

Functional properties of high-entropy $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ shape memory alloy

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Functional properties (superelasticity, recoverable strain variation on cooling and heating under stress) were studied in new high-entropy $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ shape memory alloy. It was shown that this alloy demonstrated a superelastic response in a temperature range of -125 to 100°C , which is the maximum range for such materials. Maximum value of the superelastic strain was 4.5%. This alloy revealed a high value of the recoverable strain which value was 6% on cooling and heating under 300 MPa.

Keywords: high-entropy shape memory alloys, superelasticity, shape memory effect, Ti–Hf–Zr–Ni–Cu–Co.

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Last ten years, scientists have been developing high-entropy shape memory alloys which combine the properties of high-entropy alloys such as a high yield limit for dislocation slip and sluggish diffusion and the properties of the shape memory alloys as shape memory effect and superelasticity [1]. To obtain such materials, a low-entropy NiTi-based alloys are taken as the basis in which the main atoms are substituted by doping atoms. So, a lot of Ti–Hf–Zr–Ni–Cu–Co alloys were designed, where Ti atoms were substituted by Hf and Zr atoms, while Ni atoms were replaced by Cu and Co atoms. It was shown that depending on the concentration of one or other atoms or atom groups, it was possible to change in a targeted manner the temperatures of the martensitic transformation from extremely high to extremely low values which did not exceed the temperature of liquid nitrogen [2]. It was shown that such alloys revealed a very wide temperature range of the superelasticity and high recovery strain ratio [3,4]. Both these phenomena are due to the hindering of the dislocation movement due to a high yield limit for dislocation slip [5,6].

Nowadays, the efforts of scientists are aimed at a search of the optimal composition of Ti–Hf–Zr–Ni–Cu–Co alloys demonstrating the best functional behaviour. The studies which were carried out by authors for the medium-entropy $\text{Ti}_{40}\text{Hf}_{2.5}\text{Zr}_{7.5}\text{Ni}_{40}\text{Cu}_5\text{Co}_5$, $\text{Ti}_{40}\text{Hf}_5\text{Zr}_5\text{Ni}_{40}\text{Cu}_5\text{Co}_5$ and $\text{Ti}_{40}\text{Hf}_{7.5}\text{Zr}_{2.5}\text{Ni}_{40}\text{Cu}_5\text{Co}_5$ shape memory alloys (mixing entropy was $1.3R$, where R — universe gas constant) showed that an increase in the Zr concentration compared to the Hf concentration improved the functional properties. So, one may expect that Zr-rich high-entropy shape memory alloys would reveal better functional properties than Hf-rich alloys. Thus, this paper aimed to study the functional properties of the $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ high-entropy shape memory alloy and to compare the results to the properties of the $\text{Ti}_{16}\text{Hf}_{17}\text{Zr}_{17}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy (mixing

entropy is $1.79R$) which were published previously in [7]. In these alloys, the sum of the Zr + Hf concentration was the same and equal to 34 at.%, whereas in the alloy studied in the present paper, the ratio of the Hf concentration to Zr concentration was equal to 1/3.

Mixture of pure elements (99.99%) was prepared to correspond to the alloy composition in atomic %. Ingot with a mass of 20 g was obtained by manufactured in a vacuum arc furnace under an argon atmosphere (described in details in [2]). Mixing entropy was calculated using known expression [2] and it was equal to $1.73R$.

To study the structure, ingots with a diameter of 20 mm and a height of 8 mm were sliced by electro-discharge machine to plates with a thickness of 2 mm, which were devoted to grinding (abrasive paper with a number from 120 to 400) and electro-polishing (using 10% HClO_4 + 90% $\text{C}_2\text{H}_5\text{OH}$ electrolyte at a temperature of -20°C). Alloy structure was studied using plate polished samples by X-ray analysis (2θ range from 20 to 110° , scanning step of 0.02° , $\text{CuK}\alpha$ radiation) and scanning electron microscopy. Chemical composition was detected by energy-dispersive X-ray. Martensitic transformation was studied by resistivity measurements using 4-probes technique on cooling and heating in a temperature range from 100 to -170°C with a rate of $10^\circ\text{C}/\text{min}$. To study the functional properties, the dog-bone samples were cut from the plates with a thickness of 0.8 mm (working width and length of 1 and 7 mm). To study the superelasticity, the samples were subjected to tension with intermediate unloading at a temperature from a range of -125 to 100°C . Using the stress vs strain curves, the critical stress for the martensite nucleation σ_{SIM} was measured as $\sigma_{0.2}$ value and the superelastic strain ϵ^{SE} was determined as the maximum strain nonlinear recovered on unloading. To study the recoverable strain, the samples were subjected to cooling and heating under constant stress in a

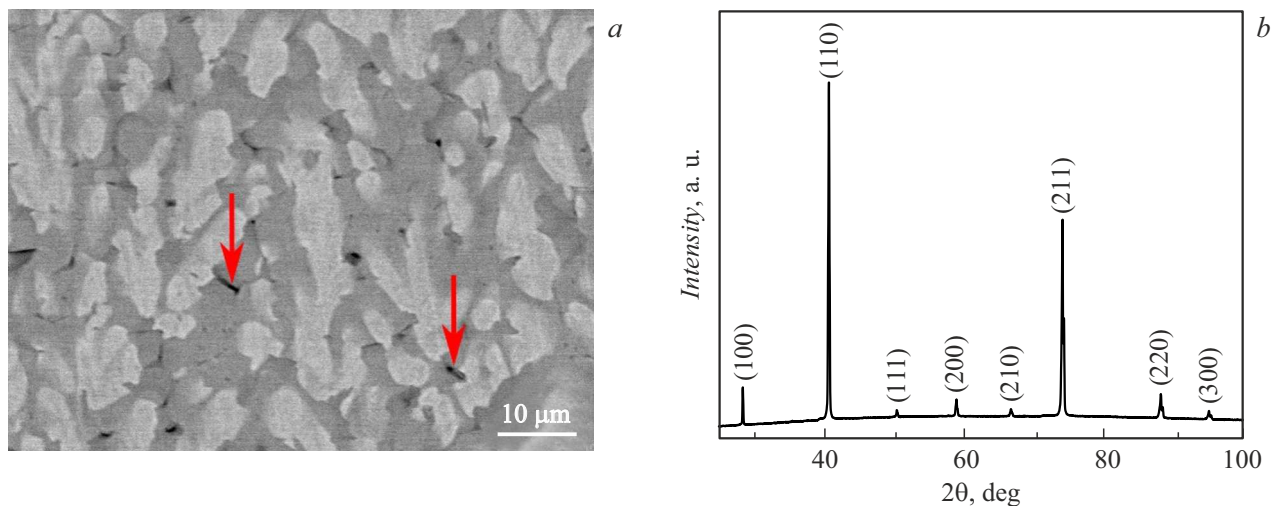


Figure 1. *a* — image of structure of $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy obtained by SEM. Arrows show the precipitates. *b* — X-ray pattern obtained at room temperature, indexes show the *B2* phase planes.

temperature range of 100 to -150°C (minimal value which may be attained in thermal chamber). Using $\varepsilon(T)$ curve, the recoverable strain ε^{SM} was measured as strain recovered on heating, the irrecoverable strain ε_{ir} was determined as the difference between the strain accumulated on cooling and recovered on heating. The M_s and A_f temperatures (start of the forward and the finish of the reverse transformations) were also measured. All experiments were carried out in Shimadzu AG-50kN testing machine equipped with thermal chamber and video-extensometer for non-contact strain measurement.

A study of the structure showed that the alloy had a typical cast structure. Matrix contained the dendritic cells and the secondary precipitates located in inter-dendritic space (Fig. 1, *a*), that is typical for multi-component shape memory alloys [1,2,8]. Dendritic cell core was depleted

by Cu and Zr atoms ($\text{Ti}_{15}\text{Hf}_{11}\text{Zr}_{23}\text{Ni}_{17}\text{Cu}_{14}\text{Co}_{20}$), the dendritic cell boundary was enriched by these elements ($\text{Ti}_{17}\text{Hf}_7\text{Zr}_{26}\text{Ni}_{16}\text{Cu}_{20}\text{Co}_{14}$). The secondary phase precipitates found in inter-dendritic space were also enriched by Cu and Zr atoms ($\text{Ti}_{24}\text{Hf}_5\text{Zr}_{28}\text{Ni}_{13}\text{Cu}_{22}\text{Co}_8$) compared to the nominal composition of batch. The total concentration of Ti + Hf + Zr atoms in precipitates was equal to 57 at.% in precipitates. This value was less than real due to a small precipitates size which made possible to obtain the signal from matrix with less Ti + Hf + Zr concentration besides the signal from precipitates. Thus, one may conclude that these precipitates were the intermetallic $(\text{Ti,Hf,Zr})_2(\text{Ni,Cu,Co})$ phase, as it was found previously in [2,8].

According to X-ray analysis, the matrix was in the austenite *B2* structure (Fig. 1, *b*). Besides lattice reflexes where the sum of indexes was even number, the super lattice reflexes were observed with odd value of sum of indexes. This pointed out that the alloy was ordered, i.e., Hf and Zr atoms were in the Ti sublattice, while Cu and Co atoms were in Ni sublattice that was typical for such alloys [2].

Figure 2 shows that dependences of the resistivity on temperature measured in the studied alloy. It is seen that in a range of -110 to -170°C , anomalous resistivity behaviour was observed with hysteresis (it increased on cooling and decreased on heating). This may be due to the phase transformation took place in the temperature range, however on cooling to -170°C it was at the beginning stage and a small fraction of the alloys transformed to martensite.

The superelasticity behaviour — non-linear strain recovery on unloading was observed on deformation of the samples (Fig. 3, *a*). On loading, unelastic strain was caused by the stress induced martensite formation, whereas a non-linear strain variation on unloading was due to the reverse transformation from the martensite to austenite. When the

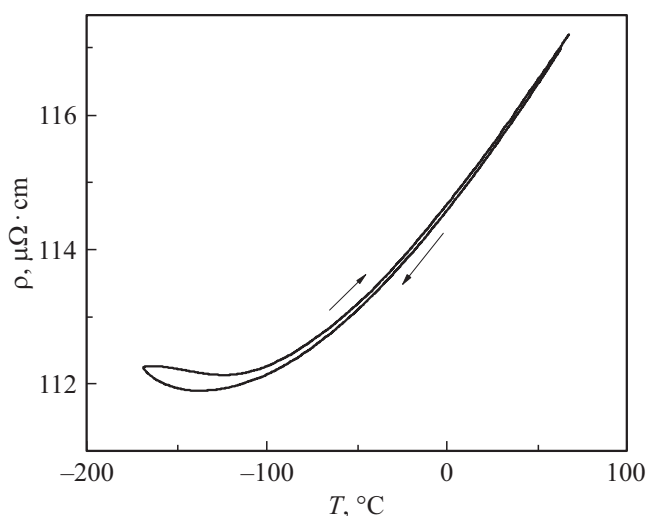


Figure 2. Resistivity variation on cooling and heating of $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy.

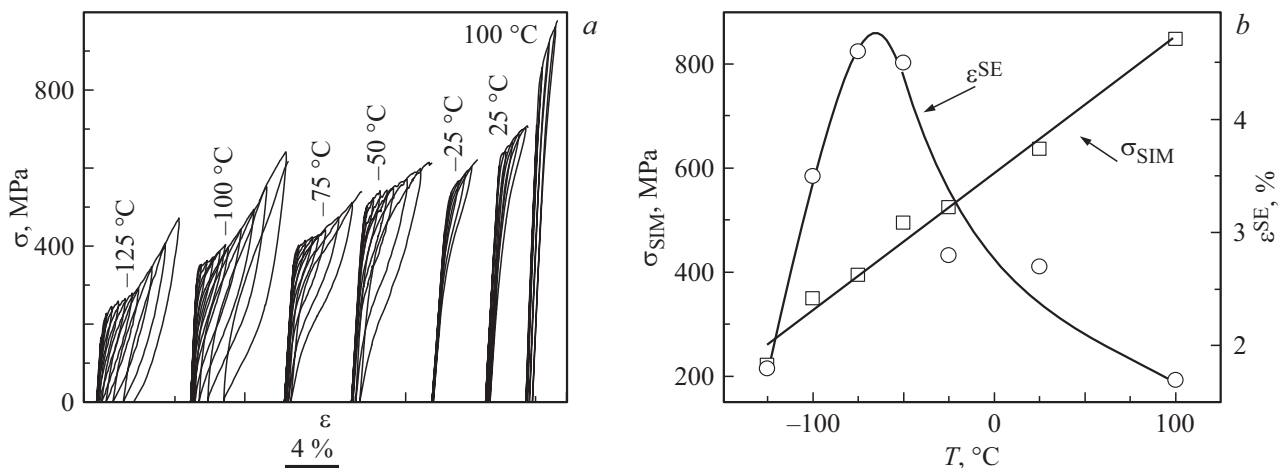


Figure 3. *a* — stress vs strain curves obtained at various temperatures. *b* — the dependences of the critical stress for martensite nucleation and superelastic strain on the deformation temperature.

deformation temperature was less than -75°C , martensite did not completely disappear because this temperature was less or close to the A_f temperature (finish temperature of the reverse transformation). As some martensite did not undergo the reverse transformation, then the residual strain accumulated in the sample. At temperatures which were higher than A_f temperature ($> -100^{\circ}\text{C}$), the martensite completely transformed to the austenite on unloading and the strain fully recovered (Fig. 3, *a*). It is important to note, that non-linear strain recovery was observed on unloading even at a temperature of 100°C . This allows one to conclude that the temperature range at which the martensite may be induced by stress during deformation was at least 225°C in the studied alloy.

The $\sigma_{SIM}(T)$ dependence was linear with angular coefficient of $d\sigma/dT = 2.6 \text{ MPa}/^{\circ}\text{C}$ (Fig. 3, *b*). Analysis of known data [3,4,7] showed that the value of $d\sigma/dT$ was the smallest for the high-entropy Ti–Hf–Zr–Ni–Cu–Co shape memory alloys. So, this coefficient was $2.9 \text{ MPa}/^{\circ}\text{C}$ in $\text{Ti}_{16}\text{Hf}_{17}\text{Zr}_{17}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy [7]. Figure 3, *b* presents that the dependence of the superelastic strain on the deformation temperature was non-monotonic and the maximum of 4.5% was observed in a temperature range from -75 to -50°C . The value of the superelastic strain was close to the same which was measured on compression of the $(\text{Ti,Hf,Zr})_{50}\text{Ni}_{25}\text{Co}_{10}\text{Cu}_{15}$ single crystal [3,9] or on tension of thin ribbons or fiber with the same chemical composition [4,10].

To study the recoverable strain, the samples were cooled and heated under constant stress. On cooling, strain accumulated due to the forward martensitic transformation, while on heating, it recovers due to the reverse transformation (Fig. 4, *a*). The data obtained showed that an increase in stress led to a rise in the recoverable strain to 6% (Fig. 4, *b*), that was the maximum value measured in this alloy system [4,9,11]. Moreover, such a recoverable strain was observed at a relatively low stress (300 MPa). The

irrecoverable strain was found only on cooling under stress of 300 MPa and it was equal to 0.4 %. Thus, regardless of the existence of irrecoverable strain, the recovery coefficient which was equal to the ratio of the strain recovered on heating to strain accumulated on cooling, was a little bit less than 94 %.

The temperatures of the martensitic transformation increased linear on stress (Fig. 4, *c*), however they did not exceed room temperature even at the maximum stress. This allows one to use this alloy for low-temperature applications. Using the $M_s(\sigma)$ dependence, the slope angle was determined which was equal to $0.313^{\circ}\text{C}/\text{MPa}$. The reverse value was equal to $3.2 \text{ MPa}/^{\circ}\text{C}$, which was close to the coefficient of $2.6 \text{ MPa}/^{\circ}\text{C}$, measured using the $\sigma_{SIM}(T)$ dependence given in Fig. 3, *b*.

The comparison of the functional properties of the $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy (labeled as S-1/3), which was studied in the present paper, to the same properties of $\text{Ti}_{16}\text{Hf}_{17}\text{Zr}_{17}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy (labeled as S-1/1), given in [7], showed that the Zr-rich alloy had the advantages. First of all, the temperature window for the superelasticity in S-1/3 alloy was 100°C higher than in S-1/1 alloy. Maximum superelastic strain was 4% in S-1/1 alloy, however, it was attained at -150°C . This strain decreased on an increase in deformation temperature. So, it decreased by 2.5% at temperatures of -75 and -50°C , whereas, the superelastic strain was 4.5 % at these temperatures in S-1/3 alloy. This was due to martensitic transformation temperatures in S-1/3 alloy were higher than in S-1/1 alloy, so the optimal conditions for the superelasticity observation were fulfilled at higher temperatures that is important for application.

The value of the recoverable strain in S-1/1 alloy did not exceed 1% even on cooling under a stress of 400 MPa, whereas this value was 6 times larger in S-1/3 alloy at a stress of 300 MPa. This was caused by the temperatures of the martensitic transformation in Zr-rich alloy were higher than in equiatomic alloy, so on

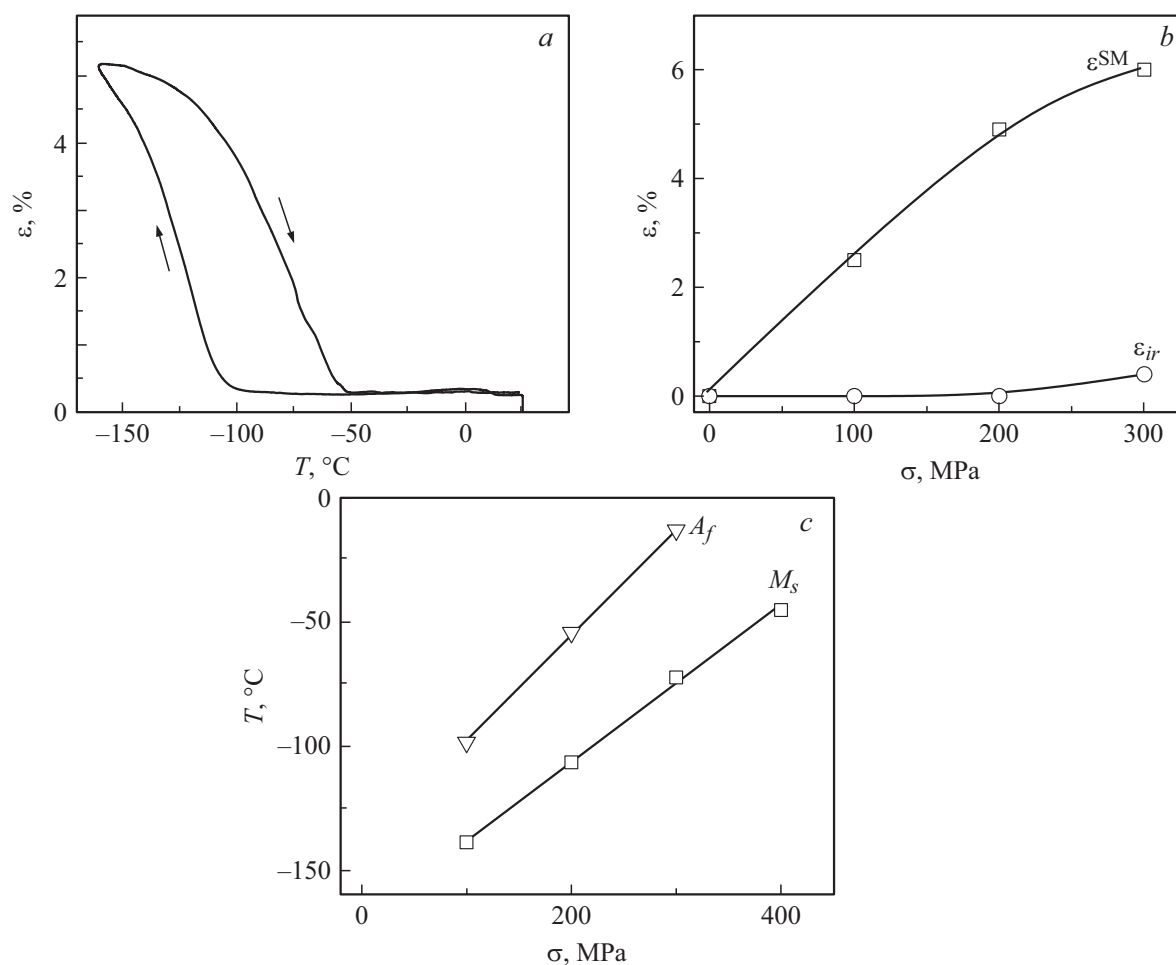


Figure 4. Strain variation on cooling and heating under 200 MPa (a) and the dependences of recoverable and irrecoverable strain (b) and M_s and A_f temperatures (c) on stress.

cooling to the minimum temperature the completeness of the martensitic transformation in S-1/3 alloy was larger compared to S-1/1 alloy. This led to a higher recoverable strain. Thus, the results of the paper showed that new $\text{Ti}_{16}\text{Hf}_{8.5}\text{Zr}_{25.5}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy developed in this study demonstrated the better functional properties compared to the equiatomic $\text{Ti}_{16}\text{Hf}_{17}\text{Zr}_{17}\text{Ni}_{16}\text{Cu}_{17}\text{Co}_{17}$ alloy and other high-entropy shape memory alloys. This alloy may be applied for the cryogenic technologies.

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Conflict of interest

The authors declare that they have no conflict of interest.

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