscopy, SEM, TEM and in-situ optical microscopy in a CuAlNiMn and a CuAlNiMnFe SMA with increased ductility. It was revealed that an exothermic process occurred in these alloys upon heating starting at around 300°C. The process produced a stable structure destroying the shape memory effect. This stable structure contained fine plate-like structure and very fine precipitates. The exothermic process turned out to be an austenite→bainite transformation upon heating. The relief evolution of this transformation was monitored by in-situ optical microscopy, a technique used in the 60's. A proposal is given to explain the mechanism of the transformation.

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