FORMATION OF ZrB_2-AlN POWDER MIXTURE BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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Abstract: *Formation of ZrB_2-AlN mixed powder by self-propagating high-temperature synthesis (SHS) was investigated. Powders of Zr, B, BN and Al (purity >99 %) was used as the starting materials. Two initial mixtures were prepared and mixed at specific ratios. The first mixture was made of Zr and B, which were weighed at stoichiometric amounts to form ZrB_2. The second mixture contained Zr, BN and Al; amounts of which were calculated so as to form ZrB_2 and AlN.*

The starting powders were mixed in a mortar and pestle, and then the reactant mixture was slightly pressed in a steel die. The SHS reactions were conducted in high purity argon atmosphere, in an SHS chamber. The reactant pellet was ignited from one end with a tungsten wire. The reaction products were examined with scanning electron microscopy and they were subjected to X-ray diffraction analyses.

It was found that when the reactants contained 40 % mixture-1 and 60 % mixture-2, according to the XRD results of the products, the peaks related to ZrB_2 were dominant. The product contained some AlN and ZrN. When the amount of mixture-2 was increased to 90 %, the amounts of AlN and ZrN both were observed to increase. When Al amount in mixture-2 was increased by 30 % and mixture-2 was added as 90% into mixture-1, amount of AlN in the reaction products increased and amount of ZrN decreased. According to SEM examinations, ZrB_2 particles were seen to be mixed with AlN particles in the reaction products. Size of ZrB_2 particles were about 1 micron and AlN particles were larger.

Keywords: ZAMAK 3 ALLOY, AGING, MECHANICAL PROPERTIES

1. Introduction

Aluminum nitride (AlN) is important for electronic industry due to its good properties such as high electrical resistivity, thermal conductivity and low thermal expansion. In addition, its corrosion resistance and oxidation resistance make it a suitable material for high temperature boats that are used in various metal melting and similar processes [1].

Zirconium diboride (ZrB_2) is in the class of ultra-high temperature ceramics. It has also high thermal conductivity and thermal shock resistance. It is used in high temperature applications and as high temperature boats [2].

Self-propagating high-temperature synthesis (SHS) is a procedure that utilizes the exothermic character of the reactions for sustaining the formation of the products. One chief benefit of this practice is that it requires little amount of energy, which is necessary to initiate the reaction. Low equipment cost, uncontamination of the products, fast production rate are a few of the other rewards [3].

AlN was prepared through combustion synthesis by heating Al powder in high pressure nitrogen atmosphere. AlN was used as diluent. It was reported that reaction did not take place when the Al content of the mixture was less than 20 wt % [1].

For high temperature applications, there are some disadvantages of single phase ceramic materials, such as low ablation resistance. Therefore, they are combined with other ceramics. Addition of secondary or tertiary compounds enhances their properties and density [2]. Addition of SiC to ZrB_2 increases its strength and addition of $MoSi_2$ to ZrB_2 increases its high temperature strength [2].

In the study of Liu, ZrB_2 based ceramics were produced by reactive spark plasma sintering [4]. Zr, ZrH_2, Si, B_4C, BN were used as the starting materials and ZrB_2 and SiC or AlN or ZrN containing ceramics were obtained.

In the study of Zhang et al. [4], boron carbide and boron nitride were used as reactants for producing boride containing ceramic composites. ZrB_2 and AlN ceramics were obtained by in situ reactive hot pressing technique.

In this study, formation of ZrB_2-AlN mixed powder by self-propagating high-temperature synthesis (SHS) by using of Zr, B, BN and Al powders, was investigated.

2. Experimental Procedure

Formation of ZrB_2-AlN mixed powder by self-propagating high-temperature synthesis (SHS) was investigated. Powders of Zr, B, BN and Al (purity >99 %) was used as the starting materials. Two initial mixtures were prepared and mixed at specific ratios. The first mixture (mixture-1) was made of Zr and B, which were weighed at stoichiometric amounts to form ZrB_2 according to Reaction (1).

$$Zr + 2B = ZrB_2 \quad (1)$$

The second mixture (mixture-2) contained Zr, BN and Al; amounts of which were calculated so as to form ZrB_2 and AlN according to Reaction (2).

$$Zr + 2Al + 2BN = ZrB_2 + 2AlN \quad (2)$$

Three samples were produced by using different amounts of starting materials. The first composition was contained 40 wt % of mixture-1 and 60 wt % of mixture-2. The second composition contained 10 wt % of mixture-1 and 90 wt % of mixture-2. The third composition contained 10 wt % of mixture-1 and 90 wt % of mixture-2, but the amount of Al in mixture-2 was 30 % in excess of the stoichiometric amount (Table 1).

Table 1: *Produced samples and amounts of the reactants powders in them*

	Amounts of Reactants (g)			
Sample	Zr	B	BN	Al
Sample-1 (%60M1-%40M2)	0.4525	0.0575	0.1146	0.1247
Sample-2 (%10M1-%90M2)	0.37	0.0134	0.1604	0.1746
Sample-3 (%10M1-%90M2 (Al 30%xs))	0.37	0.0134	0.1604	0.2275

The starting powders were mixed in a mortar and pestle, and then the reactant mixture was slightly pressed in a steel die. The SHS reactions were conducted in high purity argon atmosphere, in an SHS chamber. The reactant pellet was ignited from one end with a tungsten wire. The reaction products were examined with scanning electron microscopy and they were subjected to X-ray diffraction analyses.

3. Results and Discussion

After self-propagating high-temperature synthesis reaction the pellets preserved their shapes. Some swelling was observed, along with increase in the porosity. In addition, the pellets had a lamellar morphology, a typical result of the SHS reaction. The pellets were ground in a mortar and pestle into powder form.

XRD Analyses

The ground samples were subjected to XRD analyses at a rate of 2 ^{o}/min. XRD patterns of the product obtained from the sample containing 40% mixture-1 and 60% mixture-2 (Sample-1) is presented in Fig. 1(a). The peaks related to ZrB2 were dominant. The product contained some AlN and ZrN. The intensity of AlN peaks are much lower as compared to that of ZrB2 peaks. The intensity of the AlN peaks are believed to be not directly proportional with the amount of AlN phase in the products.

The reaction was conducted in argon atmosphere. Thus, the only source of nitrogen in the system is BN. There was no sign of unreacted aluminum or boron nitride in the system, indicating that the reaction was completed. In the present study, BN was used to provide nitrogen, whereas in literature AlN production by combustion synthesis is frequently performed in high pressure nitrogen [1].

When the amount of mixture-2 was increased to 90 % in the reactants (Sample 2), the amounts of AlN and ZrN both were observed to increase (Fig 1(b)). Mixture-2 contains BN, which is the nitrogen source in the system, and the products of Reaction (2) are ZrB2 and AlN. Therefore AlN is expected to increase in the products, as a result of increase in the amount of mixture-2 in the reactants. On the other hand, amount of ZrN also increased in the products, due to increase in the amount of BN in the reactants.

In the third sample, Al amount in mixture-2 was increased by 30 % and mixture-2 was added as 90% into mixture-1, (Sample 3). It was seen that the amount of AlN in the reaction products increased and amount of ZrN decreased (Fig. 1(c)). It can be deduced that in sample-2, there was a loss of aluminum during the SHS reaction. Adding excess aluminum into the reactants may have compensated for the loss of aluminum from the system and led to formation of more AlN. In addition, this decreased the formation of ZrN. According to XRD pattern given in Fig. 1(c), there was trace amount of unreacted aluminum in the reactants, when 30 % excess aluminum was used in mixture-2.

Microstructure

Scanning electron micrographs of the products are given in Figs 2-4. These images were obtained in the backscatter electron mode. Therefore, compositional contrast was obtained. The white particles are believed to be ZrB_2 (or ZrN in some cases), with higher average atomic weight. Gray particles are believed to be AlN (or Al), with lower average atomic weight.

According SEM examinations, ZrB_2 particles were seen to be mixed with AlN particles in the reaction products. The microstructure is very similar to the ZrB_2-AlN system synthesized by in situ reactive hot pressing [5]. Size of ZrB_2 particles were about 1 micron and AlN particles were larger.

Amount of AlN phase was seen to be higher in Sample-3 (Fig. 4), as compared to other samples.

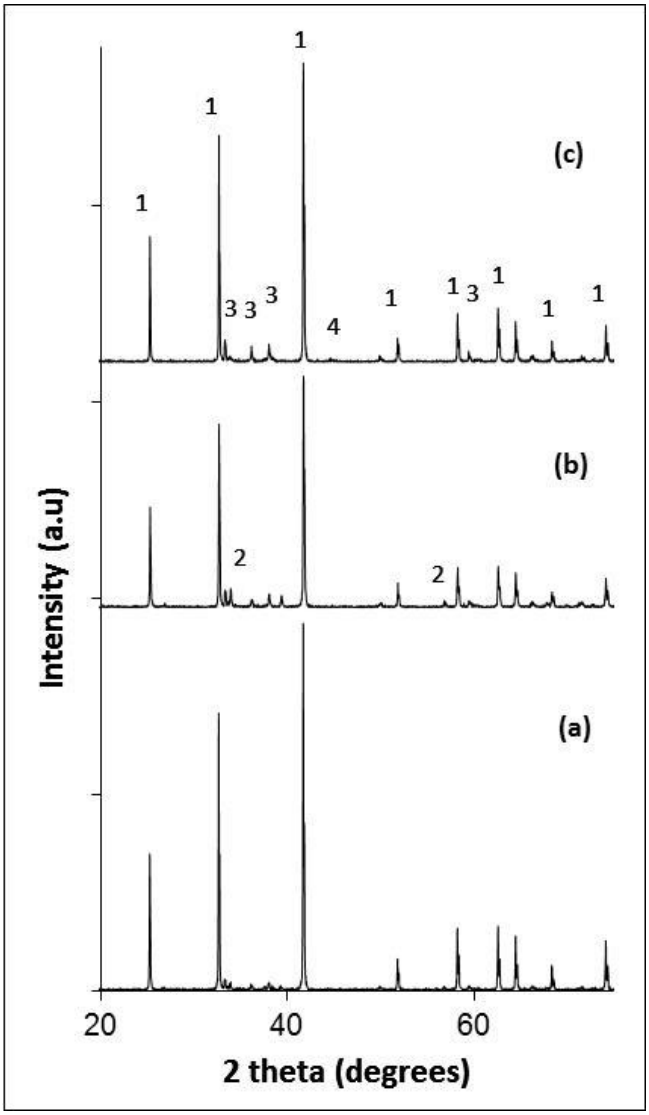

Fig. 1 *XRD patterns of the products (a) S1 (%60M1-%40M2) (b) S2 (%10M1-%90M2) (c) S3 (%10M1-%90M2 (Al 30%xs)), 1. ZrB_2, 2. ZrN, 3. AlN, 4. Al*

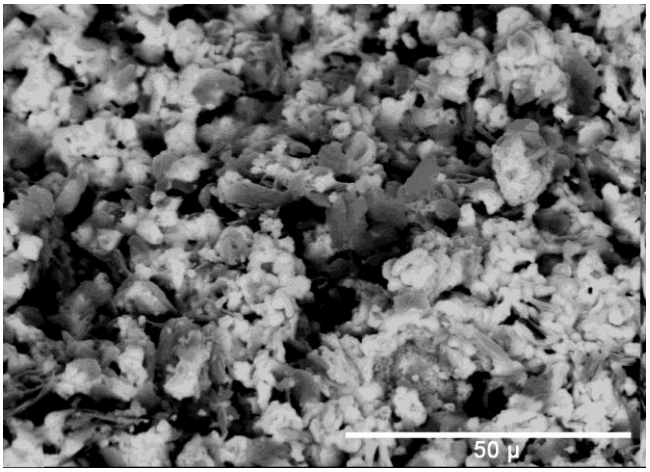

Fig. 2 *Scanning electron micrograph of the products obtained from reactants containing 40% mixture-1 and 60% mixture-2 (Sample-1).*

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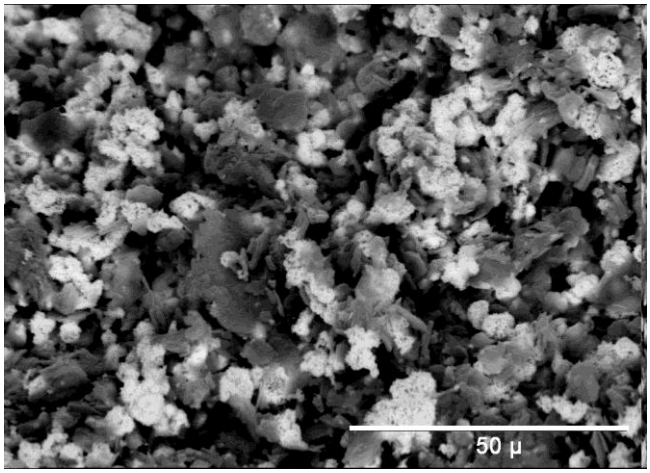

Fig. 3 *Scanning electron micrograph of the products obtained from reactants containing 10% mixture-1 and 90% mixture-2 (Sample-2).*

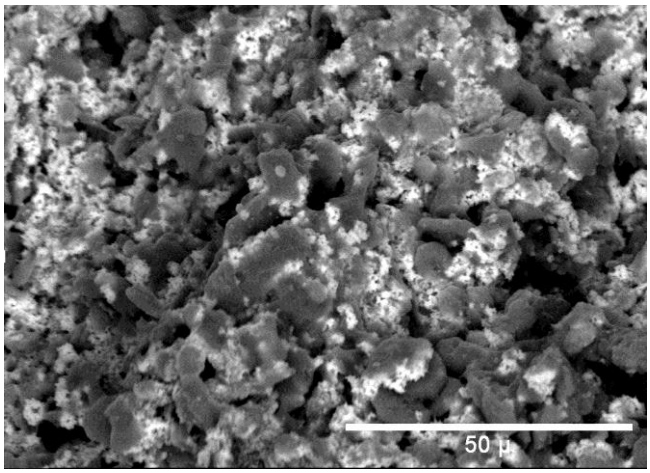

Fig. 4 *Scanning electron micrograph of the products obtained from reactants containing 10% mixture-1 and 90% mixture-2 (Al 30%xs) (Sample-3).*

4. Conclusion

ZrB_2-AlN powder mixture was produced from Zr, B, BN and Al reactant mixtures by self-propagating high-temperature synthesis. Increase in the amount of BN and Al in the reactants, resulted in an increase in the amount of AlN in the products.

ZrB_2 and AlN particles could be visualized by compositional contrast in SEM. ZrB_2 particles were seen to be mixed with AlN particles in the reaction products. Size of ZrB2 particles were about 1 micron and AlN particles were larger.

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