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Titanium- and nickel-based alloys for medical applications, obtained by a powder metallurgy technique♣

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Titanium- and nickel-based alloys find a wide application in implantology and dentistry. Here we demonstrate the possibilities and advantages of powder metallurgy (PM) for the synthesis of these alloys. Using metal powders as reagents and specific operations such as cold pressing and sintering, traditional metallurgical processes have been avoided. PM gives the possibility for application of mechanochemical methods in obtaining amorphous or nanostructured products. In this work, the TiNi alloy is obtained by the mechanical alloying (MA) method. The structural and mechanical characteristics of the Ti-Ni alloy, suitable for human implants, and the Ni-Cr alloy, designed for metal-to-ceramic dental constructions, are studied in the present paper.

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1. Introduction

Different materials such as metals, alloys and ceramics find applications in the field of bone regeneration. The ideal scaffold material is biocompatible and possesses high mechanical strength, interconnected porosity and high corrosion resistance. Titanium and its alloys such as TiNi and Ti6Al4V are largely used in implantology due to their excellent biocompatibility and appropriate mechanical and chemical properties [1, 2]. The effects of shape memory, two-way shape memory and superelasticity are other remarkable characteristics for equiatomic TiNi alloys. TiNi alloys have also attracted interest for their potential use as biomedical materials, due to the similarity of their mechanical properties to that of human bone tissue. The traditional metallurgical methods used for manufacturing medical titanium alloys include subsequent processes of melting, hot rolling, intermediate annealing and, finally cold rolling. The disadvantages of these processes are connected with oxidation, leading to degradation of the properties and to material losses. The development of simple methods for obtaining TiNi bodies with a porous structure similar to that of human bone is of great interest from a practical point of view. Powder metallurgy (PM), with its specific methods of treatment and densification of metal powders such as cold pressing, hot pressing, pressureless sintering, etc. gives many possibilities for structural design. As a result of the process of controlled particle consolidation, it is possible to obtain an end body with desirable structural properties and appropriate porosity. Contemporary Ni-Cr-based dental alloys find large applications in dentistry for metal-to-ceramic constructions. They have become superior to the gold-based alloys in hardness, elasticity, tensile strength and particularly in their price [3].

Here, we show the possibilities of PM for creating TiNi alloys and Ni-Cr dental alloys. The main advantages of the PM method and the possibilities for direct mechanical alloying (MA) and synthesis of nanostructured alloys are also shown. Phase changes after thermal or mechanical treatment of a Ti-Ni mixture are demonstrated using XRD, DTA, and SEM.

2. Experimental

Pure Ni and Ti powders, both obtained from *Fluka*, were used as reagents for the synthesis of TiNi alloys. The mechanical treatment of powders was performed in a *Pulverizette 5/4* planetary ball mill. Thermal alloying of an

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008 inactivated Ti-Ni powder mixture was carried out at 950 ^{o}C for 120 min in Ar. Densification of mechanically activated Ti-Ni powders was performed using cold pressing at 500 MPa and sintering at 800^{o}C in Ar. The sintering of the dental alloy was carried out at 1300^{o}C. DTA analysis was performed in the temperature range 20-1000^{o}C under Ar using *Stanton Redcroft* apparatus. The specimens for DTA investigations were obtained by quenching at 1100^{o}C. The phase changes were studied by XRD using a *Philips APD 15* diffractometer and Cu Kα radiation.

3. Results and discussion

Dealing with metal powders as starting materials and some specific technologies, PM is a convenient method for obtaining bulk materials with a fine and dense structure. Fig. 1 presents a

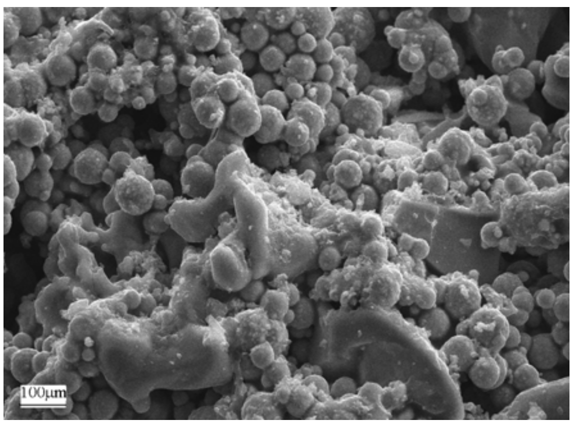

Fig. 1. SEM of Ti-Ni particles, X1000

SEM image of the initial Ti-52at.% Ni powder mixture subjected to thermal and mechanical treatment. The reagent particles differ in their morphological properties: those of Ti are flat and bigger (about 200 µm) and those of Ni are-globular and smaller (about 50 µm in diameter). It is impossible to

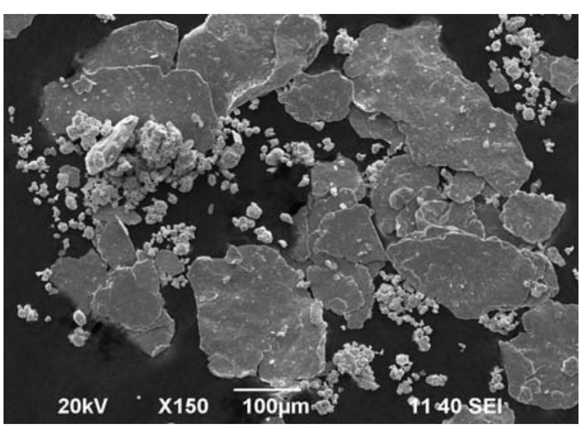

Fig.2. SEM of Ni-Cr particles, X 150

obtain dense bodies from such a powder mixture using the simplest and cheapest PM procedure: cold pressing and sintering. The same is especially valid for the powers shown in fig. 2. This is a SEM image of Ni and Cr particles which are the main components (about 80 wt.%) of nickel-chromium dental alloys. The Cr powder is obtained by milling and its particles are absolutely flat, with a mean size of about 120-150 µm, while those of Ni are globular with a size of 10-15µm. Fig. 3 presents XRD data of the starting Ti-Ni (1), the same after 30 and 40 hours mechanical treatment (2, 3), and a thermally treated at 950^{o}C for 120 min inactivated Ti-Ni mixture. As a result of 30 hours milling, the peaks become broadened and flattened due to lattice distortions and the appearance of small crystallites. Prolongation of the milling time

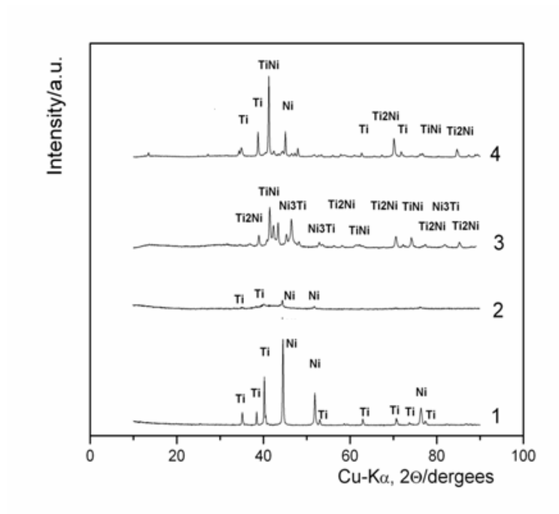

Fig.3. XRD of Ti-Ni mixture: (1) reagents; (2, 3) 30 and 40 h milling; (4) thermal alloying at 950^{o}C

to 40 hours leads to direct mechanical alloying and synthesis of TiNi, as curve 3 shows. Some amounts of Ti_2Ni and $TiNi_3$ are present. Phase analysis of the product obtained by "classic" thermal alloying at 950 ^{o}C shows that in addition to the phases of TiNi, Ti_2Ni and $TiNi_3$, the product contains some amount of reagents: Ti and Ni (curve 4). TG curves of the Ti-Ni powder mixture and the same mixture mechanically treated for 30 and 40 hours are shown in Fig. 4. The TiNi parent phase has a B2 (CsCl) type structure which transforms at 1090^{o}C to BCC. The latter is retained upon quenching or slow cooling to room temperature. Depending on the experimental conditions, the TiNi parent phase undergoes a direct B2 (cubic) – R19' (monoclinic martensite) phase transformation at 33^{o}C. This phase plays a basic role in the martensitic transformations and related effects such as shape memory and superelasticity. Two other martensite transformations are also possible: B2 - B19 (orthorhombic) - B19' and B2 – R (trigonal) - B19'. The first is typical of TiNi

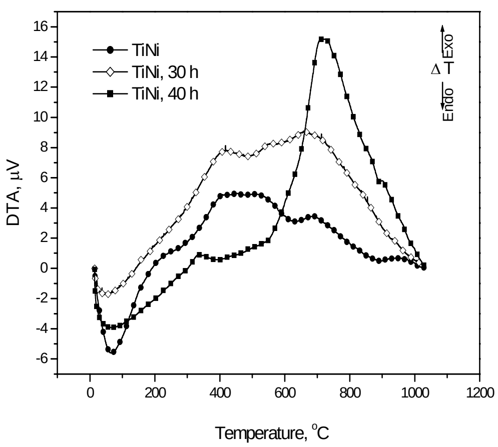

Fig.4. TG curves of "pure", 30h and 40h mechanically treated Ti-Ni.

containing Cu, the second, of TiNi subjected to aging. The phase R also appears if TiNi is heat-treated at temperatures appropriate for the production of Ti_3Ni_4 precipitates or if the parent phase is cold worked before annealing to produce structural defects. On heating mechanically untreated samples, the endothermic peak at 65 °C registers a direct B19'-B2 transformation (Fig. 4). A similar behaviour of aged TiNi alloys was discussed in [4]. The authors studied TiNi after quenching and aging for different times and temperatures, i.e. conditions which correspond to slow? cooling. The two-stage transformation B19'-R-B2 is typical of TiNi subjected to additional aging when a finely dispersed Ti_3Ni_4 precipitate appears in the B2 matrix, which favours the formation of a R phase. The broadening of the endothermic peaks for mechanically treated Ti-Ni and the change in their sharpness at the same temperature reveals a change in the phase transformation path (Fig. 4). Probably, a B19'-R-B2 transformation occurs, which is typical of cold worked Ti-Ni enriched in point defects [1]. The presence of $TiNi_3$ in the phase composition of the product obtained by MA (Fig. 3-curve 4), is a result of the transformations: Ti_3Ni_4-Ti_2Ni_3-$TiNi_3$, and proves the presence of a Ti_3Ni_4 precipitate responsible for the appearance of a R-phase. The exo-effects in mechanically untreated TiNi could be associated with phase transformations as a result of eutectoidal decomposition of TiNi to Ti_2Ni and $TiNi_3$. After 30 hours of mechanical treatment of Ti-Ni, the results are similar: there is a higher intensity of peaks and a shifting of the third of them to lower temperatures as a result of the higher activity of milled powders. After 40 h activation, the corresponding peak appears at a more than 70° lower temperature. The distinct exo-peak at 718 °C registers the transition from the amorphous to the crystalline state.

The possibility to produce end bodies with desirable structures is one of the advantages of the PM technique. Controlling the morphological properties of powders and the parameters of the processes of pressing and densification, it is possible to achieve end bodies with controlled densities and porosities. Fig. 5 shows a SEM image of TiNi obtained by MA and densified by sintering at 800°C. The presence of open interconnected pores is a precondition for the successful penetration of bone tissue into TiNi implants. The balance between porosity and mechanical strength of implants is very important for their practical application. , we show a pore structure characterized by interconnected porosity and a pore size of about 2-4 μm. It has been shown that similar porosity is appropriate for the purposes of implantology [5]. The mechanochemical methods are widely used in the synthesis of

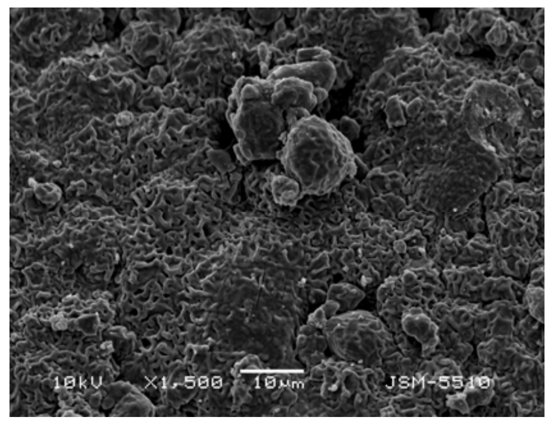

Fig. 5. Pore structure of a sintered TiNi alloy

nanostructured materials. High productivity and simple technological design are among their main advantages. The flexibility of these methods is another of their features. Mechanical alloying (MA), mechanically assisted methods of thermal synthesis (MATS), and self-propagating high-temperature synthesis (MA SHS) give many possibilities for the production of nanostructured materials. Due to the high activity of mechanically treated Ti-Ni powders, the thermal synthesis of TiNi alloys proceeds at temperatures lower by 400° than the traditional metallurgical procedure. It was shown by XRD, SEM and TEM that the crystallite sizes of the TiNi and Ti_2Ni phases obtained by MA and MATS ranged from 30-50 nm [6, 7]. The mechanical treatment of the reagents by high-energy equipment such as planetary mills and attritors allows the enlargement of the possibilities of the PM technology. The products obtained after mechanical impact on metal powders have a specific globular shape with enhanced pressability and sinterability. This allows applications in practice of powders that have inappropriate, from a technological viewpoint, properties, being similar to those shown in Figs. 1, 2. Using a homogeneous mixture of mechanically activated metal powders and a PM route for their densification, e.g. cold pressing and sintering in vacuum, some difficulties of the traditional metallurgical method for the synthesis of Ni-based dental alloys have been avoided. Fig. 6 shows types of dense pellets of a multicomponent dental alloy containing Ni, Cr, Mo, Si, Mn and Ce [8]. The traditional method for dental alloys preparation consists of

Fig.6. Ni-Cr dental alloy pellets

consecutive melting of alloy components under a protective atmosphere. The difference in the melting temperatures and densities of the alloy components is the main reason for obtaining an inhomogeneous melt and segregation of the alloy components after the melting. This leads to an

Fig. 7. Metal-ceramic dental bridge

uncertainty in the properties of the alloy, and reflects upon the quality of the dental construction. The excellent mechanical properties: an elongation limit of 480 MPa, a tensile strength of 660 GPa, a hardness (HV_{10}) of 220 and an appropriate coefficient of thermal expansion (14.0 μm/mK) determine the high aesthetic and technological properties of the dental alloy. Fig. 7 demonstrates a dental construction obtained after casting and porcelain veneering.

The overcoming of the obstacles during alloy formation and the difficulties of mechanically machining of the end bodies are among the advantages of the PM. The economic advantages of this ecologically friendly technique have been discussed elsewhere [9]. Here we have demonstrated results when combining PM and MA in the production of Ti- and Ni-based alloys, with applications in implantology and dentistry.

Acknowledgements

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