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In-situ formation of borides and enhancement of powder metallurgy properties

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ABSTRACT

Considering the demands for the high strength and corrosion resistant powder metallurgy parts, the most direct yet cost effective method of production of borides can be possibly be routed through the in-situ solid-state reaction in powder metallurgy. Going by the known reaction paths, a composition of boron carbide and silicon carbide in combination with aluminum was investigated at three different sintering temperatures in order to see the effect of boron carbide on mechanical properties of aluminum under conventional high temperature sintering conditions. The limited study on high temperature sintering using SiC and B_4C showed gradual improvements in strength sintering above 750 ºC, which can be attributed to the in-situ formation of Si as well as SiB_n, where n= 2, 4, 6 ….

1. Introduction

Low density materials have attracted much interest as structural materials, particularly for use in the medical, marine, automotive and aerospace industries. In that respect of Beryllium (Be-alloys), Magnesium (Mg-alloys), Aluminum (Al-alloys) and Titanium (Ti-alloys) are of only interest in the lightweight alloy category because of their high strength-to-weight ratio. Excepting Be alloys, these alloys are mostly of low toxic nature compared to heavy metals.

Several past studies on Mg alloys have shown that adding hard metal boride particles improved mechanical properties of Mg alloys with high workability. These studies typically used the alloys, AlB_2 and MgB_2 and results showed progressive improvement in strength with the increase in boride content. However, the process requires that the reaction system be carefully screened. Favorable thermodynamics of the anticipated reaction is the pre-requisite for the process to be applicable. Reasonably faster reaction kinetics is also required to make the process viable in all practical purposes. The process of in-situ formation of few metal borides was discussed recently elsewhere with reference to strengthening boron carbide B_4C [1,2]. However, it is still very challenging to improve the material properties of Al and Mg matrices during sintering. The use of metal silicides, carbides, and borides to induce major microstructural rearrangement for improving strength is the general trend.

In this communication, mostly the compositions with Al is reviewed where various complex borides form in-situ in the presence of reactive compositions like B_4C and Silicon Carbide (SiC). A yet another important objective of the present study was to see their effects on the mechanical properties of Al under conventional high temperature sintering conditions.

2. Materials and methods

B_4C of 99% purity was obtained from American Elements and aluminum alloy powder 601 was obtained from Reade Metal Powders. Micro-fine SiC powder was obtained from Washington Mill. In all formulations studied, a small quantity of graphite was intentionally added for its function as a lubricant and also as a reduction aid. SiC was used as a reactive additive for both Al and B_4C. The formulations studied are given below in Table 1.

Transverse rupture (TR) strength bars were compacted using pressures of 250 MPa to determine the static mechanical properties of each formulation. Cylindrical

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Table 1. The formulations studied in the experiments

Formulation	Al%	B_4C%	SiC%	Graphite%
1	92	7.8	0	0.2
2	91	7.8	1	0.2
3	87	11.3	1.5	0.2
4	83	14.8	2.0	0.2
5	80	17.3	2.5	0.2

test slugs of a diameter of 0.5 (~13 mm) inches were compressed to a height of approximately 1 inch (25 mm) as per the MPIF standard test procedures. Test samples were compacted to ~ 2.1 g/cc green density. All test samples were then subjected to hot vacuum degassing (HVD) at around 500ºC prior to being sintered at temperatures ranging between 650-850ºC for an average of 140 minutes. HVD was employed for the purpose of minimizing voids and to minimize dimensional changes during sintering. Total sintering time of 140 min included the time in pre-heating zone, heating zone and cooling zone. To achieve best condition of the sintered parts, the residence time in each zone was selected between 60-65 min, 15-20 min and 60-65 min respectively.

The sintered densities were measured using a volume displacement technique. The sintered samples were tested for bending strength and compressive strength. The method of preparation of the powder matrices comprised cold-pressing of uniformly mixed Al powders and the in-situ boride formers. Then by heating the cold-pressed compacts under vacuum or in an inert atmosphere, to a temperature above the melting point of Al and then cooling the heated compact to solidify Al. The in-situ boride formers can be any suitable metal oxide, carbide or metal powders like Si, Co, Ni etc.

By using metal oxides, individual metal borides can be produced in-situ through B_4C reduction. B_4C with its inherent carbon impurity further accelerates the in-situ reductions as the reduction process requires the presence of some carbon (Eq. 1.).

$$2MO_{n\ (n=1\ or\ 2)} + B_4C + 3C \rightarrow 2MB_{m\ (m=2,\ 3,\ 4,\ 6)} + 4CO \qquad (1)$$

However, for Al powder metallurgy the in-situ boride formers can be very effectively carried out using SiC instead of other metal oxides or carbides. The use of fine metal powders like Si, Co and Ni, preferably Si and Co, in combination with B_4C form complex borides and carbides in-situ providing excellent mechanical property [1,2]. Those reactive metal powders show very good chemical affinity for boron and carbon. For example, Si with B_4C forms SiC and complex silicon borides like SiB_4, SiB_6 and also B_6SiC_2. The advantage of using silicon over other reactive metals is, the reaction and migration across the Al grain boundary occurs at a relatively lower sintering temperature. Moreover, Al even in its liquidus state interacts well with B_4C to form various binary and ternary phases such as aluminum boride, aluminum carbide and aluminum borocarbide (AlB_{10}, Al_4C_3, Al_3B_4C etc.), of which, the ternary phase aluminum borocarbide is most commonly formed.

There have been several powder metallurgy studies carried out in the past on Al in the presence of B_4C. These studies revealed the temperature dependencies for improved mechanical properties of Al where B_4C interacted with Al, forming various borides and boro-carbides, complex forms of boron and carbon, [3-5,6].

3. Results and discussion

B_4C is a very hard (9.5+ in Mohs scale), low specific gravity (2.52), covalent ceramic which offers distinct advantages when used for applications requiring low density, high strength metal composites involving Al and Mg. The experiments demonstrated that the mechanical properties of Al can be significantly improved through its association with B_4C. The main advantage of the compositions studied is, the low-melting-point metal phase of Al, which can probably wet the surfaces of B_4C and SiC effectively starting from its liquidus state during sintering at near or above the melting point of Al. As shown in Figure 1, the densities of all formulations studied indicates that densification significantly improved as the temperature increased above the melting point of Al. In addition, the resulting composites also showed improved mechanical properties. For the composites assessed through the present study, processing temperatures were kept below 1000°C. The primary interest of this study was to investigate the behavior of B_4C and its reactivity with Al in the presence of SiC. Al being the low melting component, Al wetted B_4C and SiC particulates were brought into close proximity for controlled reactions within the system. Wetting was necessary to achieve strong interfacial bonding and to allow liquid rearrangement during sintering. In order to allow consistent wetting to happen, the green parts were subjected to hot vacuum degassing at approximately 450-500°C. The hot vacuum degassing process minimizes the formation of pores.

The nature of the interfacial reaction between Al particulates and SiC below the melting point of Al is well known [1]. The reaction begins in-situ around 600°C. Aluminum reduces SiC to form Al carbide and Si (Eq. 2.):

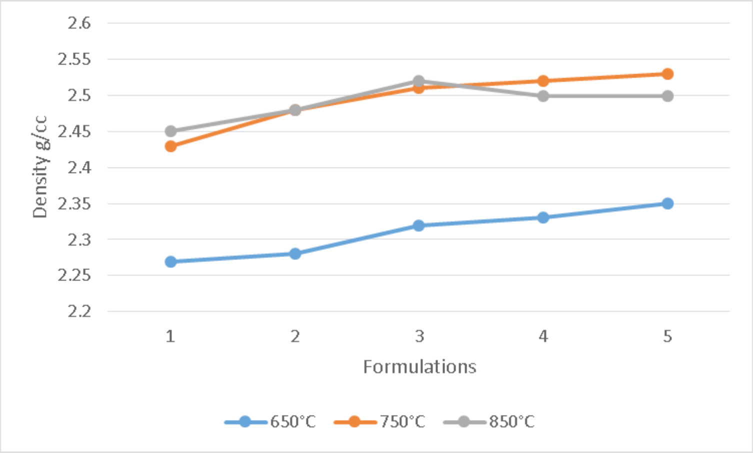

Figure 1. Density of the sintered compositions studied at three different sintering temperatures.

$$4Al + 3SiC = Al_4C_3 + 3Si \qquad (2)$$

Si thus formed in-situ can act two ways; (1) it can get dissolved into Al quickly, and (2) trans-migration of Si occurs towards B_4C bringing about changes in the structural property of B_4C during sintering [1,2].

Variation in density of the sintered parts is shown in Figure 1. At a lower sintering temperature (650°C) the rise in density was very modest. However, at sintering temperatures above 750°C there was a sharp rise in density approaching near true density of the composite indicating the flow of liquid and space filling during the sintering process. The density trend also suggests that the maximum density achieved by the formulations with 1-1.5% SiC at 850°C is probably due to the formation of adequate Si to act as glue between Al and B_4C.

A three-point bending test was employed to assess the mechanical properties of sintered compacts using the INSTRON 5869 machine having a 1000 kN maximum load. Transverse rupture strength (TRS) was calculated using the Eq. 3 [7,8] as follows:

$$\sigma_T = 3F_BL / 2W\tau^2 \qquad (3)$$

Where σ_T is transfer rupture strength, F_B is bending failure load, L is distance between the lower support rods, W is the width of the specimen and τ is the thickness of the specimen. A compression pressure of 480 MPa was used. For compressive strength, the area of the specimen varies upon compression. The stress (the force divided by the area) and compressive strength can be expressed as Eq. 4,

$$\sigma_e = \frac{F}{A_0} \qquad (4)$$

A_0=Original specimen area, and F=load applied just before crushing. Correspondingly, the strain is expressed as Eq. 5,

$$\varepsilon_e = \frac{l - l_0}{l_0} \qquad (5)$$

where l = specimen length before crushing. The hard-

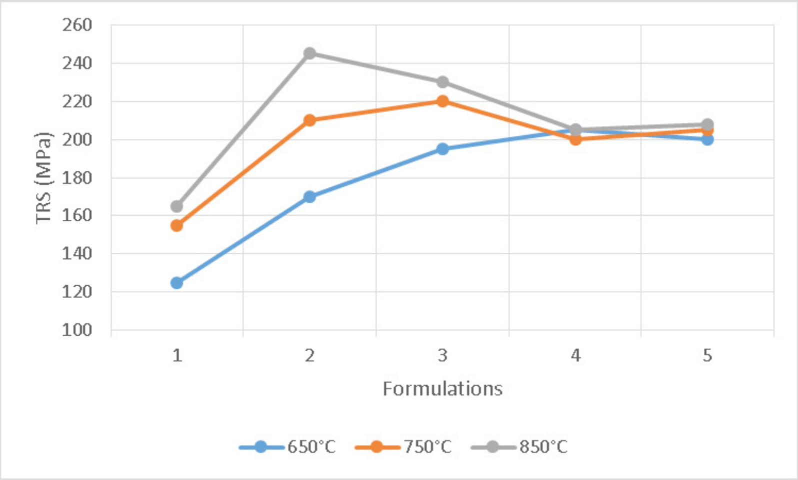

Figure 2. Transverse Rupture Strength of the compositions studied at three different sintering temperatures.

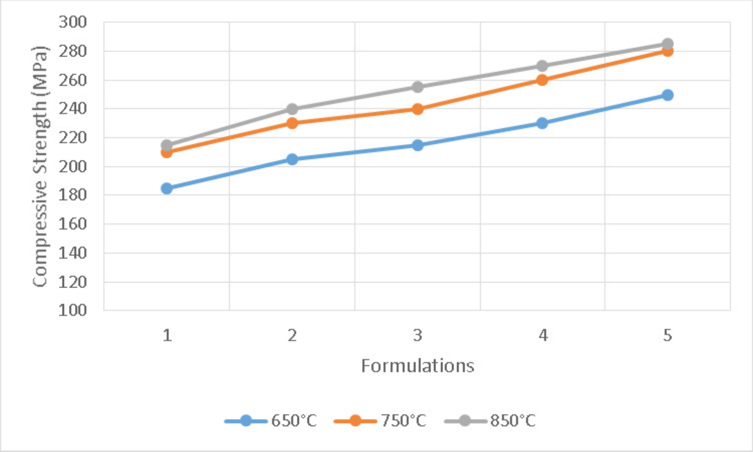

Figure 3. Compressive strength of the compositions studied at three different sintering temperatures.

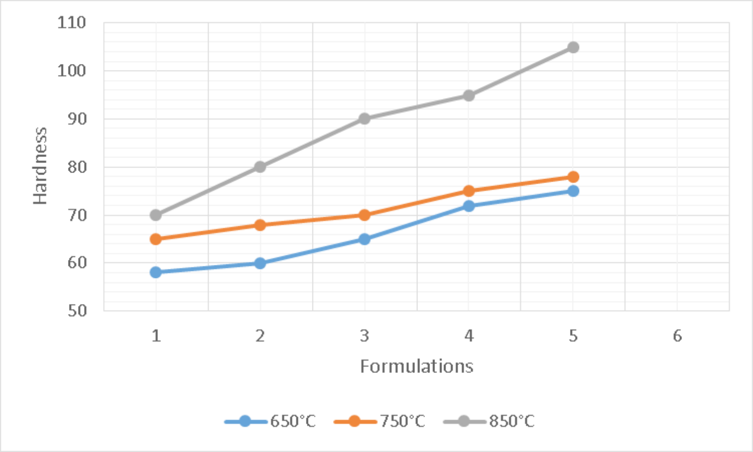

Figure 4. Vickers Microhardness of the compositions studied at three different sintering temperatures.

ening of the compacted sintered matrix of the formulations studied are shown Figure 2-4.

It is interesting to note from both the transverse rupture strength and compressive strength graphs that there exists some sort of optimized synergy between B_4C and SiC in compositions 3 and 4, where SiC varied between 1.5-2%. However, vickers hardness revealed a sharper rise in hardness at sintering temperatures above 750°C.

Further studies are in progress to carry out detailed spectral analysis of the microstructures of the composites to confirm interfacial compositions at the grain boundaries. Nevertheless, previous studies on the interaction of B_4C with other metal oxides and carbides [1,2] and various other existing literatures suggest that the observed increase in hardening is most probably due to the chemical reaction. In-situ formation of complex borides along with the formation of Si further accentuates the effect. Si helps to bind B_4C with Al as it is interactive with both Al and B_4C at their interfaces, thereby improving the mechanical properties of the composites.

4. Conclusions

The results obtained in the experimental studies can be summarized as follows;

- The primary interest of this study was to investigate the behavior of B_4C and its reactivity with Al in the presence of SiC following the primary reaction paths:

  $Al_2O_3 + 3B_4C + C = 2AlB_{2\text{--}12} + 3CO$ (i);

  $4Al + 3SiC = Al_4C_3 + 3Si$ (ii); and

  $4Si + nB_4C = 4SiB_n + C$ (iii)

- The limited study on high temperature sintering using SiC and B_4C showed gradual improvements in strength, which can be attributed to the in-situ formation of Si as well as SiB_n, where n = 2, 4, 6, ….

- Si being highly soluble in Al, the strengthening of Al also suggest the transmigration of Si as well as SiB_n across the Al grain boundaries.

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References

[1] Chattopadhyay A. K., Selective migration of metals and metal borides to strengthen boron carbide, Met. Powder Rep., 71(2), 106, 2016.

[2] Chattopadhyay A. K., Yilmaz O., Bilen M., Baris M., Strengthening boron carbide and prevention of high pressure amorphization by inducing metals or metal borides across the grain boundary during hot pressing or sintering, Adv. Powder. Metall. Part. Mater., 7, 1–12, 2015.

[3] Viala J.C., Bouix J., Gonzalez G, Esnouf C, Chemical reactivity of aluminium with boron carbide, J. Mater Sci., 32, 4559-4573, 1997.

[4] Oh S.Y., Cornie J.A., Russel K.C., Wetting of ceramic particulates with liquid aluminum alloys: Part II. Study of wettability, Metall. Trans. A, 20, 533-541, 1989.

[5] Nobel B., Trousdale A.J., Haris S.J., J. Mater Sci., 32, 5969, 1997.

[6] Gokmese H., Bostan, B., Baris, M., Fabrication and characterization of nanoceramic particle al_2o_3/b_4c composite by mechanochemical approach, Inorganic and Nano-Metal Chemistry, 47 (3), 416-422, 2017.

[7] German R. M., Powder metallurgy and particulate materials processing, MPIF, 377-78, 2005.

[8] MPIF Standard: Method for determination of transverse rupture strength of powder metallurgy materials, MPIF Standard Test Methods, 2006.