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The Effect of Copper Doping on Martensite Shear Stress in Porous TiNi(Mo,Fe,Cu) Alloys

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Abstract—The properties of alloys based on porous nickel-titanium (TiNi) with copper additives have been studied. It is established that the copper doping of porous TiNi(Mo,Fe,Cu) alloys fabricated by the method of self-propagating high-temperature synthesis leads to a significant decrease in the martensite shear stress (below 30 MPa). Low values of the martensite shear stress (σ_{min}) in copper-doped TiNi-based alloys allows medical implants of complex shapes to be manufactured for various purposes, including oral surgery. The optimum concentration of copper additives (within 3–6 at %) has been determined that ensures high performance characteristics of TiNi-based porous alloys for medical implants.

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The development of implantology based on the use of metal-based materials and alloys makes it necessary to create biocompatible materials with properties similar to those of living tissues of the organism [1]. Porous alloys based on nickel titanium (TiNi) are characterized by high biocompatibility that ensures long-term functioning in the organism without being rejected, stable cell regeneration, and reliable adhesion due to the fusion and growth of tissues in pores of implants [1]. The main characteristics of these alloys for medical applications include the temperature interval of shape memory effect manifestation and critical boundary values of martensite shear stress (σ_{min}, σ_{max}), which depend on variations of the internal structure caused by deviations of the alloy composition from a homogeneity region, thermomechanical treatments, and doping [1, 2].

Doping with elements such as Mo, Fe, and Al provides effective purposeful control of the accumulated strain, interval of martensitic transformations, and strength and plasticity of shape memory alloys [3]. However, in some TiNi-based porous alloys, the minimum martensite shear stress σ_{min} (responsible for the material rigidity) does not correspond to the desired level. This circumstance limits the flexibility of implants and restricts the possibilities of modeling with respect to configurations of replaced tissue defects. In monolithic TiNi alloys, these problems can be solved by doping with copper. A porous material possessing chemical-phase inhomogeneity represents a conglomerate of regions with different compositions and structures close to that of cast alloys. By analogy with monolithic TiNi alloys, it is possible to use copper doping to solve problems encountered in modeling with porous alloys. The present study was aimed at studying the effect of copper additives on the main characteristics of porous TiNi-based alloys in order to create a porous material with an optimum combination of mechanical properties.

Porous alloys of the $TiNio_{49.9-x}Mo_{0.1}Fe_{0.1}Cu_x$ system (x = 0, 1, 3, and 6 at %) were obtained by the method of self-propagating high-temperature synthesis (SHS) from powdered titanium (PTM and PTOM grades), powdered nickel (PNK-10T2 and PNK-1L5 grades), and powdered copper (Table 1). The porous alloys were doped through partial replacing of nickel

Table 1. Compositions of TiNi-based porous alloys studied

Alloy	Doping element, at %				
	Ni	Mo	Fe	Cu	Ti
No. 1	49.9	0.1	0.1	–	Balance
No. 2	48.9	0.1	0.1	1	Balance
No. 3	46.9	0.1	0.1	3	Balance
No. 4	43.9	0.1	0.1	6	Balance

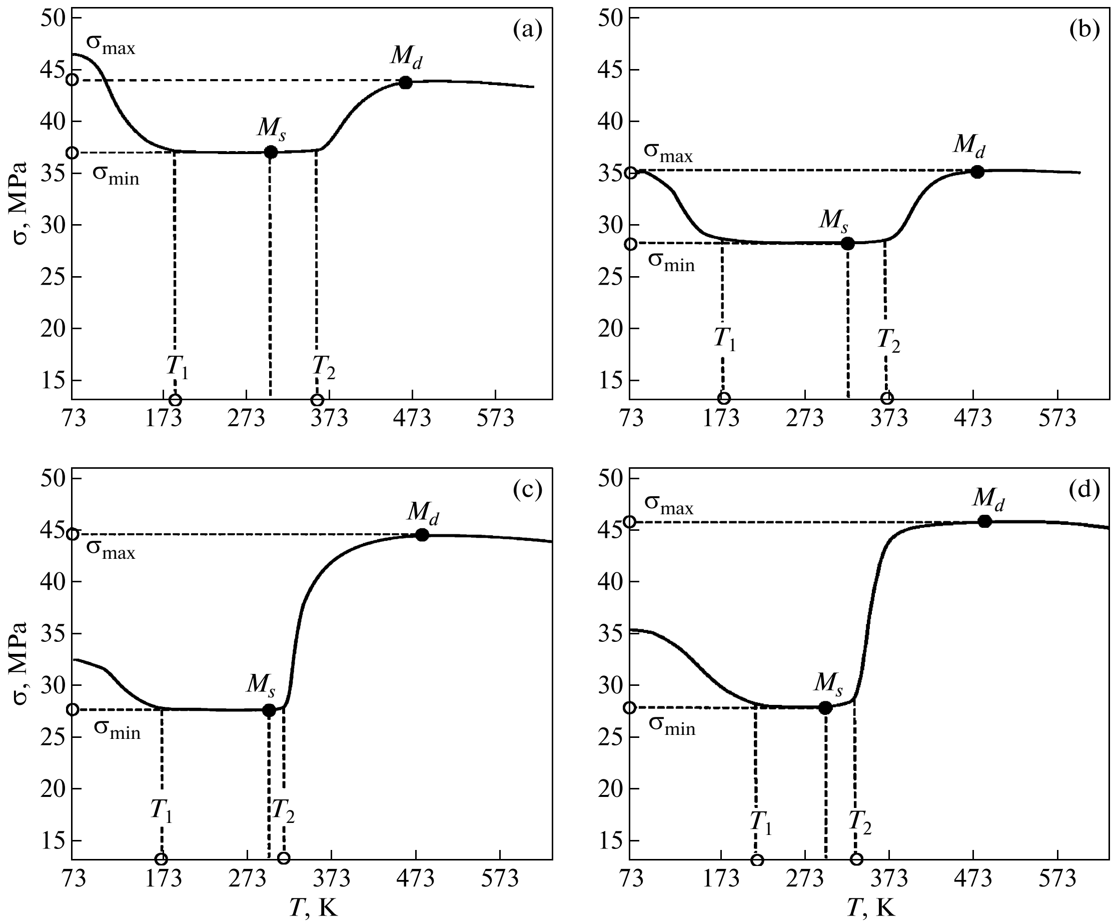

Fig. 1. Temperature dependences of the martensite shear stress σ in porous TiNi alloys (a) No. 1, (b) No. 2, (c) No. 3, and (d) No. 4.

by copper at an amount of 1–6 at %. Initially, the Ti, Ni, and copper powders were dried in a thermal box at 350–360 K and then mixed in a blender. The obtained mixture was charged into a silica flask (reactor), densified on a shaker, and placed into an electric furnace. The SHS process was initiated on attaining the reaction onset temperature $T = 747$ K, which was experimentally selected depending on the charge volume, homogeneity of the mixture, size of powder particles, reactor wall thickness, and desired porosity of the final material [1, 4].

The properties of synthesized alloys were studied on samples with dimensions of 2.5 × 2.5 × 35 mm, which were cut by electric spark erosion from SHS semiproducts. The minimum and maximum martensite shear stresses (σ_{min}, σ_{max}) were determined from temperature dependence of martensite shear stress $\sigma(T)$ [5, 6]. For this purpose, the porous alloy samples were tensile strained in a broad temperature range (73–600 K) below the temperature interval of martensite transformations. The heating was then (without unloading) continued, and the level of stresses that had developed in a sample due to its shape memory and the tendency to restore the initial shape was measured.

Analysis of the obtained $\sigma(T)$ curves showed that alloy No. 1 is characterized by a broad temperature

Table 2. Elemental compositions of copper-doped TiNi-based porous alloys

Element		Composition, at %	
		Matrix	Dendrite body
Ti	Alloy No. 2	49.7	49.9
Ni		48.4	48.7
Cu		1.9	1.4
Ti	Alloy No. 3	48.7	49.1
Ni		49.4	47.6
Cu		1.9	3.3
Ti	Alloy No. 4	48.5	49.6
Ni		49.0	45.4
Cu		2.5	5.0

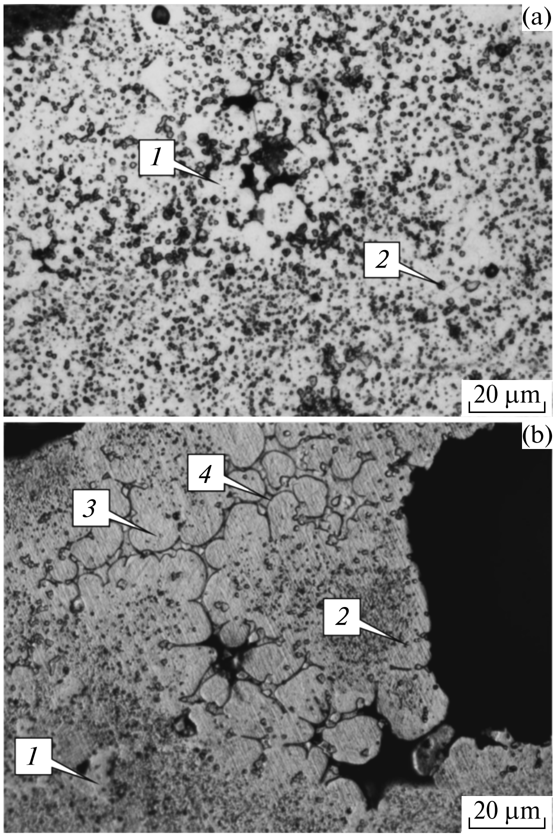

Fig. 2. Structure of porous TiNi alloys (a) 1 and (b) 4: (*1*) matrix, (*2*) Ti_2Ni particles, (*3*) dendrite body, and (*4*) dendrite interlayer.

interval of manifestation of the shape memory effect (T_1–T_2) ~ 170 K (Fig. 1a). This is related to inhomogeneity of the structure of this porous alloy obtained by SHS. This material consists of a large number of Ti_2Ni and $TiNi_3$ particles with dimensions of from 1 to 4.3 μm, which are not involved in the martensite transformation (Fig. 2a). Because of this phase inhomogeneity, the martensite transformation is extended over some temperature interval, since phase transformations begin at different temperatures in various regions [7, 8].

The large minimum martensite shear stress (σ_{min} ~ 40 MPa) in alloy No. 1 restricts the flexibility of implants and limits their modeling possibilities with respect to configurations of replaced tissue defects (Fig. 1a). The synthesis of porous alloys with a lower level of critical martensite shear stress in the temperature interval from 283 to 313 K opens wide possibilities of using these materials for the replacement of tissue defects [9].

Table 3. Characteristics of porous TiNi-based alloys

Alloy	No. 1	No. 2	No. 3	No. 4
σ_{min}, MPa	37	28	27	27
σ_{max}, MPa	44	35	45	47

Modification of the structure of TiNi-based porous alloys by doping with copper leads to narrowing of the temperature interval of shape memory effect manifestation to (T_1–T_2) ~ 120 K. As the content of Cu additives in TiNi allows increases, the formation of rarely encountered coarse liquation formations (dendrites) and lower amount of Ti_2Ni and $TiNi_3$ precipitates lead to significant purification of the matrix phase that is responsible for the development of martensitic transformation (Fig. 2b). The involvement of dendrites (with a composition close to that of the matrix phase) in the transformation increases the volume of material participating in this process (Fig. 2b, Table 2). The start and finish of martensitic transformation is observed almost simultaneously over the entire volume of the alloy.

The introduction of copper at an amount of 1 to 6 at % into alloy No. 1 leads to a decrease in the minimum martensite shear stress below σ_{min} ~ 30 MPa in the interval of working temperatures from 283 to 313 K (Figs. 1b–1d, Table 3). For practical applications in medicine, the most acceptable porous TiNi alloys are those doped with Cu to 3–6 at %, for which the minimum martensite shear stress σ_{min} is below 30 MPa and the difference σ_{max}–σ_{min} characterizing the degree of shape recovery is at maximum. As is known from the available literature, an increase in the difference σ_{max}–σ_{min} leads to growth in the contribution of martensitic transformation-related strain and, hence, in total deformation of the material [1].

The obtained results are of considerable practical value, since a decrease in the minimum martensite shear stress below 30 MPa will allow the reconstructive surgery implants to more precisely model living tissue defects of large volumes and complicated configurations. It should be emphasized that a further increase in the copper content in TiNi alloys leads to sharp narrowing of the temperature interval of shape memory effect manifestations (T_1–T_2).

Thus, the results of our investigation lead to the following conclusion. The doping of porous TiNi-based alloys with copper leads to substantial optimization of the properties of these materials and ensures the obtaining of porous materials with characteristics acceptable in the oral surgery. The most acceptable porous TiNi alloys for practical applications in medicine are those doped with Cu to 3–6 at %, for which minimum martensite shear stress σ_{min} is below 30 MPa in a temperature interval of 283–313 K. This result is new and undoubtedly of interest for both basic science and practical applications.

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