Engineering and Technology Research 3(0): 000-000, November 2019
DOI: 10.15413/etr.2019.0108

ISSN: 2682 5716

Research Paper

Study of commercially pure aluminum grain refining by TiB_2, processed by high-energy ball milling

Accepted

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ABSTRACT

The present study was conducted to analyze the effect of processing of titanium diboride (TiB_2) by high-energy milling, in grain refinement of commercially pure aluminum. TiB_2 powders were milled during 8 and 16 h and subsequently mixed with aluminum powder at 0.15 and 0.3%(in wt.-%) for the final melt load. The samples were compacted into pastilles ("carriers") of 3 mm diameter and sintered with and without the presence of copper. These pastilles were added in the molten aluminum,to promote its dissolution and disperse the boride particles. The molten aluminum was subsequently poured in a thermal analysis cup, where the solidification occurred. The results showed a significant grain refining for the samples inoculated by pastilles with TiB_2 milled, as compared with samples inoculated with TiB_2 without milling.

Key words: High energy ball milling, titanium diboride, grain refining, casting and solidification, aluminum.

INTRODUCTION

Commercially cast aluminum alloys require a refined and equiaxial grain structure (Rooy, 1992; Quested, 2005). It is dependent on several factors such as chemical composition, solidification rate, and the addition of inoculants that provide heterogeneous nucleation sites (Rooy, 1992). The addition of these inoculants takes place typically by insertion of solid particles to the molten aluminum; thus, generating a higher number of nucleation sites in the liquid metal, producing grain refining by either nucleation and suppression of grain growth mechanisms (Easton and John, 1999; Quested, 2005).

Industrial inoculants for aluminum alloys are based in the Al-Ti-B system (Greer, 2003; Quested, 2004, 2005), whose most common composition is Al-5%Ti-1%B (in wt.%)(Ghadimi et al., 2013; MCcartney, 1989; Quested, 2004; Wang et al., 2012; Wannasin et al., 2013). The inoculation involves the addition of a master alloy, generally in the form of a rod, to the molten aluminum, to allow the introduction of TiB_2 and Al_3Ti particles inα-aluminum matrix (Quested, 2004). Thus, the α-aluminum works as a "carrier" and the Al_3Ti particles dissolve (Quested, 2005) in the bath due to the tendency of dissolution of titanium, while the TiB_2 particles remain stable. The refining power of Al-Ti-B master alloy is only useful when the titanium amount is in excess, to promote its combination with boron in the TiB_2 form. Therefore, the titanium in excess serves as solute next to the solidification front (Greer et al., 2000), which restricts the α-aluminum grain growth (Easton and StJohn, 1999; Quested, 2004; Quested, 2005). In this case, the role of TiB_2 is acting as an effective nucleant(Quested, 2005).

However, there are some problems related to the use of Al-Ti-B system like inoculant, such as the tendency to agglomeration and "poisoning" (Greer, 2003). When TiB_2 particles are added to the molten metal, even though they have a relatively small initial size, they tend to form agglomerates reaching the micrometric scale. One of the possible solutions for this problem is the use of high-energy ball milling,which is the main objective of this study. This technique is proven to be useful in obtaining materials with a refined and homogeneous structure, as well as nanometric-sized powder particles. The central idea is to get pastilles with milled TiB_2 particles involved in aluminum powder so that each particle acts as a single substrate to the α-aluminum during the solidification. Thus, there would be a higher number of nucleation sites dispersed in the bath, possibly leading to a more refined and equiaxial grain structure.

MATERIALS AND METHODS

The TiB_2 powders were processed by high-energy ball milling in a SPEX mill, during two different periods (8 and 16 h)to investigate the effect of milling time on microstructural refining. Stearic acid was used as a process control agent in the $C_{18}H_{36}O_2$ composition. A commercially pure aluminum (99.7 wt.-%) powder was used as the base material for "carriers." Particle size distribution analysis was performed by laser scattering.The mean diameter of TiB_2 particles was 16.72 μm before milling. The aluminum powder particle size varied between 10 and 50 μm. The milling products were mixed with elementary aluminum powders in proportions as shown in Table 1. This also provides a design of the experiments, including the TiB_2 content in the molten aluminum bath.

TiB_2 powder without milling was used for comparison with samples inoculated with milled material. After the mixture, the powders were compacted in a cylindrical matrix with 8 mm in diameter, using a maximum tension of 100 MPa. Due to the difficulty of incorporating the pastilles into the molten aluminum, sintering process in a tubular furnace was performed at a temperature of 600°C during 30 min. To promote liquid phase sintering, an addition of 5% of Copper(in wt.-%) was conducted in the samples 4 to 7.

Melts were prepared with 99.7% pure aluminum ingots provided by CBA(Brazilian Aluminum Company). Table 2 shows the chemical composition supplied by the manufacturer.

Aluminum strips with approximately 300 g were cut from an ingot. The casting process was conducted by charging the pieces into a graphite crucible, which was inserted in a Muffin furnace at a temperature of 800ºC. After the complete melting of aluminum, the inoculant sintered samples ("carriers") were introduced in the molten metal. A graphite rod was used to stir the molten metal aiding the dissolution and homogenization of bath. A time of about 15 min was observed to the bath homogenization.

The aluminum melt was poured at 800ºC into thermal analysis cups, and the solidification takes place.

The solidified samples were cut in a half-cross-section, grounded, polished and chemically attacked with concentrated Keller reagent (66 ml of HNO_3, 33 ml of HCl and 1 ml of HF) to reveal the macrostructure of grains.

Additionally, the samples were analyzed in a magnifying glass, and the images are used to determine the grain size, according to ASTM E112-96 standard.

RESULTS AND DISCUSSION

Figure 1 shows the morphology of TiB_2 powders processed by high-energy ball milling at different times (8 and 16 h).

For both milling times, a significant reduction of the particle size occurs when compared with the material without milling. However, the morphology does not change significantly between 8 and 16 h of milling. As the particle size decreases, a substantial increase in the surface area of the powders is observed.

In the casting step, a preliminary run with the addition of Al + 20% TiB_2 (as-received) was performed to compare the macro- and microstructures obtained via the addition of TiB_2 processed by high-energy ball milling. Figure 2 shows the solidification macrostructure of the mentioned sample.

One can observe that the presence of TiB_2 in the bath caused refining of the solidification macrostructure, probably by enhancing nucleation and suppressing columnar growth, providing a more equiaxial grain structure. However, the refinement was not accentuated. The next six melts were performed with the addition of TiB_2 processed by high-energy ball milling. Figure 3 shows the comparison of the grain structure of the sample without milling with the samples prepared in different milling times (8 and 16 h), different sintering conditions (with and without copper), besides TiB_2 contents in the bath (0, 0.15 and 0.3% inwt.%).

The efficiency of TiB_2 processing by high-energy milling is remarkable, observing the differences between the macrostructure of the sample inoculated with Al-20% TiB_2 without milling (a), and that of the melts in which the carriers were prepared with TiB_2 milled: (b) to (g). These samples had a much more significant degree of grain refining.

Samples (d) to (g) were inoculated with sintered carriers with the addition of copper (5% in wt.) since the sintering of aluminum alloys occurs via liquid phase. As can be observed, the addition of copper did not affect the grain structure, as compared with the macrostructures of samples (b) and (c) sintered without the presence of copper.

Another essential variable to be observed in Figure 3 is the milling time of TiB_2. The macrostructures did not change significantly with milling time, as can be seen by comparing samples (b) to (e), obtained in samples milled during 8 h, with samples (f) and (g), milled during 16 h. This behavior was expected since Figure 1 shows that there was no relevant difference in the morphology and particle size of the milled powders at different times. Therefore, the final result of the molten aluminum grain structure should be similar.

The increase in the content of TiB_2 from 0.15 to 0.30%(in wt.%) in the castings did not result in a higher degree of grain refining, as shown in macrographs (f) and (g), for TiB_2

Table 1: Composition of the loads, milling time, and type of sintering used.

Test run number	Amount of aluminum powder (% by weight)	Amount of TiB_2 powder (% by weight)	Milling time (h)	TiB_2 content in the bath (% by weight)	Type of sintering
01	80	20	-	0.15	Without copper
02	80	20	08	0.15	Without copper
03	80	20	08	0.30	Without copper
04	80	20	08	0.15	With copper
05	80	20	08	0.30	With copper
06	80	20	16	0.15	With copper
07	80	20	16	0.30	With copper

Table 2: Ingot chemical compositions (% by weight) used in the melting.

Element	Amount (%)
Al	99.7
Si	0.08
Fe	0.18
C	0.01
V	0.01

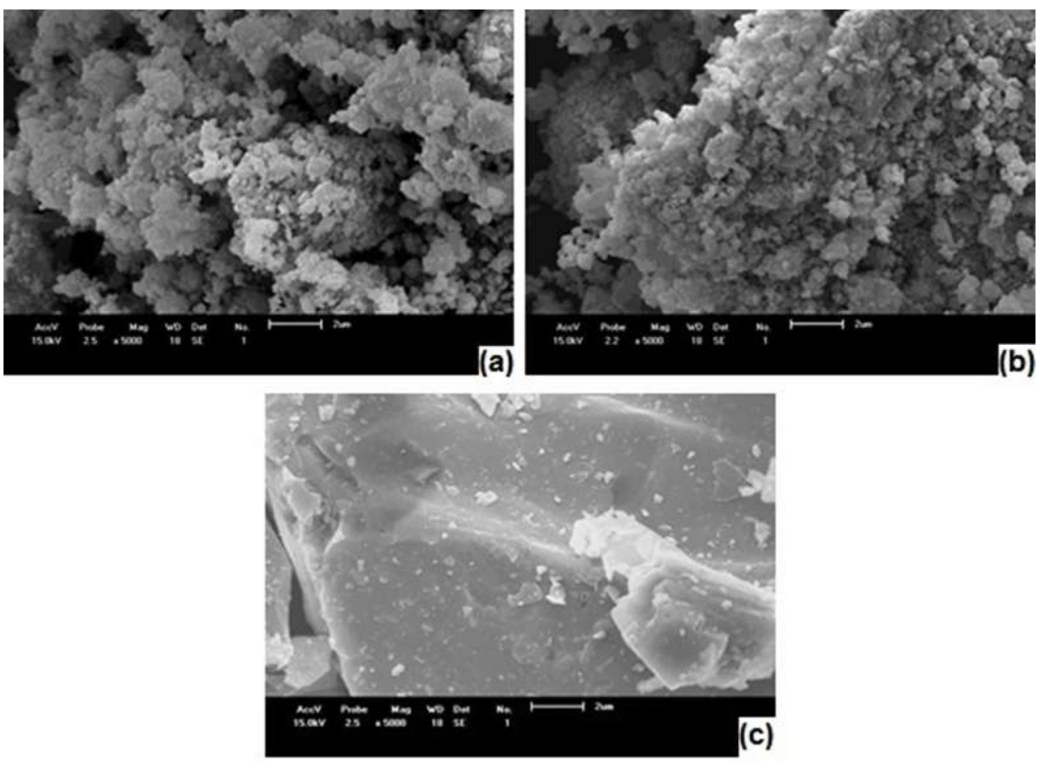

Figure 1: Comparison between the morphology of TiB_2 powders. (a) milled for 8h; (b) milled for 16h e (c) without milling.

additions of 0.15 and 0.30% (in wt.%), respectively. The sample inoculated with 0.15% TiB_2 presented a slightly higher refinement, suggesting that concentrations of about 0.15% may result in higher refinements.

For grain size quantification, the mean grain diameter calculations of each sample were performed. Figure 4 shows the images taken with the aid of a magnifying glass, together with the highlighted grain boundaries. The

Figure 2: Test run 1 macrography: Addition of 0.15% (in wt.%) of TiB_2 in the bath.

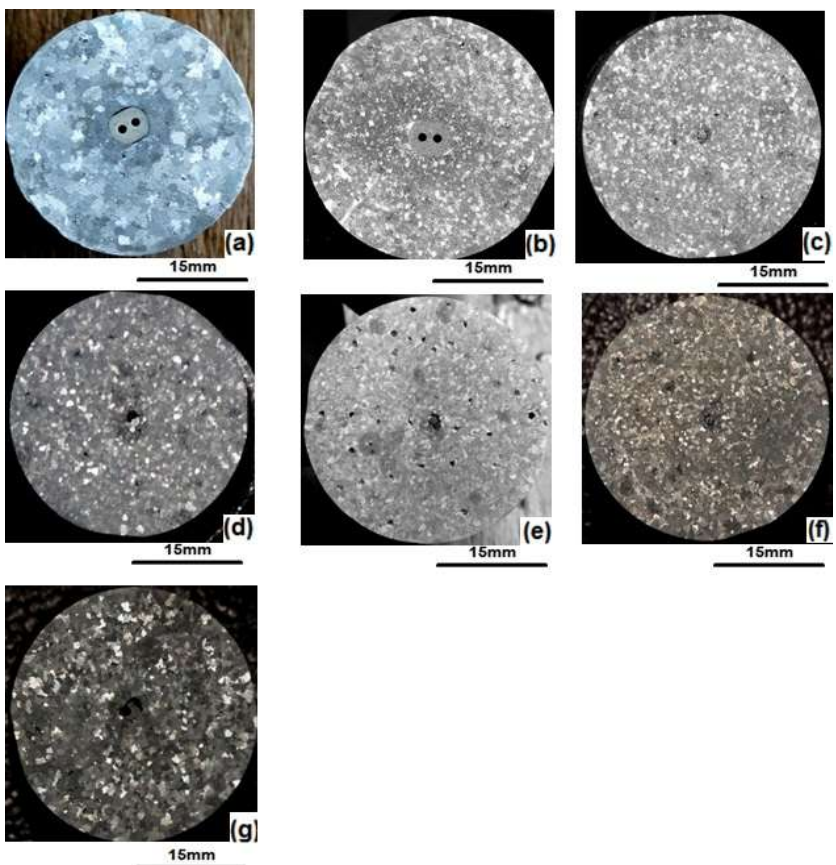

Figure 3: Comparison of test runs with and without milling in different conditions. (a) inoculation with Al-20% TiB_2 pastilles without milling (0.15% TiB_2 in the bath); (b) inoculation with Al-20% TiB_2 pastilles (0.15% TiB_2 in the bath), milling in the Spex mill for 8 hours, sintering without copper; (c) inoculation with Al-20% TiB_2 pastilles (0.30% TiB_2 in the bath), milling in Spex mill for 8 h, sintering without copper; (d) inoculation with Al-20% TiB_2 pastilles (0.15% TiB_2 in the bath), milling in the Spex mill for 08 hours, sintering with copper; (e) inoculation with Al-20% TiB_2 pastilles (0.30% TiB_2 in the bath), milling in the Spex mill for 8 h, sintering with copper; (f) inoculation with Al-20% TiB_2 pastilles (0.15% TiB_2 in the bath), milling in the Spex mill for 16 h, sintering with copper; (g) inoculation with Al-20% TiB_2 pellets (0.30% TiB_2 in the bath), milling in the Spex mill for 16h, sintering with copper.

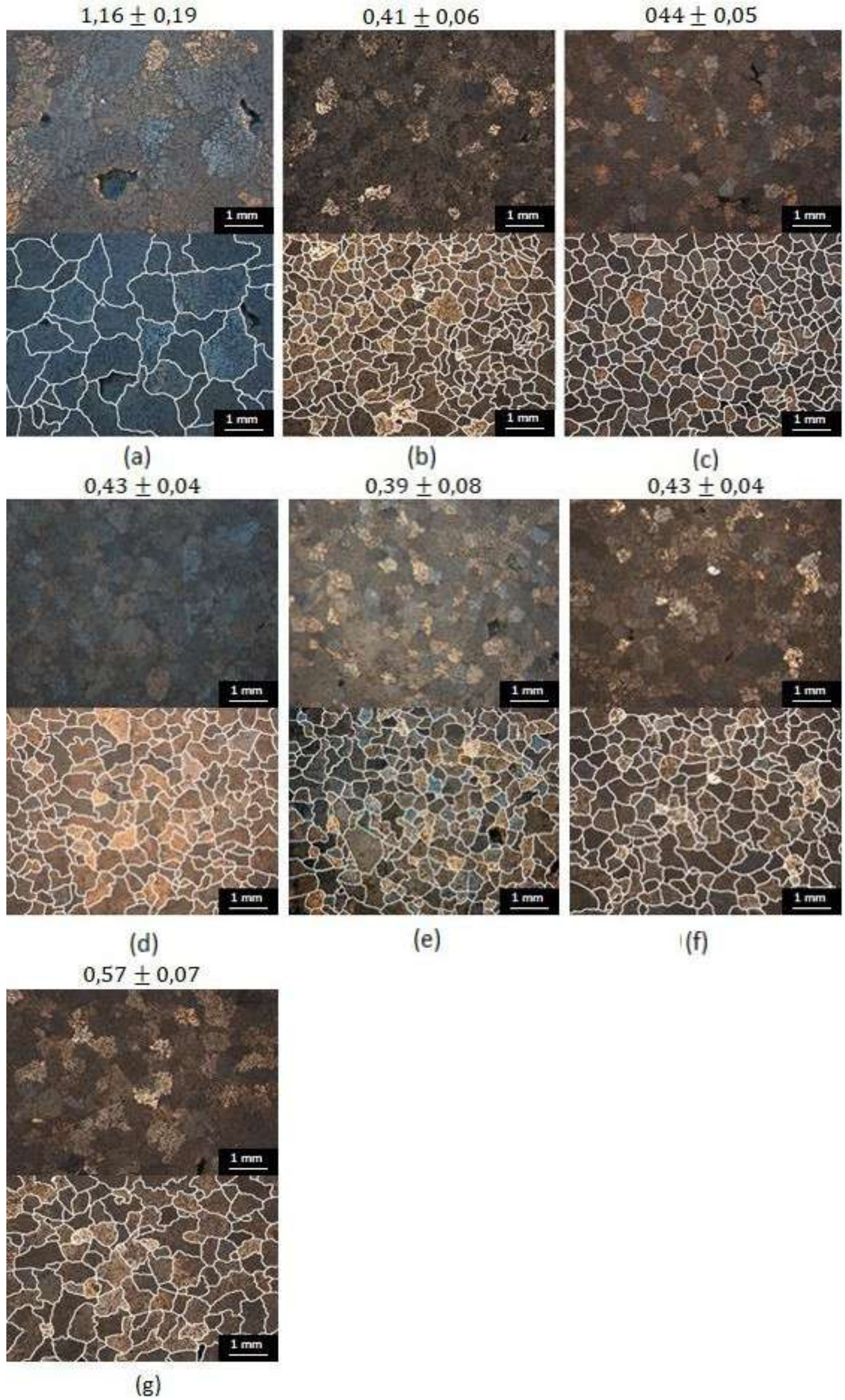

Figure 4: Magnifying glass images of samples, featuring grain boundaries. Grain boundary mean diameter and standard deviation (in mm). (a) Sample 13; (b) Sample 14; (c) Sample 15; (d) Sample 16; (e) Sample 17; (f) Sample 18; (g) Sample 19.

average grain diameters of each sample and their respective standard deviations are also shown.

It can be observed again the discrepancy between the grain size of the sample where it was used TiB_2 without milling and the samples with milled TiB_2, which have on average a value of 61.2% lower average grain diameter. This fact demonstrates the effectiveness of decreasing the size of the inoculant particles to provoke a higher number of solidification nuclei per unit area, and suppression of grain growth, and consequently reducing grain size.

Conclusions

Based on the results presented in this study, the following conclusions can be drawn:

1) The use of high-energy ball milling as an alternative route for the preparation of inoculant carriers from commercial TiB_2 powders provided higher grain refining, under all investigated processing conditions.
2) The presence of copper used in the sintering step did not change the resulting grain structures.
3) The high-energy milling of TiB_2 for 8 h proved to be useful in the preparation of inoculant carriers.The resulting grain structures did not vary significantly for higher milling times.The increase of TiB_2 content in the bath from 0.15 to 0.30% (in wt.%) did not result in an enhancementof the degree of the grain refining.

ACKNOWLEDGMENTS

The authors are grateful to the Coordination for the Improvement of Higher Education Personnel (CAPES) and National Council for Scientific and Technological Development (CNPq) for the doctoral scholarship.

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