Conference paper

Crystallization Features of Porous TiNi Fabricated by SHS

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Abstract

The surface layers and fracture surfaces of porous titanium nickelide obtained by self-propagating high temperature synthesis (SHS) in a flow reactor in an argon atmosphere are studied by SEM and energy dispersive analysis. It is alleged that primary pores 5–15 μ in size and the related granular layer are formed due to segregation and capillary force effect during peritectic crystallization of some porous alloy areas. Coarsening and deformation of pores, as well as migration and growth of granular layers, is caused by reaction gases. Carbon and oxygen impurities present in the reaction gases and the protective atmosphere penetrate into the melt film on the pore surface to form strong and corrosion-resistant nanostructured layers of intermetallic carbides, nitrides and oxides.

1 Introduction

The effectiveness of the porous implant integration into biological tissue and its long-term functioning depends on its biochemical and biomechanical compatibility. Porous NiTi alloys exhibit superelasticity that ensures biomechanical compatibility with living tissues. Synthesis of porous TiNi in the inert atmosphere with a considerable amount of impurities of oxygen, nitrogen and carbon provides conditions for gradient crystallization of intermetallic carbides and nitrides on the alloy surface. Formation of surface intermetallic carbides and nitrides does not affect superelasticity and shape memory and improves electrochemical passivity of the porous alloy [1, 2, 3].

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Information on the content of impurities of oxygen, carbon and nitrogen in the TiNi phase grains and grain boundary phases is required to analyze the corrosion-resistance and strength properties of porous titanium nickelide alloys. The presence of intermetallic oxycarbonitride in titanium nickelide alloys in the form of grain boundary precipitates and secondary precipitates in grains, and surface oxide layers and surface layers of nitrides and titanium carbides has been repeatedly discussed in literature [4, 5, 6]. Very little is reported on surface oxycarbonitride layers observed in powder metallurgy of titanium nickelide.

2 Experimental

The Philips SEM 515 microscope and EDAX ECON IV microanalyzer were used to study the surface layers and fracture surfaces of porous NiTi obtained by SHS in a flow reactor.

The content of impurities in the titanium and nickel powders used in the experiment is specified in regulatory documents [7, 8, 9]. The non-gasifiable impurities form metal and nonmetal precipitates. The impurities such as hydrogen, carbon, nitrogen and oxygen are gasified during SHS and form reaction gases (Fig. 1). In addition, the inert gas that was used as a protective atmosphere during the alloy synthesis contains impurities of oxygen, nitrogen and carbon.

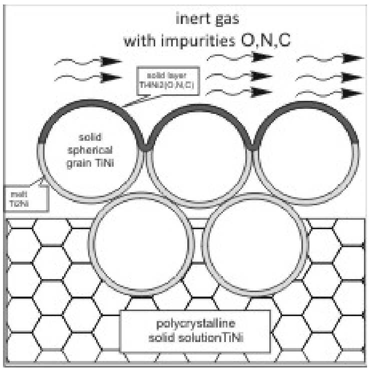

Fig. 1. Crystallization of the outer surface of the granular layer affected by carbon and nitrogen impurities

The study of the fracture surfaces was carried out for granules produced through disintegration of porous titanium nickelide. The disintegration implied fracture of the largest interporous partition walls with 500–1000 μm cross section between open macropores. The fractures disclose numerous pores ranging in size from 5 to 100 μm (Fig. 2).

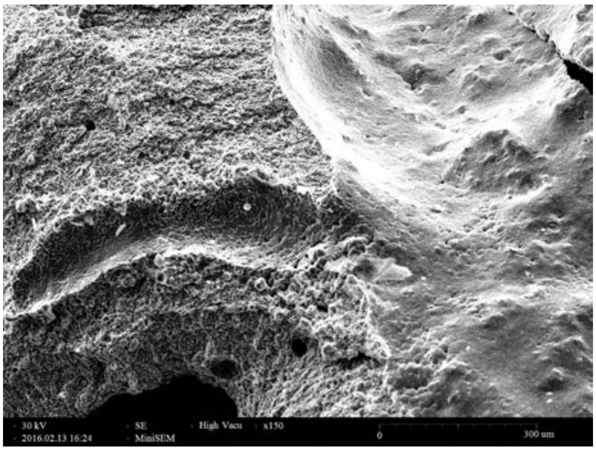

Fig. 2. SEM image of the granular surface that resulted from fracture of the partition walls between large pore channels

3 Results and discussion

All the investigated pores can be divided into four types: type 1 includes dead-end acute-angled pores with 5–15 μm cross section (Fig. 3); type 2 is represented by smoothed dead-end pores in the form of channels with a cross section of 20–100 μm, which are connected with the pores of the third type, smoothed open macropores in the form of channels with a cross section of 200–500 μm and more (see Fig. 2); type 4 includes closed 5–50 μm spherical pores (Fig. 4). The surface of all the pores is formed by clusters of rounded TiNi grains of 5–15 μm.

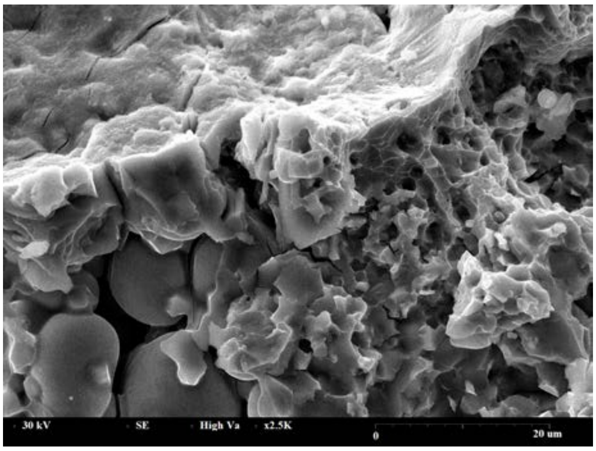

Fig. 3. Quasi-brittle fracture surface of the interpore partition walls including the acute-angled pore

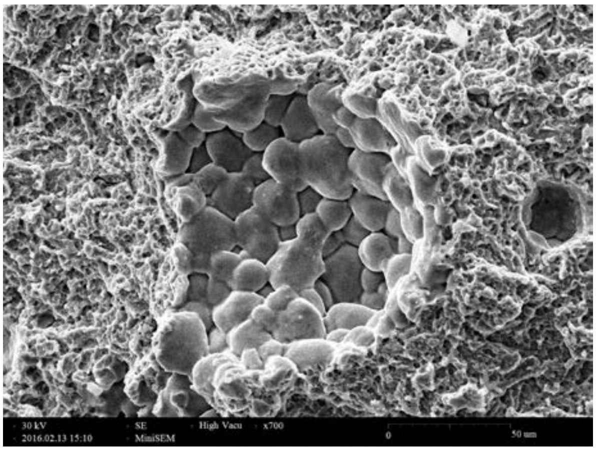

Fig. 4. Ductile transgranular fracture surface of the TiNi phase including the granular layers surrounding the pores

It is known that aluminum, magnesium and titanium alloys contain pores with a acute-angled section referred to as shrinkage porosity. These pores are formed as a result of interdendritic shrinkage due to lack of supply liquid during dendrite crystallization [10]. In powder metallurgy of alloys of the Ti–Ni system, rounded TiNi phase grains play the role of dendrites. The appearance of the observed shrinkage micropores similar to that of interdendritic shrink pores allows us to conclude that our acute-angled pores are formed as a result of the lack of supply melt in the areas of peritectic crystallization. Melt deficiency leads to the formation of gaps between the TiNi grains due to the capillary force effect. As a result, 5–15 μm acute-angled closed and dead-end pores are formed inside the clusters of rounded grains.

Reaction gases containing carbon, nitrogen and oxygen are accumulated in acute-angled pores. Excessive pressure of reaction gases causes growth of movable closed micropores ranging in size from 5 to 50 μm and makes them spherical in shape (see Fig. 4). Gases freely filter out from dead-end pores into larger open pores with no excessive pressure generated. Therefore, the cross-sectional shape of small dead-end pores remains acute-angled .

Channel pores of the second and third types are formed by coalescence of the first and fourth type pores. The coalescence can be observed at the stage of porous alloy structuring under the thermal effect of reaction gases when the TiNi phase is mainly formed. The granular layers surrounding the pores coalesce into larger structures simultaneously with the pore coalescence.

The reaction gases with a temperature of nearly 1300°C are mixed in macropores with a protective atmosphere and filtered by the alloy pores through interaction with their surface (see Fig. 1). As a result of this interaction, the pore surface is covered with the layers of products of reactive diffusion of the interstitial impurities into the peritectic melt which surrounds the TiNi phase grains. In addition, the surface layers comprise numerous slag inclusions of 2–60° μm.

The degree of surface coating with the layers of products of reactive diffusion greatly varies for different pores. The surface of the third type open macropores is covered to the most extent, the surface of the second type dead-end pores is less covered and the layers on acute-angled dead-end and closed pores of the first and fourth types are almost invisible. Obviously, the coating degree depends on the amount of gases passing through the pore and amount of impurities penetrated in its surface.

It is worth mentioning that in the fracture of interpore partition walls the fracture of the surface layer is brittle if compared to ductile fracture of the main partition walls array (Fig. 5). Large cracks in the surface granular layer occur at the boundaries of rounded grains (Fig. 6). The cracks can also be observed on the dead-end and closed pores of the first and fourth types, respectively, exposing the surface of rounded smoothed grains separated by V-shaped gaps of 1-2 μm (see Fig. 3).

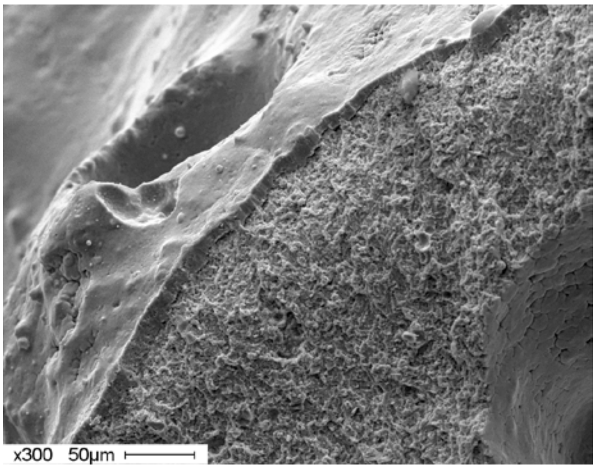

Fig. 5. Cleavage of the surface layer hardened with interstitial impurities

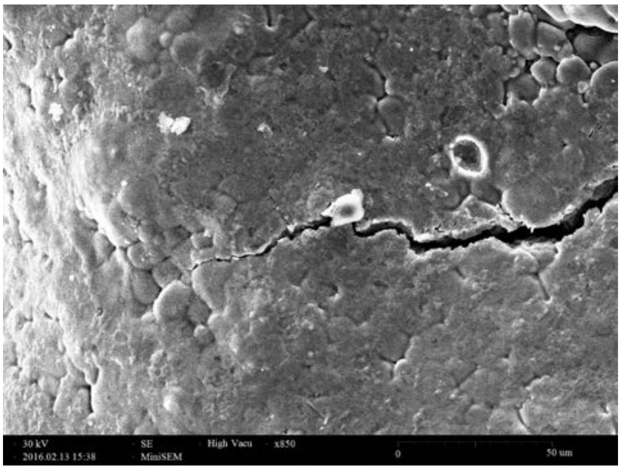

Fig. 6. Crack propagation of the partition walls between large pores

The crack opening direction in partition walls indicates the fracture initiation in the surface granular layer at the Ti_2Ni–TiNi interface and its propagation into the depth of the partition walls up to its complete fracture (see Fig. 6). The primary crack formation is accompanied by the additional crack formation that does not lead to fracture. The cracks enable tracing the fracture origin and propagation. This kind of crack formation and opening is typical of quasi-brittle fracture [11] and corresponds to the multi-phase alloy, which contains brittle, ductile and hardened phases (see Fig. 3).

Intergranular phase is more brittle than rounded grains. The brittle fracture cracks with smoothed edges often run through the phase. The cracks can be observed on the rounded grains formed by the TiNi phase and partition walls between them. The cup fractures typical of transgranular ductile fractures occurin these areas (see Figs. 3 and 4). The fracture of the surface layer hardened with interstitial impurities leads to its brittle cleavage from the ductile base. The layer cleavage results in a patching relief with ductile ridges on the ductile TiNi phase (see Fig. 5).

Due to the different nature of fracture, the surface layer is clearly visible. Its thickness does not exceed 12-15 μm. The hardened diffusion layer has the same thickness throughout. The thickness depends on the depth of reactive diffusion of interstitial impurities from reaction gases into liquid (melt) that covers the pore surface.

Although there is no precise data on thickness and structure of the brittle surface layer, it is obvious that it has a thickness significantly greater than that of the carbonitride layer, which should not exceed 1 μm. The oxidized layer depth can be estimated approximately according to the brittle cleavage thickness, assuming that embrittlement to a depth greater than 1 μm occurs due to oxidation. Other studies state that changes in the depth of the TiNi phase structure may be up to 100 μm due to its oxidation [12]. The brittle layer cleavage is mainly ductile in nature; in some areas the cleavage is quasi-brittle as it runs through the partially oxidized array that has not lost its original ductility.

4 Summary

The study of fracture surfaces of porous NiTi obtained by SHS in a flow reactor suggests that formation of pores and the granular layer associated with them is caused by segregation, formation and preservation of the melt surrounding the grains in the areas of peritectic alloy crystallization. The intergranular shrinkage pores are formed due to the capillary force effect. Excessive pressure of reaction gases in micropores promotes their growth and coalescence into macropores. At the same time, granular layers surrounding the pores become larger. The impurities of carbon, nitrogen and oxygen in reaction gases and protective atmosphere penetrate into the surface melt of open pores, forming strong and corrosion-resistant layers of intermetallic oxycarbonitride.

5 Acknowledgments

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