Structure formation and functional properties of thin-gauge tapes made of copper-based alloys obtained by melt spinning

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Abstract. The article presents evidence proving that the alloys of the CuZnAl system, unlike the CuAl (Ni, Mn) system, have a smaller contact area with the quenching disk. It is caused by the condensation of Zinc vapors from the melt on its quenching surface. In addition, it is shown that Bronze alloys, in comparison with Brasses, are preferable for obtaining tapes by spinning. The main patterns of changes in critical points and the value of the Shape Memory Effect ($\varepsilon_{SME}$), depending on the types of heat treatment are also analyzed in this paper. Exposure of the alloy to the mold setting temperature of $T = 800\text{÷}850^\circ C$ is accompanied by grain growth, increase in critical points, and decrease in the value of Shape Memory Effect. In this regard, the holding time at the mold setting temperature should not exceed $t = 3\text{÷}5$ min.

1. Introduction

Due to their unique properties, materials with the Shape Memory Effect are widely used in many areas of technology. Among these materials, Copper-based alloys occupy a special place. They are characterized by the ability to restore significant (up to 8–15%) inelastic deformations, corrosion resistance, high technological properties, relative cheapness, high thermal conductivity and, as a result, rapid response to temperature changes. Along with massive materials, a worthy place in this group is occupied by thin-gauge tapes obtained by melt spinning. The microcrystalline structure of tapes provides a variety and severity of such phenomena as Shape Memory Effect, Multiple Shape Memory, Reversible Shape Memory, etc.

The application field of such materials in engineering is rapidly expanding due to the development of new alloys and significant progress in their production technology. The ability to change form in a certain temperature range and a small cross-section area distinguish the tapes as promising materials for the production of heat-sensitive elements. The widespread use of thin-gauge tapes of Copper alloys is hampered only by the lack of knowledge of their functional properties. This restricts information about the kinetics of the formation of the tape structure in both isothermal and thermocyclic conditions. It is impossible to design and develop devices based on the work of tapes possessing Shape Memory Effect without obtaining this data.

In order to increase the efficiency of practical use of such materials in technology, it is necessary to find new ways to manage their special properties. For this reason, there has recently been an increased interest in studying the structural state and functional properties of thin-gauge tapes made of materials with Shape Memory Effect. The thermal stability and mechanical resistance of various structural states...
and their role in the implementation of martensitic transformations (MT) responsible for the complex properties of shape memory are still the most essential factors in this process.

2. Results and discussion

The above-mentioned points indicate the relevance of developing original methods and creating experimental conditions for studying the functional properties of thin-gauge tapes, as well as identifying patterns of their mechanical behavior under various types of external influence that are of scientific and practical interest [1, 2, 3].

The objective of the research is to study the structure formation and forming functional properties of thin-gauge tapes of Copper alloys for their use as heat-sensitive elements. In accordance with the objective, the following tasks are formulated:

- to investigate the influence of technological factors on the formation of the tape structure in the conditions of high-speed solidification of the melt;
- to study the influence of various types of thermal and thermomechanical processing on the functional properties of thin-gauge tapes;
- to set optimal modes for creating the Shape Memory Effect in the unloaded state, which ensure high performance of tapes in bending conditions with multiple implementation of shape memory properties;
- to develop the basics of engineering calculations for selecting the modes of creating the Shape Memory Effect for the operation of a thermosensitive element in a given deformation space.

Experimental studies were conducted on two specially created installations that allow obtaining tapes of the required geometry and measuring their functional properties under bending conditions during thermal cycling, both in the unloaded state and under the influence of constantly applied stress. Diagrams of these installations are given.

Traditional methods of measuring physical (electrical resistance) and mechanical (tensile testing) properties were implemented in the course of the experiment. Research methods utilizing optical metallography, X-ray diffraction analysis and electron microscopy are described in this paper. Theoretical research was carried out using the methods of mathematical planning of the experiment.

Alloy systems possessing the Shape Memory Effect (SME) were used as objects for research: CuZnAl (Cu-14Zn-7,6Al; Cu-21Zn-5,8Al; Cu-10,2Zn-8,4Al) and CuAl(Ni,Mn) (Cu-13,5Al-4,8Ni; Cu-12,5Al-4,5Mn; Cu-14,7Al-4,3Ni-1Ti).

Here and subsequently, throughout the paper, the chemical composition of the alloys is given in % by weight. The tapes were divided into the following quality categories: I – absence of transverse pores, smooth edges; II – random pores along the length of the tape, minor edge defects (burrs); III – through porosity (waste materials).

The results of experiments have shown that a steel disk, in comparison with the copper one, under the same casting conditions, always forms a tape of a smaller thickness (figure 1). At the same time, the interval of variation in casting modes for obtaining tapes of categories I and II on a steel disk, in comparison with the copper one, is shorter, especially from the side of low pressure of the ejecting gas.

It was found that at pressures (0.13–0.15)•10^5 ≤ P ≤ (0.32–0.35)•10^5 PA, the thickness of the tape when casting on a copper disc can be approximated with sufficient accuracy by a linear dependence on the pressure. When the pressure increases P > 0.35•10^5 PA, the dependence of the tape thickness deviates from the linear one. In this case, the casting process is always accompanied by the appearance of a "back" release of the melt and a decrease in the quality of the tape surface.

The quality of the contact (internal) surface of the tapes is mainly determined by the contact interaction (adhesion) of the disk surface with the melt. Copper disk, unlike steel, when casting both types of alloys, provides a tighter contact with the melt. At the same time, the Brasses, unlike Bronze, in all cases contacts the quenching disk on a smaller area.
Figure 1. The influence of the pressure of the ejecting gas and the casting speed on the thickness and quality of the tapes when spinning the melt on: copper disk (a); steel disk (b). I, II, III – areas of tape thickness of the corresponding categories. Alloys of the CuAl system (Ni, Mn) (bronze), nozzle b = 0.6 mm, gap h = 0.25 mm.

It is also found that the main cause of low adhesion of the Brass tape is the condensation of Zinc vapors from the melt on the quenching surface of the disk, which leads to a violation of their mutual thermal contact. The results obtained made it possible to reasonably select the intervals of technological factors variation and ultimately obtain tapes of categories I and II in order to further optimize the spinning process.

The regression equations describing the influence of the main technological factors on the thickness of the tape (Y) are derived using the experiment planning method. When casting alloys of the CuAl(Ni,Mn) system, this dependence is represented by a polynomial of the first degree:

\[ Y = 57.5 - 16.3x_1 + 15x_2 + 5x_3 + 8.8x_4 \]  (1)

For alloys of the CuZnAl system, this dependence has the form:

\[ Y = 64.9 - 13.5x_1 + 10.2x_2 + 7.6x_4 \]  (2)

where: \( x_i \) is the encoded \((-1,+1)\) value of the \( X_i \) factor. The following technological factors were selected: \( X_1 \) – circumferential speed of the disk (20÷40) m / s; \( X_2 \) – pressure of the ejecting gas (0.15÷0.35)•10^5 PA; \( X_3 \) – the gap between the nozzle and the quenching surface of the disk (0.2÷0.3) mm; \( X_4 \) – the width of the nozzle gap (0.3÷0.5) mm.

Based on equations 1, 2, it is concluded that the thickness of the Brass tape is independent of the gap (factor \( X_3 \)) and the values of all coefficients for variable factors are relatively low compared to the Bronze tape. The results obtained are an additional confirmation of the weak adhesion of the Brass melt to the quenching surface of the disk.

The presence of texture is noted as one of the features of the structural state of the tapes. In cross-section, the grains have a columnar shape and are located perpendicular to the contact surface
of the tape. In the longitudinal section, there is a tendency to tilt the crystal axis at an angle of 15\(^\circ\)–20\(^\circ\) in the direction of the tape movement during casting.

X-ray diffraction analysis of the tapes showed that in all cases, the axis of the preferred orientation of the grains perpendicular to the outer surfaces of the tape is the direction [110]\(\beta\).

Studies conducted using metals with a different crystal lattice from the Body-Centered Cubic alloys – BCC (Cu, Al, Zn) revealed a correlation between the type of crystal lattice at the time of crystallization, the preferred orientation of the grains and the main direction of heat removal.

It is shown that the grains with the orientation [111]HCC and [001]GPU are located perpendicular to the outer surfaces of the tapes (the main direction of the heat removal). On the basis of the Le Chatelier-Brown principle, possible causes of this effect are established. The size of the Shape Memory Effect was determined by bending. The deformation was calculated from the outer layer of the sample under the assumption of an ideal plastic body.

In the process of spinning the melt, it was noticed that the tapes are on the surface of the disk for a very short time (\(\tau \approx 0.5\div2\) micron) and leave its surface in a "hot" state. As a result, there is a strong distortion of the tape from interaction with air, requiring additional heat treatment to correct the shape.

Heat treatment was carried out by holding at the temperature of stable \(\beta\)-phase existence (T\(\approx 850\) °C) with subsequent quenching in water. Experiments have shown that with increasing exposure time, all characteristic temperatures increase, with the greatest change in the \(M_t\) temperature, and the value of the Shape Memory Effect decreases.

X-ray analysis revealed that the phase composition of all alloys after this type of heat treatment does not change, so the change in the properties of the tapes is associated with a change in their microstructure: grain growth, reduction of the number of quenching defects, etc. Grain in CuZnAl alloys has the maximum tendency to grow.

It is shown that intensive grain growth is observed in all alloys at the initial stages of exposure (\(\tau \approx 3\div5\) min). With a further increase in the holding time, the grain growth occurs at a very low rate. Optical analysis indicates that a noticeable decrease in the grain growth rate, as well as a change in the functional properties of the tapes, are observed when the average grain size becomes commensurate with the thickness of the tape itself. In this case, the outer surface of the tape is a natural obstacle to further increase in grain size.

It is established that the thermal stability of Copper alloys significantly depends on their chemical composition. For example, in conditions of artificial ageing (T\(\leq 300\) °C), the CuZnAl system has minimal thermal stability, since changes in the functional properties in the alloys of this system are observed after heating to T\(=120\div150\) °C, and exposure for \(t = 3\) hours at T \(= 300\) °C leads to the complete decay of the matrix phase. Alloys of the CuAl system (Ni,Mn) retain their functional properties up to temperatures T\(\approx 220\div250\) °C.

CuAlMn system is the most thermally stable of all the studied alloys. The main reason for this is the presence of Manganese, which lowers the temperature of eutectoid transformation (\(\beta \leftrightarrow \alpha + \gamma\)) and the release of the Cu2MnAl during the ageing phase (Geissler phase), which tests materials in areas depleted by Aluminum, which appear in the material due to the diffusion decay of the matrix phase.

X-ray structural analysis has shown that in metastable Copper-based alloys, diffusion processes occurring at the initial stages of artificial ageing do not cause the formation of equilibrium phases (\(\alpha, \gamma\), AlNi, etc.), but contribute to the formation of a different type of martensite in relation to the existing one. So, if the structure before heat treatment included martensite with an increased electronic concentration, after the artificial aging, the formation of martensite is characterized by a reduced electronic concentration, and vice versa. Both processes cause the Martensitic Transformation (MT) temperature range to expand and the Shape Memory Effect to decrease. Equilibrium phases appear at later stages of ageing.

It is shown that depending on the chemical composition of the alloy, natural ageing affects the characteristic temperatures in different ways. In the CuZnAl alloy system, all temperatures during ageing remain almost at the same level. In CuAlNi alloys with relatively low temperatures of Martensitic Transformation – MT (\(A_t \leq 100\div115\) °C) there is an expansion of the temperature range of MT.
However, as a result of thermal cycling through the MT interval, all points return to their original values. At relatively high MT temperatures (AT ≥ 120 °C), there is no change in MT temperatures during natural ageing.

The X-ray diffraction analysis shows that changes in the properties of tapes under natural ageing conditions occur as a result of diffusion processes that lead to the formation of Guigner-Preston zones in the structure of alloys. The possible causes of this phenomenon are analyzed and recommendations on the choice of material for thermosensitive elements working in reusable and single-use devices are offered.

The methods of creating the Shape Memory Effect in the free state in relation to the chemical composition and loading conditions are studied. The Reversible Shape Memory was set by active deformation of the tapes in the martensitic state, as well as by heating in the deformed and pinched state (the mode of generating reactive stresses). Heating was carried out to temperatures no higher than T=300 °C, since at these temperatures the matrix phase decay processes are intensified. Before testing, the samples were deformed in the martensitic state by the value of Extension Limit (εEL) around the mandrel at an angle of 90°, fixed in this position and subjected to heat treatment under various temperature and time factors.

The advantage of creating the Shape Memory Effect by heating in the deformed and pinched state in comparison with isothermal active deformation is shown. For all alloys, the Shape Memory Effect is formed with a pronounced maximum when heated under conditions of reactive stress generation (figure 2). Moreover, the formation time εRSM max [RSM = Reversible Shape Memory] decreases both with an increase in the heating temperature and with an increase in the Aluminum content in the alloy.

![Figure 2. The influence of heating time on the Shape Memory Effect value in alloys: Cu-21Zn-5,8Al (1); Cu-14Zn-7,6Al (2); Cu-10,2Zn-8,4Al (3). T = 130 °C.](image)

Thus, the presence of Aluminum in the alloy reduces the thermodynamic stability of the β1-phase. It was found that with an increase in the processing temperature and a decrease in the AT temperature, the stability of the Shape Memory Effect formed in this way increases.

With an increase in the duration of exposure at the temperature of the Shape Memory Effect setting, the interval of reversible shaping gradually shifts towards pre-deformation (figure 3).
Figure 3. Changes of the Shape Memory Effect value (a); location of the area of reversible shaping (b) in the alloy Cu-10.2Zn-8.4Al. Ageing at $T = 130^\circ$C.

The identified feature makes it possible to create a Shape Memory Effect in any deformation space of $0 \varepsilon_{EL}$, which is important for the application of this effect in engineering.

It was found that the stability of the Shape Memory Effect created in this way depends on the processing temperature and the $A_t$ temperature.

The reduction in the Shape Memory Effect when thermocyclocycling in the free state has been determined as the common feature of all alloys. The greatest changes are observed at the initial stages of cycling (8–12 cycles). If the temperature of the Reversible Shape Memory (RSM) formation is close to the terminal temperature of the reverse martensitic transformation MT ($A_t$), consequently, thermal cycling of 4÷10 cycles through the MT interval results in the complete degradation of the RSM effect.

3. Conclusion
The speed of the quenching surface of the disk (casting speed) has the greatest influence on the thickness of the tape. It was found that the thickness of tapes of satisfactory quality is in a certain range $t \approx (40\div120$ microns).

Natural ageing causes an expansion of the MT temperature range and a decrease in the Shape Memory Effect in alloys of the CuAl (Ni, Mn) system. Increasing the ductility of the alloy (CuZnAl system) reduces the tendency to change properties. It is established that the main mechanism for the creation of the Shape Memory Effect is the diffusion of alloy components in the areas of reactive stress initiated by preliminary deformation of martensite. The value of the reversible deformation of the Shape Memory Effect depending on the duration of heating is described by a maximum curve, and the value $\varepsilon_{RSM}^{\max}$ [RSM = Reversible Shape Memory] is determined only by the degree of pre-deformation of the Extension Limit ($\varepsilon_{EL}$) and is observed in the middle part of the deformation space $0 \varepsilon_{EL}$. The revealed regularities make it possible to create the Reversible Shape Memory in any area of the $0 \varepsilon_{EL}$ deformation space, which is important for applying this effect in engineering.

The stability of the Shape Memory Effect depends on the $A_t$ temperature and decreases when the temperature rises. This fact limits the upper range of performance temperatures of Copper alloys at the level of $T \approx 100\div120^\circ$C.

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