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The Role of Autogenic Halide Gas in the Production of Metal Borides

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Synthesis of metal borides is typically undertaken at high temperature using direct combinations of elemental starting materials[1]. Techniques include carbothermal reduction using elemental carbon, metals, metal oxides and B2O3[2] or reaction between metal chlorides and boron sources[3]. These reactions generally require temperatures greater than 1200°C and are not readily suitable for an industrial setting nor scalable to bulk production.

Shi et al.[4] have demonstrated a lower temperature reaction process at 650°C which utilizes solid-state synthesis between metal chlorides, NaBH₄ and Mg in an autoclave. Zhang et al.[5] produce a range of rare earth hexaborides at temperatures as low as 400°C in an autoclave using metal chloride precursors. Wang et al.[6] used a similar procedure using Mg and I₂ to assist in the reaction. More recently, Portehault et. al.[7] developed a general solution route for producing a range of nano-scale metal borides. This process uses metal chlorides as metal precursors and sodium borohydride as a boron source in a molten salt eutectic of LiCl/KCl to enhance the reaction. These studies show a significant improvement in reaction kinetics by including halides as part of the boride synthesis.

However, there are limited data on the pressure(s) that may be developed during these low temperature reactions. Given the vapour pressures and volatility of some halides, it is surprising that to-date the role of associated pressure with halide type is not well documented. Here we report a systematic investigation on the role of autogenic halide gas, generated during the synthesis of metal borides. The reactions are carried out in an instrumented closed system using a 50ml Parr reactor at temperatures up to 500°C and a maximum pressure of 20 MPa.

For YB₄ or VB₂ synthesis, stoichiometric ratios of chloride starting materials (e.g. YCl₃; VCl₃) are mixed with NaBH₄ in an oxygen-free environment, transferred to the Parr reactor and heated to 500°C for periods up to 20 hours. Production of gases is dependent on the initial volume of reactants with maximum pressure during the reaction of 4.5MPa for up to two hours. The autogenous pressure reduces gradually over time while the reactor is held at maximum temperature and reflects the formation of boride product which is also accompanied by the formation of NaCl and other trace phases. In general, micron-sized euhedral forms of VB₂ and YB₄ intermixed with salts and other phases are formed by this process.

References