THERMOCHEMICAL CALCULATIONS AND EXPERIMENTAL INVESTIGATIONS ON Mo-Ni-B ALLOY SYSTEM PRODUCED BY COMBUSTION SYNTHESIS

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Abstract: In this study, Mo-Ni-B alloy system which can be a new hard alloy alternative to tungsten base cemented carbides, was investigated by means of thermochemical calculations and experimental trials. Thermochemical calculations were carried out to estimate the adiabatic temperatures and possible product compositions in the alloys by using FactSage 7.0 thermochemical software. The combustion synthesis process was performed under normal gravity and air in Cu copper crucibles by using metal oxides (MoO3 and NiO), boron oxide (B2O3) as a boron source and aluminum (Al) as a metallic reductant. Alumina, (Al2O3) as a functional additive (diluent), were also added in order to reduce the adiabatic temperature of the reaction. Since the attained reaction temperatures for this system during the exothermic SHS process is so high (above 2000 °C), the reaction is self-sustaining and the melt consists of insoluble mixture of metallic compound and oxide phase which can be segregated under normal gravity force.

KEYWORDS: COMBUSTION SYNTHESIS, Mo-Ni-B, HARD ALLOY, THERMOCHEMICAL CALCULATIONS, FACTSAGE.

1. Introduction

Today, WC-Co MMCs are the mainstay of the manufacturing industry with a variety of applications including machining of many different metallic and nonmetallic materials [1]. According to the recent investigations, new hard alloys can also be successfully applied to wear resistance applications such as injection molding machine parts. For example, borides which have high corrosion resistance and strength can replace cemented carbides for some specific applications. A new hard alloy composite alternative contains a metal matrix of nickel as a binder and MoNiB-type boride as a hard phase. However, due to the poor sintering behavior of borides and the formation of brittle phases with metals during sintering, reaction boronizing sintering technique are mostly used in previous studies which requires high power and consequently higher costs [2].

Combustion Synthesis (or Self Propagating High Temperature Synthesis) is one of the alternative production techniques that can be used to produce refractory metal compounds such as carbides, nitrides, silicides, borides as well as other intermetallics and metal matrix composites. The process has several advantages such as very short processing time, simple operation, low initiation energy requirement and low cost. In a SHS process, after ignition, the combustion front is formed and propagates throughout the reactant mixture yielding the desired product [3]. This work aims to establish a scientific background for high energy efficient, fast and low-cost production of Mo-Ni-B hard metal system starting from the cheap oxides by combustion synthesis method.

2. Experimental Studies

The raw materials of the SHS experiments are MoO3 (99.5 wt. % pure, particle size < 60 μm), Al (99.6 wt. % pure and particle size <100 μm), NiO (99.0 wt. % pure and particle size <40 μm), Al2O3 (99.0 wt. % pure and particle size <50 μm). B2O3 was obtained by the calcination of 99.5 % pure boric acid (H3BO3, Eti Holding Inc.) in a nickel crucible at 800 °C for 2 hours followed by milling and sieving. After drying procedure of the powders in an oven at 110 °C for 2 hours, the mixture was prepared at different molar ratios. The SHS process was carried out in a copper crucible with the inner height of 200 mm and the inner diameter of 40 mm. The dried powder was mixed thoroughly in a Turbula mixer for 30 min. After the charge mixture was poured into the crucible and compacted thoroughly, a tungsten resistance wire was placed on the top of the compacted powder. The weights of the raw materials used in the experiments were shown in Table 1. The reaction was initiated by passing electricity through the resistance wire. After initiation, electricity was cut off and the crucible was left to cool to room temperature. The characterization studies were performed by using atomic absorption spectroscopy (AAS), X-ray florescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometers (WDs-EDS), and micro-hardness testing methods.

Table 1. Weights of initial raw materials for Mo-Ni-B systems

<table>
<thead>
<tr>
<th>Initial Raw Materials</th>
<th>Exp. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO3, g</td>
<td>N1</td>
</tr>
<tr>
<td>NiO, g</td>
<td>N1</td>
</tr>
<tr>
<td>B2O3, g</td>
<td>N1</td>
</tr>
<tr>
<td>Al, g</td>
<td>N1</td>
</tr>
<tr>
<td>Al2O3, g</td>
<td>N1</td>
</tr>
</tbody>
</table>

3. Results and Discussions

A thermochemical calculation was carried out to estimate the adiabatic temperature (Tad) value and the possible product composition of the SHS reaction by using the advanced “Equilib” module of FactSage 7 developed by CRCT-ThermFact and GTT-Technologies®. In the calculations, FactPS, STGE2011, and FToxide were chosen as the most appropriate databases. In order to simulate the SHS reaction, 2 moles of MoO3, 0.5 mole of NiO, 1 moles of B2O3 were equilibrated with different moles of Al. The reactions of the process were assumed as adiabatic (ΔH=0) and the initial reaction temperature was selected as 25 °C. The adiabatic temperature value (Tad) is an important indicator to estimate whether a reaction is self-propagating or not. The adiabatic temperature change versus Al addition in the combustion synthesis process was performed under normal gravity and air in Cu copper crucibles by using metal oxides (MoO3 and NiO), boron oxide (B2O3) as a boron source and aluminum (Al) as a metallic reductant. Alumina, (Al2O3) as a functional additive (diluent), were also added in order to reduce the adiabatic temperature of the reaction. Since the attained reaction temperatures for this system during the exothermic SHS process is so high (above 2000 °C), the reaction is self-sustaining and the melt consists of insoluble mixture of metallic compound and oxide phase which can be segregated under normal gravity force.
Figure 1. Thermochemical calculation for adiabatic temperature versus Al addition.

Figure 2. Thermochemical calculation for product composition versus Al addition.

The obtained SEM image of the specimen coded with NI1 is given in Figure 3. The EDS analysis shows that nickel reacted with excess aluminum to produce NiAl intermetallic which formed the matrix phase (1). The inner region of angular grains belong to MoB2 phase (2) whereas the inner region are MoB (3). The mean hardness value of the specimen was found as 938.65 HV.

Figure 4 represents the obtained SEM image of the specimen coded with NI7. Since the initial NiO quantity is comparably higher than that of NI1, the excess Al reacted with high amount of Ni to form Ni3Al phase. In the specimen, Mo2NiB2 region was also observed as gray angular form. The grains with white region represents MoB phase (3). The mean hardness value of the specimen was found as 943 HV.

4. Conclusion
It is possible to produce a Mo-Ni-B containing metal matrix composites from oxides by aluminothermic reaction. The formation of ternary boride Mo2NiB2 in the product is possible with nickel oxide addition. Due to the high amount of excess Al in the alloy, NiAl or Ni3Al phases form in the matrix. This study is an ongoing project and further experiments and analyses will be carried out in the near future.

5. Acknowledgement
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6. References