Announcing the Final Examination of Zhilin Xie for the degree of Doctor of Philosophy

Time & Location: October 27, 2014 at 10:30 AM in ENG 288
Title: Rhenium, Osmium and Iridium Diborides by Mechanochemistry: Synthesis, Structure, Thermal Stability and Mechanical Properties

Borides are implemented in a range of industrial applications due to their unique mechanical, electrical, thermal and catalytic properties. In particular, transition metal diborides are of special interest. In the recent years, borides of rhenium (Re), osmium (Os) and iridium (Ir) have been studied as for their ultra-hardness and superior stiffness. In this dissertation, a mechanochemical method is introduced to produce rhenium diboride (ReB$_2$) powder, a novel hexagonal osmium diboride (h-OsB$_2$), and iridium borides' powders. Densification by Spark Plasma Sintering, thermal stability and mechanical properties of h-OsB$_2$ were also studied.

ReB$_2$ was recently reported to exhibit high hardness and low compressibility, which both are strong functions of its stoichiometry, namely Re to B ratio. Most of the techniques used for ReB$_2$ synthesis reported 1:2.5 Re to B ratio because of the loss of the B during high temperature synthesis. However, as a result of B excess, the amorphous boron, located along the grain boundaries of polycrystalline ReB$_2$, would degrade the ReB$_2$ properties. Therefore, techniques which could allow synthesizing the stoichiometric ReB$_2$ preferably at room temperature are in high demand. ReB$_2$ powder was synthesized at low temperature using mechanochemical route by milling elemental crystalline Re and amorphous B powders in the SPEX 8000 high energy ball mill for 80 hours. The formation of boron and perrhenic acids are also reported after ReB$_2$ powder was exposed to the moist air environment for a twelve month period of time.

Hexagonal osmium diboride (h-OsB$_2$), a theoretically predicted high-pressure phase, has been synthesized for the first time by a mechanochemical method, i.e., high energy ball milling. X-ray diffraction (XRD) indicated the formation of h-OsB$_2$ after 2.5 hours of milling, and the reaction reaches equilibrium after 18 hours of milling. The lattice parameters of the h-OsB$_2$ are $a=2.916\,\text{Å}$ and $c=7.376\,\text{Å}$, with a P6$_3$/mmc space group. Transmission electron microscopy confirmed the appearance of the h-OsB$_2$ phase. The thermal stability of h-OsB$_2$ powder was studied by heating under argon up to 876 °C and cooling in vacuo down to -225 °C. The oxidation mechanism of h-OsB$_2$ has also been proposed. The hexagonal phase partially converted to the orthorhombic phase (20 wt.%) after spark plasma sintering of h-OsB$_2$ at 1500°C and 50MPa for 5 minutes. Hardness and Young's modulus of the h-OsB$_2$ were measured to be 31 ± 9 GPa and 574 ± 112 GPa, respectively by nanoindentation method.

Prior to this research a number of compounds have been prepared in Ir-B system with lower than 2 boron stoichiometry, and no IrB$_2$ phases have been synthesized experimentally. In this dissertation, three new iridium boride phases, ReB$_2$-type IrB$_2$, AlB$_2$-type IrB$_2$ and IrB have been synthesized with a similar mechanochemical method. The formation of these three phases has been confirmed by both X-ray diffraction (XRD) and transmission electron microscope (TEM) after 30 hours of ball milling and 48 hours of annealing. The IrB$_2$ phases have hexagonal crystal structures and the new IrB phase has an orthorhombic crystal structure. The segregation of iridium from iridium borides' lattices has also been studied by high resolution TEM.

Major: Mechanical Engineering

Educational Career:
Bachelor's of Process and Control Engineering, BS, 2010, China University of Petroleum
Master's of Mechanical Engineering, MS, 2012, University of Central Florida

Committee in Charge:
Nina Orlovskaya, Chair, Department of Mechanical and Aerospace Engineering
Richard Blair, Co-Chair, Department of Mechanical and Aerospace Engineering; Department of Physics
Jan Gou, Department of Mechanical and Aerospace Engineering
Seetha Raghavan, Department of Mechanical and Aerospace Engineering
Linan An, Department of Materials Science and Engineering

Approved for distribution by Nina Orlovskaya, Committee Chair, on October 12, 2014.

The public is welcome to attend.