Structure and Phase Transformations in Copper-Alloyed Rapidly Melt-Quenched Ni$_{50}$Ti$_{32}$Hf$_{18}$-Based Alloys with High-Temperature Shape Memory Effect

A. V. Pushin$^a$, V. G. Pushin$^{a,b,*}$, N. N. Kuranova$^a$, N. I. Kourov$^*$, T. E. Kuntsevich$^a$, V. V. Makarov$^a$, and A. N. Uksusnikov$^a$

$^a$Mikheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, ul. S. Kovalevskoi 18, Ekaterinburg, 620990 Russia
$^b$Ural Federal University, ul. Mira 19, Ekaterinburg, 620002 Russia
$^*$e-mail: pushin@imp.uran.ru

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Abstract—Methods of transmission and scanning electron microscopy, chemical microanalysis, electron diffraction, and X-ray diffraction have been used to carry out the comparative study of the structure and chemical and phase composition of thin ribbons of four quasi-binary alloys (Ni$_{50}$Ti$_{32}$Hf$_{18}$, Ni$_{45}$Ti$_{32}$Hf$_{18}$Cu$_{5}$, Ni$_{35}$Ti$_{32}$Hf$_{18}$Cu$_{15}$, and Ni$_{25}$Ti$_{32}$Hf$_{18}$Cu$_{25}$) obtained in the amorphous state by rapid quenching from the melt by jet spinning. The critical temperatures of the devitrification and $B_2 \leftrightarrow B_{19'}$ martensitic transformation of the alloys have been determined based on the data of temperature dependences of the electrical resistivity. The specific features of the formation of the ultrafine-grained structure upon the devitrification and of the phase transformations have been studied depending on the heat-treatment regimes and chemical composition of the alloys (concentration of copper atoms).

Keywords: rapid quenching from the melt, microstructure, amorphous state, thermoelastic martensitic transformation, alloying with copper and hafnium

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INTRODUCTION

Since the end of the last century, a great deal of attention has been paid to developing new technologies of the synthesis of materials based on titanium nickelide which experience thermoelastic martensitic transformations (TEMT) and exhibit the related shape-memory effects (SME) [1–22]. These technologies include, e.g., precision multicomponent alloying, megaplastic deformation, and rapid quenching from the melt (RQM). The spinning of a melt jet with high rates of cooling ($10^5$–$10^7$ K/s) makes it possible to produce homogeneous alloys of titanium nickelide with enhanced copper contents (up to 25 at %) in the form of long thin ribbons or bands with uncommon properties and structure [8–20]. They are widely used in the development of original microelectromechanical systems, such as thermoactuators, thermosensors, and a number of other devices with SME. At the same time, these materials by no means always ensure the required physicomechanical parameters because of the small level of stresses of the martensitic shear $\sigma_M$ (less than 100 MPa) and low critical temperatures at which the SME is achieved (330–370 K) [8, 13, 16–18]. Elements such as Pd, Au, or Pt introduced in large quantities into titanium–nickelide alloys upon substitution for nickel substantially increase the critical temperatures of the $B_2 \leftrightarrow B_{19'}$ TEMT and, consequently, the temperature parameters of the realization of the SME [3, 4]. However, this leads to a drastic rise in price of these materials and does not ensure an increase of $\sigma_M$.

Alloying with 10–30 at % hafnium substituted for titanium in Ti$_{50}$Ni$_{50}$ alloys makes it possible to increase the temperatures of the $B_2 \leftrightarrow B_{19'}$ TEMT to 870 K and the critical stresses $\sigma_M$ up to 400–500 MPa [23–27]. An important feature of alloying with hafnium with concentrations that exceed 10–12 at %, as in the case of alloying with copper up to 25 at %, is the possibility of synthesizing these alloys in the amorphous state by spinning. As a result of subsequent optimum heat treatment, a high-strength and plastic ultrafine-grained (UFG) structure with a high-temperature SME can be obtained in these alloys [28–34]. However, the regularities of the formation of the amorphous state and subsequent devitrification upon heating, and the effect of the alloying with hafnium only and of the joint alloying with hafnium and copper on the structure and phase trans-
formations in these alloys have not been sufficiently studied.

This paper is aimed at conducting a complex study of the ternary alloy Ni\textsubscript{50}Ti\textsubscript{32}Hf\textsubscript{18} and three quaternary alloys Ni\textsubscript{45}Ti\textsubscript{32}Hf\textsubscript{18}Cu\textsubscript{5}, Ni\textsubscript{35}Ti\textsubscript{32}Hf\textsubscript{18}Cu\textsubscript{15}, and Ni\textsubscript{25}Ti\textsubscript{32}Hf\textsubscript{18}Cu\textsubscript{25} obtained in the amorphous state by quenching from the melt and in the UFG state after heat treatments.

**EXPERIMENTAL**

The alloys were melted by the electric-arc method from high-purity Ni, Cu (99.99 wt %), Ti (99.8 wt %), and Hf (99.9 wt %) in an inert atmosphere of purified helium. The ingots (certified by the chemical composition) for homogenization were subjected to remelting no less than three times, hot upsetting by pressing to 5–10%, prolonged annealings in argon at 1073 K, and quenching. Compared to the initial ingots, this treatment led to the formation of a substantially more uniform fine-grained structure (with a maximum grain size of up to 50–70 μm) in alloys and nearly prevented the segregation of all chemical elements. RQM spinning was performed on a copper rapidly rotating drum at rates of close to 10\textsuperscript{5} or 10\textsuperscript{6} K/s, which ensured the obtaining of the amorphized alloys in the form of ribbons with a thickness of 40 or 30 μm and a width of 1.8 or 1.5 mm, respectively. Let us emphasize that the alloys with a chemical composition equivalent to the quasi-binary (Ni, Cu)\textsubscript{50}(Ti, Hf)\textsubscript{50} alloy were selected for study.

The structure and phase transformations in the initial amorphous ribbons and in the ribbons subjected to crystallization by heat treatment according to different regimes (annealing in a temperature range of 573–873 K for 10 min) were studied using X-ray diffraction phase and structural analysis (XRD), transmission (TEM) and scanning (SEM) electron microscopy, and in situ experiments upon heating or cooling of samples. The X-ray diffraction analysis by the θ/2θ method was carried out using a DRON-3M diffractometer in the Cu Kα radiation monochromatized by a graphite single crystal. The electrical resistivity of the alloy samples in the form of ribbons was measured in a wide temperature range. The electron-microscopic studies were performed at the Center of Collaborative Access, Institute of Metal Physics, Ural Branch, Russian Academy of Sciences using JEM-200 CX (maximum accelerating voltage of 200 kV) and Tecnai G2 30 (maximum accelerating voltage of 300 kV) transmission electron microscopes and Quanta 200 scanning electron microscope (maximum accelerating voltage of up to 30 kV), which was equipped with a Pegasus system including the fractography of fractures and energy-dispersive spectrometry.

**RESULTS AND DISCUSSION**

As has already been noted, an analysis of the chemical composition of the melted ingots and RQM ribbons was initially carried out using an EDAX X-ray energy-dispersive spectrometer entering into the Quanta Pegasus SEM setup. According to the data of the EDS analysis, the samples of nominal quasi-binary compositions Ni\textsubscript{50}Ti\textsubscript{32}Hf\textsubscript{18}, Ni\textsubscript{45}Ti\textsubscript{32}Hf\textsubscript{18}Cu\textsubscript{5}, Ni\textsubscript{35}Ti\textsubscript{32}Hf\textsubscript{18}Cu\textsubscript{15}, and Ni\textsubscript{25}Ti\textsubscript{32}Hf\textsubscript{18}Cu\textsubscript{25}, which contain 49.8 at % Ni, 31.5 at % Ti, 18.7 at % Hf; 44.5 at % Ni, 32.2 at % Ti, 17.8 at % Hf, 5.0 at % Cu; 34.7 at % Ni, 31.6 at % Ti, 18.5 at % Hf, and 15.2 at % Cu, respectively, were selected for study. This made it possible to avoid the embrittling effect of inclusions of the excess phases, which may form during the melting and heat treatment of a nonstoichiometric composition in these ternary and quaternary alloys.

The XRD analysis showed that, at room temperature, after cooling at a rate of 10\textsuperscript{6} K/s, all samples of the alloys in the initial RQM state were amorphous (Figs. 1, 2) and, after cooling at a rate of 10\textsuperscript{5} K/s, they were in an amorphous crystalline state [32]. The isochronous isothermal treatments (for 10 min) at temperatures in the range of 573–673 K hardly changed the structural state of the alloys. Annealing at 773 K enabled devitrification with the formation of a polycrystalline UFG state in all the alloys. The lattice parameter of the B2 phase of the alloys at room tem-