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Effect of sintering methods and cobalt addition on the shape memory properties of porous TiNi-based alloy

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Abstract

The changes of shape memory characteristics and properties of the porous sintered TiNi-based alloy are possible by a choice of the sintering methods or use of cobalt doping additive, as the present investigation has showed. The comparative analysis of the temperature dependences of electric resistance and macrodeformation both alloys, obtained by reaction and diffusion sintering was conducted. Diffusion-sintered alloy have showed high shape memory parameters and a more uniform passing of martensitic transformations. This is connected with a larger fraction of TiNi phase (about 90 vol.%) after diffusion sintering. It was found that the martensitic transformation characteristics and reversibility of martensitic strain in the porous nickelid titanium depend on level of intrinsic stresses in the TiNi phase and stresses caused by Co impurity. The addition to 1.0 at.% Co decreases the internal stresses in the TiNi phase, and more than 1.0 at.% Co increases their due to the effect of precipitation hardening of the alloy.

1 Introduction

A great interest in porous TiNi-based alloys is associated with the fact that they have shape memory effect. It is based on the mechanism of martensitic transformation. Due to their biochemical compatibility, it is possible to use them for

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bone tissue replacements in medicine [1, 2]. The porous TiNi-based alloy obtained by sintering has a high degree of structural-phase inhomogeneity. It is a limitation of powder metallurgy methods. Inhomogeneity of the structure and phase composition of porous sintered TiNi-based alloys greatly affects their physicomechanical properties. Volume fraction of TiNi phase in porous alloy is a major factor affecting superelastic properties and shape memory effect. The fraction of TiNi phase at the reaction sintering is much less than at the diffusion sintering, that affects SME. Besides, the fraction of TiNi phase after the liquid-phase sintering is more than after the solid phase sintering due to larger degree of conversion [3, 4].

Doping is an additional procedure for management of physical and mechanical properties of TiNi-based alloys [1, 2]. In the nickel powder, there is always a considerable admixture of Co. Therefore, there is interest in the use of cobalt as a dopant during sintering. There are few studies on cobalt effect on the structure and physico-chemical properties of alloys obtained by casting [5, 6]. In general, cobalt alloying of monolithic alloy results in the broadening and shifting of the martensitic transformations interval towards a decrease in the temperature, as well as in an increase in the amount of residual austenite.

2 Experimental

In the work specimens of the porous permeable TiNi alloy obtained by reaction sintering (RS) and diffusion sintering (DS) were studied. For RS electrolytic titanium powder and carbonyl nickel powder were used. The sintering temperature was 950 °C and the sintering time was 90 min. For DS, nickelide titanium powder, PN55T45, is used. Diffusion-sintered specimens were prepared at 1270 ºC for 5-6 min. Cobalt powder, PC-1y, was used as a dopant .

For mechanical test, sintered porous blanks were cut by the electric spark method to the plates with a size of 35×7×1 mm. The analysis of the physico-mechanical properties was conducted using temperature dependences of macrodeformation under loading (at constant stress) (the repeated shape-memory effect under loading) and temperature dependences of electric resistance.

The method of macrodeformation reflects the changes of the repeated shape-memory effect of porous specimens under doping, even though, that TiNi phase is only one of the components of the multiphase alloy when RS [3, 7]. This method reliably detects values of the maximum accumulated strain, residual, reversible strains and strain of specimen under load in a high temperature state.

In the work, the effect of cobalt additives from 0 to 2 at % with step 0,5 on the shape memory parameters and characteristics of martensitic transformations of porous TiNi alloys obtained by DS was studied.

3 Results and discussion

As a result of the comparative analysis, main distinctions of the temperature dependences of electric resistance of both specimens obtained by RS and DS were found (Fig. 1)

The analysis was conducted according to the following parameters:

- maximum value of electrical resistance at phase transition;
- value of temperature hysteresis of direct and reverse transition;
- inclination of temperature dependences of electric resistance at temperatures above room temperature;
- martensitic transformation start temperature - M_{s}.

Distinctions of the temperature dependences according to the parameters are associated with the different phase composition of sintered specimens and the volume fraction of TiNi phase for RS and DS [3, 4, 8]. Maximum value of electrical resistance for DS is greater than for RS, where it is close to zero. This fact corresponds to the difference in the amount of the TiNi phase and its location in the specimens. It should be noted, that the reaction-sintered specimen is multiphase.

The TiNi phase is formed as a layer inside a reaction cell (RC), but a periphery of the RC is formed by Ni_{γ} solid solution. The fraction of the latter amounts to 50–60 vol.% [9] that significantly affects the electric resistance of whole specimen. The TiNi phase fraction in this specimen is small, that is why the electrical resistance change of the specimen, associated with martensite formation, weakly affects the overall temperature dependence of the electric resistivity specimen.

Analogously, the value of temperature hysteresis for RS is markedly smaller, than for DS. Probably, the fact is related not only to a lesser fraction of TiNi phase at RS, but also with its formation by a solid-state diffusion reaction. The TiNi phase is visually homogeneous and free from secondary precipitates. However, its crystal structure is defective due to the impurities in it, which significantly affect its properties. During DS, the TiNi phase is taken fully from TiNi powder, including the secondary precipitations and the impurities [4].

It will be noted the incongruence inclination of temperature dependences of electric resistance for RS and DS above room temperature. It deals with a larger fraction of Ni_γ phase in the reaction-sintered specimen. In addition, its electric resistance is different from the electric resistance of the TiNi phase. M_s temperature of the specimens obtained by DS and PC differs by 75 ° C (Fig. 1).

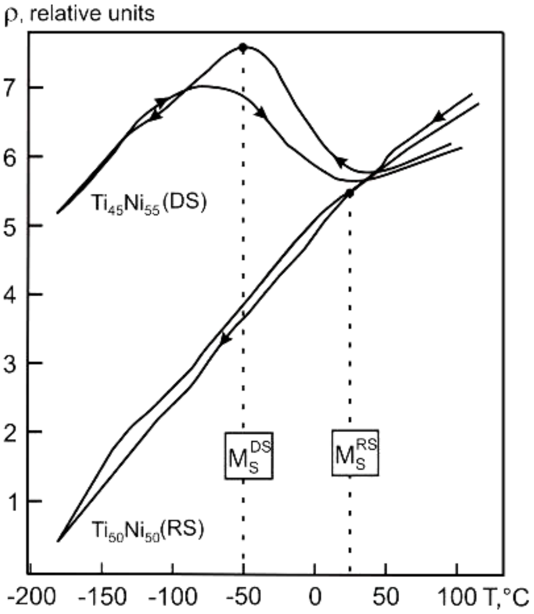

Fig. 1. Temperature dependences of electric resistance of diffusion-sintered specimen and reaction-sintered specimen

The investigation has showed that the temperature dependences of macrodeformation both specimens obtained by RS and DS have significantly distinctions too. The shape memory effect of these specimens is exhibited in different ways. In different cases it has different parameters (Fig. 2):

- values of maximum accumulated strain, residual, reversible strains and strain of specimen under load in a high temperature state;
- sequence of phase transformations.

In present work a behavior of the specimen at the repeated shape-memory effect can be explained in consideration of connection of the phase composition, its features, macrostructure of the sintered specimens and their physical and mechanical properties.

In the dependence of the repeated shape memory effect four components of deformation are distinguished [1]: maximum accumulated strain, residual, reversible strains and strain of specimen under load in a high temperature state, as a result of the parent-martensite-parent phase transition cycle (A↔M) under load (at constant stress).

The main factors influencing on deformation characteristics at shape memory effect are the TiNi phase volume undergoing a phase transformation and the porosity of sintered specimens [4, 8, 10]. The values of all deformation characteristics of the diffusion-sintered specimen at the repeated shape memory effect are larger in compared with the reaction-sintered specimen. It is related to a larger volume of the TiNi phase and the large porosity. The analysis of strain values in a high temperature state has showed that its value is less for reaction-sintered specimen, then for diffusion-sintered specimen (0.55 rel. units), because in this case the influence of the sintered array based on nickel particles is great (Fig. 2). The volume fraction of the N_{γ} spongy array is much higher than the fraction of other parts of RC. Occupying a main part of the specimen, the spongy array firstly receives the external load, deform plastically and transmit a load to the TiNi phase with shape memory. The value of this strain is affected by not only ductility of nickel particles but also the total porosity of the specimen. Thus, a smaller porosity and a smaller average pore size of reaction-sintered specimen, as compared with diffusion-sintered specimen (to 1,55 rel. units) are another reasons of smaller strain value of the reaction-sintered specimen under load in a high temperature state.

The value of maximum accumulated strain of reaction-sintered specimen behaves similarly. A lesser volume fraction of the TiNi phase and its isolation in RC by other phases cause a lesser value of accumulated strain – 7.99 rel. units, while the TiNi phase of the diffusion-sintered specimen takes a greater coupled volume and value of its strain is 11,13 rel. units.

The specimen, obtained by DS, also showed a large value of reversible martensite strain (Fig. 2). This is indicative of a high level of intrinsic internal stresses in the TiNi phase, which is usually characteristic of RS.

As shown in Fig. 2 the martensitic transformation in porous TiNi-based alloy obtained by RS is two-stage. While, the first stage of direct and reverse martensitic transitions has a higher speed, than the second stage. Martensitic transformation in the diffusion-sintered specimen occurs in one stage and more uniform in comparison with the reaction-sintered specimen.

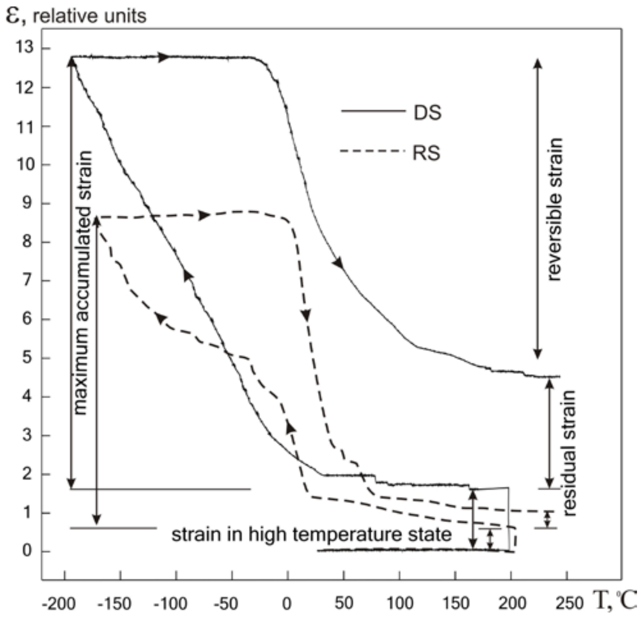

Fig. 2. Temperature dependences of macrodeformation of diffusion-sintered specimen and reaction-sintered specimen

Thus, the choice of method for obtaining of porous TiNi-based alloy (DS or RS) is one of the control methods of martensitic transformations sequence in it, underlying shape memory effect.

Furthermore, the effect of Co alloying addition was examined in this paper as a method allowing to control the properties and parameters of shape memory effect of porous alloys.

Fig. 3 shows the temperature dependence of the electric resistance of porous TiNi specimens obtained by DS, which exhibits a clearly pronounced maximum in the region of martensitic transformation. The addition to 1at.% Co causes a sharp decrease in extreme values of electrical resistance in comparison with the undoped specimens (Fig. 4). The Co content above 1.5 at % causes an expansion of the temperature interval of martensitic transformation. The expansion is associated with a shift of the martensitic transition finish temperature (M_f) toward negative temperatures, and with a deceleration of martensitic transformation.

These results allow to conclude that the decrease and the broadening of temperature dependence peak of electric resistance in the region of A→M transformation upon adding 0.5–2.0 at % Co corresponds to a deceleration of direct martensitic transformation, decrease in its completeness and an increase in residual austenite.

Strain characteristics of the repeated shape-memory effect are strongly influenced by the Co concentration. At cobalt concentrations from 0.5 to 1,0 at.% the strain under load in a high temperature state and the residual strain sharply increase in diffusion-sintered specimen. This is evidence of the fact that the level of intrinsic internal stresses in the austenite sharply decreases. Applied external load becomes an obstacle to completion of the reverse martensitic transformation, reduces reversible strain, but accompanies direct martensitic transformation (Fig. 4). For specimen with addition of 1.0 to 1.5 at.% Co, a sharp decrease in all the components of deformation is observed. We assume that this is related to the precipitation hardening of austenitic phase and a growth of internal stresses in it, which again lead to possibility of the reverse martensitic transformation under opposite load and a growth of reversible strain, but values of different kinds of strain are decreased.

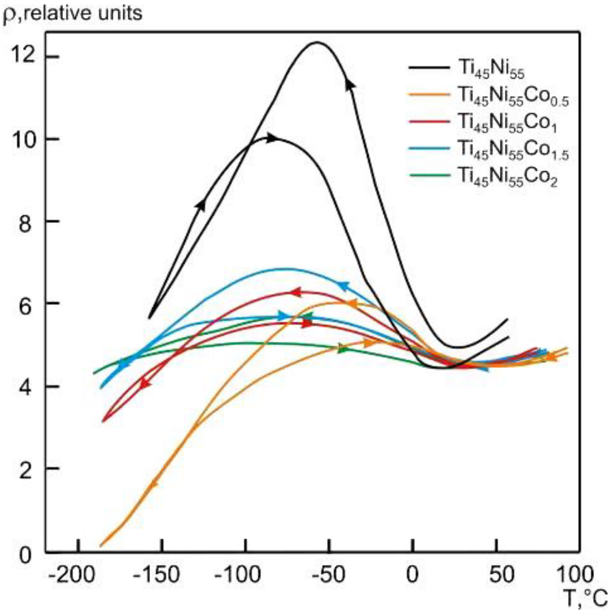

Fig. 3. Temperature dependences of electric resistance of diffusion-sintered specimens with cobalt additives

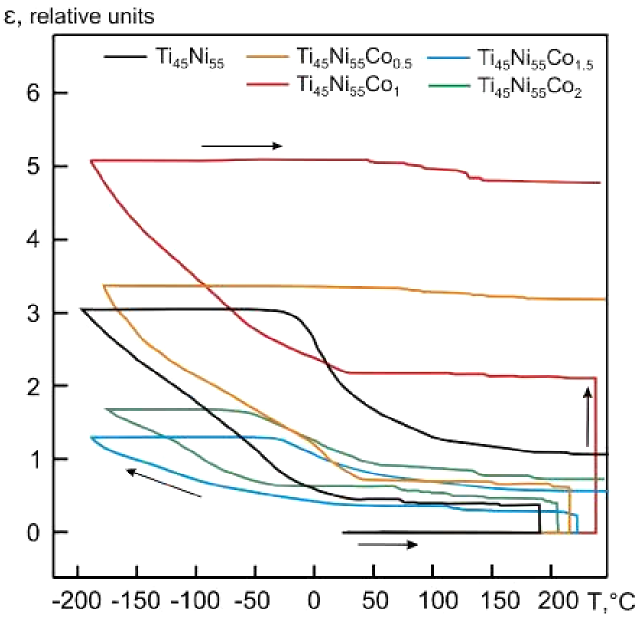

Fig. 4. Temperature dependences of macrodeformation with cobalt additives

4 Summary

The present investigation has showed that shape memory parameters and characteristics of martensitic transformations are sensitive to the amount of alloying addition and the choice of sintering method of porous TiNi-based alloy (DS or PC). Shape memory parameters of the diffusion-sintered specimen are determined by properties of the original NiTi powder. The parameters are better, than those of the reaction-sintered specimen. In specimen after DS the martensitic transformations carried out more fully and uniformly, than after RS. Analysis of the temperature dependences of electric resistance and shape memory effect have showed that martensitic transformations in the porous nickelid titanium obtained by DS and RS largely depend on the level of intrinsic stresses in the TiNi phase, including the stress, caused by Co addition. The Co content of 0.5 to 1.0 at % decreases the reversible strain due to the reduction of internal stresses in the TiNi phase. The reversible strain of specimen with the addition 1.0-2.0 at.% Co corresponds to that of the undoped alloy. Thus, the value of reversible strain with an optimum value that is different for the porous TiNi-based alloy in different operating conditions may be regulated. In conditions no load the addition of 1.0 to 2.0 at.% Co expands the temperature interval of martensitic transformation, shifts the martensitic transition finish temperature (M_f) to the low-temperature region, down to the liquid nitrogen temperature.

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References

[1] V.E. Gunther, V.N. Khodorenko, T.L. Chekalkin, Medical materials with shape memory. Medical materials and shape memory implants [in Russian], first ed., NPP «MIC», Tomsk, 2011.

[2] V.E. Gunther, G.Ts. Dambaev, P.G. Sysoliatin, Delay Law and New Class of Materials and Implants in Medicine, MA: STT, Northampton, 2000.

[3] N.V. Artyukhova, Yu.F. Yasenchuk, V.E. Gyunter, Shape-memory effect in porous alloys obtained by the reaction sintering of the Ti-Ni system, Russian journal of non-ferrous metals. 54 (2013) 178–185

[4] N.V. Artyukhova, Yu.F. Yasenchuk, V.A. Novikov, V.E. Gyunter, Structure and shape memory effect properties of the porous TiNi produced by diffusion sintering, News of Higher Educational Institutions. Physics [in Russian]. 57 (2014) 41–45.

[5] J. Bhagyaraj, K.V. Ramaiah, C.N. Saikrishna, S.K. Bhaumik, Behavior and effect of Ti2Ni phase during processing of NiTi shape memory alloy wire from cast ingot, J Alloy Compd. 581 (2013) 344-351.

[6] N. El. Bagoury, Microstructure and martensitic transformation and mechanical properties of cast Ni rich NiTiCo shape memory alloys, N. Mater Sci Tech. 30 (2014) 1795-1800.

[7] M. Whitney, S.F Corbin., R.B. Gorbet, Investigation of the mechanisms of reactive sintering and combustion synthesis of NiTi using differential scanning calorimetry and microstructural analysis, Acta Materialia. 56 (2007) 559–570.

[8] N.V. Artyukhova, Yu.F. Yasenchuk, Kim Ji-Soon, V. É. Gunther, Reaction sintering of porous shape-memory titanium nickelide-based alloys, Russian Physics Journal. 57 (2015) 1313–1320.

[9] N.V. Artyukhova, Yu.F. Yasenchuk, T.L. Chekalkin, V.E. Gunther, J-S Kim, J-H Kang, Structure and properties of porous TiNi(Co, Mo)-based alloy produced by the reaction sintering, Smart Materials and Structures. 25 (2016) (7pp).

[10] Yu.F. Yasenchuk, N.V. Artyukhova, T.L. Chekalkin, S.G. Anikeev, J-S Kim, J-H Kang, V.E. Gunther, Effect of cobalt addition on shape memory effects in porous TiNi - based alloys obtained by reaction and diffusion sintering, Adv. Mater. Lett. 7 (2016) 630-634.