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Amorphous–crystalline Ti_2NiCu alloy rapidly quenched ribbons annealed by DSC and electric pulses

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ABSTRACT

Samples of Ti_2NiCu rapidly-quenched alloy with different fractions of crystalline phase were prepared from as-spun amorphous ribbons by two different techniques: applying electric pulse and annealing in differential scanning calorimeter (DSC). The structure and thermomechanical properties of these samples were studied. Spherulites were found in a structure of the samples prepared by DSC. And the mixture of amorphous and nanocrystalline structures with mean grain size less than 10 nm was observed by TEM for samples annealed by electric current. The two-way shape memory was induced in the fractionally crystallized samples by single deformation at cooling below the martensite transformation temperature.

1. Introduction

Ti_2NiCu alloy attracts great interest and find new applications in microsystem technology [1–4]. It is known, that the reduction of the grain size in Ti-containing alloys with shape memory effect (SME) causes their functional properties improvement [5]. Equal channel angular pressing (ECAP) technique is often used to get submicrocrystalline and nanostructure. This method, however, needs significant power consumption and is very complicated. There are alternative ways to obtain the alloy with defined proportion of amorphous and crystalline state and different grain size. Annealing amorphous alloy inside the differential scanning calorimeter (DSC) was previously tested [6]. The annealing process in this technique is executed inside the calorimeter's chamber under the control of measurement system. This process is interrupted in intervals by liquid nitrogen injection into calorimeter's chamber. The annealing of amorphous alloy by pulses of electric current of specially calculated duration is used in works [1,7]. The aim of the present work is to compare the results of investigation of the structure and thermomechanical properties of rapidly quenched Ti_2NiCu alloy ribbons produced by both techniques.

2. Materials and methods

Ribbons of Ti_2NiCu alloy for further samples production were prepared by rapid quenching technique on fast rotating copper wheel (melt spinning) [8]. Due to the high cooling rate and large copper content in the melt the initial structure of the ribbons was mainly amorphous.

To produce ribbons with different fractions of crystalline phase Φ two sets of samples were prepared. The first set underwent thermal treatment using the controlled annealing in calorimeter's chamber technique [6]. Amorphous ribbons were exposed in DSC at 440 °C for various times. As a result of the exposure samples with crystalline phase content of $\Phi c = 2\%$, 15%, 29%, 34%, 57%, 74%, 89% and fully annealed samples with additional exposure time of 1 and 24 min were obtained. The energy of the crystallization process was determined by DSC. The percentage ratio of the fractional crystallization energy to the energy of full crystallization was calculated. This ratio was used to approximate the crystalline phase content (Φc) in the sample.

The second set of samples underwent annealing by the application of electric current pulses as described in [1]. In the latter, pulses are applied repeatedly to the sample (up to hundreds of times). The electrical resistance of the sample was measured during the pause between pulses. Because the resistance depends on the fraction of crystalline phase in the sample, the crystalline phase content was estimated using the expression $\Phi r = (Ra - R)/(Ra - Rcr) * 100\%$. Here Ra – the resistance of initial amorphous sample; Rcr – the resistance of fully annealed sample; R – the resistance of the sample. A set of samples with fractions of crystalline phase of $\Phi r = 21\%$, 22%, 29%, 43%, 50%, 60%, 69%, 80%, 89% and 96% was produced. It should be noted that the values Φc and Φr qualitatively describe the process of crystallization, but they may significantly differ quantitatively.

3. Experimental

Calorimetric measurements were made using a Mettler Toledo 822^e DSC. The structural studies were conducted using a

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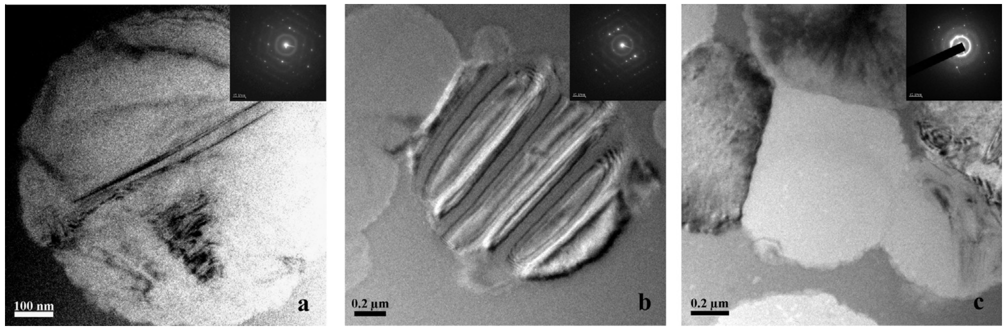

Fig. 1. TEM studies of the first set of samples. (a) $\Phi c = 15\%$; (b) $\Phi c = 29\%$; and (c) $\Phi c = 34\%$.

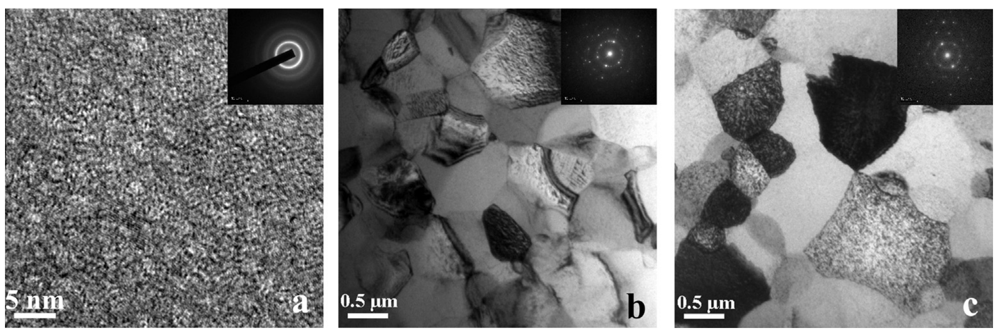

Fig. 2. TEM studies of the second set of the samples. (a) $\Phi r = 63\%$; (b) $\Phi r = 80\%$; and (c) $\Phi r = 89\%$.

transmission electron microscope (TEM) JEOL JEM-2100F. The mechanical properties of the samples were studied by the instrumentality of special designed experimental setup. This setup allows the measurement of the bending deformation of the sample loaded by different loads in the temperature range of −100 to 100 °C.

4. Results and discussion

Data measured by DSC qualitatively coincide for both sets of samples. An increase of the amount of crystalline phase in a sample causes the increase of amplitude and area under the peak of a curve. Also one can observe the shift of phase transformation to the higher temperatures.

The observation by TEM showed different ways of crystalline phase formation in the two sets of samples. Single spherical grains (spherulites) were found in the structure of the sample with $\Phi c = 15\%$ annealed in DSC (Fig. 1a). The spherulites grow up to the size of several micrometers in diameter with an increase of Φc to 29% (Fig. 1b). The martensite twins appear in the volume of the spherulites. The spherulites coalescence with flat boundaries formation beginning at $\Phi c = 34\%$ (Fig. 1c).

TEM studies of the second set of the samples differed from the first one. Fine grains were observed in the structure of the samples annealed by electric pulses. Typical grain size was around 10 nm in the sample that had $\Phi r = 63\%$ (Fig. 2a). Further annealing caused large grains formation in samples with $\Phi r = 80\%$ and $\Phi r = 89\%$ (Fig. 2b and c).

The nanostructure with grain size about 10 nm in the sample with $\Phi r = 63\%$ can be explained in the following way: the resistance of crystalline grains is smaller than the resistance of amorphous phase. So the heating of the amorphous fraction of the alloy is larger than the crystalline one due to Joule law. Thus new crystalline grains nucleate during the pulse of electric current,

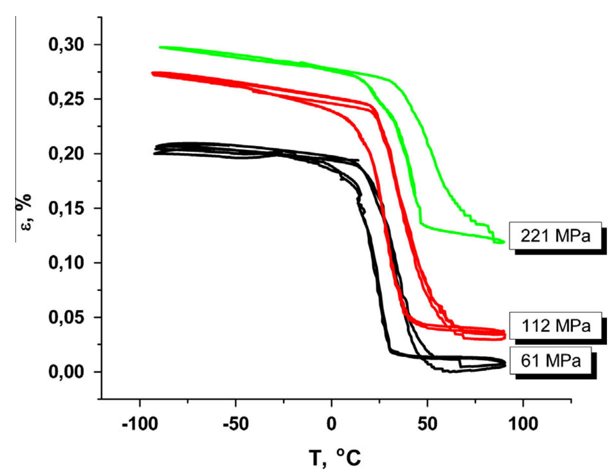

Fig. 3. Bending deformation versus temperature for the sample from 1-sr set. $\Phi c = 89\%$. Three different loads are applied.

and the growth of crystal grains formed during previous pulses is insignificant. This sample was annealed by 435 pulses. Samples with $\Phi r = 80\%$ and $\Phi r = 89\%$ were treated by 4 and 373 pulses respectively.

Studies of the thermomechanical properties of both sets of samples showed that the SME manifests itself more sharply with the increase of the fraction of crystalline phase in the sample. For example Fig. 3 shows the dependence of bending deformation on the sample temperature from the first set with $\Phi r = 89\%$. This dependence has hysteresis behavior, which is typical for an alloy with SME. It is clearly seen that the pseudoplastic deformation sharply increases with the decrease in temperature below the onset of martensite transformation.

Another unique feature observed in both samples sets is two-way SME in fractionally crystallized samples. This effect manifests itself even after one-time deformation of the sample. The effect is the result of presents of two phases: amorphous and crystalline. The deformation of the sample causes plastic deformation of amorphous phase while crystalline martensite deforms pseudoplastically. Thus the sample obtains composite properties. More details about the effect are reported in [1].

5. Conclusion

Samples of Ti_2NiCu alloy were obtained from the amorphous state by two different techniques of annealing. The structure, phase transitions and thermomechanical properties of these samples were experimentally compared in present work. The spherulites nucleation and growth was observed in samples annealed in DSC. The nanostructure with grain size about 10 nm was found in the structure of the samples annealed by multiple electric current pulses. Two-way SME was discovered in intermediate samples with mixture of crystalline and amorphous phases.

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