Comparative Electron-Microscopic Study of Shape Memory Alloys of Systems Cu-Ni-Al and Ni-Mn-Al

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Abstract

The microstructure of Cu-Ni-Al and Ni-Mn-Al alloys in a wide range of chemical compositions has been studied by transmission and scanning electron microscopy methods, diffraction of electrons and X-rays. The phase composition of all the investigated alloys and the mechanism of the fracture under deformation have been determined.

Keywords: thermoelastic martensitic transformation, brittleness, fractography, long-period lattice, electron-microscopic studies.

1. Introduction

Thermoelastic martensitic transformations (TMTs) were observed in many binary and multicomponent intermetallic atomic-ordered alloys based on titanium, nickel, and copper: Ti-Ni, Ni-Mn, Ni-Al, Cu-Al, Ti-Ni-Me, Ni-Mn -Me, Ni-Al-Me, Cu-Al-Me and others [1-13]. Doping with third chemical elements allows one to control their critical temperatures \( M_s \), \( M_f \), \( A_s \), \( A_f \) and to design alloys with specified TMT parameters. At the same time, many aspects of the effect of doping on the features of TMT and the mechanisms of destruction in such alloys remain unexplored.

The most important problem that impedes the practical application of many polycrystalline alloys based on most intermetallic compounds is their relatively low strength, plastic and fatigue characteristics and their tendency to brittle fracture. Thus, polycrystalline Cu-Ni-Al and Ni-Mn-Al alloys experience brittle intercrystalline failure after deformation by 2-3%. The main reasons for this destruction include: a very large elastic anisotropy of their metastable austenite; large grain sizes; the presence of grain-boundary segregations and precipitates of embrittling phases.
2. Materials and Methods

In this study we used eleven Cu–Al – 3 wt% Ni ternary alloys with the content of aluminum varied from 9 to 14 wt% (with an accuracy of ±0.1 wt%), taking into account a triple-point phase-equilibrium diagram of the vertical section of the Cu–Al–Ni three-component system. The alloys were produced by the electric-arc melting from high-purity Cu, Al and Ni (99.99%) in a refined helium atmosphere. For the sake of homogenization, the alloys selected by their chemical composition were subjected to long annealing at (1173 ± 25) K in an inert argon atmosphere. The alloy ingots were cooled in air. The alloys heated to 1223 K were forged to form a 12×12 mm bar, followed by cooling in air. Then they were quenched into water at room temperature after heating of the bars at 1223 K for 10 min.

The alloys based on Ni-Mn-Al system were prepared by induction melting in a purified argon atmosphere. For homogenization, they were remelted (at least three times) and then vacuum annealed at 1173 K for up to 30 h. High-purity (99.99% purity) metals served as starting materials for the alloys. Ingots were spark cut into plates, which were then again subjected to homogenizing annealing for 6 h in the state of β (B2) phase followed by water quenching or slow cooling at a rate of ~100 K/h from 1073 or 1173 K.

The structure, phase composition, and martensitic transformations were investigated using the methods of X-ray diffraction at θ/2θ and electron microscopy. The X-ray diffraction analysis by the θ/2θ method was carried out using a DRON-3M diffractometer in the Cu Kα radiation monochromatized by a graphite single crystal. The following facilities of the Ural Branch of RAS, Institute of Metal Physics Collaborative Access Center were used in the investigations: JEM 200 CX (maximum accelerating voltage 200 kV) and Tecnai G2 30 (maximum accelerating voltage 300 kV) transmission electron microscopes and a Quanta 200 scanning electron microscope (accelerating voltage 30 kV) equipped with a Pegasus system. Electron diffraction patterns were taken from a selected area to identify phases.

3. Results and Discussion

In the present work, a comparative study of alloys with TMT and the related shape memory effects (SME) of the two doping systems Cu – Ni – Al (9–14 wt.%) and Ni – Mn – Al (0–25 at.%), created by based on binary alloys Cu-Al and Ni-Mn, is performed.
By the method of temperature resistometry, it was found that doping with aluminum within the specified limits reduces the critical temperatures of TMT from high to cryogenic. The phase composition of the alloys and the structural types of martensitic phases were determined by X-ray diffraction and the complete phase diagrams of TMT in them were constructed. As aluminum was alloyed, the structural type of martensite also changed: in Ni-Mn-based alloys in the sequence 2M (L1₀) - 14M - 10M, on the basis of Cu-Al-Ni - from 18R to 4H. The presence of long-period martensitic phases (14M, 10M, 18R, 4H) is one of the main differences between these alloys.

According to the TEM data, a common feature of the studied alloys is the multi-packet morphology of pairwise twin martensitic phases (Fig. 1 a, c). The main crystal structure characteristics of the packet morphology of martensite include flat boundaries of primary pairwise twin-oriented crystals and internal nanotwins with crystallographic habits close to {110}, and special size and orientation relationships. The observed morphology of martensite is, on the whole, typical for martensite in single-crystal alloys of the same compositions. Interpretation of selected area electron diffraction patterns made it possible to determine the structural type of phases. It is shown that the crystal lattices of the both alloys have a complex long-period structure: \( \beta \)₁ - 18R for the Cu-14% Al-3% Ni alloy and 14M for the Ni\(_{50}\)Mn\(_{32}\)Al\(_{18}\) alloy. Electron diffraction analysis data are consistent with X-ray studies.

In single crystals of low-modulus non-ferrous alloys with SME, this circumstance is responsible for their high structural-phase and physico-mechanical reversibility in the implementation of TMT under the influence of temperature or external load. However, as a rule, the high brittleness of these alloys in the polycrystalline state prevents the practical application in them of the effects of thermomechanical memory and superelasticity. Therefore, the establishment of the causes of fragility and their elimination is an important scientific and technical task.

A fractographic study of the alloys was performed using SEM in secondary electrons on the samples after testing prior to destruction. In Fig. 2, and the image of the fracture of the samples of the composition Ni\(_{50}\)Mn\(_{50}\), Ni\(_{50}\)Mn\(_{32}\)Al\(_{18}\), Ni\(_{50}\)Mn\(_{30}\)Al\(_{20}\), and Ni\(_{50}\)Mn\(_{25}\)Al\(_{25}\) is shown. It can be seen that the destruction occurs in all samples by transcrysalline (mainly along the grain boundaries) and the intercrystalline type (mainly along the joints of packages of martensitic crystals inside the grain). Intercrystalline destruction occurred as brittle as brittle-ductile type. This depends on the arrangement of the packets of martensitic plates relative to the direction of expand of the fracture crack. If the package plane is located along the crack, then brittle fracture occurs (Fig. 2, a - c). This behavior can be explained by the stress concentration in certain areas of the multicrystalline alloy.
And if a crack develops perpendicularly or at an angle to the habit of the martensitic plates of the package, then a brittle-ductile fracture pattern takes place (Fig. 2, d). With a larger increase on the surface of fracture, one can observe a number of areas characterized by lamellar relief.

The nature of fracture under tension of samples of coarse-grained Cu-Ni-Al alloys, as a rule, was intergranular brittle, and in more fine-grained alloys it became ductile (cf. Fig. 3 a, b) or mixed ductile-brittle (Fig. 3 c, d).

At the same time, according to mechanical test data, the ultimate strength \(\sigma_u\), the yield strength \(\sigma_y\), and the relative elongation \(\delta\) changed at room temperature. The increase in the mechanical properties of the alloys was due to the refinement of the grain structure of the \(\beta\)-austenite and the packet substructure. So, for fine-grained alloys with 9.2 and 9.5 wt. % Al, the value of relative elongation is maintained at a good level (> 10%), and for other alloys with an aluminum content of 10-14 wt. %, it does not exceed 5%. With a change in the aluminum content in these alloys, the nature of the destruction of the samples under uniaxial tension also changes.
4. Summary

The following main patterns of structural and phase changes occurring in the Cu-Al-Ni and Ni-Mn-Al alloys during various deformation-thermal treatments were established:

1. The factors determining the embrittlement of polycrystalline alloys in the martensitic state are the magnitude and anisotropy of the elastic moduli, the difference in the lattice parameters of martensitic phases from the corresponding parameters of the initial phase, grain sizes and the presence of excess phases, especially at the boundaries of the original grains.

2. The alloying of these alloys with aluminum makes it possible to control their critical temperatures $M_s$, $M_f$, $A_s$, $A_f$ from high to cryogenic and to design alloys with given TMT parameters.

3. As the aluminum was doped, the structural type of martensite changed: in Ni-Mn-based alloys in the sequence $2M$ ($L1_0$) - 14M - 10M, on the basis of Cu-Al-Ni - from...
18R to 4H. The presence of long-period martensitic phases is one of the main differences between these alloys.

4. It was established that a common feature of the studied alloys is the multi-packet morphology of pairwise twin martensitic phases, which are characterized by flat boundaries of primary pairwise twin-oriented crystals and internal nanotwins with crystallographic habits close to \( \{110\} \) and Bain type OR.

5. Different, depending on the aluminum content, refinement of the grain structure influences the deformation behavior of the alloys, leading to an increase in their strength and plastic properties. In this case, the mechanism of their destruction changes from brittle (along the boundaries of the former austenitic grains and / or the boundaries of martensite packets in a hot-rolled and hardened state) to a predominantly brittle-ductile fracture (with the development of significant preliminary plastic deformation).
Acknowledgment

The work was carried out within the framework of the state task of Russian Ministry of Education and Science (cipher "Structure", No. AAAA-A18-118020190116-6) and with partial support of the RFBR (project No. 18-32-00529 mol_a).

References


