

Preparation of transition metal borides through solid-gas reactions

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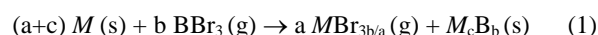
Since the synthesis of transition metal borides remains an experimental challenge, an innovative crucible-free technique was developed. A solid transition metal reacts crucible-free with a gaseous boron halide. In a first attempt some experiments with different transition metals were performed, more comprehensive investigations have been carried out on the Hf/B/Br and W/B/Br systems. The experimental results in conjunction with thermodynamic model calculations help to understand the proceeding chemical reactions and allow predictions on the applicability of this method for other transition metals.

An innovative crucible-free technique [1,2] was developed for the synthesis of transition metal borides at comparatively moderate conditions yielding products exhibiting no significant chemical impurities. The procedure is based on the crucible-free reaction of a solid transition metal with a gaseous boron halide. The applied experimental setup (Fig. 1) resembles van Arkel and de Boer's hot-wire method. A metal wire ($d = 1\text{ mm}$) is heated by an electrical current up to reaction temperatures of $1800\text{ }^{\circ}\text{C}$ in an atmosphere of gaseous boron halide. Thereby a metal boride is formed.

Since boron tribromide has a sufficient vapour pressure at room temperature and therefore needs neither cooling nor heating it is particularly suitable for this approach. Furthermore, the equilibrium state of the performed experiments is in a favourable range.

Due to some preliminary experiments with different metals the following working hypothesis was suggested: the metal reacts with the boron tribromide to a respective metal boride and a volatile metal

bromide. In general such a reaction can be expressed as follows.



Thus, the reaction proceeds at the hot metal surface. The formed metal bromide, which is volatile under these conditions, spreads in the reaction chamber and finally condenses on the cold vessel wall. The continuous removal of the halide shifts the equilibrium to the side of the reaction products. The reaction of the metal with boron tribromide can also run under the formation of elemental bromine, which exists mainly atomically at higher temperatures (equation 2).



Which reaction ((1) or (2)) dominates the process depends on the thermodynamic stability of the metal bromide. Reaction (1) will be preferred at the formation of very stable metal bromides (e.g. $HfBr_4$ with $\Delta H^0_{298} = -656.7\text{ kJ/mol}$), reaction (2) with less stable metal bromides (e.g. WBr_4 with $\Delta H^0_{298} = -113.2\text{ kJ/mol}$).

The following two examples illustrate these different reactions modes.

Synthesis of Hafniumdiboride [1]

A series of experiments with variations of reaction time (60 min up to 240 min) and wire temperature ($800\text{ }^{\circ}\text{C}$ up to $1200\text{ }^{\circ}\text{C}$) have been carried out for the Hf/B/Br system. All experiments led to the same product in form of a porous layer, which was identified as single-phase hafnium diboride by X-ray powder diffraction (PXRD). The analysis via wave-length dispersive X-ray spectroscopy measurements (WDXS) confirmed these results. Depending on reaction temperature and duration, the boride layer growth (Fig. 2) proceeds until the hafnium wire is almost completely consumed. In contrast, the composition and the ordering in the crystal structure of the hafnium diboride is independent from these parameters proven by lattice parameter refinements (internal standard LaB_6). Since hafnium

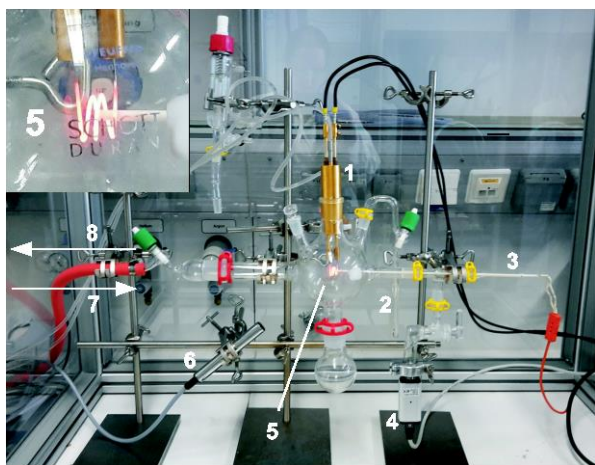


Fig.-1: Apparatus for the crucible-free synthesis of borides. (1) electrical contacts (2) BBr_3 reservoir (3) thermocouple (4) pressure sensor (5) metal wire (6) pyrometer (7) argon supply (8) pump.

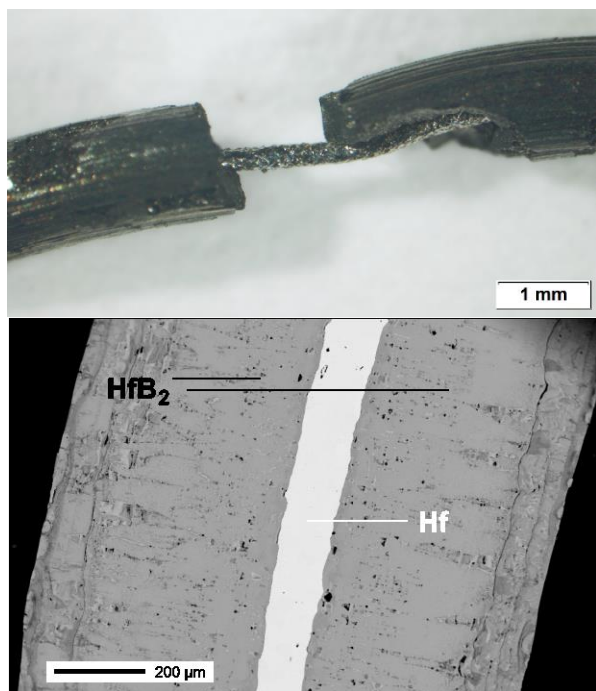


Fig.-2: Hafnium wire treated with boron tribromide at 900 °C for 240 min. The non-converted hafnium core (middle, light silvery) is surrounded by hafnium diboride (dark). Top: light microscopic image; bottom: corresponding scanning electron microscope BSE image.

forms one of the most stable oxides and taking typical contaminations of borides into account the oxygen and carbon analysis was of high importance. Chemical analyses (carrier gas hot extraction with IR-detector) of the obtained products yielded a negligible average mass fraction of oxygen of 0.05 %; significant amounts of carbon could be excluded.

Besides HfB_2 , considerable amounts of HfBr_4 were formed in the experiments. The bromide condensed at the vessel wall while the rest of the atmosphere in the apparatus stayed transparent.

This preparation technique enables a fast and easy access to single-phase samples of high purity as bulk material on a gram scale for the Hf/B/Br system.

Preparations in the Tungsten-Boron System [2]

The reaction between metallic tungsten and gaseous boron tribromide was evaluated for different reaction times (10 min up to 240 min) and temperatures (1000 °C up to 1800 °C).

Contrary to the experiments in the Hf/B/Br system the reaction progress is slowed down considerably at comparable temperatures. The formed gas phase has a brown hue and condensation occurs to a lesser extent. After 10 min at 1200 °C a compact layer on the surface

of the tungsten wire can be observed, which is shown in Figure 3. The reaction product was identified as the low-temperature phase of WB by PXRD and WDXS. From a thermodynamic perspective, the formation of WB has not been expected, since the phase coexisting with tungsten is W_2B , which itself coexists with the next boron-rich phase WB. Despite the high temperatures the sample is not set in its thermodynamic equilibrium.

After longer reaction times a second phase, identified as W_2B , is formed between the metallic core and the outer WB layer (Fig. 4). W_2B is formed in a solid state reaction without any involvement of the gas phase. The growth of the layers is significantly slower in this system. This indicates that the initially formed tungsten boride layers are mostly dense and significantly decelerate the further reaction of the metallic tungsten core with the gaseous boron tribromide.

At temperatures up to 1200 °C the solid-gas reaction dies down after a certain time. At elevated temperatures above 1500 °C an increasing crack formation at the formed layers can be observed. This leads to a further progress of the reaction under formation of two-phase samples consisting of WB and WB_2 .

In difference to the Hf/B/Br system the options for the synthesis of phase-pure tungsten borides as bulk material are rather limited in this set-up whereas the deposition of dense boride layers is possible within a short period of time.

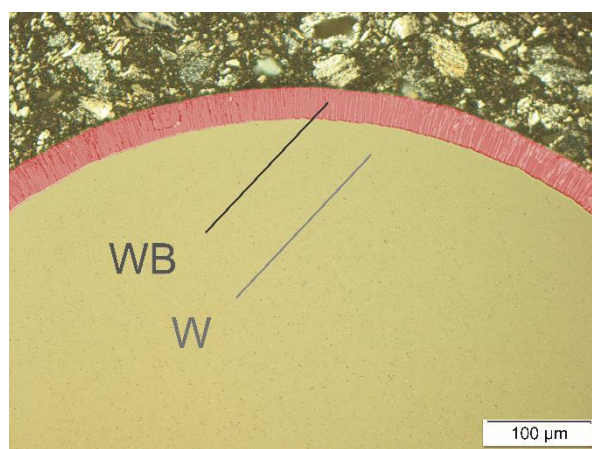


Fig.-3: Reaction product obtained at 1200 °C after 10 minutes, light microscopic image with polarised light of the wire's metallographic cross section (outer layer is false-coloured).

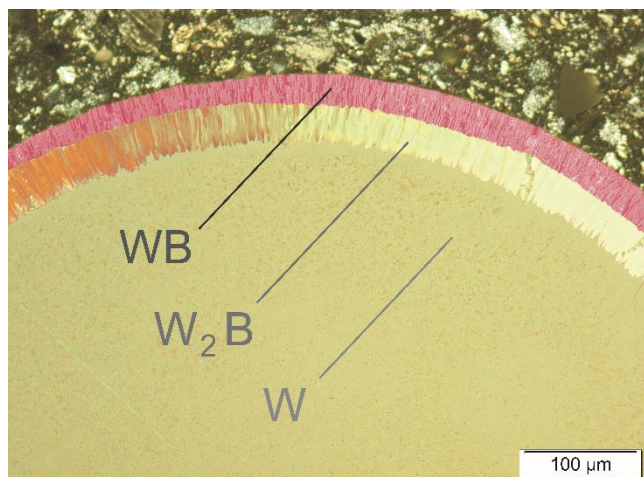


Fig.-4: Reaction product obtained at 1200 °C after 240 minutes, light microscopic image with polarised light of the wire's metallographic cross section (outer layer is false-colored).

Thermodynamic considerations

In order to obtain clarity about the proceeding chemical reactions, thermodynamic model calculations for the case of equilibrium have been performed including the known solid phases and all potentially occurring gas species in the respective system. Due to the experimental arrangement, a very high temperature gradient from the reaction temperature at the wire to almost room temperature is developed. The resulting convection leads to a continuous and fast mass exchange through the gas phase. This is why the calculations for the case of equilibrium should be seen as an approximation. This approximation is only applicable closely around the wire as the place of reaction, but allows a comparison for the different systems among each other. Figure 5 shows the partial pressures of the occurring gas species for the reaction of hafnium and tungsten, respectively, with boron tribromide in coexistence with the respective solid phases.

It becomes clear that hafnium reacts with boron tribromide to hafnium tetrabromide almost quantitatively. Free bromine and boron tribromide hardly appear at equilibrium. Based on the calculated pressures the reaction can basically be described by equation (3).



HfBr₄ is formed in high concentrations and condenses almost completely at the wall of the reaction vessel. Thus, it is constantly withdrawn from the equilibrium, which leads to a faster progress of the reaction.

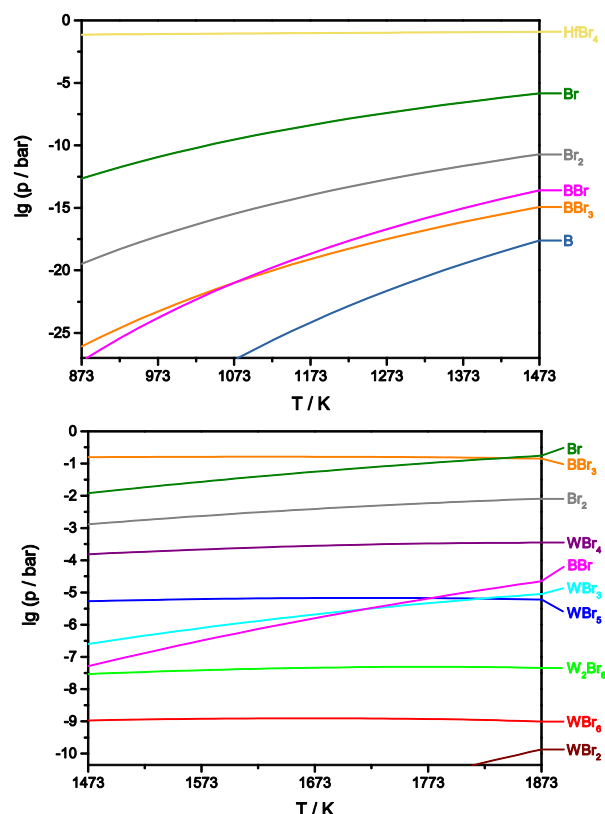
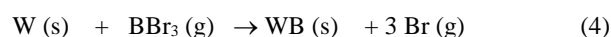


Fig.-5: Partial pressures as a function of temperature (for the state of equilibrium) of the occurring gas species for the reaction of the metal (top: hafnium, bottom: tungsten) with boron tribromide.

The W/B/Br system shows a very different behaviour: the high partial pressure of boron tribromide indicates its low reactivity with tungsten; free bromine forms while the tungsten bromides develop only minor partial pressures. Correspondingly, only small amounts of tungsten bromide condense and are withdrawn from the equilibrium. The main product remains in the gas phase in its entirety and isn't withdrawn from the equilibrium. This is a main reason for the significantly increased reaction progress. As a result the whole reaction proceedings around the formation of WB can be approximately described by the following reactions.



The formation of W₂B runs according to reaction (6).



These considerations allow certain predictions on the way of reacting in M/B/Br systems not yet investigated with this procedure.

The reaction of a solid metal with a gaseous boron halide at elevated temperatures provides an innovative access to the synthesis of borides. Orienting

experiments and thermodynamic considerations justify the expectation that a majority of the transition metals as well as the f-elements could be converted to borides with this procedure. Such reactions can be conducted crucible-free as described here; some other experimental set-ups are conceivable as well.

External Cooperation Partners

R. Köppe (Karlsruher Institut für Technologie, Germany)

References

- [1] *Crucible-Free Preparation of Transition-Metal Borides: HfB₂*, A. Henschel, M. Binnewies, M. Schmidt, H. Borrmann and Y. Grin, *Chem. Eur. J.*, **23** (2017) 15869, <http://doi.org/10.1002/chem.201703181>.
- [2] *Tungsten borides – on the reaction of tungsten with boron(III) bromide*, A. Henschel, M. Binnewies, M. Schmidt, R. Köppe, U. Burkhardt and Y. Grin, *Chem. Eur. J.*, **24** (2018) 10109, <http://doi.org/10.1002/chem.201801778>.

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