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Effect of Milling Parameters on the TiB and TiB_2 Formation in Ti-50at%B and Ti-66at%B Powders

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Abstract. This work discusses on the effect of milling parameters on the TiB and TiB_2 formation in Ti-50at%B and Ti-66at%B powders, respectively. Both powder mixtures were processed in a planetary ball Fritsch P-5 ball mill under Ar atmosphere, varying the milling parameters: rotary speed (150 and 200 rpm), size of balls (10 and 19mm diameter) and ball-to-powder weight ratio (2:1 and 10:1). In order to obtain the equilibrium structures the milled powders were heated at 1200°C for 1h. Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal analysis (DSC). XRD results indicated that extended Ti(B) solid solutions were formed during ball milling of Ti-50at%B and Ti-66at%B powders. After milling for 170h it was noted the TiB and TiB_2 formation in Ti-50B and Ti-66B powders processed under higher-energy condition. DSC analysis revealed that the TiB_2 formation was completed during heating of mechanically alloyed Ti-66at%B powders only. After heating at 1200°C for 1h, a large amount of TiB and TiB_2 was found in Ti-B powders milled under higher energy condition.

Introduction

The intermetallic compounds can be interesting for high temperature structural applications due to their physical and chemical properties such as high melting point, and oxidation resistance [1-6]. In the Ti-B system, various works involving the preparation of the TiB and TiB_2 compounds by conventional arc-melting and powder metallurgy techniques were reported [7-10].
Recent studies indicated that the mechanical properties can be improved in as-cast Ti billets after severe plastic deformation by the equal channel angular extrusion (ECAE) [11,12]. The intense structural refinement during ECAE process contributed to form nanostructures in bulk alloy. Non-equilibrium materials processing routes including the mechanical alloying and rapid solidification techniques are potentially attractive to prepare metastable structures such extended solid solution and amorphous phases [13-16]. During ball milling, the phase transformations can occur depending on the milling parameters and alloy composition [16].
Previous work reported on the preparation of Ti-50B and Ti-66B (at-%) powders by ball milling in order to obtain the TiB and TiB_2 compounds [17]. The milling process was conducted in a planetary ball milling using hardened steel balls (10mm diameter), rotary speed of 150rpm, and a ball-to-powder weight ratio (BPR) of 2:1. Results indicated that the B atoms were dissolved into the Ti lattice in order to form extended Ti solid solutions, but no intermetallic peak was identified in Ti-50B and Ti-66B (at-%) powders milled at lower energy condition. In addition, it was noticed that the mechanical alloying process was accelerated in TiH_2-50at%B powders. The XRD results revealed that a significant amount of TiB and TiB_2 was formed in Ti-50B and Ti-66B powders after different heat treatments (700-1200°C). However, other phases such as Ti_{SS} (ss-solid solution) and Ti_3B_4 were also noticed in heat-treated Ti-50B and Ti-66B powders. This fact could be minimized after ball milling at higher energy condition. The present work discusses on the effect of milling parameters on the TiB and TiB_2 formation in Ti-50at%B and Ti-66at%B powders.

Materials and Methods

The following high-purity starting powders were used to prepare the Ti-50at%B and Ti-66at%B powder mixtures by high-energy ball milling using: Ti (99.9wt-%, spherical, <150 mesh) and B (99.5wt-%, angular, <120mesh). The Ti-50at-%B and Ti-66at-%B powder mixtures were referred in the text hereafter as Ti-50B and Ti-66B powders, respectively.
The milling process of Ti-50B and Ti-66B powders was carried out in a planetary Fritsch P-5 ball mill under argon atmosphere. The following milling parameters were adopted for processing under lower-energy condition: stainless steel vials (225mL) and balls (10mm diameter), rotary speed of 150rpm, and a BPR of 2:1. In order to evaluate the effect of milling parameters on the TiB and TiB_2 formation the Ti-50B and Ti-66B powders were also milled at higher-energy condition: stainless steel balls (19mm diameter), rotary speed of 200rpm, and a BPR of 10:1. The two different milling parameters adopted in this work were referred in the text hereafter as high-energy and low-energy ball millings, respectively. Samples were collected into the vial after different milling times. The as-milled Ti-50B and Ti-66B powders were handled in an Ar-filled glove box for minimizing the atmospheric contamination and spontaneous ignition. To obtain the equilibrium structures the as-milled Ti-50B and Ti-66B powders were heated at 1200^{o}C for 1h in argon atmosphere and gettered by titanium.
The milled and heat-treated Ti-50B and Ti-66B powders were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM), and differential scanning spectrometry (DSC) techniques. XRD experiments at room temperature were performed in a Seifert equipment using Ni filtered Cu-Kα radiation. The phases formed during ball milling and after heat treatments were indexed using the files from the JCPDS database [18]. The Powdercell computer program [19] was also used to index the phases formed in milled and heat-treated Ti-50B and Ti-66B powders. The full width at half maximum (FWHM) values were measured by the integral method while that the crystallite sizes were calculated by the Debye-Scherrer equation ($D=0.9\lambda/\beta\cos\theta$). The morphology and particles sizes of as-milled powders were observed in a LEO 1450-VP SEM. In order to understand on the phase transformation during heating of mechanically alloyed Ti-66B powders the thermal analysis (DSC) was conducted up to 1200^{o}C (20K/min).

Results and Discussion

Fig. 1 shows the XRD patterns of Ti-50B and Ti-66B powders produced by high-energy ball milling after different times. The intensity on the B peaks was promptly reduced in the initial milling times. In both powder mixtures processed at low and high energy conditions, the Si peaks disappeared after milling for 10h, suggesting that the B atoms were dissolved into the Ti lattice to form extended Ti solid solutions. In addition, the Ti peaks were continuously broadened during ball milling for both powder mixtures, but intense Ti peaks were still detected in XRD patterns of Ti-50B and Ti-66B powders milled for 45h and 60h at low-energy condition, respectively. In contrary, it was noted the presence of halos in Ti-50B and Ti-66B powders processed at high-energy condition, suggesting that amorphous structures were formed after milling for 110h. No intermetallic peak was found in Ti-50B and Ti-66B during ball milling at low-energy ball milling. In contrast, the TiB and TiB_2 peaks were detected in Ti-50B and Ti-66B powders milled for 170h at high-energy condition. XRD results revealed the reduced intensity on the TiB peaks in powders milled for 230h, suggesting that the atomic disordering of the TiB compound was achieved.
Fig. 2 displays the details on the major Ti peaks of both Ti-50B and Ti-66B powders milled at low and high energy conditions. The Ti peaks were moved slightly toward the direction of lower diffraction angles during ball milling probably due to the dissolution of B atoms into the Ti lattice in order to form extended solid solutions. The FWHM values and crystallite sizes of Ti-50B and Ti-66B powders produced by low and high-energy ball millings are shown in Fig. 2. The sizes of crystallites were exponentially reduced in the initial milling time. In Ti-50B and Ti-66B powders milled at higher-energy condition presented the increased FWHM values whereas the crystallite sizes reduced for the longest milling times. As expected, this fact was more pronounced during the

processing of Ti-50B and Ti-66B powders at high-energy condition. In addition, this tendency also occurred in powder mixtures containing smaller B amounts, denoting the more effective plastic deformation mechanisms in powder mixture with larger amount of ductile particles.

The morphology and particle sizes of Ti-50B and Ti-66B powders produced by high-energy ball milling after different times are shown in Fig. 3. Initially, the Ti and B powder particles presented spherical and angular morphology, respectively. The ductile Ti particles were frequently flattened and the harder B powders were incrusted in these softer particles during the initial milling times. Critical ball milling (CBM) behavior of Ti-50B and Ti-66B was noted during the initial milling time due to an excessive agglomeration of ductile particles on the balls and vial surfaces. This fact was attenuated after formation of brittle phases such as TiB and TiB_2 during high-energy ball milling, and the balance between the cold-welding and fracture mechanisms was achieved. The sizes of powder particles were reduced in Ti-50B and Ti-66B powders milled for 60h. Previous work reported on the TiB_2 formation in Ti-66B and TiH_2-50B, and Ti-22.2Si-11.1B powders produced by lower-energy ball milling while that the TiB compound was not found in Ti-50B powders [17]. Fine particles with rounded morphology were found after ball milling for 110h. However, it was noted a more pronounced agglomeration and aggregated particles larger than 400μm were formed in Ti-50B and Ti-66B powders milled for 170h under lower-energy condition. Previous work indicated that the presence of aggregated particles can contribute for stabilizing the metastable structures [17]. After milling for 230h, the aggregated particles were broken and the particle sizes lower than 50μm were found in mechanically alloyed Ti-50B and Ti-66B powders.

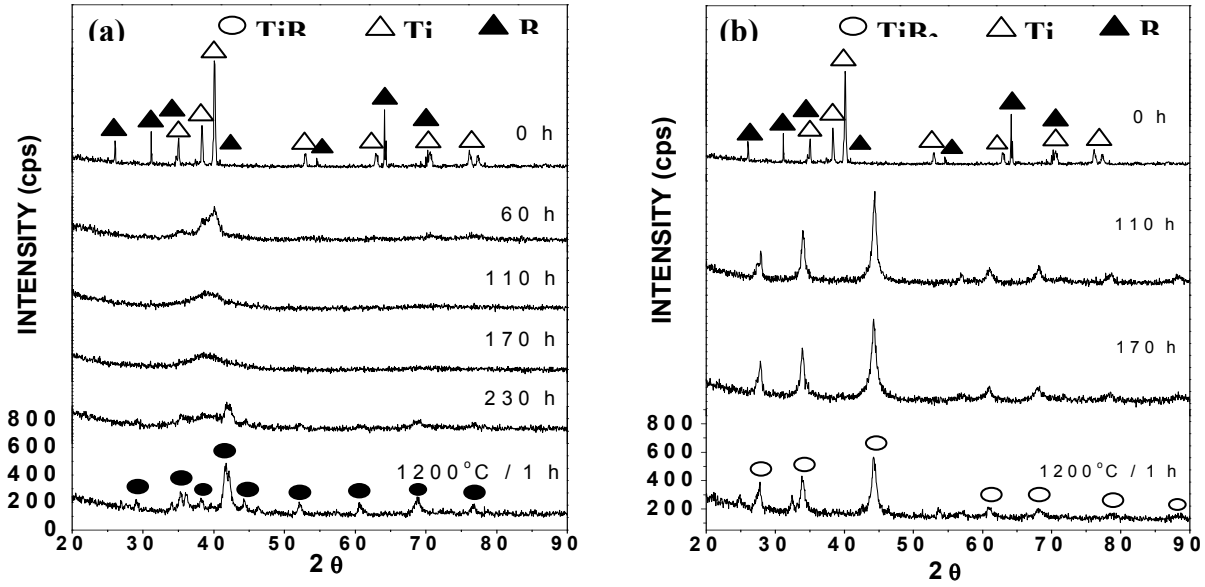

Fig. 1 – XRD patterns of (a) Ti-50B and (b) Ti-66B powders produced by high-energy ball milling after different times.

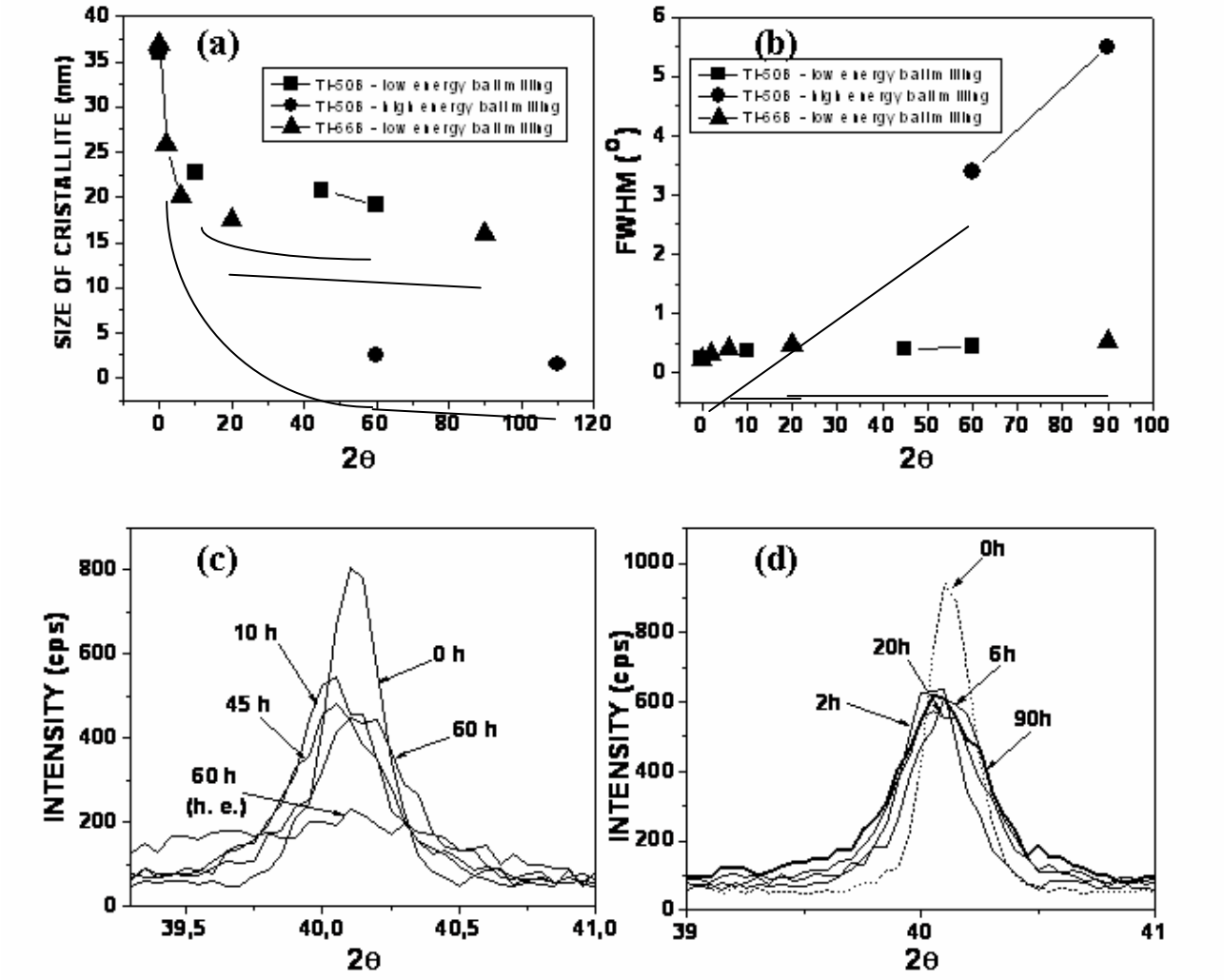

Fig. 2 – The (a) sizes of crystallite and (b) FWHM values of Ti-50B and Ti-66B powders milled at low and high energy conditions. Details on the effect of milling time on the position of Ti peaks in Ti-50b and Ti-66B powders milled at lower-energy condition are presented in (c) and (d), respectively.

The DSC curves after heating at 1200°C (20°C/min) of Ti-66B powders produced by low and high energy millings. Results indicated the presence of wide exothermic peaks located between 400° and 800°C, indicating that the TiB_2 formation was completed during heating. In this sense, the released heat from the disordered structures could have contributed for accelerating the diffusion mechanisms. As expected, the Ti-66B powders milled under higher-energy condition presented the higher released heat flow during the TiB_2 formation.

XRD patterns of mechanically alloyed Ti-50B and Ti-66B powders heated at 1200°C for 1h are shown in Fig. 1. A small amount of TiB and TiB_2 was found after heat treatments of Ti-B powders milled at lower-energy condition. In contrast, it was noted the major presence of intense TiB and TiB_2 peaks in Ti-50B and Ti-66B powders processed under higher-energy condition, denoting the effect of milling parameters on the synthesis of intermetallics.

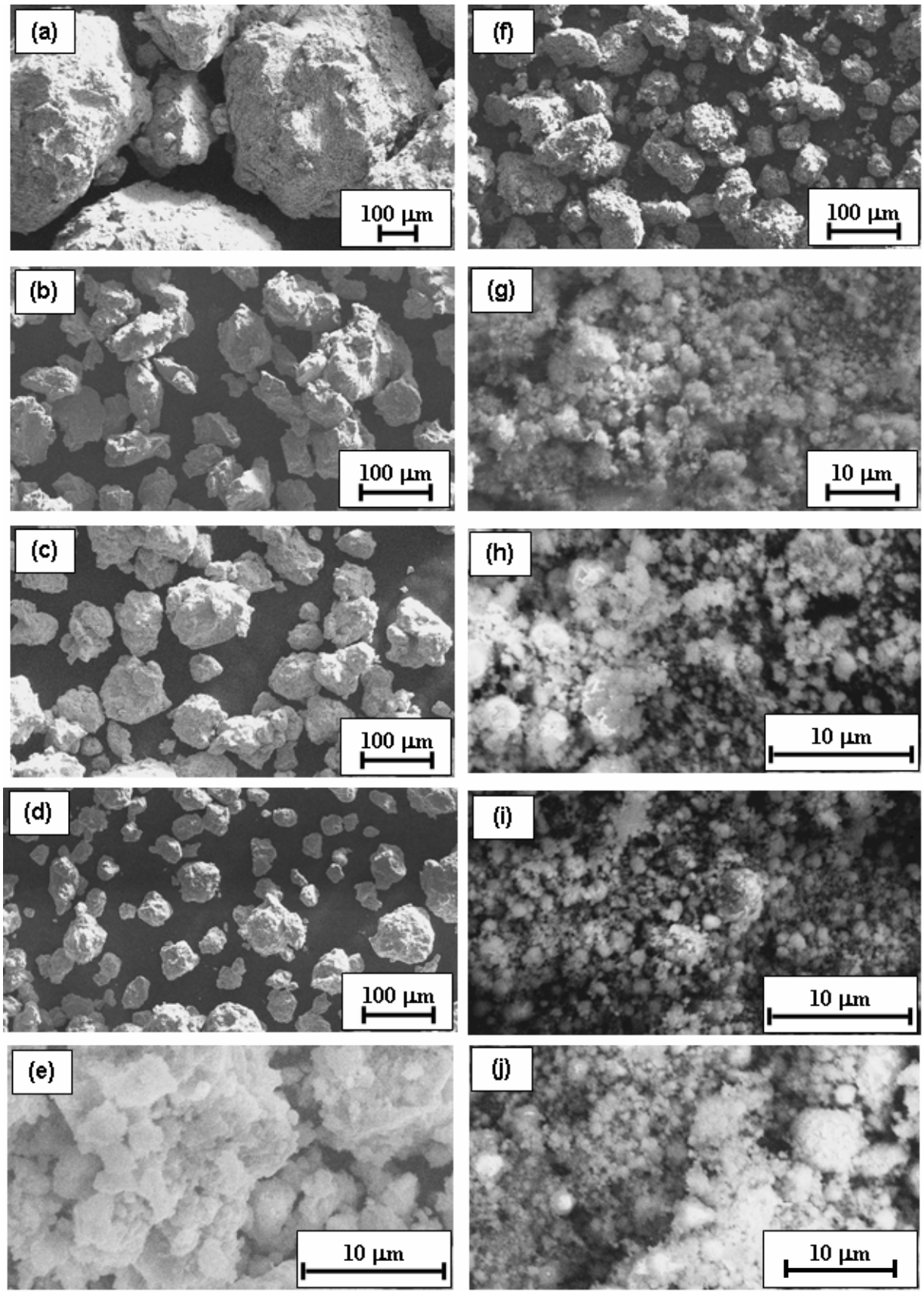

Fig. 3 – SEM images of (a-e) Ti-50B and (f-j) Ti-66B powders produced by high-energy ball milling after different times: (a,f) 10h, (b,g) 60h, (c,h) 110h, (d,i) 170h, (e,j) 230h..

Conclusions

The milling process under higher-energy condition synthesized the TiB and TiB_2 compounds while that only extended Ti solid solutions were found after ball milling under lower-energy condition. The atomic disordering of the TiB and TiB_2 compounds occurred for the longest milling times. DSC analysis revealed the presence of wide exothermic peaks during heating of previous Ti-50B and Ti-66B powder milled under higher-energy condition, indicating that exothermic reactions of TiB and TiB_2 formation were completed. In this way, the released heat from the disordered TiB and TiB_2 structures could have contributed for accelerating the diffusion mechanisms during heating of mechanically alloyed Ti-50B and Ti-66B powders.
A large amount of TiB and TiB_2 was formed after heating of Ti-50B and Ti-66B powders milled under higher-energy condition, denoting of effect of milling parameters on the synthesis of intermetallics.

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