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Distinctive Features of the Phase Composition of Porous TiNi-based Alloys Obtained by Reaction and Diffusion Sintering

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Abstract

The present article is concerned with questions of reaction and diffusion sintering of porous shape-memory TiNi-based alloys. The comparative analysis of structural features of the porous alloys obtained by diffusion sintering of TiNi powder and reaction sintering of Ti and Ni powders was conducted. It is observed that the main feature of structure of the porous alloys is related to fraction of the TiNi phase which occupies about 90 vol.% at diffusion sintering, and 20÷50 % of the total volume of multiphase alloy for reaction sintering. The mechanisms of the structure formation on the solid phase and liquid phase sintering stages of these methods were considered. The role of Ti_2Ni phase during sintering was disclosed. The Ti_2Ni phase not only provides the necessary quality of sintering, activates recrystallization processes for diffusion sintering, modifies the phase composition of the sintered specimen for reaction sintering, but also participates in the formation of the TiNi phase, increasing its fraction.

1 Introduction

The porous TiNi-based alloy obtained by powder metallurgy has a high degree of the structural-phase inhomogeneity, whose reasons are associated with features of its production technology. Preparation of TiNi porous implants by

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sintering is possible in two ways: by diffusion sintering of TiNi powder (DS) and reaction sintering of Ti and Ni powders (RS) [1, 2]. The TiNi powder for DS undergoes a recrystallization influenced by heat of a furnace heater, at that the TiNi phase fraction is 70-80 vol. % before and after sintering. The homogeneity of the powder depends on the regime of preparation by calcium hydride reduction [3, 4, 5]. Specimens for RS are synthesized during diffusion reaction from titanium and nickel powders. In this case the phase composition is greatly differs depending on synthesis regimes [6]. As a result of sintering the synthesized TiNi phase amounts to 45–55% of the specimen volume depending on a powder type and sintering regimes. The features of these sintering techniques are causes of the structural-phase differences of sintered specimens.

2 Experimental

In the work we have studied two groups of specimens of the porous permeable nickelid titanium alloy, which were obtained by RS and DS methods in an SNVE-1.31/15-14 electrical vacuum furnace. For RS electrolytic titanium powder with an average particle size of 60-80 µm and carbonyl nickel powder with an average particle size of 10–15 µm were used. The RS was carried out at a temperature of 950 °C and holding for 90 min. The diffusion-sintered specimens were prepared from $Ti_{45}Ni_{55}$ powder synthesized by calcium hydride reduction, of 1270 ° C and holding for 5-6 min. The porous specimens were sintered in quartz tubes with a diameter of 9-11 mm, length of 50-55 mm with using porous TiNi stoppers.

The temperature and time of sintering were experimentally adjusted on the basis of a liquid phase amount which was forming during sintering. Its amount determines parameters of final product such as a shrinkage, porosity, surface microrelief and transformation degree for RS. The RS temperature was determined by selection by increments of 20°C. The sintering temperature was limited by one 950°C. The maximum temperature of sintering was limited by melting temperature of the low-melting eutectic - 940–950 °C that decreases the melt amount to a minimum [1, 7]. The DS temperature was adjusted orientating on melting temperature of the TiNi phase on the basis of the Ti–Ni phase diagram [8]. The optimum quality of sintering was obtained with the appearance of low-melting Ti_2Ni phase that is necessary for the sintering activation and formation of strong interparticle necks. An obligatory sintering condition was preparation of high-porosity specimens. The melt amount was limited because of requirement of the minimum shrinkage for retention of high porosity of specimens. Specimens with a porosity of 50–60% were prepared by solid-state sintering.

The structure of the porous specimens was examined with using microsection metallographic specimens prepared by standard metallographic techniques [9]: light microscopy (Axiovert 40 Mat) and scanning electron microscopy (PHILIPS SEM 515). The phase composition was determined with an EDAX ECON IV microanalyzer.

3   Results and discussion

The investigation of structure of the porous $Ti_{50}Ni_{50}$ specimen after the RS solid phase stage have showed that its phase structure consist of repeated reaction cells. The reaction cell (RC) is formed by a solid-phase reaction diffusion due to the interdiffusion transport between the titanium particle and surrounding nickel particles. The RC consists of four layers arranged around the titanium core is formed by Ti_β-base solid solution (*1*) (Fig. 1, a). The layers are represented by a spongy array based on nickel particles (Ni_γ) – 5 at the periphery of a cell and by shells based on intermetallic phases (Ti_2Ni – 2, TiNi– 3, $TiNi_3$– 4) around the nucleus (Fig. 1, a) [6, 10]. Thus the formed structure at RS corresponds to the Ti–Ni phase diagram [8]. The layers of intermetallic phases have different thicknesses depending on the holding time of sintering.

The structure of titanium core can be represented in three variations. Firstly, it can consist of several parts Ti_β– 1 separated by dendrites and shell 2, composition of which is close to Ti_2Ni. Secondly, it can be formed by Ti_β+Ti_2Ni eutectoid (Fig. 2) or by Ti_2Ni intermetallic compound. Along with complex cores the monolithic RC cores formed by only the Ti_βphase are observed.

The solid Ti_β solution containing up to 10 at.% Ni in a monolithic RC core upon cooling can suffer an isothermal decay followed by transformation into the Ti_2Ni +Ti_β eutectoid or stay in a metastable state. In the solid N_γ solution that forms the porous periphery of the RC, the titanium content varies between 0.6 and 3.0 at.%.
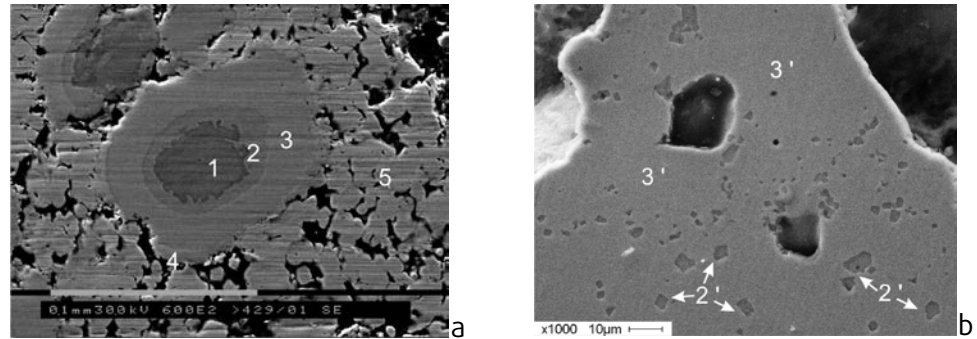
1 – Ti_β (,7 at.% Ni), 2 – Ti_2Ni (35,4 at.% Ni)

3 – TiNi (54,3 at.% Ni), 4 – $TiNi_3$ (76,3 at.% Ni), 5 – Ni_γ (98,8 at.% Ni)

2 ' – Ti_2Ni (34,9 at.% Ni)

3' – TiNi (50,6 at.% Ni)

Fig. 1. Microphotographs of the structure and concentration composition of porousTiNi-based alloy after sintering: a – DS; b – RS
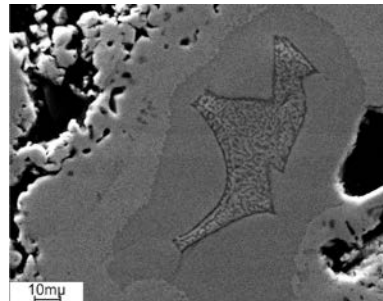

Fig. 2. The eutectoid structure of the (Ti_β +Ti_2Ni) RC core

Microscopic investigations of the porous diffusion-sintered specimen enabled us to reveal common elements of its structure such as location of the impurity diffusion zone and Ti_2Ni secondary crystals (Fig. 3). The impurity content in the sintered alloy is caused by their presence in sintering powder [3]. It will be noted that the structure of the diffusion-sintered specimen is similar to the structure of the initial NiTi powder. An average size of impurity diffusion zones is about 20-50 μm. When sintering theimpuritiesare often accompanied by Ti_2Ni secondary crystals formed during recrystallization of the powder structure.

A typical case is a presence of the closed segregation pore in the diffusion zone centre (Fig. 3, a). It is formed in place of low-melting impurity which melts during sintering and diffuses into the matrix. Wherein a part of the impurity compounds stays on a pore surface as dark microcrystals (Fig. 3, b). The Ti_2Ni secondary crystals is formed around the pore and diffusion zone upon cooling as a result of breakdown of Ti-rich matrix phase (Fig. 3, a, b).

As a result of a zone segregation some impurities produce the large Ti_2Ni crystals cluster with average size of 10-15 μm (Fig. 3, c), as well as presumably martensitic zones [11] arranged between the Ti_2Ni secondary crystals. It is demonstrated in [12], that lenticular particles can be particles of Ti_3Ni_4 phase (Fig. 3, d). Second precipitations of excess phase are often formed in Ti_2Ni phase crystals (Fig. 3, d). The crystals of Ti_2Ni phase are mainly located along a surface of sintered specimen (Fig. 3, c, b)

This is connected with fact that sintering lead to a migration of the impurities and secondary crystals in TiNi powder to a newly formed surface of the sintered specimen by recrystallization and competitive growth.

The main distinguishing feature of the structure of porous alloys obtained by DS and RS is that the TiNi phase occupies about 90% of total volume (Fig. 1, b). In contrast, porous TiNi alloy obtained by solid state RS is multiphase, and the TiNi phase occupies only about 20–50% of a specimen volume (Fig. 1, a).

The process of a structure formation in the reaction-sintered and diffusion-sintered alloys involves solid-phase and liquid-phase stages. The liquid-phase stage deals with an appearance of Ti_2Ni phase melt. This melt activates the sintering and provides sufficient strength of the porous alloy. The liquid-phase stage of RS is characterized by Ti_2Ni phase melting, its capillary spreading and a further solid-liquid interaction with TiNi, Ti_β, N_γ, $TiNi_3$ phases that were formed at the solid-phase stage earlier. The microscopic investigations of the reaction-sintered specimens after the liquid-phase stage have revealed some features of the phase structure such as a Ti_β/Ti_2Ni boundary zone, $Ti_2Ni/TiNi$ boundary zone and an additional spongy TiNi phase.

Interaction between the Ti_2Ni phase melt and solid titanium core Ti_β in Ti_β/Ti_2Ni boundary zone causes to a core cracking and formation of a ragged phase boundary (Fig. 4). This process is associated with a Rehbinder effect [13].

The detailed study of the $Ti_2Ni/TiNi$ boundary enabled to observe a transition zone with a wide of 5÷20 μm – 7 (Fig. 4, a). The solid TiNi phase interacts with the surrounding Ti_2Ni melt into RC by the peritectic mechanism to form the transition zone [14]. The transition zone consists of granulation and dendritic regions. The respective width of the regions is 3–11 and 4–10 μm. The composition of dark gray phase is $Ni_{38}Ti_{62}$, which corresponds to the ($Ti_2Ni+TiNi$) region in the phase diagram of the Ti–Ni system within the transition zone. The light gray phase – $Ni_{50}Ti_{50}$–

corresponds to the TiNi homogeneity region. A change of width of the transition zone is related to the sintering time.

A long-term exposure of sintering leads to a change in the structure of spongy shell at periphery of RC. A product of interaction of nickel array with Ti_2Ni phase melt was observed in studied specimens, despite the lack of contact between the Ni_γ solid solution and the solid phase of Ti_2Ni. A new phase is formed from a part of Ni_γ spongy array in consequence of the interaction. The phase retains a spongy morphology, but its structure becomes more complex with new composition of 49.35 at.% Ti, 50,65 at.% Ni – 8 (Fig. 4, b). The alternative TiNi phase has shape memory effect as a primary TiNi phase formed by the solid-phase reaction diffusion in RC.

The investigation of the DS solid-phase stage has shown that interparticle necks are formed, necks of contact grow by surface and volume diffusion, and binding of particles is observed. These processes are result of the solid-phase interaction and lead to shrinkage to 5 vol. %.

The analysis of the specimen structure after the DS liquid-phase stage led to the conclusion about melting and capillary spreading of the melt of the Ti_2Ni phase on the porous surface of the solid phase. A grain boundary wetting causes recrystallization of wetted fields, redistribution and consolidation of pores by coalescence. This stage is characterized by a loss of primary individual morphology of particles and acquisition of new uniform morphology of the porous alloy. During DS the capillary spreading of the porous specimen melt starts at a more heated periphery. Field of liquid-phase sintering is limited by periphery because of inefficient heating up of the centre of the porous specimen. The resultant melt activates the sintering, therefore the liquid-phase sintering is more intense.

The shape and sizes of pores in diffusion-sintered and reaction-sintered specimens are different and depend on heat distribution in sintering specimen. It is a major factor of propagation of the melt for DS.

The whole volume of the reaction-sintered specimen can be divided into two zones: central and periphery. The spongy shell of the RC is less dense on the specimen periphery than in the central zone. This results in a decrease in a distance between centers of nickel particles. In the central part of the $Ti_{50}Ni_{50}$ specimen, the average distance between centers of particles is 7 μm, while it is 11 μm in the peripheral zone. The average pore size of the spongy shell on the specimen

periphery is about 150 μm, in the central part – about 0,5–1,0 μm. The average pore size of the whole specimen is 12 μm. The transition to liquid-phase stage at RS is accompanied by the appearance of large pores in the RC core.

Zonal heterogeneity of the spongy array is connected with different temperatures on the specimen periphery and in the central zone. A less dense spongy part of RS corresponds to a lower temperature on the periphery; a more dense spongy part corresponds to a higher temperature in the center of the specimen. Such situation may occur in a case of presence of the additional heat source in specimen due to an exothermic intermetallic compound synthesis reaction.
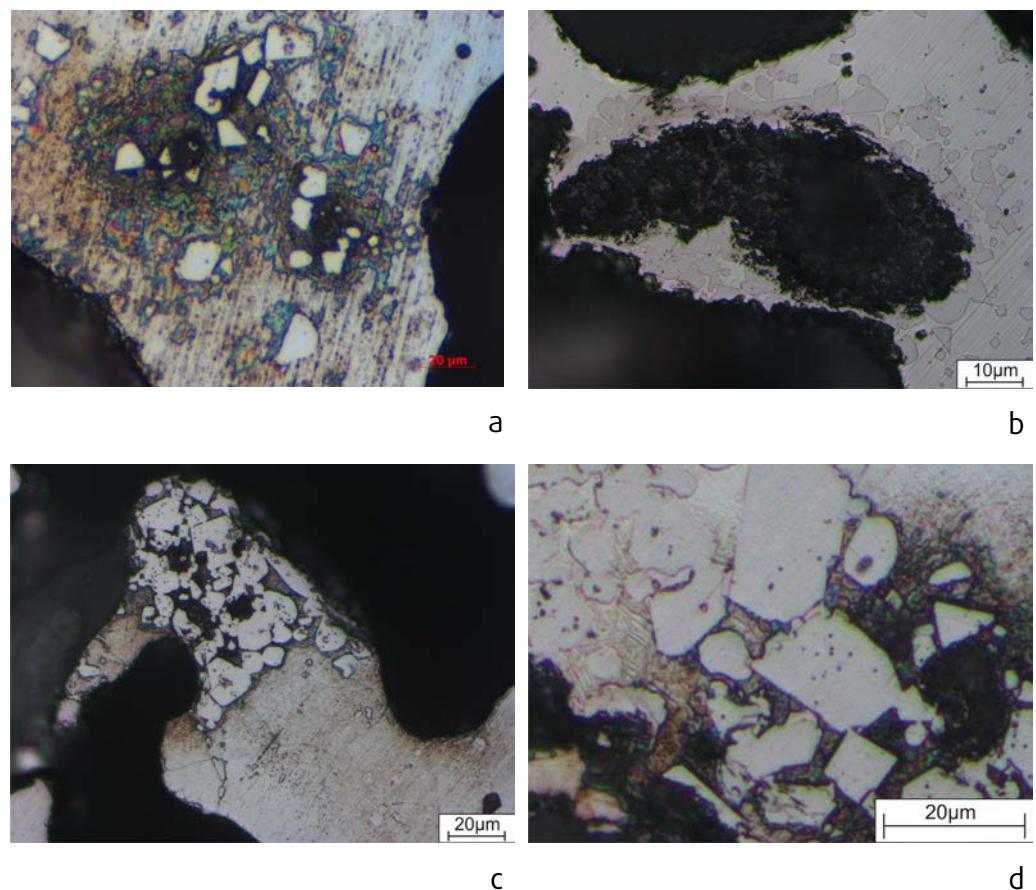

a

b

c

d

Fig. 3. The common elements of the structure of the porous diffusion-sintered specimen: a – the impurity diffusion zone; b – area of the Ti_2Ni secondary crystals around large segregation pore; c – accumulation of the Ti_2Ni secondary crystals on the periphery; d – the impurity diffusion zone with the Ti_2Ni secondary crystals and martensite between them
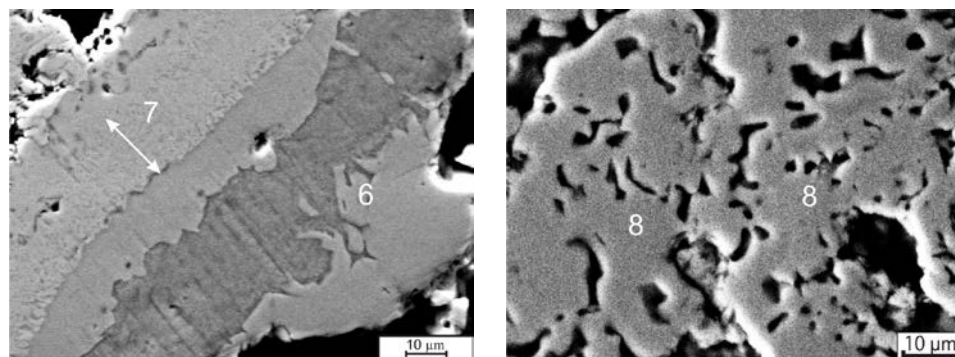
Fig. 4. SEM images of the porous TiNi-based alloy structure obtained by reaction-sintered TINi alloy: a – fragments of the $Ti_2Ni/TiNi$ transition zone, the Ti_β/Ti_2Ni boundary zone; b – the additional TiNi phase with spongy morphology is formed at the liquid-phase stage

In the specimen the powder particles shape and pores between them are retained at the initial DS solid-phase stage. Wetting by the Ti_2Ni melt and recrystallization of powder particles change a solid skeleton morphology and a pore volume. The appearance of the grain boundary layer of the melt causes sliding and rotation of TiNi grains until their contact, merger and formation of arched structures. The same type pore volume with pore size in the range $(70 \div 140)$ µm is formed by DS as distinct from RS.

The investigation have revealed differences in mechanisms of structure formation of the porous TiNi-based alloys obtained by RS and DS. The differences are associated with a lower temperature of alloying for RS and a lower holding for DS. The results of the investigation can be used to improve the technical result when creating implant constructions of TiNi alloy.

4 Summary

The phase composition of the porous TiNi-based alloy for DS is more homogeneous than for RS. A large TiNi phase fraction formed by DS requires a less sintering time. The liquid phase is needed for providing of strength of the porous alloy both in the RS and in the DS. In both kinds of sintering, the Ti_2Ni phase melt forms the TiNi phase - a main phase of TiNi alloy.

The Ti_2Ni phase melt changes the phase composition of the RC, increases the TiNi phase fraction and leads to the appearance of large pores in the sintered system. The solid-liquid interaction between the melt and primary TiNi phase leads to its additional structurization i.e. the appearance of transition zone with a dendrite

structure. The additional TiNi phase is formed as a result of interaction of the melt with a spongy nickel shell of the RC.

The impurities of TiNi powder and the Ti_2Ni secondary crystals are redistributed and located along a new surface of the sintered specimen by recrystallization of its structure. The DS process is accompanied by a reduction in surface of the sintering body and its modification.

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