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Influence of Al and Mn impurities on structural processes transformations in copper alloys

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In the work on specific examples involving real copper-based alloys containing 14 weight.%Al and 3 weight.%Mn, describes the results of a study of the process of restoring the shape of a material that was defomated according to the three-point bending scheme. The studies were carried out by measuring changes in the temperature dependence of the electrical resistance and deflection of the sample, as well as by obtaining microelectronograms using an electron microscope. Since SME alloys operate under conditions of mandatory thermal cycling, the elucidation of the thermal stability of these materials is of practical interest. It is established that martensitic crystals that occur in hardened samples have a high density of packing defects and thin twins formed on the (121) γ′ plane. One of the important features of the martensitic mechanism is the obligatory formation of martensite with defects, which is a fine structure. By comparing the curves of the electrical resistivity and the deflection, it was found that the temperature range of the increase in the deflection upon cooling coincides with the temperature range of the direct martensitic transformation. In addition to stacking faults, thin twins with a thickness of 0.01-0.04 microns are also observed in martensite crystals. It was found in the analysis that twinning in martensite occurs along the {121} γ′ plane. It is shown that the streakiness arising during martensitic transformations is caused by stacking faults, which lie in the {121} plane at a high density of stacking faults.

Keywords: metals, alloys, martensite, electrical resistance, electron microscopy, structure, alloying.
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1 Introduction

The phenomenon of thermoelastic martensitic transformation predicted at the time by G. V. Kurdyumov and later discovered on CuAlNi alloys these results have led to the appearance of many works devoted to the study of various aspects of this unique phenomenon. The most interesting and of great scientific and applied significance are the shape memory effect (SME), superelasticity, and two-way (reversible) shape memory [1,2]. The essence of the shape memory effect is as follows. Loading a material sample in the temperature range of martensitic transformation leads to its deformation in the form of stretching, bending, etc. This deformation can be «removed» by heating above the temperature of the end of the reverse transformation. In this case, the sample is deformed due to the directed growth of martensitic crystals under the action of applied stresses [5]. A similar process is observed in all materials that undergo reversible martensitic transformation. The difference can only be in the degree of restoration of the original form that existed before the transformation. It should be noted that in alloys with thermoelastic martensitic transformation, the original shape is completely restored. In materials with a large hysteresis of the forward-reverse transformation process, a partial restoration of the original shape is observed, as a result of which part of the deformation obtained during cooling under load is preserved [3,4].

Since then, a significant number of works have been performed on the study of the phenomenon associated with martensitic transformation. However, there are a number of problems that have not yet been solved, including the lack of consensus on the conditions for the existence of a complete restoration of the original shape when the material is heated after deformation[10].

Determining these conditions is extremely important when choosing materials with SME used in devices designed to solve various structural and multifunctional tasks. Let us briefly explain the essence of martensitic transformation [7, 9].

Martensitic transformation is a subspecies of polymorphic transformation in which the relative positions of the atoms that make up the crystal are changed by their ordered movement. In this case, the relative displacements of neighboring atoms are small compared to the interatomic distance [6, 11]. The rearrangement of the crystal lattice in microblasts is usually reduced to the deformation of its cell, and the final phase of the martensitic transformation can be considered as a uniformly deformed initial phase [8, 12]. The strain value is small (about 1-10%) and correspondingly small compared to the binding energy in the crystal. The microstructure of martensite has a needle-like (plate-like) or rack-and-pinion (batch) appearance. It can be observed in hardened metal alloys and in some pure metals that are characterized by polymorphism. Martensite is the main structural component of hardened steel. For steel, it is an ordered supersaturated solid solution of carbon in α-iron of the same concentration as the original austenite [17]. The memory effect of metals and alloys is associated with the transformation of martensite during heating and cooling. It received its name in honor of the German metal scientist Adolf Martens, whose name is associated with the discovery of this phenomenon [14, 15, 20].

One of the important features of the martensitic mechanism is the mandatory formation of martensite with defects, which is a thin structure [16, 19]. The latter has a certain effect on a number of properties of materials, including hardening and SME parameters. By changing the concentration of one of the elements in the alloy, you can get martensite with different substructures with the same mechanical properties of the entire system. In addition, since SME alloys operate under conditions of mandatory thermal Cycling, the determination of the thermal stability of these materials is of important practical interest. In this regard, this article will review some experimental results of the study of SME in cases where the martensite transformation proceeds with different hysteresis, and the martensite itself has a different fine structure [13, 18, 21].

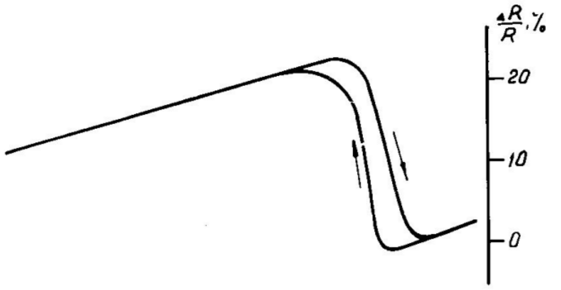
2 Fine structure of martensite and memory effect in a copper-based alloy

To study the shape recovery during the reverse transformation, the alloy samples were prepared in the following composition: Cu+14 weight.% Al+3weight.%Mn with Mn = 10oC. The samples were deformed according to the three-point bending scheme. Loading was performed above the Aк point [6]. the Load was selected in such a way that the maximum stresses arising in the sample were significantly lower than the yield strength of the high-temperature β1 phase. When cooling in a certain temperature range, the deflection of the sample increases sharply (Figure1b). A comparison of the electrical resistance curves (Figure 1a) and the deflection curve (Figure 1b) shows that the temperature range of increasing deflection during cooling coincides with the temperature range of direct martensitic transformation.

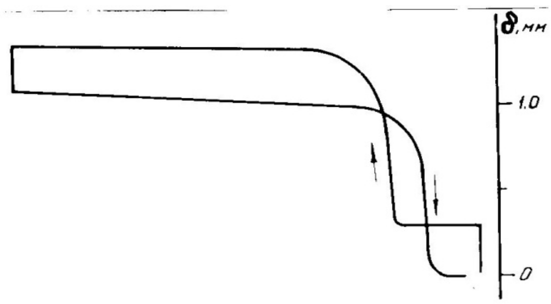
After the load is removed at the temperature of liquid nitrogen, the shape is restored during heating in the interval of reverse martensitic transformation (Figure 1 a, b). If the maximum stresses applied before loading do not exceed the yield strength, then complete straightening during heating is observed even if the sample is not unloaded before heating and it, unbending, performs work against an external force. In this case, the interval of the mold recovery temperature is slightly shifted towards higher temperatures compared to the case when the load does not prevent the mold recovery. It should be noted that the curves of the temperature dependence of the electrical resistance when heated under load remain almost unchanged. This is probably because the amount of martensitic phase that causes the shape change is at the level of the sensitivity threshold of the resistometric technique. Complete restoration of the original shape during heating was also observed after plastic deformation at -196oC. However, in this case, to obtain the same residual deflection as when cooling under load, loads 10-15 times greater are required.

During the quenching process in the studied alloy, the initial β – phase is ordered and a β1-phase is formed with a parameter 2 times greater than the parameter of the β – phase. Microelectronograms from the ordered β1 phase show superstructural reflexes, while micrographs show curved antiphase boundaries (Figure 2). A certain amount of martensitic crystals is preserved in the samples at room temperature. the γ-phase is also ordered, but the antiphase domains in martensite are smaller than in the initial phase.

Martensitic crystals that occur in hardened samples most often consist of two halves separated by a median plane. In each half of the crystal, banding is observed, which leads to the appearance of strands on microelectronograms obtained from such sites.



a)

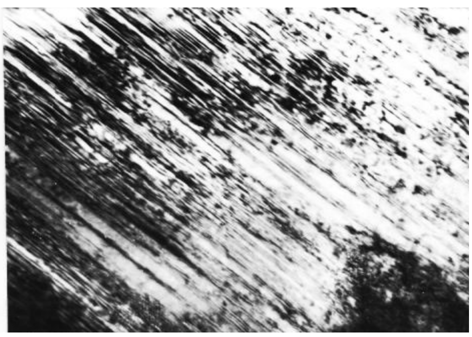


b)

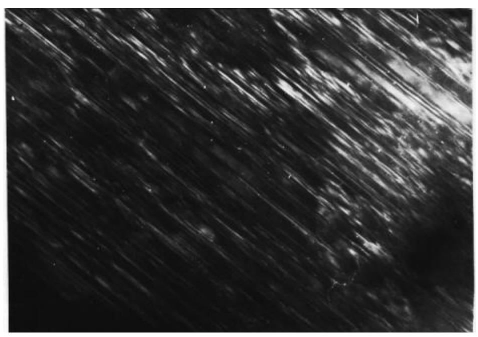
Figure 1 – Temperature dependences of electrical resistivity (ΔR/R) and deflection (δ) of CuAlMn alloy

Figure 2 – Antiphase boundaries in the β1 phase of CuAlMn alloy

a)



b)



c)

Figure 3 – Section of a Martensitic cualmn alloy crystal with packaging defects: a) light field image; b) reflection in the reflex (100)γ′; c) image in the reflex (200)γ′.

The strands are always perpendicular to the banding in micrographs. Banding is caused by packaging defects that lie in the {121} plane. The density of packaging defects is quite high. Figure 3 shows micrographs of a section of a martensitic crystal with banding in a light and dark field.

In addition to packing defects, thin twins with a thickness of 0.01-0.04 microns are also observed in martensitic crystals. During the analysis, it was found that twinning in martensite occurs along the {121}γ′ plane. A micrograph of a section of a martensitic crystal with thin twins is shown in Fig.4. Within the broader twin plots was also observed in the banding caused by defective packaging. In the initial β1 phase after quenching, the dislocation density is low, and only single dislocations are observed. After β1 → γ′ transformation, areas with high dislocation density were also found in martensitic crystals.

In addition to thin twins, relatively wide (up to 1 mm) twin sections were found in the γ′ – phase. The borders of such doubles are usually straight. These twins could be formed due to the stresses that occur during the martensitic transformation (observed after the end of β1 → γ′ upreversion at a given temperature) or as a result of the appearance of local thermal stresses in thin films when viewed in an electron microscope (the twins were formed during observation).

The direction of banding changes in the foreground areas (Figure 5). It was found that in this case, too, the twinning occurs along the {121} γ′ plane.

When cooled, martensitic crystals or plates are formed with both smooth and jagged borders (Figure 6). Compression deformation (2%) leads to the appearance of martensite plates with banding and reoriented sections with a width of approximately (0.2-0.4) microns. The boundaries of these sections are located in the {121}γ′ and {101}γ′ planes. In some areas, the density of dislocations in martensite increases. It should be noted that after deformation, martensitic crystals with jagged interfacial boundaries appear more often.

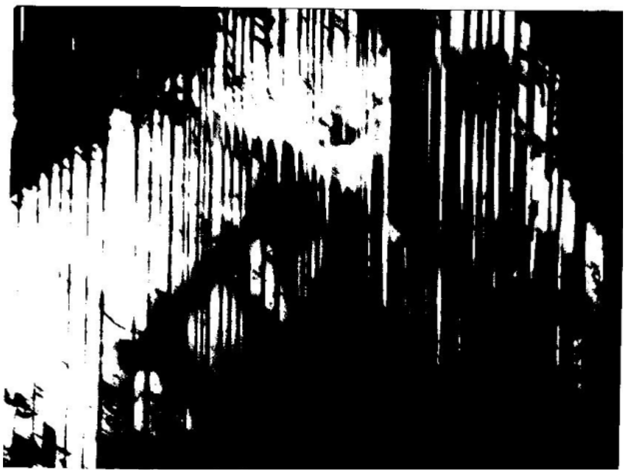


Figure 4 – Thin twins in the γ-phase of the CuAlMn alloy at the orientation [111]

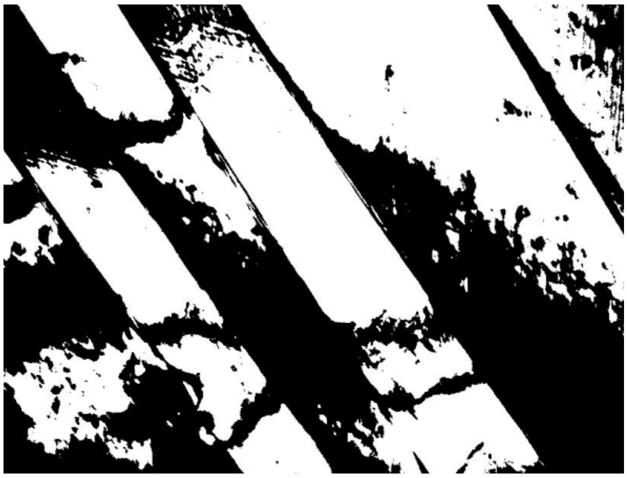


Figure 5 – Twin sections of the CuAlMn alloy in the γ-phase with the orientation [010]

3 Conclusions

Studies of the influence of al and Mn impurities on the processes of structural transformations in copper alloys subjected to plastic deformation according to the three-point bending scheme by measuring the temperature dependence of electrical resistance have shown that this dependence is practically unchanged. The main reason for this process is probably that the concentration of the martensitic phase formed in the alloy as a result of plastic deformation does not exceed the sensitivity threshold of the method based on the measurement of electrical resistance. However, if the load acting on the sample is increased by more than 10 times at a temperature of – 196oC, it is possible to achieve complete restoration of the original shape of the material. According to electron microscopic studies, the main structural disorders that occur in this case are defects in high-density packaging and thin twins, the dimensions of which do not exceed 0.01-0.04 microns in thickness. It is established that the predominant formation of the latter occurs on the plane (121) γ′.

a) b)

Figure 6 – CuAlMn martensitic crystals with smooth (a) and jagged (b) borders

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