The Structure and Functional Properties of Ti$_2$NiCu Alloy Rapidly Quenched Ribbons with Different Fractions of Crystalline Phase

Belyaev$^a$ S. P., Istomin-Kastrovskiy$^b$ V. V., Koledov$^c$ V. V., Kuchin$^c$* D. S., Resnina$^a$ N. N., Shavrov$^c$ V. G., Shelyakov$^d$ A. V., Ivanov$^d$ S. E.

$^a$ Saint-Petersburg State University, 7-9, Universitetskaya nab., St. Peterburg, 199034, Russian Federation.

$^b$ State Technological University “Moscow Institute of Steel and Alloys”, 119049, Moscow, Lenin av., 4, Russian Federation

$^c$ Kotelnikov Institute of Radio-engineering and Electronics of Russian Academy of Sciences, 125009, Moscow, Mohovaya st., 11/7, Russian Federation

$^d$ The Moscow engineering-physical institute, 115409, Moscow, Kashirskoe Highway, 31, Russian Federation

Abstract

The samples of Ti$_2$NiCu rapidly quenched alloy with different fractions of crystalline phase have been prepared by electric pulse technique from as spun amorphous ribbons. The structure and thermomechanical properties of these samples have been studied. The mixture of amorphous and nanocrystalline structures with mean grains size less than 10 nm has been observed by HRTEM. The remarkable thermomechanical properties of the samples with the ratio of crystalline fraction in the range of $r = 0.4 - 0.6$ (determined by electrical resistivity measurements) have been found. The two-way shape memory effect with the reverse deformation $\Delta \varepsilon = 0.31 \%$ has been induced in the sample with $r = 0.46$ by single deformation at cooling below the temperature of martensite transformation. The prototype of microweekers based on amorphous-nanocrystalline Ti$_2$NiCu melt-spun ribbon alloy with two-way shape memory effect has been designed and tested.

Keywords: Shape memory effect; two-way shape memory effect; Ti-Ni-Cu; amorphous-crystalline alloys;

1. Introduction

Alloys with shape memory effect (SME) are widely used in different areas of science and technology, such as electronics, medicine and space industry [1]. Ti containing alloys with SME demonstrate the most attractive combination of properties. Among them Ti-Ni-Cu alloy is easy to produce by melt-spinning technique. There are a lot of works devoted to Ti-Ni-Cu alloy investigation [2–8]. But the study of the structure and properties of these alloys is still an actual problem. Such studies will allow to improve the quality of already existing devices and to expand the area of applications of SME alloys.

* Corresponding author. Tel.: +7 926 265 03 77;
E-mail address: rexby@list.ru.

© 2010 Published by Elsevier Ltd Open access under CC BY-NC-ND license.

Keywords: Shape memory effect; two-way shape memory effect; Ti-Ni-Cu; amorphous-crystalline alloys;
Recently nanostructured alloys with SME have been produced by severe plastic deformation technique. They demonstrate enhanced reliability and functional properties [9]. The aim of the present work is to propose a technique of controlled thermal treatment of amorphous melt-spun ribbons of Ti$_2$NiCu alloy which allows to produce the samples with nanograins structure, controllable fraction of crystalline phase. Another aim is to investigate the relationship between the structure and termomechanical properties, particularly the manifestation of the two-way shape memory effect. Alloys with nanocrystalline structure may have application in MEMS and NEMS technology. Also, partly annealed samples are of special interest for fundamental study of the processes of crystallization of the amorphous Ti$_2$NiCu alloy [10].

2. Sample preparation

Melt-spun ribbons of Ti$_2$NiCu have been prepared by rapid quenching technique. As spun ribbons are in amorphous state because of the high cooling rate ($10^6$ K/sec) and great amount of copper (25 atomic percent). The size of the ribbons is 40 µm in thickness, 1.8 mm in width, the length is several meters.

The following technique of annealing of amorphous ribbons is proposed. The 20 cm samples were cut from as spun amorphous ribbon. Then samples were annealed by application of electric current pulses. It is known from the experiment that the electrical resistance of the ribbons after annealing $R_{cr}$ is less than the resistance of amorphous ribbon $R_a$. Thus, the avalanche-like process of crystallization can be controlled by measuring of instantaneous value of the sample’s resistance.

Process of annealing is illustrated on the diagrams (fig. 1). When the pulse of current strength $I_{pulse}$ is on (fig. 1a) the temperature of sample rises (fig. 1b). When the temperature reaches the $T_{cr}$ value the crystallization process starts. After switching off the pulse, the temperature begins to decrease. The process of crystallization terminates when the temperature is lower than $T_{cr}$. Thus the time of crystallization is $\Delta t = t_2 - t_1$. The length of pulse $t_{pulse}$ was selected so that the resistance of a sample changed on a small value $\Delta R$ during the pulse (fig.1c). After that the sample was annealed by the number of pulses of selected length. The resistance of the sample $R$ changed from $R_a$ (the resistance of amorphous ribbon) to $R_{cr}$ (the resistance of fully crystalline ribbon) during this process. The expression

![Fig. 1. Schematic time diagram of crystallization process.](image)

(a) – pulse of current. $I_{pulse}$ – current strength, $t_{pulse}$ – time of pulse.

(b) – temperature of a sample. $T_{room}$ – room temperature, $T_{cr}$ – crystallization temperature, $t_1$, $t_2$ – times of the beginning and the eng of crystallization process correspondingly.

(c) – electric resistance of a sample. $\Delta R$ – change of resistance per one pulse.
can be used to estimate the fraction of the crystalline phase. The described technique was used to prepare a set of samples with different fractions of crystalline phase ($r = 0.46, 0.63, 1$).

It was already mentioned that the resistance of amorphous ribbon is higher than resistance of crystallized one. We can make a hypothesis that the main part of Joule heat ($P = I^2R$) is extracted exactly in amorphous fraction of the ribbon. This will cause new grains appearing instead of old (appeared in previous pulses) grains growing.

3. **The study of structure by high-resolution transmission electron microscopy (HRTEM)**

The structure of sample with $r = 0.63$ was studied by HRTEM. The results are given in fig. 2. Halos on microdiffraction pattern (fig. 2a) are the evidence of amorphous or fine-crystalline structure. One can see crystallites of several nanometers in size in microphotographs (fig. 2b – 2d). The size of grains doesn’t exceed 10 nm (fig. 2b).

![Fig. 2. HRTEM studies of the sample with $r = 0.63$. (a) – microdiffraction pattern; (b), (c), (d) – microphotographs of the sample.](image)

4. **Studies of termomechanical properties**

The thermomechanical properties of a Ti$_2$NiCu sample with $r = 0.63$ and a fully crystallized sample were studied. The bending deformation of a sample versus temperature at different applied loads was measured. The curves in fig. 3 demonstrate hysteresis type behavior which is the result of martensite transformation in the samples.

The temperatures of transformation in the sample with $r = 0.63$ are approximately 15°C lower than in fully crystallized one. This fact can be explained by influence of the amorphous matrix on the crystalline grains in a fractionally crystallized sample.

![Fig. 3. The bending deformation of the samples versus temperature at different external stresses. (a) – for the sample with $r = 0.63$; (b) – for the sample with $r = 1$ (fully crystallized).](image)
5. Two-way shape memory effect

The two-way SME in the fractionally crystallized samples is of special interest. It was found experimentally that a pronounced two-way SME can be obtained after single deformation at a temperature below the temperature of martensite transformation. To measure the reversible deformation the sample was wound and annealed on a quartz cylinder. After annealing it attained a spiral shape (fig. 4). The sample was deformed by straightening after preparation and it obtained the ability of recoverable deformation.

The recoverable deformation $\Delta \varepsilon = 0.31\%$ was calculated as a difference between deformation of the sample in martensite $\varepsilon_M$ and in austenite state $\varepsilon_A$. Two-way SME in the sample can be explained the following way. When a fractionally annealed sample is deformed in martensite state, the amorphous matrix attains the plastic deformation, while the martensite fraction exhibits only pseudoplastic deformation. The crystalline fraction transforms to austenite and recovers its initial spiral shape on heating. The deformed amorphous matrix makes martensite to straighten on cooling.

6. The prototype of manipulator

The prototype of microtweezers was created on the basis of a sample with $r = 0.63$. Microtweezers can catch and move small (submillimeter sized) objects. Microtweezers consist of two parts attached to a resistor mounted on an insulating substrate. One part is made of a copper plate with thickness 60 μm and another part is Ti$_2$NiCu.
amorphous-crystalline melt-spun ribbon trained for reversible bending strain. When a current is on, it heats the resistor and a ribbon with SME and so it bends. Thus the microweazlers are opened at temperature above 45°C and closed at temperature below 25°C. The manipulating of objects with sizes of 50 – 150 μm was demonstrated by microweazlers (fig. 5). The measurement of the force acting upon the object gave the value of about 0.01 N.

7. Conclusion

The technique of controlled annealing proposed in this work allows producing samples of Ti2NiCu rapidly quenched alloy with different fractions of crystalline phase. It is found that the samples with r = 0.4 – 0.6 demonstrate one-way SME and can easily be trained to two-way SME even by single deformation after cooling below the temperature of martensite transformation. The prototype of microweazlers based on this effect was created. The prototype of microweazlers successfully manipulated microobjects in the experiment. This proves the possibility of application amorphous-crystalline ribbons of Ti2NiCu alloy for micromechanical device and MEMS. We can hope that micromechanical devices of extremely small sizes can be designed on the basis of these alloys because the grain size is about 10 nm.

8. Acknowledgements

The work was supported by RFBR (grants No 09-02-91348, 09-08-01177, 09-02-90437), FANI (contract N 02.513.12.3092) and research program of RAS.

References