MATERIALS FOR GENERAL PURPOSE

Mechanical and Functional Properties of Amorphous-Crystalline Ribbons of $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ Alloy

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Abstract—The mechanical behavior and functional properties in amorphous-crystalline thin ribbons of $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy with a different volume fraction (from 0 to 100%) of crystalline phase were studied. The results obtained showed that a fully amorphous sample was deformed elastically up to 6%. The existence of the crystalline phase in the sample resulting in the deformation was realized by reorientation of martensite at the early stage. The strain accumulated at this stage was fully recoverable during subsequent heating through the temperature range of reverse martensitic transformation. It was found that an increase in the volume fraction of crystalline phase led to a rise in the value of the shape memory effect. This was due to the increase in the volume fraction of the sample deforming by the mechanism of martensite reorientation. It was observed that the amorphous-crystalline $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy was deformed by three mechanisms of unelastic deformation: reorientation of martensite crystals, plastic deformation of the amorphous phase, and dislocation slip. It was shown that the change in the deformation mechanism was determined by the volume fraction of crystalline phase and the value of preliminary strain. It was found that the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy exhibited a two-way shape memory effect only if the amorphous and the crystalline phase coexisted in the alloy.

Keywords: amorphous-crystalline alloys, shape memory effect, two-way shape memory effect, mechanism of deformation.

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INTRODUCTION

Amorphous alloys are the base for creation of crystalline materials with unusual structure. Depending on the conditions of crystallization, crystalline materials with different morphology and sizes of grains can be produced, as well as alloys with an amorphous—crystalline structure.

One possible method to obtain such structures is the method of controlled crystallization [1]. In this method, an amorphous alloy is obtained by melt spun as a thin ribbon with a thickness of some tens microns and it is subjected to heating up to the crystallization temperature. The crystallization is interrupted at some stage by quenching. As a result, the structure of the alloy looks like a mixture of amorphous and crystalline phases, with the volume fractions depending on the stage of interruption [2]. The crystal size is also determined by the crystallization regime (by the temperature and duration) and may be changed from tens of nanometers to some microns. The material obtained in this way has unusual physical properties, and its mechanical behavior is of significant interest, because in fact the deformed medium is in essence an amorphous-crystalline composite with nano- or micron-sized structural components. The mechanisms and the behaviour of deformation in such materilas are known badly, especially when choosing, as an object, a TiNi based amorphous alloy (titanium nickelide). In the crystal state, such alloys undergo martensitic transformations on temperature variation and demonstrate the shape memory effect and other mechanical effects due to reversibility of unelastic deformation [3]. Amorphous-crystalline ribbons obtained by the method of controlled crystallization can be used for applications in microelectronics and microtechnology, as microsensors and actuators [4]. Therefore, a study of the kinetics of martensitic transformations and functional properties in amorphous-crystalline alloys demonstrating shape memory effects is very important. Until now, the main attention of researchers was focused on studies of martensitic transformations in amorphous — crystalline TiNi based alloys. It was found in [5] that an increase in the volume fraction of crystalline phase results in a rise in the temperature of phase transformations and a decrease in the temperature intervals and hysteresis of transition. In addition, it was shown in [6] that variation of the volume fractions of amorphous and crystalline phases may change the stages of heat transfer accompanying the

martensitic transition. Thus, it was found that the characteristics of martensitic transformations depend on the relative volume fractions of amorphous and crystalline phases. Probably it is caused by a scale effect [7] and a existence of a lot of interfaces between amorphous and crystalline phases, which are the preferable places for nucleation of martensitic plates during the phase transition [8, 9].

As the martensitic transformations are the main reason for demonstration of unusual deformation effects in shape memory alloys, hence one can assume that the variation in kinetics of phase transitions induced by variation in the volume fraction of crystalline phase may influence the functional properties of amorphous-crystalline ribbons. Therefore the aim of this work is a study of mechanical properties and deformation effects in amorphous-crystalline thin ribbons of $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy.

OBJECTS AND METHODS

The amorphous melt spun thin ribbons of $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy were used in this study. The samples with dimensions of $5 \times 2 \times 0.04$ mm were subjected to controlled crystallization using the following methods. The samples were placed inside the chamber of a Mettler Toledo 822^e differential scanning calorimeter and were kept at a temperature below the temperature of crystallization to initiate the isothermal crystallization. Variation in duration of crystallization led one to change the volume fraction of crystalline phase in the sample. In this case, the volume fraction of crystalline phase was determined as the ration of the heat released in partial crystallization to the heat released under total crystallization of the sample [2]. In this work, the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy was subjected to a partial crystallization at a temperature of 743 K, and it allowed one to produce the amorphous-crystalline samples with a volume fraction of crystalline phase (Φ_{cr}) of 40%, 70%, and 100%.

The martensitic transformations in amorphous-crystalline $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloys were studied by the method of differential scanning calorimetry. The crystalline phase in the $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy was found to undergo a martensitic transformation from the cubic $B2$ phase to the monoclinic $B19'$ phase on cooling, and reverse transformation from the $B19'$ to the $B2$ phase on heating. The temperatures of martensitic transformations occurring in the samples with different volume fraction of crystalline phase were determined on calorimetric curves and presented in the table.

A special method of deformation of thin ribbons was developed to study mechanical and functional properties. The sample was bent between two parallel plates at a constant temperature $T = 77$ K, at which the crystalline phase was in the martensite state. After that, the sample was unloaded and heated through the temperature interval of reverse martensitic transfor-

Temperatures of martensite transitions in $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy with different volume fraction of the crystalline phase

Φ_{cr}, %	M_s, K	M_f, K	A_s, K	A_f, K
40	217	204	256	285
70	246	241	275	316
100	268	265	305	325

Note: M_s—the starting temperature of direct transformation, M_f—the end temperature of direct transformation, A_s—the starting temperature of reverse transformation, A_f—the end temperature of reverse transformation.

mation up to 373 K; then it was cooled through the temperature interval of forward martensitic transformation down to 77 K. Then the sample was deformed to a higher level of deformation, and the all described procedure was repeated. At each stage, the sample was photographed against the grid scale background (Fig. 1). The images obtained were digitized and the radius of bending was found that led one to calculate the strain of the sample at each step of deformation using the equation of $\varepsilon = h/2R$, where h is the sample thickness and R is the radius of bending. The residual strain was determined as the strain after unloading (second stage); the value of the shape memory effect was determined as the difference between the strains after unloading and subsequent heating to 373 K (third stage); the value of the two-way shape memory effect was determined as the difference between the strains after heating to 373 K and subsequent cooling through the temperature interval of forward martensitic transformation down to 77 K (fourth stage).
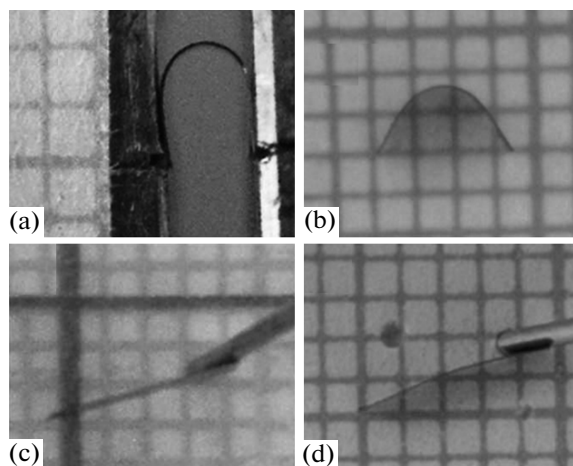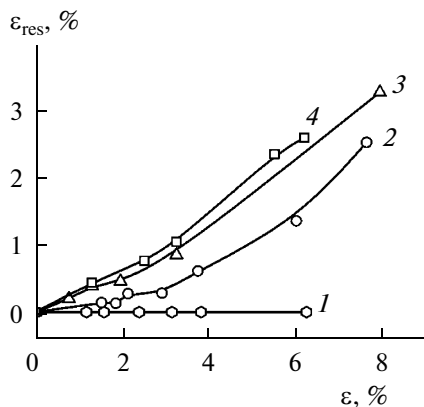

Fig. 1. Photos of a sample at different stages of deformation: (a) loaded sample, (b) unloaded sample, (c) sample after subsequent heating up to 373 K, (d) sample after following cooling down to 77 K.

Fig. 2. Dependence of residual strain (ε_{res}) on the given one (ε) in a sample of $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy with the volume fraction of crystalline phase of (*1*) 0%, (*2*) 40%, (*3*) 70%, and (*4*) 100%.

Fig. 3. Dependence of shape memory effect (ε_{sm}) on residual strain (ε_{res}) in samples with the volume fraction of crystalline phase of (*1*) 40%, (*2*) 70%, and (*3*) 100%.

RESULTS AND DISCUSSION

Figure 2 shows the dependences of residual strain after unloading (ε_{res}) on the given one (ε), corresponding to the samples of $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy with a different volume fraction of crystalline phase. It is seen that an amorphous sample fully recovers its strain when the given deformation is less than 6%. Therefore, a deformation up to 6% is elastic. In partially or fully crystallized samples, residual strain was observed even after deformation up to small strains ε. The larger the volume fraction of crystalline phase, the larger the value of residual strain. Thus, in a sample with the volume fraction of crystalline phase $\Phi_{cr} = 40\%$, a deformation up to up to 2.5% gives rise to accumulation of a residual strain of 0.27%, whereas in a sample with $\Phi_{cr} = 100\%$ the residual strain reaches 0.64%.

It is known that, in a fully crystallized TiNi-based alloy, the residual strain in the martensite state is due to a reorientation of martensite domains. This process takes place until the whole volume of martensite is transformed from the polydomain state to the monodomain one [3]. When the reorientation mechanism is exhausted, the deformation proceeds further owing to a dislocation slip. One may assume that deformation of the crystalline phase in amorphous-crystalline samples follows in the same way. At the same time, the presence of the amorphous phase can activate an additional process of unelastic deformation—a plastic deformation of the amorphous component. Therefore, the amorphous-crystalline alloys can be deformed unelastically by three mechanismas: (1) reorientation of martensite domains, (2) dislocation slip in the crystal phase, and (3) plastic deformation of the amorphous phase. Only the first one is reversible on heating. To study the contribution of reorientation mechanism to the deformation of amorphous-crystalline alloys, the ability of deformed alloys to recover the unelastic deformation on heating was carried out.
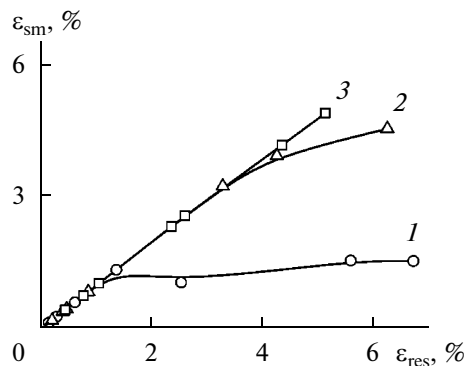
Figure 3 presents the dependences of value of shape memory effect (ε_{sm}) on residual strain (ε_{res}) for the samples with the volume fraction of crystalline phase of 40%, 70%, and 100%. Two stages can be found on these curves. At first stage, ε_{sm} increases linearly with increasing strain untill the residual strain is smaller than ε_{cr}; i.e., all strain accumulated in the alloy during deformation recovers on heating due to the shape memory effect. However, at deformations exceeding ε_{cr}, some part of the residual strain is not recovered on heating up to 373 K. The value ε^{cr} characterizes the ability of the alloy to be deformed reversibly and it depends on the sequence of phase transition. The $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy undergoes $B2 \rightleftharpoons B19'$ transition, and it is known that ε_{cr} may vary from 8 to 10% in a fully crystallized alloy. Obviously, in amorphous-crystalline alloys, the value ε_{cr} have to be determined by the volume fraction of crystalline phase, because as the volume fraction of crystalline phase increases the larger parts of alloys may undergo a reverse martensitic transformation, and as a results, a larger volume of the alloy can be deformed by reversible mechanism of martensite reorientation.

To study the ability of the amorphous − crystalline alloys for strain recovery the recovery coefficient was estimated according to the equation

$$K = \varepsilon_{sm}/\varepsilon_{res},$$

where ε_{sm} is the value of the shape memory effect, and ε_{res} is the value of residual strain. The dependences of recovery coefficient on the residual strain obtained for the samples with different volume fraction of crystalline phase are given in Fig. 4. As one can see, the stage ($\varepsilon_{res} < \varepsilon_{cr}$) where recovery coefficient is equal to 100% is observed on the $K(\varepsilon_{res})$ curves. The length of this stage increases with increasing volume fraction of crystalline phase in the alloy. If the $\varepsilon_{res} > \varepsilon_{cr}$, the recovery coefficient decreases sharply, since at deformations exceeding ε_{cr} the alloy deforms by a dislocation slip in

the crystalline phase and plastic deformation of the amorphous component.

Thus, the results showed that unelastic deformation at the initial stage of deformation in amorphous-crystalline ribbons is realized by the mechanism of reorientation of martensite domains. This process continues until the residual strain becomes larger than the value of ε_{cr}, depending on the fraction of crystalline phase. Hence the value of ε_{cr} is the maximum strain accumulated in the sample by the martensite reorientation. This value riches 6% in the fully crystallized sample ($\Phi_{cr} = 100\%$). If one may suppose that ε_{cr} is proportional to Φ_{cr}, then this value (ε_{cr}) must be about 2.4% in the sample with the volume fraction of crystalline phase being equal to 40%. However, in fig 4 it is seen that the value of ε_{cr} is only 1.23%, which is much smaller than the expected value. So, one may conclude that irreversible deformation in the amorphous-crystalline alloy appears when the accumulation of deformation through the reversible mechanism of martensite reorientation has not been completed. Such behaviour is not typical for fully crystalline TiNi alloys [3] and it takes place only in amorphous-crystalline state. Hence, one may believe that unelastic strain at $\varepsilon_{res} > \varepsilon_{cr}$ can be caused by plastic deformation of the amorphous phase. At this case a sequence of initiation of different mechanisms of unelastic deformation of amorphous-crystalline alloy may be described as following (Fig. 5). At the first stage, when $\varepsilon_{res} < \varepsilon_{cr}$, the unelastic deformation occurs by reorientation of martensite domains. At the second stage, when $\varepsilon_{res} > \varepsilon_{cr}$, along with reorientation mechanism, plastic deformation of amorphous phase takes place. At the third stage, the process of reorientation of martensite domains in crystalline phase is finished and the crystalline phase is deformed by dislocation slip. It is important to note that during the second stage not only a plastic deformation of the amorphous phase takes place, but also a reorientation of martensite domains in the crystalline phase is still continued. This is verified by an increase in the value of ε_{sm} at this stage. So, in a sample with 70% of crystalline phase, a rise in the residual strain from 3.27 to 6.25% during the second stage results in an increase in ε_{sm} from 3.27 to 4.6%, with a decrease in the recovery coefficient from 100 to 73.5%. In a sample with a 40% of crystalline phase, a rise in the residual strain from 1.36 to 6.72% leads to an increase in ε_{sm} from 1.36 to 1.56%, with a decrease in the recovery coefficient from 100 to 38.6%. An increase in the volume fraction of crystalline phase results in the displacement of the boundaries between stages, and in a fully crystallized sample, the second stage disappears because the amorphous phase is absent in the sample.

Besides the shape memory effects and deformation mechanisms, ability of the samples to demonstrate a spontaneous deformation (two-way shape memory effect) during thermal cycling through the temperature interval of martensite transitions was studied in
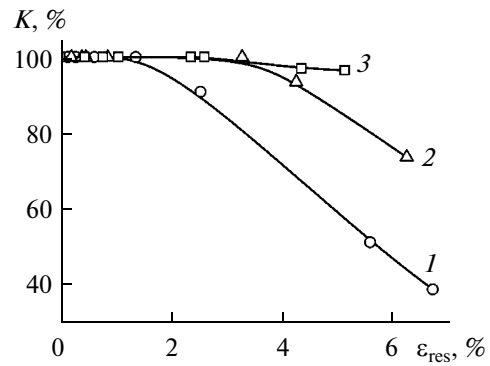

Fig. 4. Dependence of recovery coefficient (K) on residual strain (ε_{res}) in samples with the volume fraction of crystalline phase of (*1*) 40%, (*2*) 70%, and (*3*) 100%.
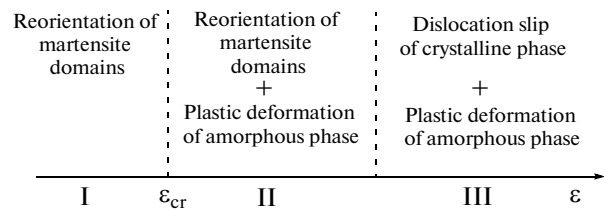

Fig. 5. Scheme of the sequence of deformation processes in amorphous-crystalline Ti$_{40.7}$Hf$_{9.5}$Ni$_{44.8}$Cu$_5$ alloy at an increase in given strain.
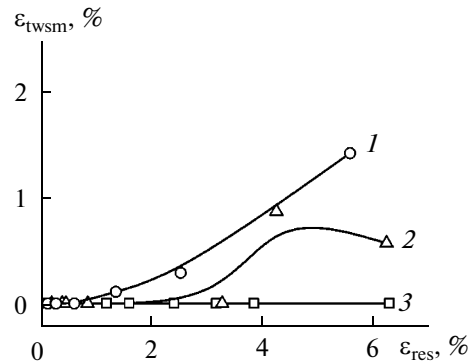

Fig. 6. Dependence of value of two-way shape memory effect (ε_{twsm}) on residual strain (ε_{res}) in samples with the volume fraction of crystalline phase of (*1*) 40%, (*2*) 70%, and (*3*) 100%.

amorphous-crystalline ribbons of Ti$_{40.7}$Hf$_{9.5}$Ni$_{44.8}$Cu$_5$ alloy. Figure 6 shows the dependences of value of two-way shape memory effect (ε_{twsm}) on residual strain ε_{res} obtained in amorphous-crystalline Ti$_{40.7}$Hf$_{9.5}$Ni$_{44.8}$Cu$_5$ alloy with a different volume fraction of crystalline phase. As one can see, in a fully crystallized sample, the two-way shape memory effect is not found, whereas spontaneous deformation is observed in the samples with the volume fraction of amorphous-crys-

talline phase of 40 and 70%; moreover, the larger the residual strain, the larger value of ε_{twsm}. It is necessary to note that, in the samples with the volume fraction of crystalline phase of 40%, the two-way shape memory effect is found at smaller residual strains than in the samples with the $\Phi_{cr} = 70\%$. It is known that, to initiate the two-way shape memory effect the oriented internal stresses should be created in the sample. In a fully crystallized sample, such stresses are created by the dislocation structure after a preliminary deformation [3]. In amorphous-crystalline alloys, oriented internal stresses can be created not only by dislocations in the crystalline state but also on the interfaces between the amorphous and crystalline phases. As the two-way shape memory effect is observed only at co-existence of amorphous and crystalline phases hence one may conclude the in the amorphous-crystalline alloys the oriented internal stresses are preferably form at interfaces between the amorphous and crystalline phases. However, it is important to note that, two-way shape memory effect will be small in the samples with the large volume fraction of amorphous phase in spite of the existence of a lot of interfaces. It is due to the two-way shape memory effect takes place only in crystalline phase. Obviously there exists some optimal relation between the volume fractions of amorphous and crystalline phases when the maximum value of the reversible shape memory effect is observed.

CONCLUSIONS

The results obtained may be summarized as following:

The mechanical properties and ability of amorphous-crystalline alloys to recover unelastic deformation on heating are determined by the ratio of volume fractions of the crystalline and amorphous phases.

Deformation of amorphous-crystalline alloys is realized by three mechanisms: reorientation of martensite domains; dislocation slip and deformation of the amorphous phase. One mechanism changes to another or to other combination of deformation mechanisms at different strains depending on the volume fraction of crystalline phase.

The two-way shape memory effect is observed in $Ti_{40.7}Hf_{9.5}Ni_{44.8}Cu_5$ alloy in the case of co-existence of amorphous and crystalline phases.

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