The Effect of Cobalt Additives on Martensitic Transformations and Deformation in Sintered Porous Nickel Titanium Alloys

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Abstract—Porous nickel titanium (TiNi) shape memory alloys with cobalt additives have been obtained by reaction and diffusion sintering. Analysis of the experimental temperature dependence of the electric resistance and multiple shape memory effect leads to a conclusion that Co additives below 1 at % in reaction-sintered, and even more so in diffusion-sintered, alloys lead to a reduction in intrinsic internal stresses in the TiNi phase. Additives above 1 at % induce dispersion hardening of the alloy. At all concentrations, cobalt additives lead to obstacles for the martensitic phase transformations.

The considerable interest in porous alloys based on the nickel–titanium system is related to the shape memory effect and superelastic behavior of these materials. In combination with biochemical compatibility, these properties allow nickel titanium (TiNi) alloys to be used in medical implants replacing bone tissues [1].

The doping of sintered porous TiNi alloys significantly expands the possibilities of controlling their mechanical properties. In particular, doping with cobalt makes fine control of the memory shape parameters of these alloys possible. It was reported [2, 3] that cobalt additives influence the structure, and mechanical characteristics of cast TiNi alloys. Usually, cobalt doping leads to expansion and shift of the interval of martensitic transformations toward lower temperatures and to an increase in the amount of residual austenite. However, no publications devoted to cobalt doping of sintered TiNi alloys have been found in the available literature. Porous TiNi alloys can be sintered by the reaction and diffusion methods [4, 5]. In fabricating porous TiNi articles, the two methods are frequently combined.

The present investigation was aimed at studying the effect of cobalt additives on the shape memory parameters of porous TiNi alloys obtained by the reaction and diffusion sintering.

The samples were prepared by diffusion sintering (DS) and reaction sintering (RS) of TiNi alloy powders doped by adding a cobalt powder. The samples for DS were prepared from $Ti_{45}Ni_{55}$ powder synthesized by calcium hydride reduction of a mixture of nickel with titanium oxide. The samples for RS were prepared from electrolytic titanium powder (with average grain size of 6–80 μm) and carbonyl nickel powder

(with average grain size of 10–15 μm). Both DS and RS samples were prepared using the same cobalt powder. The samples with porosity within 50–60% were obtained by solid-state sintering in vacuum furnace at a temperature of 677 K for 5.4×10^3 s (RS) and at 997 K for $(3.0–3.6) \times 10$ s (DS).

The sintering temperatures were empirically selected based on visual estimations of the amount of a melted phase and the degree of shrinkage. It was assumed that the optimum quality of sintering corresponds to the appearance of low-melting Ti_2Ni phase that is necessary for the formation of strong interparticle joints (necks). On the other hand, the amount of melt should be minimal in order to eliminate shrinkage and avoid pore coarsening.

Porous alloy samples for investigation in the form of plates with dimensions of $1 \times 7 \times 35$ mm were cut from sintered blanks by the electric spark method. The samples were studied by scanning electron microscopy (SEM), macrodeformation (bending) tests, and electric resistance measurements on heating and cooling [1].

The multiple shape memory effect in porous alloy plates was studied by loading samples in the central part with a constant transverse bending load under conditions of variable temperature. The load for samples in the austenite state was selected by trials so as not to leave residual deformation upon unloading. For this purpose, the most pliable sample in a series tested was loaded at a maximum experimental temperature with various loads so as to obtain a 1- to 2-mm flexture. If the flexture disappeared without residual
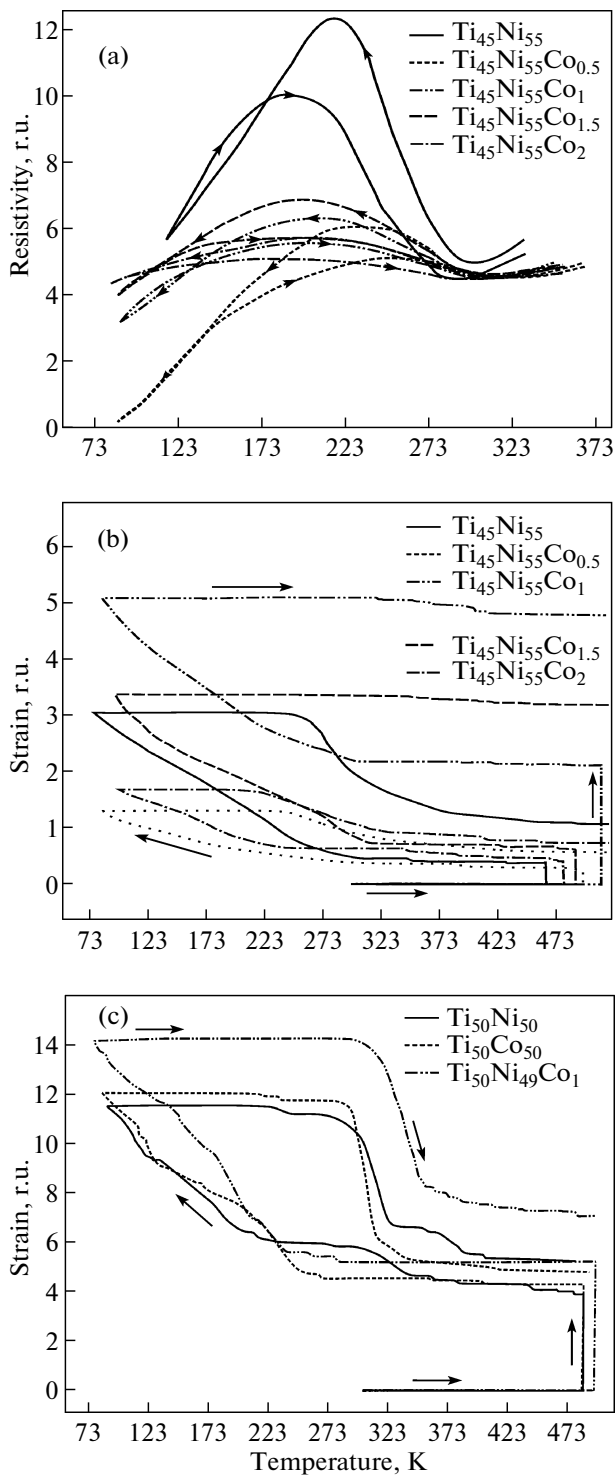
Fig. 1. Temperature dependences of (a) resistivity of diffusion-sintered samples, (b) strain of diffusion-sintered samples, and (c) strain of reaction-sintered samples of porous TiNi alloys with various cobalt additives within 0–2 at %.
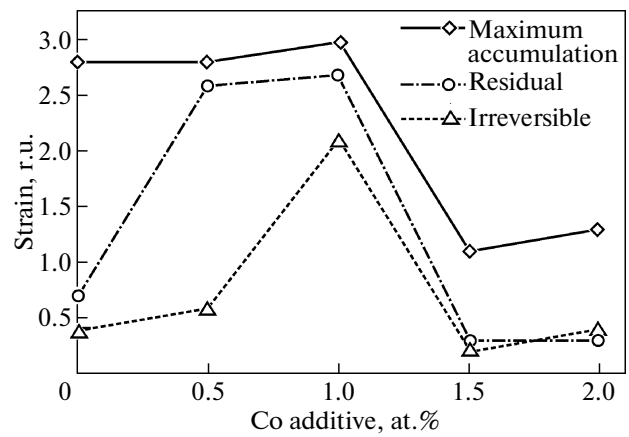
Fig. 2. Plots of the macrodeformation components vs. Co additive concentration.

Comparative analysis of the samples obtained by DS and RS can be used for assessing the role of TiNi phase in the mechanical behavior of material. The main distinguishing feature of the phase structure of porous samples upon DS is that the TiNi phase occupies about 90% of the volume. In contrast, porous TiNi alloy obtained by solid-state RS is multiphase, and the TiNi phase occupies only about 20–50% of the sample volume [4, 5].

The temperature dependence of the electric resistance of porous TiNi samples obtained by DS (Fig. 1a) exhibits a clearly pronounced maximum in the region of the austenite–martensite (A $\to$ M) transformation. Even a very small cobalt additive leads to a sharp drop in height of the resistivity peak. Simultaneously with this drop in height, the resistivity peak exhibits broadening. This behavior agrees well with the results of X-ray diffraction (XRD) investigations of porous TiNi alloys [6]. Comparison of these results leads to a conclusion that the observed decrease and broadening of the peak of electric resistivity in the region of A $\to$ M transformation upon adding 0.5–2.0 at % Co corresponds to increased amount of residual austenite, less complete forward martensitic transformation, and gradual decrease in the transformation rate.

The influence of cobalt additives on the deformation behavior of porous TiNi alloy samples obtained by RS and DS is much alike, but the effects are more clearly manifested in the diffusion-sintered material (Fig. 2). Variation of the multiple shape memory effect reveals three components of deformation [1]: irreversible initial strain, maximum accumulated strain, and residual strain upon austenite $\to$ martensite $\to$ austenite (A $\longleftrightarrow$ M) phase transformation cycle under load. All these components exhibit strong dependence on the cobalt concentration, which can be subdivided into four regions (Fig. 2).

In the first region, the introduction of 0.5 at % Co leads to a sharply increases in the residual strain as a result of the A $\longleftrightarrow$ M phase transformation cycle. In

deformation upon unloading, the given load was considered optimum and used for loading samples in the entire series. The optimum load was found to be 50 g upon DS and 60 g upon RS.

Nickel content (x, at %) in sintered porous TiNi alloys.*

Site of measurement (see Fig. 3)		
1	*2*	*3*
48.87–54.04	41.02–47.30	45.43–51.70

*Titanium to balance.

the second region, the increase of cobalt content from 0.5 to 1 at % leads to a noticeable growth in plasticity of the austenite phase and a small increase in strain recovery upon M → A transformation. The effect of Co on the accumulated strain upon A → M transformation at these concentrations is not very significant. In the third region, where the cobalt content is increased from 1.0 to 1.5 at %, all the strain components drop sharply because of increasing role of dispersion hardening of the austenite phase in the sintered alloy. In the fourth region, the growth of Co content above 1.5 at % does not significantly influence the shape memory parameters, while noticeably increasing the amount of melt and enhancing the sintering ability of $Ti_{45}Ni_{55}$ powder.

At cobalt concentrations between 1.0 and 2.0 at %, the level of internal stresses in the TiNi phase also increases, but this growth is caused by the diffusion hardening of austenite. This leads to repeated increase in the martensite strain recovery upon M → A transformation, up to a level comparable with maximum accumulated strain upon A → M transformation.

The addition of 1 at % Co to 49 at % Ni in reaction-sintered $Ti_{50}Ni_{49}Co_1$ alloy leads to the appearance of significant differences from both $Ti_{50}Co_{50}$ and $Ti_{50}Ni_{50}$ alloys in the values of initial, irreversible, and maximum accumulated strain. This fact confirms once
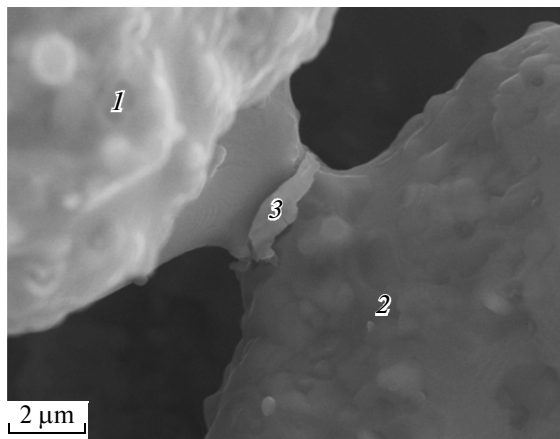

Fig. 3. SEM micrograph showing the diffusion neck of the TiNi phase (*3*) between $Ti_{1-x}Ni_x$ alloy grains (*1* and *2*).

again that the effect of cobalt in the case of both DS and RS is only manifested in combination of this additive with nickel.

A sample of $Ti_{45}Ni_{55}$ obtained by DS without cobalt additives behaves similarly to the samples of $Ti_{50}Ni_{50}$ and $Ti_{50}Co_{50}$ obtained by RS (Figs. 1b and 1c), as manifested by a large relative reversible martensite strain. This is indicative of a high level of intrinsic internal stresses in the TiNi phase, which is usually characteristic of RS. We explain this behavior by assuming that DS involves elements of RS. This idea is based on three facts. First, specific technological features of TiNi powder production by calcium hydride reduction [7] lead to strong variation of Ni content x in $Ti_{1-x}Ni_x$ composition ($x = 27.13–72.18$ at %). Second, Ni content x in $Ti_{1-x}Ni_x$ composition of TiNi alloy obtained by DS also exhibit variations (see table). Third, interparticle diffusion necks in TiNi alloy obtained by DS contain inclusions of TiNi phase (Fig. 3)

A specific feature of TiNi alloys obtained by RS is that, irrespective of cobalt concentration, the samples under loading retain an approximately constant level of reversible strain. Since the reversible strain is related to a change in the amount of martensite, it can be concluded that the new TiNi phase in the powder diffusion couple has a high level of intrinsic internal stresses. Therefore, an additional stress related to the external load (counteracting the shape restoration) is not very significant.

Thus, the effect of cobalt additives on the level of internal stresses after RS is less significant than that after DS. During the sintering, cobalt additives always counteract martensitic phase transformations in the TiNi alloy. In the presence of 0.5–1.0 at % Co in the alloy during sintering, the level of intrinsic internal stresses in the austenite sharply decreases. As a result, the external load application in multiple shape memory effect becomes an obstacle to completion of the reverse martensitic transformation (M → A). With a cobalt additive above 1 at %, the further decrease in the level of internal stresses leads to the impossibility of completion of the forward martensitic transformation A → M under the action of temperature factor alone. In the presence of 1–2 at % Co, the dispersion hardening gives rise to a growth of internal stresses in austenite, which again lead to impossibility of the reverse martensitic transformation M → A under load. Note that the influence of internal stresses in austenite is ambiguous: while the intrinsic stresses accelerate the forward martensitic transformation A → M, the stresses caused by dispersion hardening retard it.

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