REACTIONS OF BORON AND ALUMINUM NITRIDES, AND MATERIALS BASED ON THEM, WITH REFRACTORY METALS

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Boron and aluminum nitrides and certain materials based on these compounds (such as ABN and BNTs*) possess good electric insulating properties and high thermal shock resistance and chemical stability, and consequently seem to hold considerable promise for service in high-temperature engineering applications. However, nonmetallic refractory compounds dissociate in a vacuum at a temperature of \( \sim 1500^\circ C \), which sets a maximum limit to the temperature range in which they can be allowed to operate and, in particular, affects their stability in contact with metals.

In order to explore the possibility of using such materials for coatings and parts operating in contact with refractory metals, it is necessary to investigate their compatibility with the latter at high temperatures. Data upon the character of the reactions in mixtures of nonmetallic nitride and refractory metal powders during hot pressing and in a purified argon atmosphere have already been reported in the literature [1-5], but nothing appears to have been published upon the compatibility of these materials in a vaccum.

The present work was undertaken with the aim of measuring the initial temperatures of the reactions of dense specimens of boron and aluminum nitrides and ABN and BNTs materials with niobium, tantalum, molybdenum, and tungsten over the temperature range 1000-2000°C in a vacuum of \( 10^{-3} - 10^{-5} \) mm Hg and of determining the phase compositions of the products of these reactions. It was also decided to conduct a parallel study of the reactions taking place under the same annealing conditions in equimolar mixtures of powders of these materials. The experimental procedure was similar to that described in [6]. The effects of the reactions were assessed by making metallographic examinations and microhardness measurements and carrying out x-ray diffraction phase analyses. The compositions of the starting materials employed are shown in Table 1.

Thermodynamic analyses were made of the reactions of boron and aluminum nitrides with the Groups V-VI transition metals for standard conditions (Fig. 1). The results yielded by the isobaric-isothermal potential calculations for the reactions of boron nitride with the metals indicate that, with niobium and tantalum, mixtures of nitride and boride phases of the metals can be expected to form over the whole temperature range. With rise in temperature, the relative amount of the nitride phases diminishes and that of the boride phases grows. With molybdenum and tungsten, reactions resulting in the formation of boride

<table>
<thead>
<tr>
<th>Material</th>
<th>B</th>
<th>Al</th>
<th>C</th>
<th>N</th>
<th>Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>42.0</td>
<td>—</td>
<td>—</td>
<td>55.5</td>
<td>Rem. C and O</td>
</tr>
<tr>
<td>AlN</td>
<td>—</td>
<td>66.2</td>
<td>—</td>
<td>33.6</td>
<td></td>
</tr>
<tr>
<td>ABN</td>
<td>16.8-17.2</td>
<td>39-41.1</td>
<td>0.7-0.8</td>
<td>38.5-40</td>
<td>0.3-0.7B\text{O}_3; 0.5-0.6Fe</td>
</tr>
<tr>
<td>BNTs</td>
<td>53.0</td>
<td>—</td>
<td>9.6</td>
<td>36.0</td>
<td>( \leq 1% ) B\text{O}_4</td>
</tr>
</tbody>
</table>

*ABN is a composite material based on boron and aluminum nitrides (system B-\( \text{Al}-\text{N} \)); BNTs is a composite material based on boron nitride and boron carbide (system B-\( \text{N}-\text{C} \)).


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Fig. 1a: Variation of isobaric-isothermal potential with temperature for systems Me-BN and Me-AlN.

In Fig. 1a: 1) $2 \text{Nb} + \text{BN} = \text{Nb}_2\text{N} + \text{B}$; 2) $\text{Nb} + \text{BN} = \text{NbN} + \text{B}$; 3) $1/2 \text{Nb} + \text{BN} = 1/2 \text{NbB}_2 + 1/2 \text{N}_2$; 4) $5/2 \text{Nb} + \text{BN} = 1/2 \text{NbB}_2 + \text{NbN}$; 5) $3/2 \text{Nb} + \text{BN} = 1/2 \text{NbB}_2 + \text{NbN}$; 6) $2 \text{Ta} + \text{BN} = \text{Ta}_2\text{N} + \text{B}$; 7) $\text{Ta} + \text{BN} = \text{TaN} + \text{B}$; 8) $1/2 \text{Ta} + \text{BN} = 1/2 \text{TaB}_2 + 1/2 \text{N}_2$; 9) $\text{Ta} + \text{BN} = \text{TaB} + 1/2 \text{N}_2$; 10) $1/2 \text{Ta} + \text{BN} = 1/2 \text{TaB}_2 + \text{TaN}$; 11) $3/2 \text{Ta} + \text{BN} = 1/2 \text{TaB}_2 + \text{TaN}$; 12) $3 \text{Ta} + \text{BN} = \text{TaB} + \text{TaN}$.

In Fig. 1b: 1) $2 \text{Mo} + \text{BN} = \text{Mo}_2\text{N} + \text{B}$; 2) $2 \text{Mo} + \text{BN} = \text{Mo}_2\text{B} + 1/2 \text{N}_2$; 3) $\text{Mo} + \text{BN} = \text{MoB} + 1/2 \text{N}_2$; 4) $1/2 \text{Mo} + \text{BN} = 1/2 \text{MoB}_2 + 1/2 \text{N}_2$; 5) $2/5 \text{Mo} + \text{BN} = 1/5 \text{Mo}_2\text{B}_2 + 1/2 \text{N}_2$; 6) $4 \text{Mo} + \text{BN} = \text{Mo}_2\text{B} + \text{Mo}_2\text{N}$; 7) $3 \text{Mo} + \text{BN} = \text{MoB} + \text{Mo}_2\text{N}$; 8) $5/2 \text{Mo} + \text{BN} = 1/2 \text{MoB}_2 + \text{Mo}_2\text{N}$; 9) $12/5 \text{Mo} + \text{BN} = 1/5 \text{Mo}_2\text{B}_2 - \text{Mo}_2\text{N}$; 10) $2 \text{W} + \text{BN} = \text{W}_2\text{N} + \text{B}$; 11) $2 \text{W} + \text{BN} = \text{W}_2\text{B} + 1/2 \text{N}_2$; 12) $\text{W} + \text{BN} = \text{WB} + 1/2 \text{N}_2$; 13) $2/5 \text{W} + \text{BN} = 1/5 \text{W}_2\text{B}_2 + 1/2 \text{N}_2$; 14) $4 \text{W} + \text{BN} = \text{W}_2\text{B} + \text{W}_2\text{N}$; 15) $3 \text{W} + \text{BN} = \text{WB} + \text{W}_2\text{N}$; 16) $12/5 \text{W} + \text{BN} = 1/5 \text{W}_2\text{B}_2 + \text{W}_2\text{N}$.

In Fig. 1c: 1) $2 \text{AlN} = \text{W}_2\text{N} + \text{Al}$; 2) $2 \text{Mo} + \text{AlN} + \text{Mo}_2\text{N} + \text{Al}$; 3) $2 \text{Ta} + \text{AlN} = \text{Ta}_2\text{N} + \text{Al}$; 4) $\text{Ta} + \text{AlN} = \text{TaN} + \text{Al}$; 5) $\text{Nb} + \text{AlN} = \text{NbN} + \text{Al}$; 6) $2 \text{Nb} + \text{AlN} = \text{Nb}_2\text{N} + \text{Al}$.