Conference paper

Structure and Properties of Porous Alloys Based on NiTi Doped by Al, Fabricated by SHS-method

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Abstract

The effect of aluminum doping of porous TiNi-based alloy on structure, penetrability, strength properties and characteristic temperature intervals of martensitic transformations, multiple shape memory effect (MSME) parameters were studied. In this paper porous alloys from mixture of titanium, nickel and aluminum (C_{Al}=0-2.0 at. %) powders were obtained by self propagation high temperature synthesis (SHS-method). Aluminum additives allow to obtain a material which is characterized by an increased content of fine pores 10-20 μm, uniform pore size distribution, an increased level of strength. The optimum concentration of Al to obtain high properties of material was defined. The porous TiNi-based alloys doped with aluminum are promising to solve a number of complex medical problems, such as in vascular surgery and cellular technologies.

1 Introduction

Porous TiNi-based alloys manufactured by SHS-method are used in medicine as implants. Implant materials must be biochemical compatibility as well show hysteresis deformation behavior. Thereby part of main phase as TiNi must be high in porous material, material must be permeable and have specified structure

characteristics to germination bone structures and fixing of implant [1].

This work deals with researching of martensitic transformation intervals, parameters of MSME, interrelationship of macrostructure, permeability and strength properties of porous TiNi-based alloys doped by Al.

2 Experimental

Porous TiNi-based alloys with various concentration of Al were obtained by SHS-method in max equal thermodynamic conditions. For manufacture of samples Ni powder type of PNK-OT4, Ti powder type of PTOM-2, Al powder type of ASD-1 were used. Powders of Ti, Ni, Al were intermix in blending machine during 7-8 h. Working mass was put into quartz tube and was consolidated by shaking machine method during 30 min. Then working mass was heated up to beginning temperature of synthesis - 750-755 K, which was depended on volume of working mass, particles size of powders, their oxidation level etc [1]. Then synthesis was initiated. Doping of Al was carried out from 0.5 to 2.0 at. %, replacing Ni. Optimal concentration interval of doping element was determined on macrostructure that was irregular structure was appeared. Synthesis was lead in quartz tube which had diameter 15 mm, thickness 1.5 mm in argon atmosphere with cooling in water under inert gas was passed across quartz tube all time. Obtaining semi-products had follow geometric size: length 300 mm, diameter 14.5 mm.

Ultimate flexuring strength of a cylindrical rod of length l, diameter d, was determined using the formula [2]:

$$\sigma = \frac{8Pl}{\pi d^3} \quad (1),$$

where P - load at the center point of flexure.

Using the approach of [1], the calculation of deformation was carried out according to the formula:

$$\varepsilon = \frac{2dh}{l^2 + 4h^2} \cdot 100\% \quad (2)$$

where h – deflection.

Porosity was determined by weighing [3].

Coefficient of permeability and fluid flow rate through the samples were determined by the Darcy method [4]. The water was used as a liquid. Porous

samples tightly were connected with a fluid reservoir. The liquid level in the tank was kept constant throughout the experiment. Fluid flow rate Q was measured after complete wetting of the sample, and the establishment of laminar flow.

The coefficient of permeability of the porous structure was determined by the Darcy formula:

$$K = \frac{(Q\mu L)}{(\rho g \Delta H S_0 P)} \quad (3),$$

where the flow rate Q - (m^3/s); ΔH – the height of the water column; g - acceleration of free fall; S_0 – the cross-sectional area of the sample; L - length of the sample; P - porosity.

In the analysis of the macrostructure was used an optical microscope Axiovert 40 MAT.

3 Results and discussion

The presence of aluminum in the charge increases the velocity of the wave front propagation combustion. This is due to additional heat release from the melting of titanium and nickel by aluminum and an appearance of liquid phase at lower temperatures, in contacts Ni - Al at 913 K, Ti - Al at 938 K. In the case of reacting the titanium and nickel particles, the first eutectic is only achieved at 1228 K [1]. After initiating local SHS - synthesis by release of latent heat of transformation neighboring areas are heated further. This results to appearing of liquid aluminum which starts to melt nickel particles, therewith reaction diffusion of atoms high-melting component - nickel in liquid melt of aluminum have place [5].

In parallel, the "envelopment" aluminum melt of nickel particles leads to its dispersion and, as a consequence, to increase the surface area of contact and extraction even more heat. Most aluminum particles has time to react with nickel, instead of titanium, with the combustion front propagation speed will be high, and the degree of completeness of the reaction will be low. Adsorbed and dissolved gases from the powder particles form a finely porous structure [5].

With a decrease in nickel concentration and increasing aluminum concentrations above 1,5 at. %, the spreading of melt starts to limit diffusion process of penetration of aluminum atoms to titanium. Titanium-aluminum system is deactivated [5], and its distinguishing feature - low exothermicity and the lack of field solutions high-melting component in low-melting component. The reaction of

aluminum diffusing into the particles of titanium opposite directions substance transport stream associated with spreading, by capillary affect, which leads to the effect of retarding the spreading of the melt. There is a complete chemical reaction between the major components. After melting nickel by aluminum nickel liquid solution in aluminum begins to react with titanium by mechanism of chemical reaction that leads to release of additional heat and increase the temperature of combustion wave front. Upon reaching the eutectic temperature of first K 1228, according to system state diagram TiNi, titanium reacts exothermically with nickel. Accordingly completeness of chemical reaction under dissolving determines the amount released gases with surface of powders. This gives rise to appear larger pores and, as stated in the experiment with increasing concentration of Al above 2 at. % porous macrostructure of the alloy based on NiTi doped aluminum corresponds giant pores at the top and actually monolithic material at downward of reactor. Porous macrostructure of alloys based on nickel-titanium doped by aluminum visual demonstrates the effect described above in 0,5-1,0 at. % Al and its disappearance with further increase of the aluminum content in the mixture (Fig. 1).

Fig. 1. The macrostructure of porous TiNi alloys with aluminum addition, obtained by SHS-method: from left to right C_{Al} varies from 0 to 2 at. % Al, with step 0,5 at. %.

Doping of Al creates conditions for smooth pore-size distribution, wherein, the average pore size decreases from the value 37 μm to the undoped alloy to 23 μm sample doped 1,0 at. % Al (table 1). With further increase in aluminum concentration was observed since mid-sized growth up to 33 μm. It should be emphasized that the aluminum additive to 1,0 at. % beneficially affects to macrostructure of the porous samples, increases the proportion of small pores in the range from 0.7 to 30 μm, the number of large pores from 40 to 100 μm decreases. Moreover, there is homogeneity of the alloy increase with increasing Al concentration to 1,0 at. %.

Porous alloys doped with Al in the range of 1,5 - 2,0 at. % instead of nickel lose all the advantages of the macrostructure to undoped alloys NiTi. Alloy with 2,0 at. % Al has a heterogeneous pore structure which consists of small and very large pores.

The size distribution of porous alloys TiNi monolithic bulkheads shows that addition of aluminum to 1,0 at. % significantly reduces the thickness of the bulkheads (table 1). The average size of bulkheads for alloys doped with aluminum is reduced from 28 μm to 13 μm. The maximum size of bulkheads is reduced from 170 to 71 μm. As a result, nickel-titanium alloys alloyed with Al to 1,0 at. % instead of nickel have higher strength properties. Uniform distribution of bulkheads in size leads to a simultaneous load resistance bulkheads. The porous alloy doped with 1 at. % Al endures higher load as compared with the undoped alloy.

Study of permeability is integral part of a complex study of the structural properties of porous permeable materials. Permeability is physical characteristics of the porous material, which characterizes the interaction of porous material and its impregnating liquid. Water was used in the experiments as a liquid. The resulting alloys without additives of aluminum had a porous structure with average pore size of about 40 μm. Alloys doped by aluminum are characterized by small pores, as compared with unalloyed nickel-titanium alloys. The average pore size on doping is reduced to the level of 23 μm, and the average thickness interporous monolithic bulkheads reduced to 28 μm to 13 μm. This porosity affects the permeability of NiTi alloys, alloyed with aluminum. Permeability coefficient alloy doped to 1 at. % Al, three times less than the same parameter of undoped porous alloy TiNi obtained in the same conditions SH synthesis (Table. 1). Pore size distribution is shifted by doping to a region of small pores. Increasing aluminum concentration of 1 to 2 at. % in the porous nickel titanium alloys leads to a change in the coefficient of permeability ten times due to loss of structural stability of samples and formation of pores of large cross section. The optimum concentration for both homogeneous and fine-pored structure should be considered as a concentration range of aluminum additives in the range of 1,0 - 1,5 at. %.

Strength properties of porous TiNi alloys were evaluated by ultimate strength of flexure, plastic - at maximum strain at break (see Table 1). Studies of strength properties showed that the maximum strength and plastic characteristics of alloy has most uniform and fine-pore structure that is porous alloy TiNi doped 1 at. % Al. This alloy is different from other by formed macrostructure, in which the average

thickness of bulkheads has the smallest possible value in a series of samples of 13 μm, and thus there is not any pronounced rises in diagram of distribution of bulkheads in size and there is a monotonic decrease of bulkheads amount in interval from 20 μm to 60 μm. Alloys different stoichiometry have bulkheads thickness up to 170 μm, which, in our opinion, influences the negative impact on the physical-mechanical properties.

There are special features of the phase transitions in porous TiNi alloys. Alloys based on NiTi produced by SHS are characterized by high chemical heterogeneity, which makes multiphase porous NiTi. The porous structure of such alloys is determined by the amount and ratio of phase reaction products at given temperature. This occurs due to the fact that bulkheads porous structures have different thicknesses, respectively, and internal stress will be different as well.

In order to find the temperature interval of martensitic transformations, the value of the characteristic temperature direct and reverse martensitic transition interval, how many degrees separated these intervals, how many stages undergoes high-temperature phase B2, before symmetry was lowered to monoclinic phase B19 ′ and purchase options of B19 ′, you can use either temperature dependence of the resistivity or differential thermal analysis. However, as experience shows, the DTA method for porous alloy TiNi is applicable only in part, namely it is possible to estimate approximately the interval of martensitic transformations and get the approximate value of a certain temperature, named by Ms and As. This is due to the fact that the DTA method based on registering the temperature difference between the test and etalon alloy in which no phase transformation. Extracted heat from the porous NiTi in a phase transition of the first order is within the sample body, and accumulate so much heat effect washes out the boundaries of both in the forward and the reverse martensitic transformations [6].

Therefore, greater accuracy in the study of martensitic transformations of porous NiTi alloys can be obtained by measuring the temperature dependence of the electrical resistivity. The temperature dependence of the resistivity of porous NiTi alloy depending on the concentration of alloying element aluminum is showed in Fig. 2. Quantitative characteristics are summarized in Table 2. From these data and on the basis of multiple radiographic studies conducted by other authors found that the initial transition to martensitic phase B2→B19 ′ goes through an intermediate R-phase.

There is a shift start temperature transition B2→R, TR with increasing aluminum content in the porous TiNi alloys towards lower temperatures relative analog parameter alloy doped with 0.5 at. % Al, up to 20 °C

Table 1. Structural and strength properties of porous TiNi alloy doped with Al

C_{Al}, [at.%]	T_{start} [° C]	K,·10^{-12} [m²]	P, [%]	$\overline{d_{por}}$, [μm]	$\overline{d_{bulkhead}}$, [μm]	σ_f, [MPa]	ε_f, [%]
0,0	482	1,975	66	37	28,4	40	20
0,5	482	2,329	63	26	15,3	54	21,2
1,0	482	0,6785	62	23	13,4	54	21,2
1,5	482	3,517	62	30	25	52	19,3
2,0	482	6,836	66	33	21,5	44	20,5

where T_{start} - mixture temperature at the time of SH-synthesis initiation, K - permeability coefficient, P - porosity, $\overline{d_{por}}$ - the average pore size, $\overline{d_{bulkhead}}$ - the average thickness of the monolithic bulkheads moreover. The peak of the curve resistivity corresponding to a point on Ms with increasing the aluminum content increases.

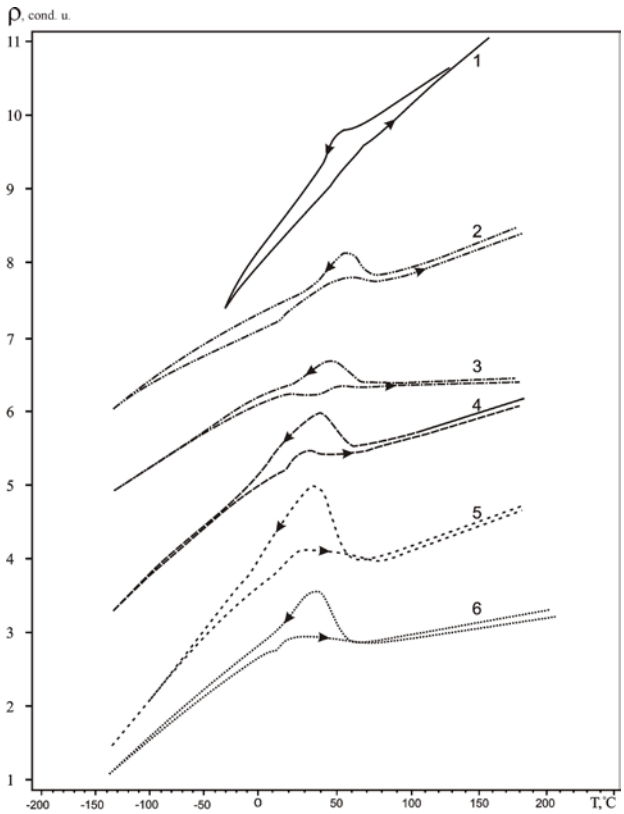

Fig. 2. The temperature dependence of the resistivity of porous NiTi alloys, depending on concentration of Al additive:

1 - 0.0 at. % Al, instead of Ni, T_{start} = 482 °C;

2 - 0.5 at. % Al, instead of Ni, T_{start} = 482 °C;

3 - 1.0 at. % Al, instead of Ni, T_{start} = 482 °C;

4 - 1.0 at. % Al, instead of Ni, T_{start} = 380 °C;

5 - 1.5 at. % Al, instead of Ni, T_{start} = 482 °C;

6 - 2.0 at. % Al, instead of Ni, T_{start} = 482 °C

It was found that the temperature range of martensitic transformations of porous NiTi alloys increases with increasing the concentration of aluminum. This is due to the influence of obstacles to the movement of the phase boundary. These obstacles may be either loss $Ti_4Ni_2(O,Al)$ particle, and the effect of porous macrostructure of alloys. In the previous section it was shown that the doping of 1 at. % Al porous TiNi alloy leads to the formation of more uniform and small pore structure of the alloy, and the reduced average thickness bulkheads. With further increase in the aluminum concentration of from 1.5 at. % or higher alloy characterized by a loss of structural stability and a large spread in thickness bulkheads monolithic porous body. It can be assumed that this inhomogeneous structure porous sample field of internal stresses arising during melt-crystallization in the synthesis of SHS will be uneven and the phase transformations in the thick and thin bulkheads will occur at different temperatures. This explains the expansion of the temperature interval of martensitic transformations porous alloys, alloyed with aluminum. It should be noted that the direct martensitic transformation range extends from 7 °C in the absence of aluminum additives to 46 °C in aluminum concentration of 2.0 at. %. In spite of the fact that high temperature phase B2 transformation in the low temperature phase B19' clearly defined by changing the angle of the slope, the reverse transition has not clear boundaries, and we can only approximate estimate the characteristic temperatures As and Af.

Therefore, the martensitic transformation in porous NiTi alloys, alloyed aluminum, are highly dependent on structural features of the porous body obtained by SH-synthesis samples.

It should be noted that chemical characteristics of porous TiNi alloys obtained by the SHS-method are high heterogeneity. To obtain more homogeneous macrostructure has to sacrifice the completeness of the reactions taking place in

the combustion zone of powders mixture, because the increase in burning time leads to precipitation of charge to bottom wall of the reactor, and resulting alloy has large pores at the top of the preform and fine pores until molten state the bottom of the porous rod.

All this is reflected in the statistical scatter of the data obtained experimentally. Thus, based on obtained temperature dependency of deformation under a constant load, it follows that the more uniform macrostructure and smaller average pore size and monolithic bulkheads, the porous TiNi alloys doped by Al is most evident MSME. TiNi alloys are doped with aluminum can be deformed to 2% in the martensitic state, and residual strain tends to zero wherein.

4 Summary

1. Porous alloys based on TiNi produced by SHS-method doped with aluminum are characterized by a finely porous macrostructure with increased content of very fine pores (10-20 μm), a uniform distribution of solid interporous bulkheads, and as a consequence, high strength properties (to 54 MPa).
2. The optimal doping level of Al in TiNi alloys for high-level properties corresponds to 1-1,5 at. % Al instead of nickel.
3. The permeability of the porous TiNi alloy with aluminum additive, when there is formation of superfine porous structure is reduced three times.
4. As resistivity curves can be approximately estimated amount of NiTi phase in the test sample. Since there is a well marked peak both direct and reverse martensitic transformation can assume significant amount of NiTi phase and, as a consequence, high physics-mechanical properties of porous alloys doped with Al, and obtained by SHS-method.

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