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Abstract

Combination of good oxidation resistance, thermal stability, hardness and high strength are great interest properties in engineering and, that are possible to obtain with the Ni-Ti-B ternary system. Mechanical alloying (MA) is an alternative method and cheapest for the synthesis of this kind of metal-ceramic materials with respect to the traditional melt and quench process. The transformation sequence of all the mixtures reported the formation of \( \gamma \) Ni phase with a nodular morphology and identified the additional presence of the TiB\(_2\) phase (needle morphology), which was more evident with the increase of titanium content (M2 and M3 mixtures) after 24 h of milling. Thermal activation of the milled powders showed the nucleation and growth of the Ni\(_3\)B (O boride) and TiB\(_2\) (Hex) as the main phases after heat treatment, where the TiB\(_2\) phase (thin flakes morphology) was nucleated onto Ni\(_3\)B matrix. Ternary alloy by MA took place under a metastable equilibrium, offering the possibility to form glassy alloys for compositions, which are not accessible by melting or quenching techniques.

Keywords: mechanical alloying, metal-ceramic materials, Ni\(_3\)B and TiB\(_2\) phases, composite powder, high density

1. Introduction

Metal-ceramic materials (glassy metals) from ternary-eutectic alloys experiment several crystalline transformations where more than two phases or two stages of crystallization have been reported because they are a complex transformation. Different ternary alloys prepared
by melt spinning with a high content of Ni and B (78 and 18.2 at.% respectively, Ti as complement) have reported the formation of the orthorhombic Ni₃B (O boride), complex cubic boride (NiTi)₃B₆ (ɣ phase), and f.c.c. nickel (γ Ni) nucleates onto it, where the variation in the number of crystals and eutectic colonies by nucleation and growth processes were activated thermally [1].

B-Ni-Ti system is of great interest for scientist and technologist due to the combination of good physical properties of TiB₂ such as low density, high hardness, good electrical and thermal conductivity, high strength and good oxidation resistance. TiB₂ is a reinforced second phase with a great potential in the development of cutting tools that request high speed and the minimum dimensional variation (tolerances) and associate with their thermal stability. In combination with the Ni₃B phase in the nickel matrix, this metal matrix composite was studied to work out the requirements of the heat-resistant alloys. Physical and chemical stability at high temperature of this combination suggests the use of this compound as a corrosion and wear-resistant material under aggressive environments between other industrial applications.

Eutectic phase T,Ti₅Ni₁₅B₂₀ at high temperature transform in the compounds of (Ni)-Ni₃B, (Ni)-TiB₂ and (Ni)-TiNi₃, which are surrounding to the T phase during the solidification as shown in Figure 1 [2]. Investigations since 1958 by different methods, such as sintering of

Figure 1. Partial liquidus surface projection of Ni-Ti-B in at.% [2].
powders, induction melting, arc melting, and milling of commercial powders, have reported the TiB$_2$ phase at 1073 K (800°C) [2]. Because the B solubility in the Ni-Ti phases is very small at temperature lower than 1073 K, making it difficult to obtain the $\tau$ phase as a single phase at high temperature. Transformation sequence from the liquid phase reported four invariant equilibria in the Ni-Ti-B system where the $\tau$ phase is present in all time, such equilibria are:

$$L \leftrightarrow \tau + (Ni), L \leftrightarrow \tau + TiNiB, L \leftrightarrow \tau + TiB_2 \text{ and } L \leftrightarrow \tau + Ni_3B$$

(1)

Some authors have determined the possible phases theoretically calculated in the Ni-Ti-B system, where the results shows the transformation sequence according the most negative value of free energy $\Delta G^\circ$, as follows: (Ni), TiB$_2$, NiB, Ni$_4$B$_3$, Ni$_3$B, and Ni$_3$Ti, observing that (Ni) and TiB$_2$ are easiest to occur thermodynamically than the other phases [2].

The self-propagating high temperature synthesis (SHS) reaction has been used for the formation of TiB$_2$ compound. Due to the high exothermic energy, some difficulties in the growth control during the heat transfer and solidification are associated with the concentration of strong internal stresses and the subsequent cracks formation. For these reasons, the addition of a metallic element like Ni as diluent of the Ti-B system was necessary to reduce the heat evolution during SHS reaction and synthesize finer TiB$_2$ particles (4–6 μm) [2]. Studies in the Ni-Ti-B system by SHS reported the formation of TiB$_2$ and (Ni) as main products, with transient phases such as Ni$_4$B$_3$, Ni$_3$B, NiB and Ni$_3$Ti with a Ni content in the range from 30 to 70 wt.%, showing a minimum particle size of 0.6 μm with 70 wt.% Ni [3].

Ni$_3$Ti-TiB$_2$ obtained by SHS showed that during the combustion reaction, a eutectic liquid corresponding with Ni-76 at.% Ti transforms into NiTi and Ni$_3$Ti at 1215 K (940°C) with the characteristic that NiTi phase was observed at the combustion front during the quenching. TiB$_2$ phase was formed by reducing the NiTi with boron. So, the reaction sequence from the eutectic liquid at high titanium concentration can be indicated as [4]:

$$4Ni + 2Ti \rightarrow Ni_3Ti + NiTi$$

(2)

$$3NiTi + 4B \rightarrow Ni_3Ti + 2TiB_2$$

(3)

The glassy metallic alloys obtained by rapid quenching from the liquid phase have special features and different from those of crystalline alloys. Some problems in the production of bulk metallic glasses by casting techniques, are the changes in composition by the occurrence of many eutectic reactions in equilibrium during the rapid quenching, which affect the glass forming ability [5]. Metallic glass formation is not restricted to quenched process because a variety of methods based on the disordering process result in a crystal-to-glass transition such as the mechanical alloying (MA) of elemental powders, where a crystalline phase can be obtained from a disordered amorphous state to transform after that, in a crystalline stable phase activated thermally.

Through high temperature melting processes has been reported the formation of (Ni)-TiB$_2$ and (Ni)-Ni$_3$B composites with low titanium content. (Ni)-TiB$_2$ and (Ni)-Ni$_3$Ti composites were identified at high titanium content. The synthesis of the Ni-Ti-B system by high
temperature processes implies some problems during the solidification (out of equilibria), due to the changes in composition by the occurrence of a lot of eutectic reactions during the rapid quenching, that affect the glass forming ability \[ 5 \]. The glassy metallic alloys obtained by rapid quenching or melting process demand more energy consumption and elevated cost; for this reason, the mechanical alloying process was explored as an alternative method for the synthesis of this important glassy material.

2. Mechanical alloying of boride compounds

Since their beginning in the 1970s, mechanical alloying (MA) was used in the synthesis of base nickel alloys, expanding its applications to various alloy systems. MA is a non-equilibrium process similar to rapid solidification and tempering, where is possible to synthesize amorphous phases, intermetallic compounds and hardened materials by second phases, impossible to obtain with other techniques.

Conventional methods for preparing refractory compounds like boride, carbide and nitride phases are expensive with a long time-consuming. Mechanical alloying (MA) has been a one-step successful route in synthesizing these compounds, like an inexpensive and faster way \[ 6 \].

Thermodynamic studies have demonstrated that MA may reproduce crystalline, quasicrystalline, nanocrystalline and amorphous alloys \[ 6 \]. High melting point materials have been obtained with high-energy mills, under a strict atmosphere control and trying to reduce the wear at the mill wall and steel balls. Titanium diboride (TiB\(_2\)) is one example of this kind of compound of high melting point (2790 °C) synthesized by MA, with a wide use by their excellent physical stability at high temperature.

Some researchers have reported the synthesis of TiB\(_2\) by the mechanochemical reaction between Al-TiO\(_2\), B\(_2\)O\(_3\) and Al-B\(_2\)O\(_3\)-Ti, where the reduction of the oxide compounds catalyzes the formation of TiB\(_2\) \[ 7 \]. This possibility has been proposed for the manufacturing of nanocomposites materials in the solid state, with a ceramic reinforcement (TiB\(_2\)) dispersed in an oxide matrix that could be Al\(_2\)O\(_3\), TiO\(_2\) or SiO\(_2\) \[ 8 \].

Phase transformation in the Ti-B system synthesized by mechanical alloying (MA) have reported the formation of TiB\(_2\) by gradual diffusion reaction (GDR) mechanism \[ 9 \]. Ni-B system assumes some solubility of B in the Ni matrix with an increase in their lattice parameter to transform in (Ni) + Ni\(_3\)B, being more stable than the NiB phase, which need more dissolution of B in their structure \[ 6 \].

Composition of the mixture, process time, steel ball-to-powder ratio, balls diameter, atmosphere and the process control agent are some important variables in the MA process that determinates the result; so that, more studies about the synthesis of TiB\(_2\) and Ni\(_3\)B in the solid state are necessary. In this document, the effect of titanium content in the development of titanium and nickel borides by mechanical alloying was analyzed.
3. Experimental

Elemental powders of Ni, Ti and B with high purity (99.7, 99.5 and 99.3%, respectively) were used as started materials. To evaluate the effect of Ti content in the formation of TiB₂ and Ni₃B compounds, three mixtures were synthetized by mechanical alloying according to the compositions shown in Table 1. Stainless steel vial with the powder mixture and hardened balls of 4.76 and 12.7 mm in diameter was loaded into a glove box, evacuated during 1200 s (20 min) with a mechanical vacuum pump and after filled with argon gas to prevent the powder oxidation. Ethyl alcohol (2 c.c.) was used as process control agent (PCA) to maintain the balance between fracture and cold welding of the powders. High-energy equipment SPEX mill 80 was used with a ball-to-powder weight ratio of 10:1 until a maximum milling time of 86.4 ks (24 h). Structural evolution of the powders in function of milling time (each 21.6 ks) was characterized by X-ray diffraction (XRD) in a Bruker D8 advanced diffractometer with Cu-Kα (λ = 1.542 Å). Morphology of the powders at the maximum milling time (86.4 ks) was characterized by scanning electron microscope (Jeol 2000). Particle size was validated with a Zeta Sizer equipment, model Malvern MPT-2. Determination of powder’s density was evaluated at the end of the milling and after heat treatment at 1173 K (900°C), during 7.2 ks (2 h) under argon atmosphere.

Isothermal section at 1073 K (800°C) in Figure 2 shows the position in the ternary diagram of each synthesized composition, indicating the equilibrium phases to obtain. Yellow circle in the figure shows the composition of the TiB₂ phase under equilibrium condition. Each line concentrated at this point is projected to the main phases from the Ni-B and Ni-Ti binary alloys to indicate the equilibrium phases according to the eutectic reactions. The equilibrium phases for each composition used are indicated in Table 2, where the TiB₂ phase was reported in the three mixtures; however, the Ni₃B phase was not observed with the maximum content of titanium (24.36 at.%), indicating the formation of a phase between titanium and nickel (TiN₃).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Ni content</th>
<th>Ti content</th>
<th>B content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt. %</td>
<td>at. %</td>
<td>wt. %</td>
</tr>
<tr>
<td>M1</td>
<td>80</td>
<td>54.77</td>
<td>10</td>
</tr>
<tr>
<td>M2</td>
<td>70</td>
<td>47.25</td>
<td>20</td>
</tr>
<tr>
<td>M3</td>
<td>60</td>
<td>39.82</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 1. Composition of the mixtures obtained by mechanical alloying.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Equilibrium phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Ni₃B, NiB, TiB₂</td>
</tr>
<tr>
<td>M2</td>
<td>T, TiB₂, NiB</td>
</tr>
<tr>
<td>M3</td>
<td>TiN₃, TiB₂, T</td>
</tr>
</tbody>
</table>

Table 2. Equilibrium phases according to the isothermal section at 1073 K (800°C).
4. Results and discussion

4.1. Mechanical alloying

X-ray diffraction patterns taken each 21.6 ks (6 h) from the M1 mixture are shown in Figure 3. At 0 h of milling, the diffraction peaks of crystalline Ni, Ti and B were characterized. After 6 h of milling, the Ti and B peaks were not identified, observing the reduction in the relative intensity and widening of the nickel’s peaks. Between 6 and 18 h of milling, the intermetallic compound Ti₃B₄ (unstable) and the (Ni) phase were identified. At the maximum milling time (24 h), only the diffraction peaks corresponding with a solid solution of nickel (Ni) were characterized, identifying an asymmetric widening and reduction of the relative intensity from the nickel’s peaks, due to various factors such as the refinement of grain size and the increase of structure deformation, associated with the tendency to the formation of amorphous compound.

Figure 2. Isothermal section at 1073 K (800°C) of Ni-Ti-B in at.%, indicating the position of the M1, M2 and M3 mixtures respectively [2].
Powder evolution during the milling of the mixtures M2 and M3 is shown in Figures 4 and 5, respectively. For the composition M2 after 12 h of milling, the TiB$_2$ phase was identified; with more milling time and until the 24 h of milling, the TiB$_2$ and (Ni) phases with an asymmetric widening and reduction of the relative intensity from the nickel’s peaks were characterized.

Mixture M3 with more titanium concentration (24.36 at.%) reported the intermetallic compound Ti$_3$B$_4$ (unstable) and the (Ni) phase after 6 h of milling. With more milling time (12, 18 and 24 h), Ti$_3$B$_4$ was not detected and were characterized the crystalline phases of (Ni), TiB$_2$ and Ni$_2$B until the maximum milling time (24 h) with a less widening and more relative intensity from the nickel’s peaks with respect to the M1 and M2 mixtures. This condition was because the deformation energy was taken advantage in the TiB$_2$ and Ni$_2$B phases transformation and not in the formation of the solid solution over saturated of nickel (Ni).

Thermodynamic data of this system based on experimental information show that the most negative enthalpy of formation for the three types of Ti borides corresponds with the TiB$_2$ phase [10]. The structure of the titanium diboride phase is isomorphous [11] with a large homogeneity ranged from 61 to 70 at.% B, characteristic of the M2 and M3 mixtures at the maximum milling time.

According with the Figure 2 in the binary composition line of Ni-B, are identified the NiB, Ni$_3$B and Ni$_2$B phases with the increase of nickel content respectively; however, the formation of Ni$_2$B in the milled samples was more evident with the increase of titanium content. These means that the formation of the TiB$_2$ phase was more stable than the nickel borides and therefore, the largest amount of boron in the mixture reacted with titanium, resulting in a minimum relation of B/Ni in equilibrium; but enough to the formation of Ni$_2$B phase [12, 13].
Figure 4. X-ray diffraction patterns for Ni\textsubscript{70}Ti\textsubscript{20}B\textsubscript{10} at different milling times (composition in wt.%).

Figure 5. X-ray diffraction patterns for Ni\textsubscript{70}Ti\textsubscript{30}B\textsubscript{10} at different milling times (composition in wt.%).
Powder morphology after milling (24 h) for each composition is shown in Figure 6. M1 mixture has an acicular particles (Figure 6a and b) with a minimum particle size of 416.12 nm. Powder density determined by the Archimedes’ principle was 15.89 g/c.c. With the increase of titanium content (M2 and M3 mixtures), the characterized morphology showed composite particles constituted by nodular powder as matrix, with the nucleation of the TiB₂ crystalline phases like inserted needles, indicated with the black arrows in Figure 6d and f. The minimum particle size was 823.07 and 741.4 nm for the M2 and M3 mixtures, respectively. The increase of particle size in these two last mixtures respecting to the M1 mixture was due to the formation of a composite particle conformed by nodules and needles. The average density reported for both mixtures (M2 and M3) was 15.5 g/c.c. similar with the M1 mixture.

Figure 6. Characteristic particle shapes after milling (24 h). (a) and (b) Acicular powder particles in the M1 mixture; (c)-(f) nodular powder particles with inserted needles of TiB₂ phase in the M2 and M3 mixtures.
4.2. Heat treatment after milling

XRD patterns from the M1 mixture after milling and heat treatment (Figure 7) show the reflections corresponding with the $\text{Ni}_3\text{B}$, $\text{TiB}_2$ and $\text{TiB}$ phases where the deformation energy stored in the (Ni) phase at the maximum milling time was thermally activated to transform into the Ti and Ni borides. According to the number of reflections, the $\text{Ni}_3\text{B}$ phase is more crystalline and stable with respect to the $\text{TiB}_2$ and $\text{TiB}$ phases. According with the titanium content was expected more nickel boride phases ($\text{Ni}_3\text{B}$ and $\text{Ni}_2\text{B}$) as is indicated in Table 2; however the reactions between titanium and boron were more stable to transform in the two crystalline phases ($\text{TiB}_2$ and $\text{TiB}$) with a Gibbs free energy more negative with respect the reactions between Ni-B and Ni-Ti [14–16].

For the mixtures M2 and M3 (more titanium content respectively) after heat treatment (Figures 8 and 9), the phases identified in the milling change to $\text{Ni}_3\text{B}$ and $\text{TiB}_2$, moving the equilibrium towards the formation of $\text{Ni}_3\text{B}$ with less boron content, but with a higher mass relation because the relative intensity of the $\text{Ni}_3\text{B}$ peaks was taller than the $\text{TiB}_2$ peaks, resulted of a more coalescence and growth of $\text{Ni}_3\text{B}$ with respect the $\text{TiB}_2$ phase [17, 18]. Certain consistency was conserved with the equilibrium phases indicated in Table 2, with the exception that was not identified the eutectic $\text{Ti}$ phase. The representative reaction in the Ni-Ti-B system synthesized by MA and heat treated is as follows:

$$\text{Ni} + \text{Ti} + B \rightarrow (\gamma\text{Ni}) + \text{TiB}_2 \xrightarrow{\Delta} \text{Ni}_3\text{B} + \text{TiB}_2 \quad (4)$$

Powder morphology after heat treatment for each composition is shown in Figure 10. Composite particles were characterized in all the mixtures and are formed by particles with a nodular morphology as matrix and particles with thin flakes morphology as second phase.

![Figure 7. X-ray diffraction patterns for Ni$_{80}$Ti$_{10}$B$_{10}$ after milling and heat treatment (composition in wt.%).](image)
inserted at the matrix. The average particle size like composite was of 639.45 nm with a density powders that increased after heat treatment of 15.63–16.30 g/c.c. This density change was correlated with the more density of the phases Ni3B (orthorhombic), combined with the hexagonal TiB2 phase in the mixtures after heat treatment and with as a result of the nucleation and growth mechanism of both phases.

Figure 8. X-ray diffraction patterns for Ni$_{70}$Ti$_{20}$B$_{10}$ after milling and heat treatment (composition in wt.%).

Figure 9. X-ray diffraction patterns for Ni$_{60}$Ti$_{30}$B$_{10}$ after milling and heat treatment (composition in wt.%).
5. Conclusions

Ni-Ti-B system synthesized by mechanical alloying reported for the compositions with high content of nickel, a transformation sequence that consisted in the formation of (γ Ni) and TiB₂ phases after milling. With the increase in the titanium content, the formation of the TiB₂ phase was more evident, as was observed in the M2 and M3 mixtures.

Formation of the (γ Ni) phase by the accumulation of deformation energy during the milling was the first step for the subsequent transformation of the orthorhombic Ni₃B (O boride) and TiB₂ (Hex) phases thermally activated. The transformation sequence for the synthesis of Ni₃B and TiB₂ phases by MA was:

Figure 10. Nodular morphology particles with inserted thin flakes in all the mixtures after heat treatment at 1173 K (900°C). M1 (a and b), M2 (c and d) and M3 (e and f).
\[ Ni + Ti + B \rightarrow (\gamma Ni) + TiB_2 \xrightarrow{\Delta} Ni_3B + TiB_2 \]

Nanocomposite materials conformed by particles with nodular morphology and inserted needles were characterized after milling. High resolution microscopy showed the nucleation of thin flakes from the TiB₂ phase in Ni₃B matrix after heat treatment.

Titanium and nickel not showed the formation of a solid solution with the milling, so that was not enough the activation energy for the formation of the TiNi₃ intermetallic compound; indicating a Gibbs free energy (\(\Delta G^0\)) more negative for the transformation of TiB₂ and Ni₃B phases.

TiB₂ and Ni₃B intermetallic compounds, have a great potential in the development of coatings for cutting tools [19]; specialty when is necessary high speed of machining with the minimum dimensional variation (tolerances) and associate with their thermal stability, high hardness and wear resistance.

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