Combustion Synthesis of Molybdenum Containing Boride Based Hard Alloys

Sevinc Rahimi Moghaddam¹, Bora Derin¹, Onuralp Yücel¹, M. Şeref Sönmez⁴, Meltem Sezen⁵, Feray Bakan⁶, Vladimir Sanin⁷, Dimitriy Andreev⁷

¹Istanbul Technical University, ²Sabancı University, ³Institute of Structural Macro Kinetics Materials Science - Türkiye, Russia

Abstract

The ternary boride containing alloys and compounds are hard materials which can be used in applications as an alternative to tungsten based cemented carbides. In this study, molybdenum containing boride based hard alloys were prepared by self propagating high temperature synthesis method. The combustion synthesis process was carried out in copper crucible through an aluminothermic reduction in three different ternary systems of Mo-Ni-B, Mo-Fe-B and Mo-Co-B including oxides as starting materials. Synthesis of these alloys was realized under normal gravity and atmospheric conditions. During these exothermic reactions, adiabatic temperature reaches over 2000°C and the flame propagates spontaneously through the powder mixture. Thermodynamical calculations were performed using FactSage 6.4 thermochemical software in order to estimate the obtained adiabatic temperature and weight percentage of products. Mechanical test results of the obtained boride containing alloys revealed that vickers hardness amount is about 800-900HV.

1. Introduction

Hard alloys containing borides exhibit a wide range of properties that are valuable for industrial applications. In competition with tungsten carbide based composites, these ternary boride based materials possess high melting point and high wear resistance [1]. The ternary borides of Mo₂FeB₂, Mo₂CoB₂ and Mo₂NiB₂ were analyzed extensively and represented low density typically close to steels [2], high Vickers hardness of 15-20 GPa and high corrosion resistance against hydrochloric and hydro sulphuric acid aqueous solutions which make it applicable for cutting tools or plastic injection molding machine parts [3]. Composites with borides dispersed in metallic matrix have shown better capabilities by combining the high toughness of Ni as metallic binder and high hardness of boride based intermetallics as hard phase.

Self-propagating high temperature synthesis (SHS) is a method which was used for the fabrication of high temperature ceramics, intermetallics and composites in a one-step operation. This technique has the advantages of providing high purity products, low energy requirements and simplicity of the process over the conventional high temperature methods[4]. In this study, for the first time production of boride based intermetallics of Mo-Ni-B, Mo-Fe-B and Mo-Co-B systems by self propagating high temperature synthesis method using aluminothermic reduction of metallic oxides of MoO₃, Fe₂O₃, NiO, Co₃O₄ and B₂O₃ as starting materials was investigated. Combination of binary and ternary intermetallics in produced alloys shows high hardness.

2. Experimental Procedure

Starting materials were commercially pure powders of MoO₃ (99.5%), NiO (99%), Fe₂O₃, Co₃O₄, B₂O₃ (94.2%) and Al (99.7%) while they are involved in the aluminothermic reaction which takes place under atmospheric environment and normal gravity. First step of these experiments are mixing of powders and drying them at about 100°C for 30 minutes before combustion. The mixtures were placed into the copper crucible and the tungsten filament on the top of the powder connected by copper wire to power supply working with 20(VA) initiated the exothermic reaction. The generated heat in aluminothermic reaction process is calculated by FactSage programme to estimate the possibility of the self-propagation of the reaction. After the SHS synthesis process, all the obtained bulk shaped samples were metallographically prepared by grinding and polishing for consequent analyses. The samples were numbered as
NI7, FE12 and CO5 representing alloys of Mo-Ni-B, Mo-Fe-B and Mo-Co-B systems, respectively. The crystal structure of final products is determined by X-ray diffractometer (XRD, PANalytical PW3040/60 with a Cu Ka radiation), microstructure and composition of phases were characterized by scanning electron microscopy and energy dispersive spectroscopy (SEM, Jeol JSM-840) and AAS spectrometry (Perkin-Elmer 1100B). Vickers hardness test (Micro Hardness Tester, SHIMADZU CORPORATION) is also performed on the specimens to identify the mechanical properties.

3. Results and Discussion

Thermochemical simulation by using the advanced “Equilib” module of FactSage 6.4 was performed to estimate the effect of initial components on adiabatic temperature and product composition [5]. The reaction of the process was assumed as adiabatic (ΔH=0) and the initial reaction conditions were considered as ambient temperature under atmospheric pressure. SGTE and FactPS databases were selected for detecting all compounds and alloys. The adiabatic temperature values of the reactions starting from initial oxide materials for the combustion synthesis in Mo-Ni-B, Mo-Fe-B and Mo-Co-B systems were calculated by FactSage software and shown in Table 1.

Table 1. Adiabatic temperature of reactions

<table>
<thead>
<tr>
<th>No</th>
<th>Starting materials</th>
<th>Adiabatic Temp.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2MoO₃+1.5NiO+1B₂O₃+7Al</td>
<td>2703.4</td>
</tr>
<tr>
<td>2</td>
<td>2MoO₃+0.75Fe₂O₃+1B₂O₃+7.5Al</td>
<td>2679.7</td>
</tr>
<tr>
<td>3</td>
<td>1MoO₃+0.5Co₃O₄+0.5B₂O₃+4Al</td>
<td>2721.5</td>
</tr>
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</table>

The combustion temperature in these processes are so high that heat sinker additives such as aluminium oxide are required. The addition amount of Al₂O₃ in three systems was used as 5% of total weight of raw materials. The microstructure of specimen coded with NI7 in Mo-Ni-B system is shown in SEM image of Figure 1. In this sample, Mo₂NiB₂ phase was observed as gray angular shapes (2). The grains in the light region represents MoB phase (3). The excess Al reacted with Ni to form Ni₃Al in matrix (1).

The dendritic phases in light gray regions distributed in matrix (3,4) which are depicted in Figure 2 consist of Fe-Mo alloy with dissolved Al. Rectangular shapes in larger light gray regions (1,5) are consisted of ternary borides of Mo-Fe-B system. The EDS analysis result shows the presence of Mo-Fe binary intermetallics as hard phase in Mo-Fe-B systems. Unreacted Al in system combines with Fe and produces Fe₃Al phase in matrix observed in dark gray areas (2).

Therefore, the fabrication of some amounts of Mo₂NiB₂ and Mo₂FeB₂ ternary borides is detected in NI7 and FE12 samples respectively. There are two regions of a matrix and a hard phase that spreads in that matrix almost in every sample. According to the EDS elemental analysis, diffusion of Al in matrix is higher than hard phase in observed three samples.

In Mo-Co-B system, as shown in Figure 3, light regions (3,4) are consisted of ternary phases coexisting with Al containing Mo-Co phases in darker areas (1). Besides, excess Al remained from the incomplete aluminothermic reduction reacts with Co to form Co rich CoAl phase in matrix (2). In fact, the matrix phase contains brittle
Ni$_3$Al, CoAl and Fe$_3$Al intermetallics in NI7, FE12 and CO5 coded samples.

Distribution of ternary boride containing phases in ceramic background makes these samples to reach high hardness values. The Vickers microhardness test results of three samples in different systems are shown in Table 2.

![Figure 3. SEM image of CO5 (x500)](image)

**Table 2. Hardness of hard alloys**

<table>
<thead>
<tr>
<th>No</th>
<th>Hardness (HV)</th>
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<tbody>
<tr>
<td>NI7</td>
<td>943</td>
</tr>
<tr>
<td>FE12</td>
<td>885</td>
</tr>
<tr>
<td>CO5</td>
<td>854</td>
</tr>
</tbody>
</table>

### 4. Conclusions

The combustion synthesis of Mo-Ni-B, Mo-Co-B and Mo-Fe-B containing hard alloys through the aluminothermic reduction of low cost metallic oxides was performed. It was concluded that the fabrication of molybdenum containing ternary boride based hard alloys using this simple process is possible. Due to high amounts of excess Al in the alloys, intermetallic based matrix was observed. Although the hardness of produced alloys are so high but the Al based ceramic matrix of these materials avoids reaching superior mechanical properties. In order to improve the toughness of these alloys further experiments will be carried out.

### Acknowledgement

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### References