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UNTRADITIONAL SYNTHESIS OF Ni-BASED ALLOYS FOR MEDICAL APPLICATION

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ABSTRACT

Due to the combination of excellent mechanical properties, high chemical stability and appropriate biocompatibility, the Ni-based alloys find large application in implantology and dentistry. The traditional metallurgical synthesis methods of these alloys have some difficulties leading to inconstancy of the composition, degradation of properties and escalation of the product price. Here we show how to overcome the disadvantages of the traditional methods of synthesis and production of Ni-based alloys for medical application using combination of mechanochemical and powder-metallurgical routes. The structural properties of the products were studied using SEM/TEM and XRD methods. It was shown that the mechanically assisted synthesis allows obtaining nanosized Ni-Ti alloy with mean particle size of 20-30 nm at significantly lower temperature in comparison with the traditional metallurgical high-temperature alloying. It was also shown that after 40 hours of intense mechanical treatment of the starting Ni and Ti powders, a direct synthesis of Ni-Ti alloy proceeds. The product has excellent sinterability which allows producing bodies with controlled structural properties appropriate for application in implantology. Using standard mechanical tests and structural examinations it was demonstrated that the Ni-Cr dental alloys obtained by mechanically assisted sintering and casting possess excellent mechanical, technological and aesthetic properties. These alloys are suitable as dental restoration materials and production of porcelain veneered constructions like crowns and bridges using the so called metal-to-ceramic technique.

Keywords: nickel (Ni), dental alloys, mechanochemical synthesis, powder metallurgy, sintering, microstructure.

1. INTRODUCTION

The range of traditional application of nickel-based alloys covers different areas that require high performance at elevated temperatures. The formation of continuous matrix austenitic γ phase, that usually contains various percentages of Cr, Mo, W, Fe, Co, the presence of coherently precipitating γ′ phases and carbide or boride grain boundary segregates gives possibilities to form variety of alloys working at extremely high temperatures subjected to a combination of mechanical stresses and thermal shocks. The large number of Ni-based superalloys and the multiplicity of their properties and areas of application are a good example in this respect. Due to the attractive combination of good mechanical properties, chemical resistivity and biocompatibility Ni-based alloys also find a broad application in the fields of dentistry and implantology. Nickel-chromium and nickel-titanium alloys are the most popular representatives in these two medical branches.

Dental alloys could be categorized as noble, containing as a main element gold or palladium and base nickel or cobalt metal alloys (Morris *et al*., 1992). The significant increases of the noble metals price since 1960-s stimulates the development of non-precious nickel-based dental alloys. Nowadays Ni-based alloys used in dentistry have become superior to the gold-based alloys in hardness, elasticity, tensile strength and particularly in their prices (Pretti *et al*., 2004). The ideal dental alloy is biocompatible, possesses high mechanical strength and corrosion resistance. These alloys also have low prices, appropriate value of the thermal expansion coefficient conformable to that of the veneering ceramic mass and good technological and aesthetic properties. The current nickel-based dental alloys are multicomponent systems containing in addition to the main metal components of Ni, Cr, Mo (totally about 90-95 wt. %) also elements like Be, Mn, Nb, Si (5-10 wt% totally) and some additives like Ce, B, C, N in amounts of part of the percent. Dental alloys are traditionally prepared by consequent melting and thermal alloying of their components in the form of cylindrical ingots weighting 5-10g. Using centrifugal lost-wax-casting of pellets and metal-to-ceramic techniques for porcelain veneering, different dental constructions such as crowns and bridges are produced. The homogeneity of the multicomponent melt and the exact composition of every pellet are of decisive importance for processes of production and for the quality of the end dental constructions. The traditional method of thermal alloying and casting of nickel-chromium dental alloys is characterized by significant difficulties in obtaining products with constant composition. The considerable differences in the melting and boiling points and densities of the starting components strongly impede obtaining of homogeneous melt in the process of thermal alloying and consequently achieving equal and desired composition and the corresponding set of properties of each dental alloy ingot/pellet. To maintain the high level of similar production processes, expensive melting techniques and strict composition control of every dental pellets batch are required.

The effects of shape memory, two-way shape memory and superelasticity are among the remarkable properties for equiatomic Ni-Ti or some close in composition Ni-Ti-based alloys. These characteristics are based on the martensitic transformation and its reversion and can be provoked by thermal or mechanical impact. These alloys show an unexpectedly low elastic anisotropy and as a consequence very high ductility determining a cold working up to 60%. The excellent bio compatibility and the high corrosion resistance resulting from the stable TiO_2 layers formation are other remarkable properties of Ni-Ti alloys. The combination of these unique properties makes Ni-Ti the most successful commercial shape-memory alloys (Otsuka, 2002). In the last decade these alloys have attracted much interest as functional materials, sensors and actuators, guide wires, medical devices and surgical tools, orthodontic wires, etc. Spring like temperature sensitive stents for cardio-vascular surgery produced from shape-memory Ni-Ti alloy are a good example in that respect. Compressed and super cooled stent is inserted into the artery where under the influence of the human body temperature it recovers its initial shape, thus expanding the blood vessel. The Ni-based shape memory alloys (SMAs) attracted also attention for their potential use as implants because of their appropriate from a medical viewpoint mechanical properties and the technological possibility to obtain bodies with a porous microstructure similar to that of the human bone tissue. The traditional method of Ni-Ti synthesis includes serial technological steps such as melting, hot rolling, cold rolling, intermediate annealing and final cold rolling. During these processes the high-temperature oxidation causes material losses and degradation of the product properties (Ebato, 1994). The described disadvantages make the traditional metallurgical method for synthesis of Ni-Ti time-consuming with reduced economical efficiency.

Here we show how to overcome disadvantages of the traditional metallurgical methods in obtaining Ni-containing alloys with application in dentistry and implantology. The methods of mechanically assisted synthesis and sintering are based on intense milling of components of alloys. In combination with cold pressing and sintering or thermal treatment, high quality Ni-based dental alloys and Ni-Ti SMAs have been obtained.

2. MATERIALS AND METHODS

2.1. Synthesis of Ni-Cr alloys

Figure-1(a) shows schematic representation of planetary ball mill in which the high efficiency of the mechanical impacts is due to the antiparallel vectors of movement of supporting disk and milling containers, a complicated trajectory of milling bodies and resulting high accelerations. Figure-1(b) shows SEM of the initial nickel particles used in the synthesis of Ni-based dental alloys. The Ni powder is produced by Novamet using carbonyl synthesis method. The particles have regular globular shape and mean particle size of 3-5 μm. As a result of their chemical purity and small particle size, characteristic of the carbonyl synthesis method, these particles have very high sinterability. Chromium particles with mean particle size 150-200 μm were obtained by milling of chromium lumps (99.9% purity) and as a consequence of the mechanical impact have an absolutely flat shape. Figure-1(c) shows a mixture of initial Ni-20%Cr particles used as main components in synthesis of multicomponent nickel-based dental alloy. Molybdenum powder with mean particle size of 5.0 μm was obtained by double hydrogen reduction of MoO_3 at 1100^oC. Ni-based dental ingots containing Cr and Mo - 95.0%, totally and the rest to 100%: Si (Elkem Silicon Materials), Mn and Ce, were obtained by mechanical treatment of reagents, cold pressing of the homogeneous powdery mixture at 15.0 GPa to obtain pellets with desire shape. These green bodies were vacuum sintered at 1295^oC for 30 min to achieve high dense ingots. Using lost-wax centrifugal casting method, standard bars suitable for mechanical tests were produced. These tests included Vickers hardness (HV10), tensile strength (Rm), elongation limit ($Rp_{0.2}$) and ductile yield (A5). The thermal expansion coefficient of the Ni-based alloy was determined by dilatometric measurements in the temperature range 20-600^oC. Using the same casting method and metal-to-ceramic technique for porcelain veneering, different dental constructions appropriate to evaluate the technological and aesthetic properties of the alloy were produced.

Titanium powder (98.5% purity) obtained by Fluka and Ni particles with globular shape and particle size below 10 μm obtained by hydrogen reduction at 600^o C of NiO (black) were used as reagents for the syntheses of equiatomic Ni-Ti alloys. Figure-1d shows SEM of the initial Ti powder used in the synthesis of NiTi. The particles have smooth shape and most of them are interconnected. The size of aggregates and some separated particles exceeds 250 μm. Ni and Ti powders in atomic ratio 1:1 were mixed and mechanically treated in a planetary ball mill (Pulverizette5/4, Fritsch GmbH) up to 40 h at a rotation speed of 200 rpm. Stainless steel bowls ($80cm^3$) and balls with a diameter of 10 mm and total volume of $25cm^3$ were used. To ensure optimal contact between milling bodies and metal particles and to achieve highly efficiency of the mechanical treatment about 30% of the reactor volume was kept free of charge. The milling containers were fitted with semi-pass flaps allowing mechanical treatment of metal powders under protective Ar atmosphere, thus preventing metal particles from oxidation. Some amount of reagents was removed periodically for structural and phase analyses. The mechanically assisted thermal synthesis of Ni-Ti alloy was carried out after 30 h intense mechanical treatment of reagents and heating in a corundum tube furnace in a hydrogen stream at 550^oC for 30 min. Sintering of dense Ni-Ti bodies with controlled porosity was performed at 800^oC under protective hydrogen atmosphere.

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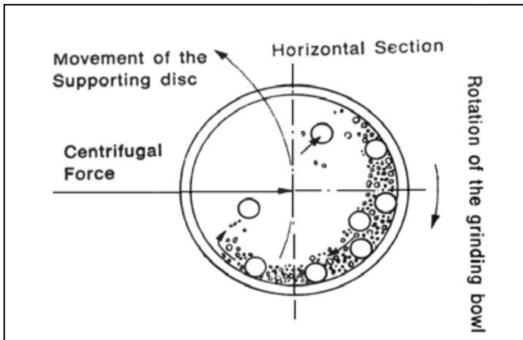

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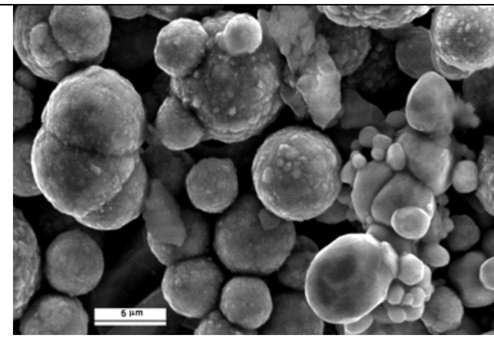

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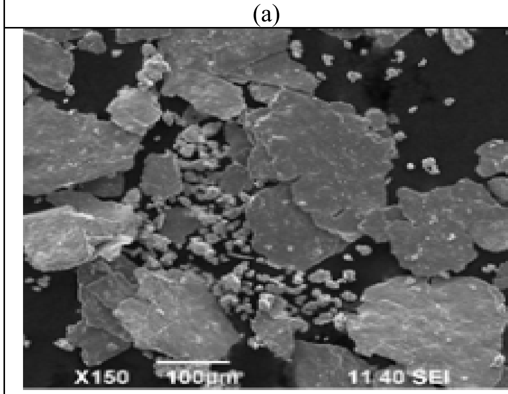

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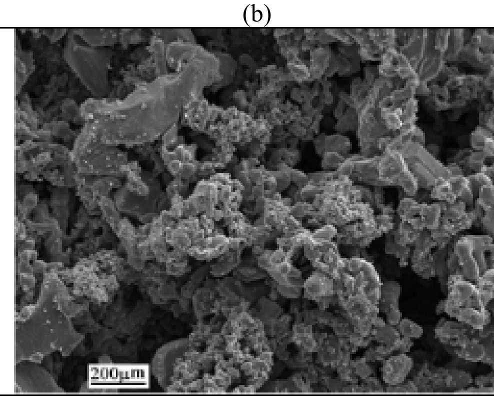

(d)

Figure-1 (a)-(d). Schematic representation of planetary ball mill, SEM images of starting Ni particles ($4.5*10^3$X), Ni-Cr powder mixture (3:1), ($1.5*10^2$X), Ti particles, ($1.0*10^2$X)

3. RESULTS AND DISCUSSIONS

3.1. Ni-based dental alloys

Figure-2 shows the SEM images of Ni-20 wt. % Cr powder mixture after 6 hours intense mechanical treatment in a planetary ball mill. The picture reveals globular aggregates with mean size of about 70-80 µm consisting of submicrometric particles. This is a typical view of mechanically treated plastic metal particles and demonstrates the morphological and structural changes resulted by the mechanical impact. Homogenization and crashing of particles, appearance of highly reactive oxygen-free surfaces, accumulation different types of structural defects, development of the processes of plastic deformation and cold welding, leading to formation of aggregates are among the effects of mechanically treated solids. Similar morphological pictures were observed after intense mechanical treatment of Ti-Ni and Ti-B powders in high energetic apparatuses like SPEX and planetary mills (Szajek *et al*., 2005; Radev, 2001 and 2010). The formation of globular aggregates containing components of the alloy is very important from technological point of view for successful implementation of the cold pressing-sintering processes and achievement of dental pellets with maximal density. Sintering of dental alloy pellets with almost theoretical density is decisive for the lost-wax casting process during which the end dental constructions are formed. The eventual presence of pores and cavities in the structure of the pellets leads to oxidation and slag formation during the process of dental construction casting. The practice of the powder metallurgy implies that Cr particles shown in Figure-1(c) would have poor pressability and sinterability resulting from their flat shape and big sizes. As a consequence, the powder mixture inherited the low sinterability of the Cr particles. The low density of the ingots is a precondition for bad quality of the end dental construction. The homogeneous distribution of Ni and Cr particles after mechanical treatment is demonstrated in Figure-4(a). The BSEI image is obtained from the metallographic section of mechanically treated Ni-Cr powder mixture. The content of Ni and Cr exceeds

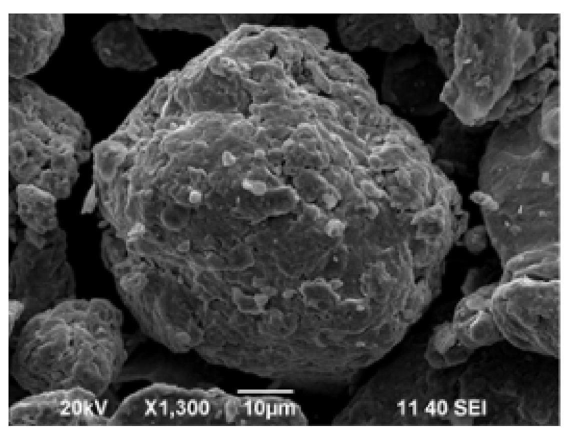

Figure-2. SEM images of Ni-Cr after 4h mechanical treatment, ($1.3*10^3$X).

85 wt% which makes the picture of homogeneous distribution of components representative for the alloy. Figure-3(a) shows images of densified by sintering dental alloy pellets produced on the basis of mechanically treated Ni-Cr powder mixtures. The picture reveals the technological advantages and flexibility of the production method which includes mechanical treatment of component, densification by the methods of powder metallurgy and obtaining dense pellets having 99% relative density, desired shape and weight. The pellets of the Ni-based alloy obtained in this way have perfect castability demonstrated by casting of a standard tiny lattice model and constant composition of the components (Radev, 2002). It is very important to notice that the mechanical treatment of the alloy components results in a perfect homogeneity of the composition and leads to morphological changes of metal particles associated with improved pressability and sinterability. The homogeneity of the powder mixture is inherited by ingots, thus ensuring constancy in the properties of the batch.

Figure-3(b) demonstrates the excellent technological and aesthetic properties of the alloy and the large possibilities to obtain highly complicated porcelain veneered dental constructions. The composition of the nickel-chromium dental alloy is well balanced which means that elements like Si, Mn and Ce are present in amounts sufficient to improve some properties of the alloy without deteriorating others. For example, it is known that the presence of some amounts of Mn, B and Ce improves the bonding strength between the alloy surface and porcelain veneer. At the same time, excess addition of Mn tends to decrease the corrosion resistance and aesthetic properties of the dental construction, discoloring the porcelain veneer. Furthermore, it is crucial that the B content does not exceed ca. 0.05-0.1 wt% since it tends to increase the brittleness of the dental constructions. The same could be said for Si, which in amounts exceeding 6 wt. % decreases the mechanical strength of the alloy. These examples clearly indicate the necessity of perfect homogenization of the alloy components, thus providing exact and constant composition of every ingot of the dental alloy. The precisely balanced composition of dental alloys is responsible for the combination of their mechanical, technological and aesthetic properties. Among these properties the value of the linear coefficient of thermal expansion (CTE) is decisive for the compatibility between the ceramic veneer and metal construction. In order to produce compressive stress in the porcelain during cooling there is a general consensus that the alloy should have higher CTE than the porcelain (De Hoff, 1998; Walton, 1985 and Lopes, 2009). The value of $13.9.10^{-6}.C^{-1}$ in the temperature interval 25-600^{o}C was determined by dilatometric tests and is similar to the data for most of the market available Ni-based dental alloys. In ductile materials, at some point, the stress-strain curve deviates from the straight-line relationship and the Hooke's law no longer applies as the strain increases faster than the stress. From this point on, some permanent deformation in the specimen occurs and the material is said to react plastically to any further increase in load or stress. That is why the level of the elongation limit ($Rp_{0.2}$) of nickel-chromium dental alloys is a very important mechanical characteristic showing the limit of their application. The standard mechanical tests after casting of ingots show mean value of 482 MPa. This value overcomes the elongation limit of most of the market available nickel-based alloys and is similar to that of some cobalt-based dental alloys which are generally stronger (Patent, 2001; 2002; 2003). The alloy is characterized by tensile strength (Rm) of 670 MPa, low value of ductile yield (5%) and Vickers hardness (Hv10) of 220 units. The well balanced composition, the chemical purity of the alloy components and the high density of the dental ingots determine the high level of mechanical and technological properties of the alloy. It should be accentuated that these results were obtained in the absence of Be or other toxic additives to the alloy composition. The role of beryllium which often presents in small amounts (about 2 wt. %) in some base metal dental alloys is to lower the melting temperature and surface tension, thus facilitating castability and improving porcelain-metal bond strength (Leinfelder, 1997; Covington *et al*., 1985; Bezzon, 1998 and Huang, 2005). It is believed that acting as a grain refiner, Be improves tensile strength and ductility of the alloy. However, exposure to beryllium vapor or particles is associated with a number of health risks from contact dermatitis to chronic lung disease, known as chronic beryllium disease (CBD). In addition, Be and its compounds in vapor or particulate form have been shown to be carcinogenic (Kuschner, 1981; Fodor, 1997 and Sanderson *et al*., 2001) The exact composition of nickel based dental alloys is decisive also for the biocompatibility and for the level of the nickel cations released in contact with the human saliva. Investigations in that area unambiguously show the mutual role of Cr, Mo and Mn on the formation of stable passive layer protecting from corrosion (Bumgardner, 1993 and Sian, 2010). Here described new technique for dental alloy production allows obtaining nickel-based ingots with strict composition and constant set of mechanical, technological and biological properties.

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(a)


(b)

Figure-3(a)-(b). Ni-based dental alloy pellets and Metal-to-ceramic Ni-based dental construction.

3.2. Mechanochemistry of Ni-Ti alloys

The mechanochemistry offers variety of synthesis methods like mechanically assisted thermal synthesis, mechanically assisted self-propagating high-temperature synthesis, direct mechanical synthesis, etc. Figure-4(b) shows TEM image of Ni-Ti alloy obtained after 30 h mechanical activation of equiatomic Ni-Ti powder mixture and thermal synthesis at 550^{o}C in a protective atmosphere of pure hydrogen for 30 min.

The data of XRD analysis show presence of the equilibrium TiNi, Ti_2Ni and $TiNi_3$ phases that limit the region of the system Ni-Ti with respect to it practical application. The data obtained by XRD and SEM investigations show that the product consists of nanosized particles with mean size of 20-30 nm which form an aggregate mass (Radev, 2010 and Varin, 2006). Nanosized materials possess high sinterability due to their defect structure and large contact surface area resulting in enhanced diffusion mobility. The high activity of such materials allows producing macrosized end bodies at milder conditions, for example by pressureless sintering or sintering at significantly lower temperatures. Prolonged milling time up to 40 h leads to direct synthesis of Ni-Ti alloy which phase composition is similar to that of the product obtained by mechanically assisted thermal synthesis. Figure-4(c) shows SEM image of the product which forms globular aggregates typical of the products obtained by mechanical synthesis.

Being built of particles with submicron sizes, these aggregates have complicated structure, possess high sinterability and are suitable to create dense bodies with controlled porosity. Similar porous structure with uniformly distributed pores being 1-2 μm in size is shown on Figure-4(d). The material is densified by sintering at 800^o C of Ni-Ti powders obtained by direct mechanical synthesis. The possibility to obtain bodies with controlled porous structure is very important for the application of Ni-Ti alloys in implantology. The presence of open interconnected pores with pre-determined dimensions allows penetration of the human bone tissue into NiTi implants. That is a good example for creation of macro-products with controlled properties due to the use of nanostructured particles (Kipp *et al*., 2005).

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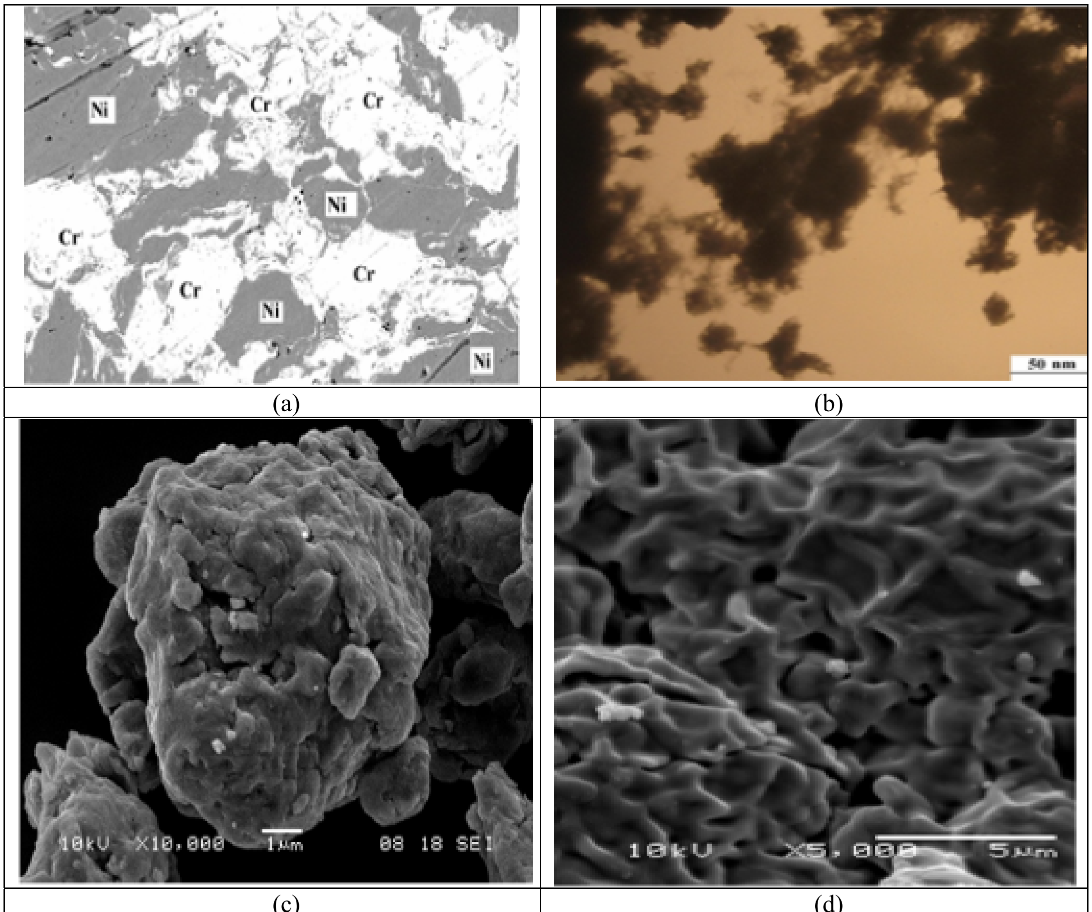

(a) (b) (c) (d)

Figure-4(a)-(d). BSEI image of Ni-Cr after 4 h mechanical treatment, ($5.0*10^2$X), TEM of Ni-Ti alloy obtained by mechanically assisted synthesis, ($2.0*10^5$X), SEM image of NiTi alloy obtained by direct mechanical synthesis, ($1.0*10^4$X); sintered Ni-Ti, ($5.0*10^3$X).

4. CONCLUSIONS

The methods of mechanochemistry allow us to overcome the difficulties associated with the traditional thermal synthesis of some Ni-based alloys for medical application. Powder metallurgical route in preparation of Ni-based alloys provides exact composition and random distribution of components in dental ingots and strict control of the nickel-titanium ratio which is decisive for the temperature range of martensite-austenite transformation of the Ni-Ti SMAs. As a result of the intense mechanical treatment the components of the alloys acquire good press- and sinterability which allows, after cold pressing and sintering producing bodies with controlled porosity. Applying the method of mechanically assisted sintering, high quality beryllium-free dental alloy ingots and finally, complicated dental constructions could be produced (Radev, 2012). The method of dental alloy production described here shows how to achieve perfect homogeneity and exact composition of every ingot and probably how to enlarge the area of application of the cheap nickel-containing dental alloys. In the case of Ni-Ti, the mechanical treatment of the reagents leads to a significant lowering of the synthesis temperature or to direct synthesis of nanosized alloy suitable for sintering bodies with controlled porosity.

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