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High-Temperature Transformation Processes in Cu-13.4Al-5Ni Shape Memory Alloy Single Crystals

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Cu-13.4Al-5Ni alloy single crystals were investigated after performing the corresponding heat treatments to reveal the formation of equilibrium α and γ_2 phases and to examine transformation processes occurring in the alloy during heating-cooling cycles between room temperature and 970 K. Transformation processes were examined using heat flux DSC, structure examinations were performed using optical microscope and SEM devices, and phase identifications were carried out by XRD method. Identification of the equilibrium α phase using XRD method was not possible on the single crystal samples. According to the results, the equilibrium phases (α and γ_2) form only after long-term heat treatments. Because of that, aging processes do not affect the thermoelastic martensitic transformation of the CuAlNi alloy. This phenomenon is probably caused by the high Ni content that decreases the diffusion rate in CuAlNi alloys.

Keywords advanced characterization, metallography, nonferrous metals

1. Introduction

Cu-based shape memory alloys (SMAs) may be suitable in high-temperature applications because of their high transformation temperatures (320 to 420 K) compared to other SMAs (Ref 1, 2). However, after exposing to higher temperatures, aging process can advance and the metastable parent (austenite) phase can decompose into equilibrium phases. Examinations of the aging process were reported in many papers. These examinations were carried out on alloys containing 3 to 4% w/w Ni. V. Recarte et al. (Ref 2) examined the Cu-13.15Al-3.25Ni alloy from room temperature to 970 K. In their experiments, the samples, processed by powder metallurgy, were homogenized and quenched before the examination. During quenching, an ordering process started in the body centered cubic (bcc) β (parent) phase solid solution which could not be finished. On further cooling, partially ordered β phase transformed to β′ martensite. The martensitic sample was heated at 10 K/min up to 970 K. In situ neutron diffraction was carried out at temperatures located before and after the DSC peaks to examine the evolved phases. The first endothermic peak, connecting to the β′ (martensite) → β (austenite) transformation was followed by the first exothermic peak which could be connected to the continued ordering of the β phase. The second exothermic peak was ascribed to the dissolution of the β phase to equilibrium α and γ_2 (eutectoid) phases. The second endothermic peak was associated to the transformation of α and γ_2 to β phase (Ref 2). The processes can be traced on the section of the Cu-Al phase diagram (Fig. 1).

In this article, a Cu-13.4Al-5Ni with higher Ni content was examined. The aim of our research was not to characterize the aging process quantitatively but to examine the processes of the alloy when heated far above its transformation temperature.

2. Experimental

The CuAlNi single crystals were produced by Bridgeman method at the Catholic University of Leuven, Belgium. Samples were spark cut from the 3 mm diameter rods. According to optical microscopic examinations, the samples were not actually single crystals, since they contained three to six crystals. Inductive coupled plasma (ICP) examinations (Metalcontrol Kft) revealed that the Al content of the alloy is 12.6 to 12.9% w/w and the Ni content is 4.4 to 4.6% w/w. The initial samples were homogenized at 1170 K for 1 h in furnace then quenched in room temperature water. Samples were etched in HCl-$FeCl_3$ solution. DSC examinations were carried out by a NETZSCH 404 heat flux device using 10 K/min scanning rates under Ar atmosphere. SEM examinations were performed with an AMRAY 1830 (with installed EDS microprobe) instrument. Four-point electrical resistance measurements were carried out in vacuum using AGILENT 34970A data acquisition unit by means of the Department of Solid State Physics, University of Debrecen.

3. Results

The as-quenched Cu-13.4Al-5Ni sample was identified as NiK5. The DSC curves of the alloy are seen in Fig. 2.

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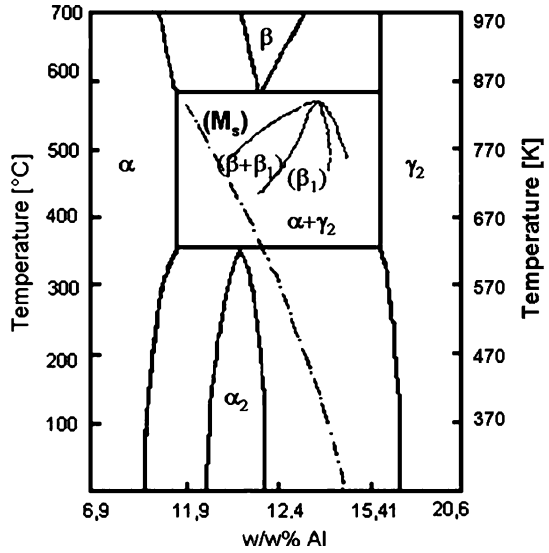

Fig. 1 The specified Cu-Al phase diagram

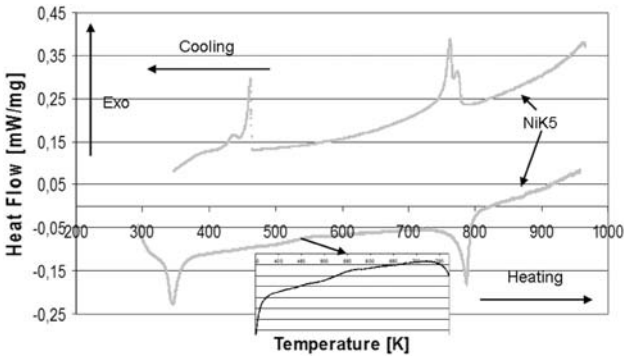

Fig. 2 DSC curves of the as-quenched Cu-13.4Al-5Ni alloy (NiK5)

During heating, the first endothermic peak would correspond to the β′ (martensite) → β (austenite) transformation at around 320 K. This is followed by a small exothermic peak at around 570 K which could be associated to the continued ordering of the β (Ref 2) phase. The next transformation is illustrated by the second endothermic peak at around 750 K in contrast to the results from the literature (Ref 2, 3). After that no peak can be seen during heating. During cooling there are two exothermic peaks which consist both of larger and smaller maxima. These peaks seem to be the pairs of the endothermic ones. The one on higher temperature will be identified later with its endothermic pair. The one on lower temperature indicates the formation of martensite. This is confirmed by the fact that after DSC cooling the sample was in martensitic state (Fig. 3).

The endothermic martensite → austenite transformation is on lower temperature (starts at around 320 K) than the exothermic peak of the austenite → martensite transformation (starts at around 470 K). This shift of the martensite → austenite transformation is often observed during the first heating cycle of the samples.

To reveal what process causes the second endothermic peak during heating, a series of examinations were performed. First,

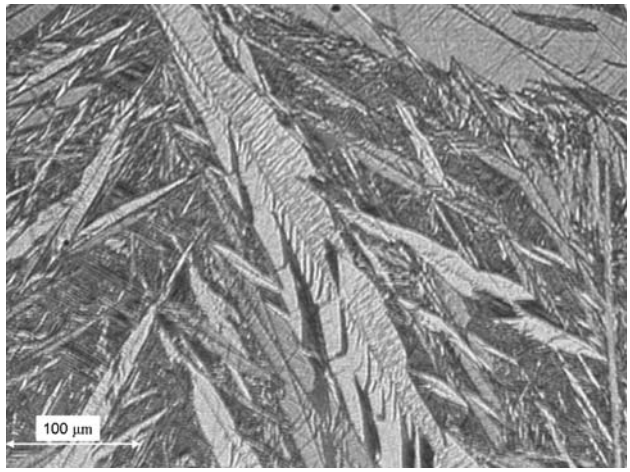

Fig. 3 Optical microscopic image of the martensitic state of NiK5 sample after DSC examination

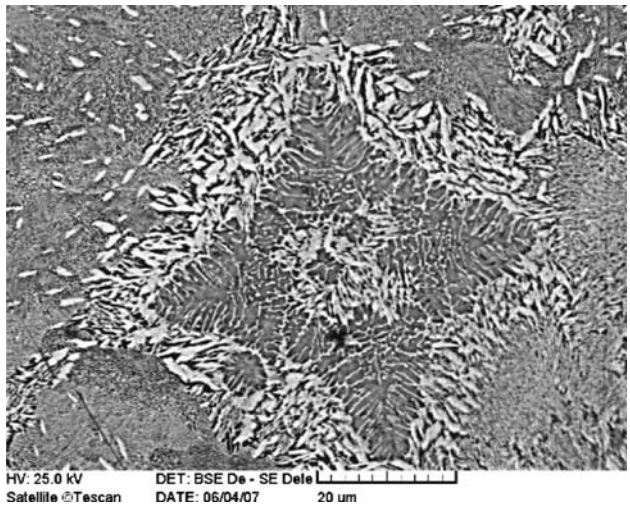

Fig. 4 SEM image of a γ_2 precipitate in the slowly cooled NiK8 sample

samples were produced with equilibrium phases. For that a sample was heat treated in the furnace at 1170 K for 1 h, and then the furnace was turned off and let to slowly cool down with the sample in it. The estimated average cooling rate was 0.9 K/min. The SEM images of the sample cooled in the furnace (identified as NiK8) can be seen in Fig. 4.

Figure 4 shows a single, cross-shaped γ_2 precipitate with α crystals in its vicinity as it evolved. The identification of the phases was carried out by EDS method. The NiK8 sample contained purely eutectoid phases in both single precipitate and lamellar forms. The small cooling rate enabled the formation of the equilibrium phases. However, the sample was not purely eutectic, it also contained some martensite.

The DSC curves of the NiK8 sample (dark gray) together with as-quenched NiK5 sample (light gray) are seen in Fig. 5.

The β′ (martensite) → β (austenite) transformation (first endothermic peak) shifted to higher temperature (to around 650 K) and became less intense in the NiK8 sample. This is because the precipitation of the eutectoid phases changed the composition of the matrix. The γ_2 phase has high Al content

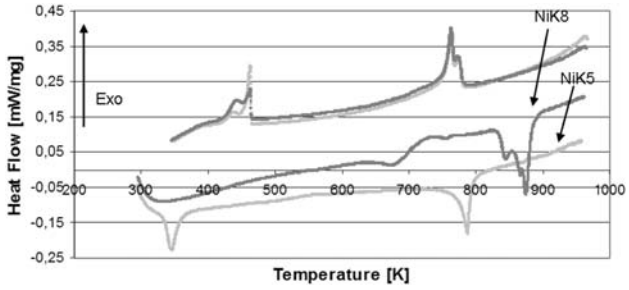

Fig. 5 DSC curves of the NiK5 and NiK8 samples

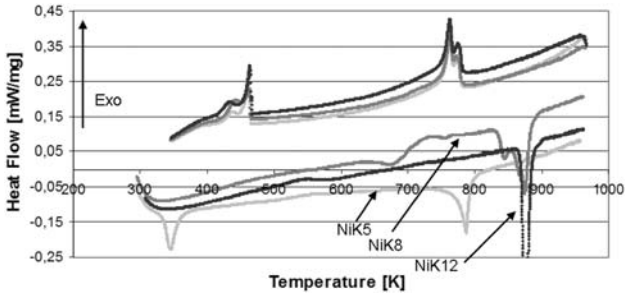

Fig. 7 DSC curves of the long-term heat-treated NiK12 sample together with the NiK8 and NiK5

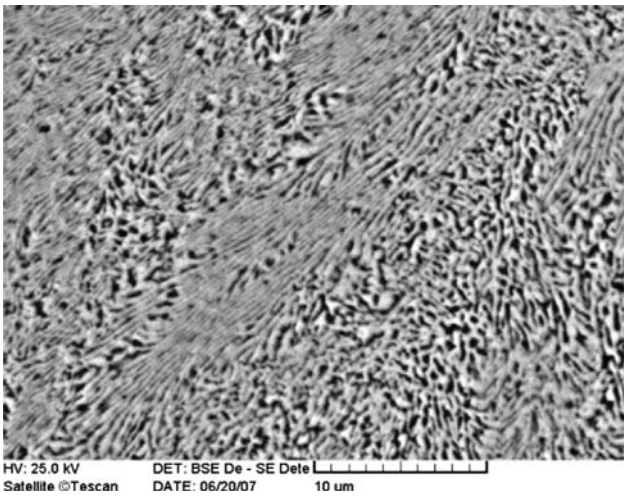

Fig. 6 SEM image of the long-term heat-treated NiK12 sample

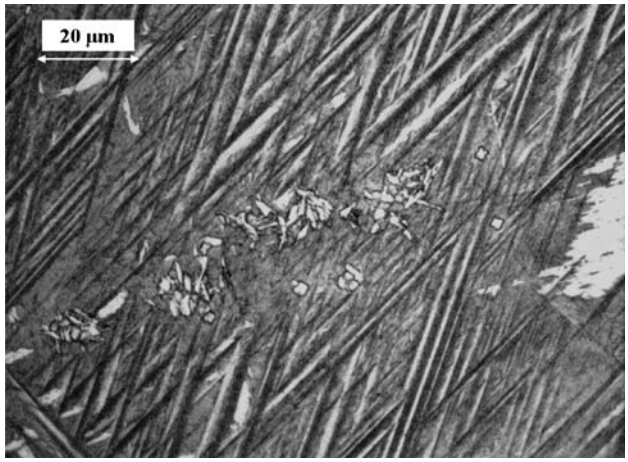

Fig. 8 Optical microscopic image of the sample heat treated at 670 K for 2 h

compared to the overall composition of the alloy (see Fig. 1). The remaining matrix is depleted in Al, which causes the martensite transformation to shift to higher temperature (Ref 4). The sample has less martensite than the NiK5; therefore, NiK8 has lower martensite → austenite peak. There is a second endothermic process with three peaks at around 830, 860, and at around 870 K. One of these peaks correspond to the $\alpha + \gamma_2 \rightarrow \beta$ transformation. We assume that the peak at 870 K corresponds to the eutectoid reaction, being the sharpest peak. We assume that the other two peaks correspond to the same process as in the case of NiK5 sample. This process is also shifted because the composition of the matrix was changed. The peaks during cooling are the same as in the previous NiK5 sample. They will be discussed later.

To produce a purely equilibrium α and γ_2 phase structure, a sample was heat treated in furnace at 690 K for 20 h. The sample was identified as NiK12. SEM image of the NiK12 sample can be seen in Fig. 6.

The sample was in a purely lamellar eutectoid state. The DSC examination of this sample will clearly indicate the $\alpha + \gamma_2 \rightarrow \beta$ transformation. The DSC curves of the NiK12 sample (heat treated for 20 h at 690 K) is seen in Fig. 7 (black curves).

There is one sharp endothermic peak during the heating of the NiK12 sample at around 870 K. This peak is the $\alpha + \gamma_2 \rightarrow \beta$ transformation. The transformation occurred in one step due to the fine lamellar eutectoid structure. The cooling stage is the same as the previous ones. This shows that the processes occurring during cooling are independent of the structure of the sample before the examinations. The same processes occur during cooling in the sample that was in purely martensitic state before the DSC examination (NiK5) as in the one that contained both martensite and eutectoid (NiK8) and as in the one that was in purely eutectoid state (NiK12). This shows that, at the end of the heating, the same structure evolved in all the samples.

The next step was to make samples with the structures before and after the second endothermic peak of the martensitic NiK5 sample. For this, a sample was heat treated before the endothermic peak at 690 K (Fig. 8) and another one after the endothermic peak at 870 K (Fig. 9) for 2 h with subsequent quenching.

The sample heat treated at 670 K (before the endothermic peak) contained martensite and some γ_2 precipitates with α crystals in their vicinity.

The sample heat treated at 870 K (after the endothermic peak) contained martensite matrix with small γ_2 precipitates in it. The α phase was not found in this sample. This is intelligible because the $\alpha \rightarrow \beta$ transformation starts at 830 K (Fig. 5) which means that at this temperature no α phase can be formed. If the starting or the finishing structure of the endothermic process was an equilibrium structure, it would have remained during quenching and the whole sample would have an equilibrium structure. However, the samples heat treated at 670 and 870 K both had predominantly martensitic structure. This means that the samples before and after the endothermic

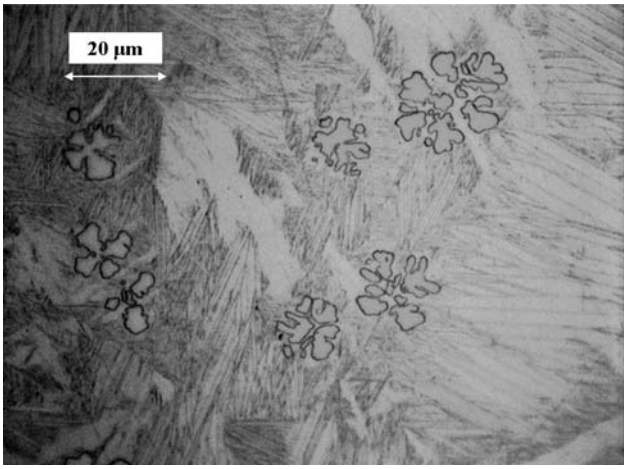

Fig. 9 Optical microscopic image of the sample heat treated at 870 K for 2 h

process both had β structures. The β phase transformed to martensite during the subsequent quenching.

The second endothermic process of the martensitic NiK5 sample and its exothermic pair must be the heat effects of the order-disorder processes of the β phase. This explains why the samples had β structure both before and after the endothermic process. These processes occur at the temperatures where the peaks appeared (Fig. 2). To demonstrate the order-disorder process, electrical resistance measurement was performed on the as-quenched NiK5 CuAlNi sample (Fig. 10).

There are two shifts in the resistance. The first shift indicates the martensite ↔ austenite transformations at 330 K during heating and 470 K during cooling. The resistivity of the sample drops as it transforms from martensite to austenite. Note that the martensite → austenite transformation during heating is on lower temperature than the austenite → martensite transformation during cooling. This is the abovementioned first cycle effect. A small decrease in the resistance can be seen at around 570 K. This decrease could be caused by the continued ordering process, previously observed on DSC curves, as well-ordered solid solutions are more electrically conductive than disordered ones. The second shift indicates the order ↔ disorder transition starting at around 750 K. The resistivity of the sample shifts to higher value as the ordered structure becomes disordered. This transition occurs about between 730 and 790 K at 12.6 to 12.9 w/w Al content (Fig. 1). The latent heat of the transition was about 22 kJ/kg, while of the martensitic transformation was about 13 kJ/kg. The continued ordering of the β phase at 570 K during the first heating of the as-quenched sample occurred with only a small peak because most of the process took place during the quenching of the sample. In contrast to the as-quenched Cu-13.15Al-3.25Ni alloy, the equilibrium $\beta \rightarrow \alpha + \gamma_2$ transformation did not take place in the as-quenched Cu-13.4Al-5Ni alloy during the DSC examinations. This phenomenon could be caused by the larger Ni content since Ni decreases the diffusion velocity in the CuAlNi alloys (Ref 5). Since formation of the equilibrium phases is retarded by the increased Ni content, the resistance to aging is believed to be increased.

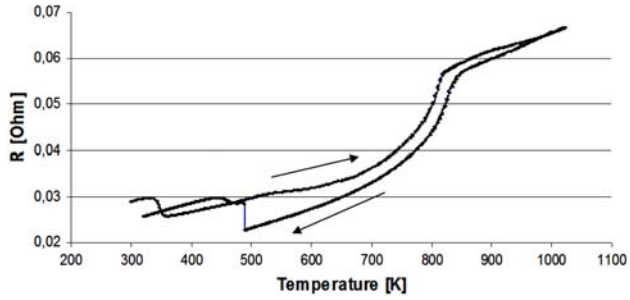

Fig. 10 Electrical resistance curve of the as-quenched NiK5 CuAlNi sample

4. Summary

DSC heating-cooling scans of high (nominal 5% w/w) Ni content CuAlNi alloy single crystals in various heat-treated states were performed between room temperature and 970 K. The equilibrium $\beta \rightarrow \alpha + \gamma_2$ transformation did not occur during DSC cooling in as-quenched sample. The formation of the equilibrium phases is retarded by the larger Ni content which hereby makes the alloy more resistant against aging. The order ↔ disorder transition of the β phase was detected with larger amount of latent heat as compared to the martensitic transformation.

Acknowledgments

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