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Preparation of 50Ni–45Ti–5Zr powders by high-energy ball milling and hot pressing

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ABSTRACT

This study reports on the preparation of the 50Ni–45Ti–5Zr (at.%) alloy by high-energy ball milling and hot pressing. The elemental powder mixture was processed in silicon nitride and hardened steel vials, and samples were collected after different milling times. To recover the previous powders in addition wet milling isopropyl alcohol (for 20 min) was adopted. The mechanically alloyed powders were hot-pressed under vacuum at 900 °C for 1 h using pressure levels close to 200 MPa. The milled powders were characterized by means of scanning electron microscopy, X-ray diffraction, and energy dispersive spectrometry techniques. It was noted that the ductile starting powders were continuously cold-welded during ball milling. This fact was more pronounced during the processing of 50Ni–45Ti–5Zr powders in hardened steel vial. After milling for 5 h, the results suggested that amorphous and nanocrystalline structures were achieved. The complete consolidation was found after hot pressing of mechanically alloyed 50Ni–45Ti–5Zr powders, and a large amount of the B2–NiTi phase was formed mainly after processing in stainless steel balls and vial.

1. Introduction

Titanium and its alloys have been widely used in orthodontic devices such as dental implants, palatal expanders and endodontic instruments [1]. The NiTi compound is characterized by the presence of an ordered lattice which can contain twins that allow the crystallographic reversibility from the martensite (B19' body monoclinic) to austenite (B2 body centered cubic) structures. This material has application in orthodontic wires due to its corrosion resistance, biocompatibility characteristics, superior superelastic values and memory shape effect [2]. Recent work involving the preparation of ternary Ni–Ti–Zr alloys was evaluated varying the zirconium amount between 5 and 10 at.%, where a large amount of the B2–NiTi phase was achieved [3]. However, the microstructure of the ternary alloys indicated the presence of other binary phases. High-energy ball milling techniques have been used as initial preparation stage of metal and ceramic powders, and may produce homogeneous materials. In addition, nanostructured materials and metastable structures such as extended solid solutions and amorphous structures can also be achieved [4]. The kinetic on the phase transformation and final product characteristics depends on the type of mill, milling parameters, and starting components characteristics [5]. The present work reports on the preparation of the Ni–45Ti–5Zr (at.%) by high-energy ball milling and hot pressing aiming future dental implant applications.

2. Materials and methods

The following high-purity starting powders were used in this work in order to prepare the Ni–45Ti–5Zr (at.%): Ti (99.9 wt%, spherical, -150 mesh), Ni (99.9 wt%, sponge, -100 + 200 mesh). Zirconium chips (99.8 wt%, containing 4 wt% Hf) were used as raw-material.

The Ni–45Ti–5Zr powder mixture was processed in a planetary Fritsch P-5 ball mill at 300 rpm (rotary speed) with a ball-to-powder weight ratio of 10:1. The milling process was performed in silicon nitride and stainless steel vials (225 mL) with silicon nitride (10 mm diameter) and stainless steel (19 mm diameter) balls. Samples were collected in the vials after different milling times: 20, 60, 120, 180, and 300 min. To recover the previous cold-welded Ni–45Ti–5Zr powders, 20 min more wet milling (isopropyl alcohol) was adopted. The mechanically alloyed powders were handled in Ar-filled glove box in order to minimize the atmospheric contamination and a spontaneous ignition. The mechanically alloyed Ni–45Ti–5Zr powders were hot-pressed at 900 °C for 60 min using pressure levels close to 200 MPa.

The milled and hot-pressed samples were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive spectrometry (EDS) techniques. SEM images were obtained in a LEO-435-VPI SEM using the secondary and back-scattered electron detectors. XRD experiments at room

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temperature were performed in a Philips PW 3719 diffractometer using Ni-filtered Cu-Kα radiation. The phases formed in milled powders and hot-pressed alloy were indexed in accordance with the files from the JCPDS database [6]. The Powdercell software [7] was also used for indexing the phases. EDS analysis was conducted in terms of Ni, Ti, Zr, and Fe contents.

3. Results and discussion

The final processing of mechanically alloyed Ni–45Ti–5Zr powders in wet medium (isopropyl alcohol) with balls and vials of silicon nitride and stainless steel contributed to increase the yield of powder from 63% to 88% (silicon nitride) and 18% to 89% (stainless steel).

XRD results of Ni–45Ti–5Zr powders milled in different milling times and vials are shown in Fig. 1. Similar behavior was noticed during the initial milling time. After milling for 120 min, the powder mixture processed with hardened steel balls (19 mm diameter) provided a reduction on the intensity of peaks more pronounced than that milled with nitride silicon nitride balls (10 mm diameter). Both the powder mixtures processed in hardened steel and silicon nitride vials indicated the presence of halos, suggesting that amorphous structures were achieved. Previous work reported the formation of amorphous structures in Ni–Ti–Zr powders [8,9]. Intermetallic phases were not identified in XRD patterns of mechanically alloyed Ni–45Ti–5Zr powders.

Fig. 2 shows the crystallite sizes values of Ni–45Ti–5Zr powders processed at different milling times. The crystallite sizes were reduced up to 10 nm, denoting the severe plastic deformation provided during ball milling of 50Ni–45Ti–5Zr powders.

SEM images of Ni–45Ti–5Zr powders milled for different times are presented in Fig. 3(a–j). Initially, the nickel and titanium powder particles presented sponge and spherical morphologies, respectively. Zirconium chips can be also observed in Fig. 3(a and b). After milling for 20 min, the presence of flattened particles can be observed. As expected, a continuous cold-welding was noticed during ball milling of ductile Ni, Ti and Zr particles. The increase

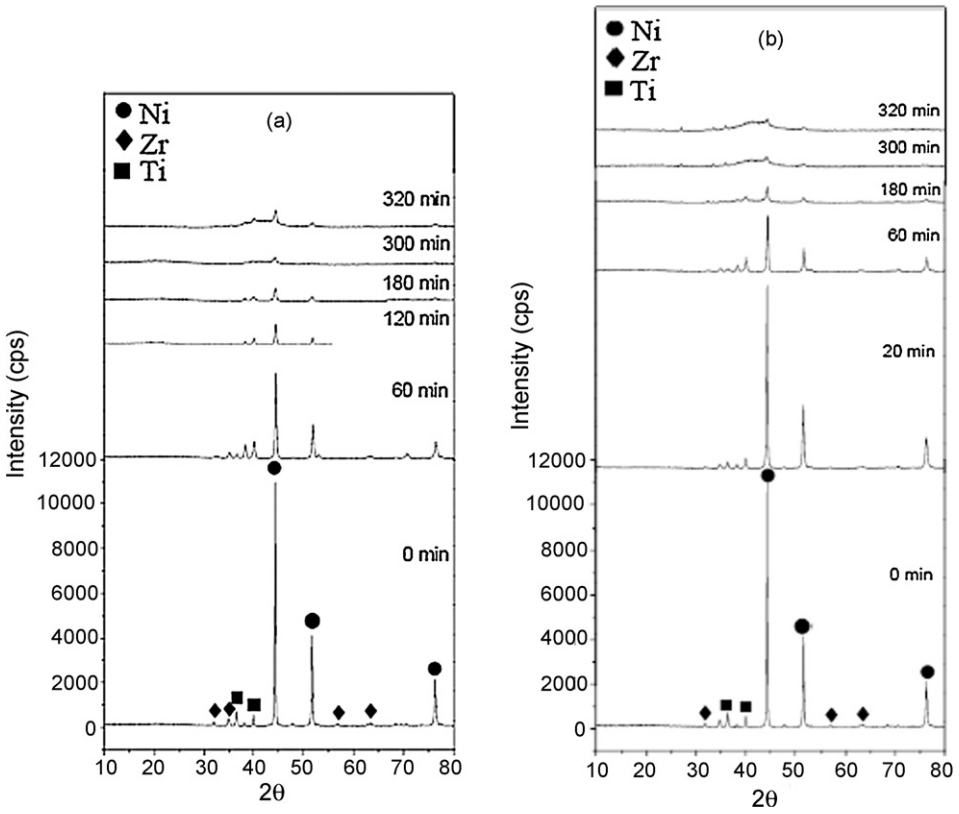

Fig. 1. XRD patterns of Ni–45Ti–5Zr powders milled for different times in (a) stainless steel and (b) silicon nitride balls and vials.

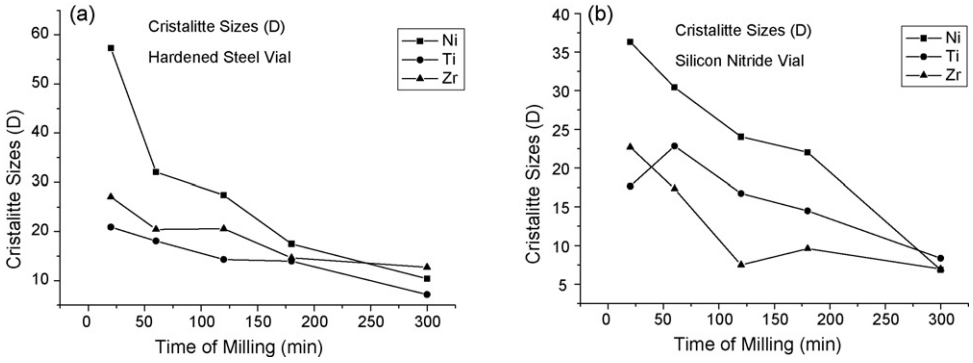

Fig. 2. Crystallite sizes of Ni–45Ti–5Zr powders processed at different milling times with balls and vials of silicon nitride (a) and stainless steel (b).

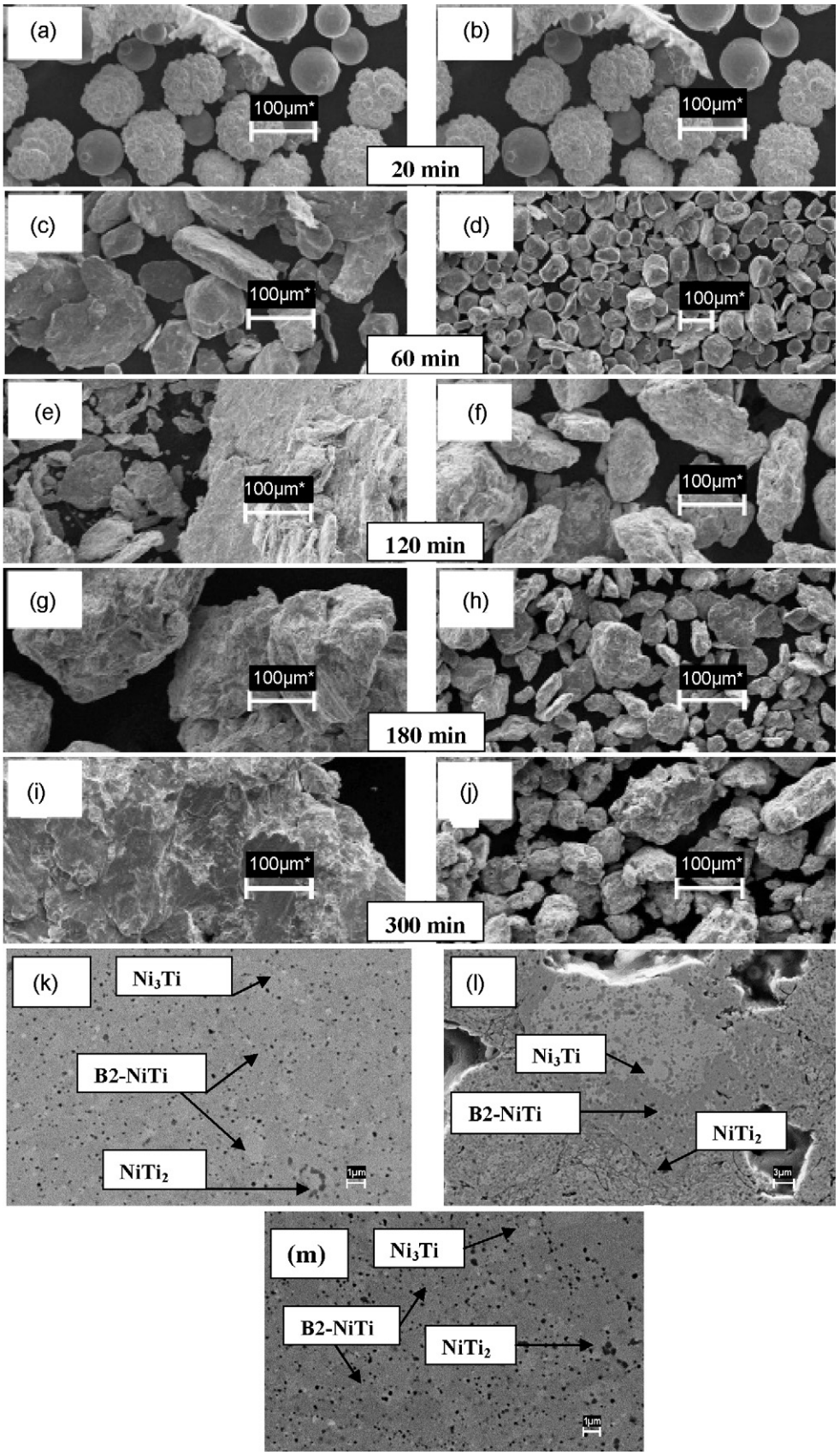

Fig. 3. SEM images of Ni–45Ti–5Zr powders milled for different times (20, 60, 120, 180, 300 min) with balls and vials of stainless steel (a, c, e, g and i) and silicon nitride (b, d, f, h and j). SEM images of hot-pressed Ni–45Ti–5Zr alloys previously milled with hardened steel (k) and silicon nitride balls and vials (l). Microstructure after hot pressing of wet-milled Ni–45Ti–5Zr powders (m).

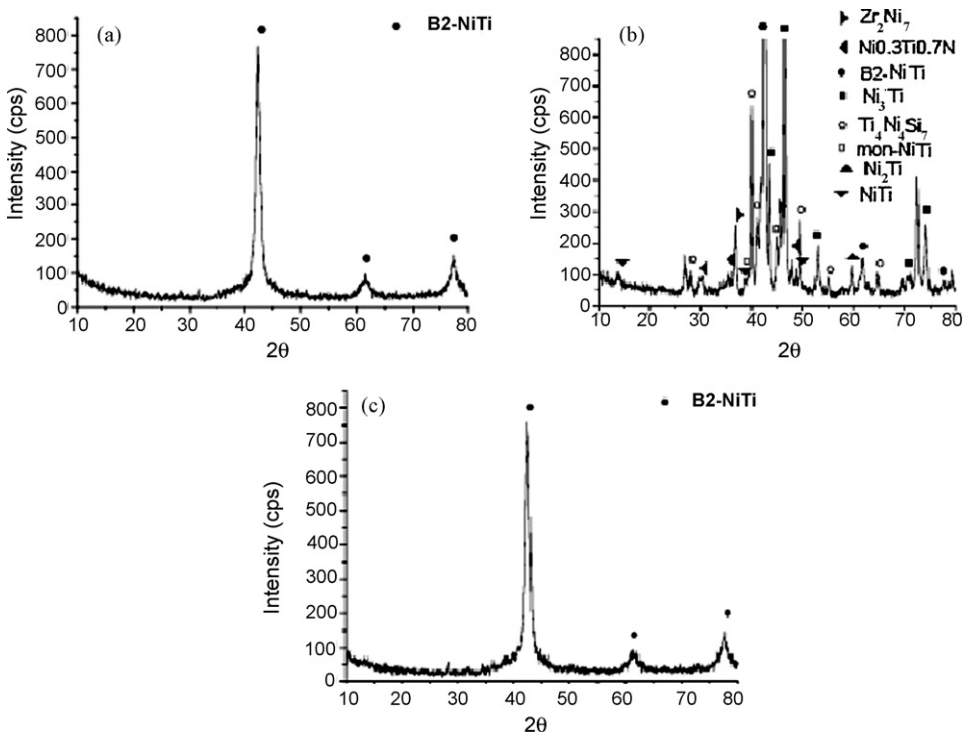

Fig. 4. XRD patterns of Ni–45Ti–5Zr alloys after hot pressing of powders previously processed with (a) stainless steel and (b) silicon nitride balls and vials. (c) XRD pattern after hot pressing of Ni–45Ti–5Zr powders milled in wet medium.

of particle sizes was more pronounced in Ni–45Ti–5Zr powders milled with hardened steel balls. Nevertheless, the reduced particle size provided during the processing of powders with silicon nitride balls and vial can contribute to reach the complete consolidation during the further hot pressing process [5]. The Ni–45Ti–5Zr powders milled with hardened steel balls and vial presented irregular morphology as shown in Fig. 3(a, c, g and i), while the rounded particles were found in powders processed with silicon nitride balls and vial as shown in Fig. 3(b, d, f, h and j). SEM images of mechanically alloyed and hot-pressed Ni–45Ti–5Zr powders are shown in Fig. 3(k–m). The microstructures of the hot-pressed alloys with different milling mediums revealed the major presence of the B2–NiTi phase as matrix. However, the microstructure of the hot-pressed alloy which was previously processed with hardened steel balls and vial (wet milling) presented a superior chemical and structural homogeneity, as shown in Fig. 3(k and m) than that processed in silicon nitride balls and vial shown Fig. 1. That a small amount of Ni_3Ti (bright region) and $NiTi_2$ (dark region) phases uniformly disperses in a B2–NiTi matrix was also identified in microstructure of the homogeneous hot-pressed alloy. In addition, the microstructure of the hot-pressed Ni–45Ti–5Zr alloy which was previously processed with silicon nitride balls and vials indicated a larger amount of pores, shown Fig. 1, suggesting that the diffusion mechanisms were more pronounced from partially mechanically alloyed powders. EDS analysis revealed that the zirconium was preferentially dissolved into the B2–NiTi phase, and an iron contamination close to 5 at.% was detected in Ni–45Ti–5Zr powders processed with hardened steel balls and vials.

Fig. 4 shows the XRD patterns of mechanically alloyed and hot-pressed Ni–45Ti–5Zr powders. Only peaks of the B2–NiTi phase were indexed in X-ray diffractogram of the powders milled with hardened steel balls and with wet milling processed from hardened steel balls, shown in Fig 4(a and c), respectively. This fact indicates that the chemical homogeneity was achieved during the previous ball milling. In contrary, other intermetallic peaks like traces were identified in X-ray diffraction of Ni–45Ti–5Zr powders milled in silicon nitride vial as shown in Fig. 4(b).

4. Conclusions

The final processing in wet medium (isopropyl alcohol) of mechanically alloyed Ni–45Ti–5Zr powders with balls and vials of silicon nitride and stainless steel contributed to increase the yield of powder from 63% to 88% (silicon nitride) and 18% to 89% (stainless steel). The starting powders were severely plastically deformed during ball milling of Ni–45Ti–5Zr powders, and the crystallite sizes of Ni, Ti and Zr were reduced. After hot pressing, a superior chemical and structural homogeneity was found in powder mixture processed with stainless steel balls and vial. The microstructures of the hot-pressed Ni–45Ti–5Zr alloy processed with silicon nitride and hardened steel balls and vials indicated the major presence of the B2–NiTi phase as matrix. For powder mixture milled with silicon nitride balls and vial, a large amount of pores was observed, while the uniformly disperse Ni_3Ti and $NiTi_2$.were observed in homogeneous microstructure of hot-pressed Ni–45Ti–5Zr alloy previously processed with hardened steel balls and vial.

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