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The structure and functional properties of Ni–Ti–Cu alloy rapidly quenched ribbons with different parts of crystalline phase*

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Abstract. The structure and thermomechanical properties of Ni-Ti-Cu alloy partially crystallized rapidly quenched ribbons were studied. The technique of controlled isothermal annealing of the initially amorphous ribbons in the differential scanning calorimeter was used for preparation of the samples with determined relations of extracted thermal energies to the full crystallization energy. The thermomechanical properties of the ribbons were studied in temperature interval -100..100 C. It was found that temperature dependence of bending deformation demonstrates hysteresis for the samples with more then 29% of crystalline phase. The shape memory effect manifests itself in these samples. The value of the reversible strain rises with the crystalline phase increase. The HRTEM studies show that rare crystallites have spherical shape in samples with 15% crystalline phase. Their sizes vary from 100 to 1000 nm. The DSC studies show peaks corresponding to the direct and reverse martensitic transformation at temperatures T_{am} = 15 C and T_{ma} = 29 C. The concretion of crystallites with plane boundaries formation was observed in samples with 29% of crystalline phase. The martensitic transformation is suppressed in crystallites less than 300 nm at room temperature. Unlike this in big (~ 1 μm) crystallites the structure of martensitic twins were observed. The transition zone between crystal and amorphous phases of the alloy on crystallites' boundaries was studied by HRTEM technique. The model for the explanation of the observed phenomena is discussed.

1. Introduction

The present work is devoted to exploration of structure and thermomechanical properties of Ni-Ti-Cu rapidly quenched alloy. There are a lot of works devoted to Ni-Ti-Cu alloy investigation [1–7]. This alloy has unique deformation properties, such as shape memory effect (SME) and super elasticity. These properties make the alloy very useful in medicine [8], electronics, and sensor and actuators technology and in others fields.

The samples of Ni-Ti-Cu which have not been fully crystallized from amorphous state are of special interest. This interest has fundamental as well as practical importance. On one hand the process of new phase nucleation and growth in amorphous matrix isn't well studied yet. On the other hand samples we study are amorphous-crystalline composites, which may have useful properties such as two way shape memory effect.

The aim of the present work is to study the samples of the Ni-Ti-Cu alloy with different part of crystalline phase and to compare the structural data and the data on their martensite transformation and termomechanical properties.

2. Samples

The special technique of the controlled isothermal crystallization of the alloy inside the differential scanning calorimeter (DSC) was used to produce the ribbons with different part of crystalline phase [9]. The technique includes of several steps. The pieces of amorphous ribbon are put into calorimeter's chamber. Then the temperature inside the chamber is enhanced by 10 C per minute till 440 C (the temperature of isothermal crystallization). Then temperature is stabilized. The heat evolution during crystallization is registered by DSC

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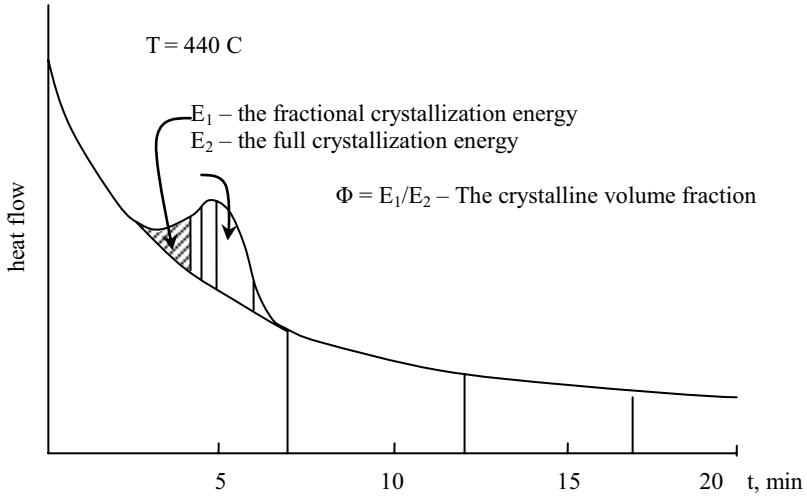


Fig. 1. The experimental crystallization curve of Ni-Ti-Cu alloy with diagram of crystalline volume fraction calculation.

curves. The crystallization process is interrupted by liquid nitrogen supply.

The crystalline volume fraction (Φ) may be calculated as the relation of extracted thermal energy E_1 to the full crystallization energy E_2: $\Phi = E_1/E_2$ (fig. 1). The described method was used to prepare specimens with different part of crystalline phase from 2 to 89% and fully crystallized specimens with additional annealing for 1 and 14 minutes.

3. Results

3.1. Martensite transformation study of Ni-Ti-Cu alloy by DSC

Fig. 2a shows the DSC curves of Ni-Ti-Cu specimens on cooling. DSC demonstrates picks of heat evolution during martensite transformation. The extracted energy (square under the peaks) increases with crystalline volume fraction (Φ) rise. Moreover the martensite transformation temperatures are shifted left (from 48 to 15 C for martensite transformation and from 57 to 29 for reverse martensite transformation) with Φ decrease. DSC curves of Ni-Ti-Cu specimens on heating are given in fig. 2b. The peaks of heat absorption are connected with reverse martensite transformation. As expected martensite transformation and reverse martensite transformation show the temperature hysteresis.

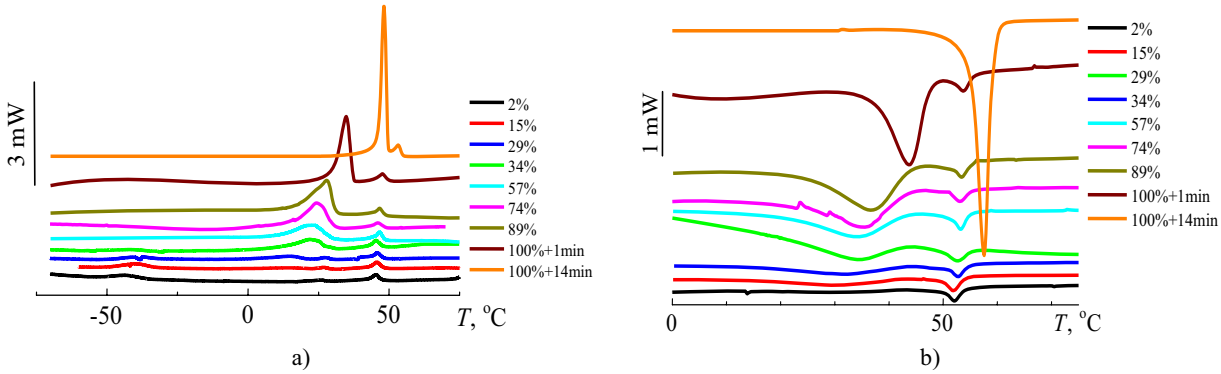
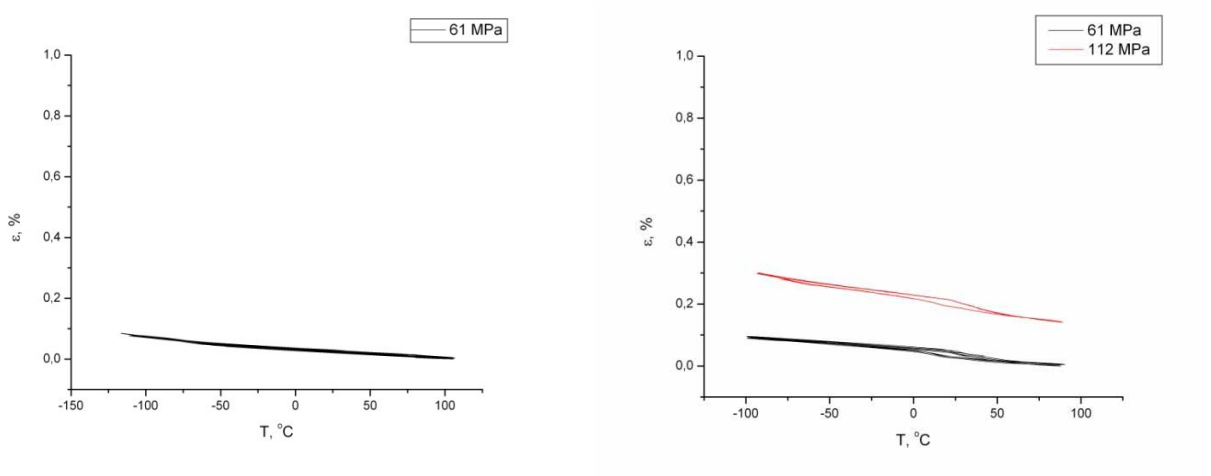


Fig. 2. The DSC curves of Ni-Ti-Cu specimens: a) on cooling; b) on heating.

3.2. Termomechanical properties study of Ni-Ti-Cu alloy

The temperature (T) dependence of bending deformation (ε) of Ni-Ti-Cu specimens under different stress was studied. The ε – T curve for the specimen with Φ = 15 % is given in fig. 3a. Bending deformation behavior doesn't have any features connected with phase transformation. It indicates that martensite transformation is suppressed by great amount of amorphous phase. Temperature dependence of bending deformation of Ni-Ti-Cu sample with Φ = 29 % shows small hysteresis of direct and reverse martensite transformations (fig. 3b). The transformation temperatures detected by thermomechanical curves (fig. 3) are A_s = 17 C, A_f = 52 C, M_s = 30 C,



a) b)

Fig. 3. The temperature dependence of bending deformation of Ni-Ti-Cu specimens under different stress: a) sample with Φ = 15 %; b) sample with Φ = 29 %.

M_f = 3 C. These temperatures correlate with thermograms (fig. 2). The reversible deformation of the sample with Φ = 29 % is equal to 0.02 % under stress 61 MPa.

The dependence of SME versus Φ may be extracted from termomechanical data. The dependence of reverse deformation versus Φ for Ni-Ti-Cu samples with different parts of crystalline phase under the stress 61 MPa is given in fig. 4. One can see that SME is suppressed in samples with Φ < 15 %. The SME appears in sample with Φ = 29 %. Strong increase of reverse deformation manifests itself when Φ = 74 %.

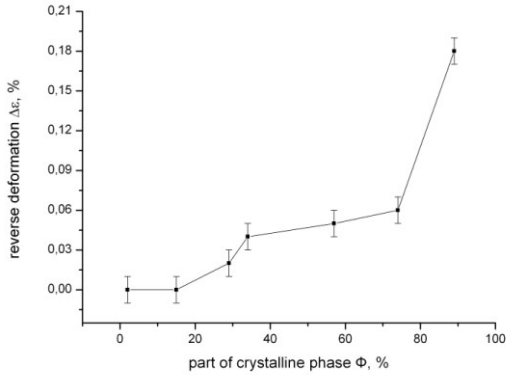


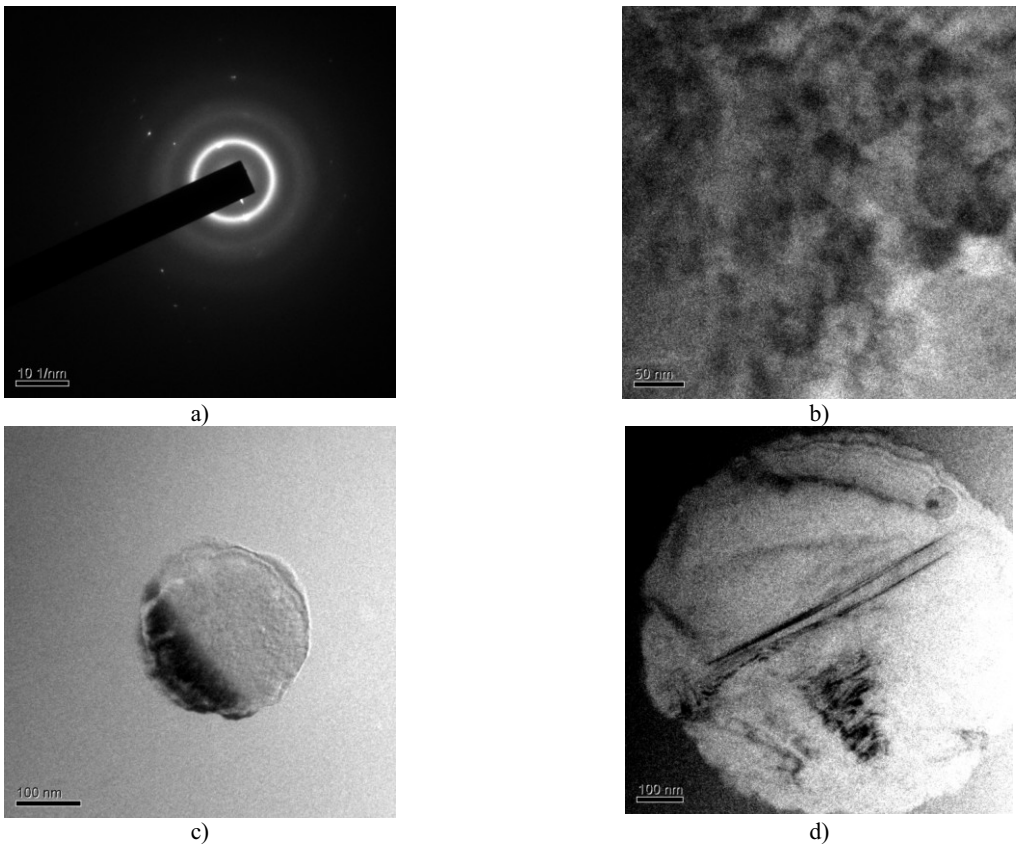
Fig. 4. The dependence of reverse deformation for Ni-Ti-Cu samples verse Φ.

3.3. HRTEM researches of Ni-Ti-Cu alloy

The structure was explored with the use of high-resolution transmission electron microscopy (HRTEM). Micro-diffraction patterns of the sample with Φ =15 % show that it mainly consist of amorphous phase (halo in fig. 5a). But there are some diffraction reflections that belong to crystalline structure of grains. The crystalline structure can be seen in some regions. Grains of 20 -50 nm size have irregular shape (fig. 5b). The larger grains have regular spherical shape (fig 5c). The diameter of spherical grains can reach ~ 1 micron. The first features of martensite transformation were found in the largest grains (fig. 5d).

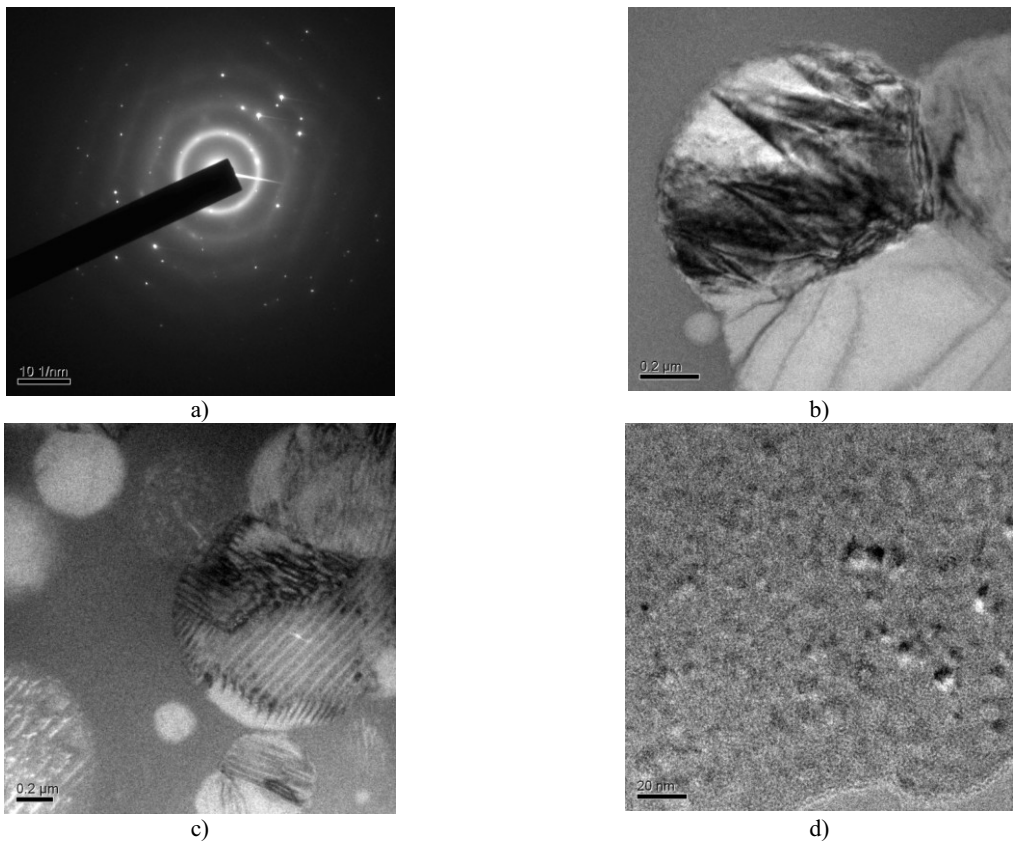
The results of HRTEM studies of sample with Φ = 29 % are given in fig. 6. The amorphous state is still present in volume in spite of longer thermal treatment (fig 6a). One can see nucleation and new spherical crystals growth in this sample in comparison with the previous one. The spherical grains grow until they reach another spherical grain. The process of spherical grains interaction is shown in fig. 6b. New spherical grains of small size don't have martensite structure (fig 6c). The fine martensite structure is replaced by big martensite plates in the largest spherical grains. The martensite plate's size reaches 0.1 – 0.2 μm.

The largest spherical grains have been studied and the transition zone between the amorphous and crystalline states (fig. 6d) has been observed. This zone has thickness about 5 – 7 nm. We can propose that it is



a) b) c) d)

Fig. 5. HRTEM studies of Ni-Ti-Cu alloy with Φ = 15 %: a) micro-diffraction; b), c) and d) microphotography of the sample.



a) b) c) d)

Fig. 6. HRTEM studies of Ni-Ti-Cu alloy with Φ = 29 %: a) micro-diffraction; b), c) and d) microphotography of the sample.

rich of lattice vacancies because of the difference in the amorphous and crystalline phases' densities. The material of the transition zone could behave as quasi liquid due to the large density of lattice vacancies. This should make the tangent stresses small in the transition zone on grain's boundaries. So, this would be the explanation why the crystal grains have regular spherical shape.

4. Discussion

We can conclude that comparative study of the structure and thermomechanical properties of melt spun Ni-Ti-Cu alloy with different part of crystalline phase has revealed some characteristic features of phase transformations: non equilibrium transformation from amorphous to crystalline state via transition zone and martensite transformation in micron and submicron size grains.

- HRTEM show the existence of the transition zone between the amorphous and crystalline states. As we have already mentioned the spherical shape of crystals can be explained by the large number of lattice vacancies in this zone. But this zone should have an extra energy because of the vacancies. During the crystallization some volume of transition zone becomes a part of crystal. This process is exothermal. So some part of the extracted energy of the transition provides the transition zone formation. Thus the motion of the transition zone reminds soliton propagation.
- DSC measurements show thermal shift of the picks, corresponding to martensite transformation in samples. HRTEM researches demonstrate that Φ increases because of the crystals growth. We make a conclusion that the smallest spherical grains are strongly stretched by amorphous matrix than others, because the tensile stress make martensite structure unfavorable. That is why martensite transformation is suppressed in spherical grains less than 200 nm at room temperature.
- The thermomechanical studies didn't show SME in the sample with Φ = 15 %. HRTEM observations show only solitary spherical grains of 0.2 – 1 μm size. The sample with Φ = 29 % demonstrate SME. The structure of this sample consists of spherical grains clusters. Thus, only groups of grains provide SME. Sharp increase of reverse deformation at Φ = 74 % can be explained as follows. The maximum packing density of solid spheres takes place at $(\pi\sqrt{2})/6 = 0.74$ [10].

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