Investigation of the Mechanism of Boron Interaction with High-Melting Metals

VLADIMIR A. NERONOV[1] and MIKHAIL A. KORCHAGIN[2]

[1]*Institute of Theoretical and Applied Mechanics, Siberian Branch of the Russian Academy of Sciences, Ul. Institutskaya 4/1, Novosibirsk 630090 (Russia)*

[2]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630090 (Russia)*

Abstract

The electron microscopic *in situ* technique was developed and used to study boron interaction with titanium, zirconium, hafnium, niobium and tantalum in samples prepared as a particle of one component lying on the film of another. By means of microdiffraction and dark-field imaging, the phase composition of the formed products has been determined along with their distribution over the reaction zone formed in the vicinity of the separate particle. Melts play an important part in the systems studied. A scheme that describes the interaction between the components in powder mixtures is proposed. The existence of some borides is verified.

INTRODUCTION

Self-propagating high-temperature synthesis (SHS) has opened broad possibilities in the technology of high-melting inorganic compounds including borides [1]. The borides of titanium, zirconium, hafnium, vanadium, niobium, tantalum and other transition metals were obtained from elements by means of SHS. The effect of technological factors on the regularities of combustion of metal powders with boron has been considered in detail. However, the mechanism of interaction between the reagents, especially on a separate particle scale, has not been adequately studied yet.

These investigations are hindered by very rapid development of SHS processes and high temperature. Because of this, the possibilities of research techniques are limited. The notions of the mechanisms of SHS processes are mainly based on the results obtained during the studies of combustion rate dependence on various parameters, measurement of temperature within combustion wave using thermocouples, as well as on the results of investigations of microsections prepared from rapidly cooled (quenched) samples.

Recently, new methods have been developed for the investigation of the mechanism of components interaction directly in the combustion wave. In particular, X-ray phase analysis has been applied to combustion, either with the use of usual X-ray tubes or synchrotron radiation [2–4]. In spite of high information content, since these methods are integral they do not allow one to obtain the data on the initial stages of interaction at the contacts between particles. It is initial stages that determine the interaction mechanism, chemical and phase composition of the products formed. First of all, this is true for the phase state of the reagents, the nature of particles being transported, methods of their transfer, phase composition of intermediate products and the sequence of stages through which the formation of final product occurs.

In the present study, a model electron microscopic technique proposed by M. A. Korchagin [4, 5] has been used for these purposes. This technique was used earlier to study the mechanism of interaction in a series of SHS systems: metal–metal, metal–carbon and Ti–B [2–6]. Besides, the use of electron microscopic technique can help clearing up the problem concer-

ning the existence of one phase or another in every specific system. It is important for the present case because no reliable state diagrams are known till now for some boride systems under consideration.

EXPERIMENTAL

A model technique is based on direct (*in situ*) electron microscopic observation of the interaction process between the components of powder systems using samples prepared as a particle of one component placed on the film of another component. The interaction is initiated by stepwise heating of the sample by electron beam of the microscope (the beam intensity being increased), or by a special microfurnace used as a heater. In the first case, initially the temperature of the particle is higher than that of the film because of the difference in the fraction of absorbed electrons and cooling mechanisms. The start of reaction is accompanied by temperature equalizing due to heat conductance through the film which leads to the appearance of temperature gradients about ~10^6 ^oC/cm which is also characterisic of SHS wave [6].

The technique allows not only to visualize the reaction process at the contact between reagents but also to directly determine, by means of microdiffraction and dark-field image, the phase composition of the products formed and their distribution over the reaction zone that is formed in the vicinity of separate particle. A minimal area from which microdiffraction patterns can be obtained is about 1 μm^2. In order to get more complete information on the character of interaction, the components of the sample can be exchanged.

The investigations of interactions in the Ti − B, Zr − B, Hf − B, Nb − B and Ta − B systems have been carried out using a EF/4 electron microscope ("Karl Zeiss Jena") with the accelerating voltage of 65 kV. Ti, Zr, Hf, Nb, Ta and boron films less than ≤ 100 nm thick were prepared by means of vacuum condensation under electron beam evaporation of titanium, zirconium and hafnium iodides, niobium of the NBSh-1-83 grade, tantalum (TU−95−205−73) and crystal boron of 98 % purity under vacuum ~ 10^{-5} Pa. KBr single crystals were used as substrates. The films were separated by dissolving the substrate in distilled water and taking them out of the solution with object carrier grids of the microscope. Powder particles of the second ingredient were deposited onto the film by means of dry preparation. The used powder particles include titanium (PTOM grade), zirconium (M-41), hafnium (GFM-1), niobium (M-13), tantalum (MRTU 95−124−69), and crystal boron with a particle size of 1−5 μm.

TABLE 1
Binary phases in the systems

System	Borides
Ti − B	Ti_2B, TiB, TiB_2
Zr − B	ZrB_2, ZrB_{12}
Hf − B	HfB_2
Nb − B	Nb_3B_2, NbB, Nb_3B_4, NbB_2
Ta − B	Ta_2B, Ta_3B_2, TaB, Ta_3B_4, TaB_2

RESULTS AND DISCUSSION

The features of the systems under consideration will be discussed below. Table 1 shows boride phases the existence of which has been stated reliably [10].

State diagrams for boron with the mentioned metals considered in detail in [10] are high-temperature, complicated and require verification. Because of this, any information concerning the conditions under which one or another phase is formed can be referred to as useful.

It is interesting to compare melting points of boron and metals. Metals (and systems, respectively) that are considered in the present study can be divided into three groups (Table 2):

− metals with melting points much below that of boron (Ti, Zr);

− metals with melting points much above that of boron (Nb, Ta);

TABLE 2
Melting points of boron and some metals [11]

Element	Melting point, K	Element	Melting point, K
B	2348.0*	Hf	2222.0
Ti	1941.0	Nb	2742.0
Zr	2128.0	Ta	3270.0

* 2573 K, according to another reference.

– metals with melting points close to that of boron (Hf, V).

Taking into account the reported fact that the reaction of boron with the metals under consideration starts at about 1000 °C [12–14] and the features of state diagrams considered above, we can assume that the formation of low-melting non-equilibrium eutectics cannot be excluded in the systems; in the leading zone of combustion wave in the Ti – B and Zr – B systems, the interaction between boron and liquid metal is possible, due to large differences in melting points of reagents. In spite of extremal character of SHS processes under consideration, it can be assumed that the reaction zone between the components will correlate with phase diagrams.

The versions of the interactions: boron particle upon metal film, and reversed version of metal particle on boron film – will be now analysed. Some interaction schemes are shown in Fig. 1.

As an example, we shall consider the interaction of crystal boron particle with amorphous hafnium film. The reaction zone is shown in Figs. 2 and 3. Temperature increase leads to the formation of crystallization zone 10–15 μm wide around the particle. This zone contains β-Hf. Real interaction of the reagents starts with the formation of a layer of products around boron particle. This layer is a fret film with many irregular holes. It is composed of HfB_2, according to microdiffraction patterns (see Fig. 2). The results of calculations of microdiffraction patterns here and below have been compared with reference data [15].

Further increase of temperature is accompanied by the formation of continuous crystal regions around the fret film. These regions are also composed of hafnium diboride. After this, while temperature is increased, an exhaust of liquid phase from boron surface occurs which looks like a continued boron particle (see Fig. 3). Boron particle itself does not melt either at this moment or during further interaction. Further interaction occurs while HfB_2 layer with holes grows; it is at the same time adsorbed by boron particle and the liquid phase. The particle gets detached from the edge of fret layer and moves absorbing the product and leaving a

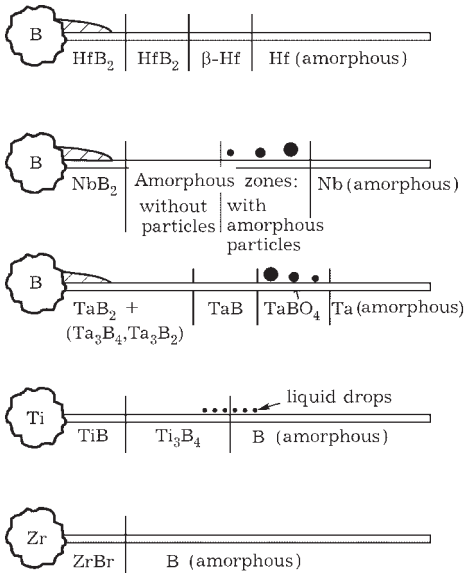

Fig. 1. Examples of the interaction in the systems: boron particle – metal film and metal particle – boron film. Shaded region is the liquid phase exhaust.

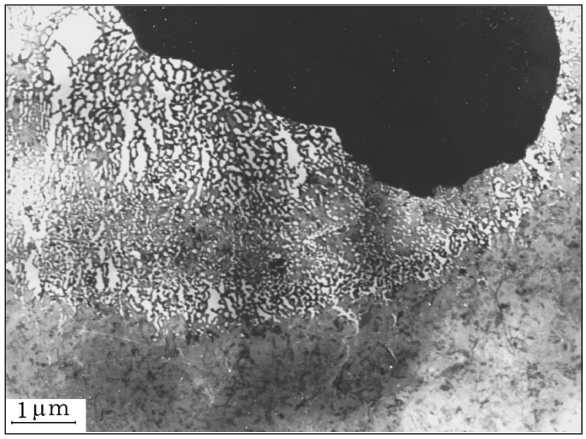

Fig. 2. Microphotograph of the product formed at the initial stages of interaction of boron particle with hafnium film.

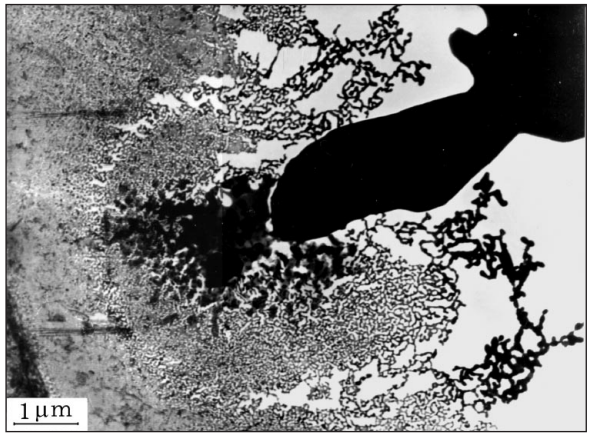

Fig. 3. The appearance of the products formed during further interaction of boron particle with hafnium film.

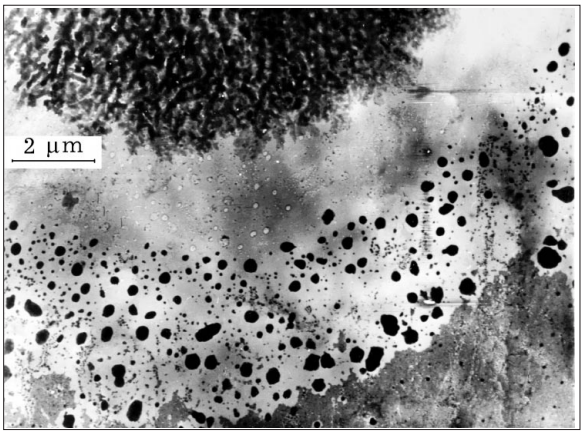

Fig. 4. Microphotograph of the products of interaction of boron particle with niobium film.

hole after it. We did not discover the formation of a continuous liquid layer around the perimeter of the particle in the fret HfB_2 layer.

The interaction of boron particle with zirconium, niobium and tantalum films also proceeds with the exhaust of liquid phase from the particle and is similar to the process described for the Hf – B system. For niobium and tantalum, fine particles are formed on the film. In the Nb – B system they are amorphous while in the Ta – B system they are composed of $TaBO_4$. This difference from the Hf – B system can be explained by the presence of small amounts of gaseous boron oxide. These particles are shown in Fig. 4 where the reaction zone is shown. It is formed during the interaction of boron particle with niobium film. Three regions can be seen: peripheral region with dark particles (amorpous); medium region which is free from particle, it is also amorphous; finally, the region adjacent to boron particle. This region is dark and contains crystal product formed in the interaction of the liquid phase exhaust with the film (NbB_2).

The interaction between rather large (3–5 μm) crystal boron particles with titanium film is somewhat different. No exhaust of the liquid phase is observed. A rapidly growing layer of product 2–3 μm wide is formed at the Ti – B boundary. This layer does not melt and is clearly facetted. Microdiffraction calculations do not coincide with any of the phases known to be present in the Ti – B, Ti – O and Ti – B – O systems. The particle starts to move when temperature is increased. The particle absorbs the interaction product and produces a hole with the edges composed, as a rule, of the initial titanium film [5, 6].

In all the systems under consideration consisting of boron particle and Ti, Zr, Hf, Nb, Ta films, boron does not melt during the interaction. The so-called exhausts are likely to be the evidence of the formation of low-melting non-equilibrium eutectics.

In the reverse version (metal particle on boron film), the interaction in the systems containing titanium and zirconium is somewhat different from the interactions in the Hf – B, Nb – B and Ta – B systems. Hafnium, niobium and tantalum particles remain solid. As a rule, no reaction zone is observed around them. On the contrary, in the Ti – B and Zr – B systems, as Fig. 1 shows, reaction zones composed of borides are formed in the vicinity of metal particles. Ti and Zr particles get fused or completely melted. The appearance of the interaction layer in the Ti – B system is presented in [5, 6] and that of the Zr – B system is shown in Fig. 5. At the initial stages of interaction, one can sometimes succeed in capturing the occurrence of amorphous boron crystallization layer near the particle. When temperature is increased, metal particles begin to move absorbing boron film and making a hole. Directly before being adsorbed, boron melts (except for Ti – B and Zr – B systems).

On the basis of the results obtained, the interaction mechanism in the systems involving the formation of the liquid phase can be represented by the following generalized scheme.

1. The interaction is initiated by heating the sample with the electron beam of increased in-

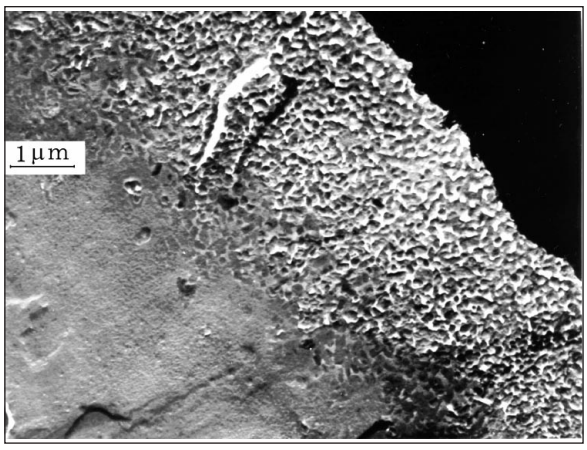

Fig. 5. The appearance of the products of zirconium particle interaction with boron film.

tensity in the microscope. One of the products by the beginning of the interaction is melted or covered with liquid eutectics. The layer of primary products is formed due to the diffusion of atoms from the liquid phase into solid.

2. After this layer achieves definite thickness, a kind of dynamic equilibrium is established. The absorption of primary products layer by the liquid phase occurs at one side; at the same time, at another side (on the border with solid component) its growth proceeds. Thus, this layer shifts into the solid component. The thickness of this layer remains constant. It carried the liquid phase with it.

3. The formation of final product occurs at later stages of interaction by means of crystallization from the melt while one component (liquid) gets saturated with the atoms of another component (solid).

The formation of the final product after a substantial delay has been confirmed with some real powder mixtures by means of X-ray phase analysis using the synchrotron radiation diffractometer [4].

When studying the products of boron interaction with titanium, zirconium and hafnium, monoboride was found only in the boron – titanium system. This can be considered as one of the confirmations that zirconium and hafnium monoborides do not exist though they were earlier for a long time thought to be existing. The existence of boride Ti_3B_4 has been confirmed.

The experiments supported the idea put forward by A. P. Savitsky and L. K. Savitskaya [16] that the dissolution of solid component in liquid is preceded by the diffusion of solvent atoms into the solid with the formation of interaction products (solid solutions or chemical compounds) in the layer near the boundary.

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