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The influence of SPS heating rates on the synthesis reaction of tantalum diboride

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ABSTRACT

TaB_2 is a material from the Ultra High Temperature Ceramics group and is rather unexplored because it is difficult to procure the raw materials and to densify TaB_2. Using SPS technique to realize reactive sintering processes of powders mixture according to the reaction $Ta + 2B \rightarrow TaB_2$ makes it possible to achieve TaB_2 in one technological step. The aim of the study was to determine the influence of heating rates on the synthesis reaction and on the multistage densification mechanisms during SPS processes. The mixture was sintered at constant parameters of 2200 °C, 48 MPa for 5 min with the usage of heating rates from 50 °C/min up to 400 °C/min. The densification processes were studied through analyzing the shrinkage of powder compacts during SPS (Spark Plasma Sintering) processes. The comparison of the densification curves indicates that the reactions do not proceed completely at slow heating rates. Namely, too low heating rates contribute to the sintering of tantalum before the synthesis reaction and demonstrate the presence of boron in liquid state. The best material obtained in this study has Young's modulus 571 GPa, Vickers hardness 20.7 GPa (HV1) and indentation fracture toughness K_{IC} 4.7 MPa m$^{1/2}$.

Influencia de las velocidades de calentamiento en la reacción de síntesis del diboruro de tántalo obtenido mediante SPS

Palabras clave:
Diboruro de tántalo
Sinterización reactiva
Sinterización por corriente eléctrica pulsada (SPS)
Materiales cerámicos

RESUMEN

El TaB_2 es un material perteneciente al grupo de cerámicas de ultra alta temperatura muy poco investigado tanto por la complejidad de encontrar materias primas adecuadas, como por su difícil densificación. Mediante la técnica SPS se consiguen procesos de sinterización reactiva de mezcla de polvos de acuerdo a la reacción $Ta + 2B \rightarrow TaB_2$ que permiten preparar TaB_2 en un única etapa. El objetivo de este trabajo fue estudiar la influencia de las velocidades de calentamiento en la reacción de síntesis, así como determinar los mecanismos de densificación durante el proceso. La mezcla fue sinterizada a parámetros constantes de 2200 °C,

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48 MPa durante 5 min y a velocidades de calentamiento de 50 °C/min a 400 °C/min. Los procesos de densificación fueron estudiados mediante análisis dilatométrico de los compactos durante los procesos de SPS (sinterización por corriente eléctrica pulsada). La comparación de las curvas de densificación indica que las reacciónes son incompletas a velocidades de calentamiento bajas. Estas contribuyen a la sinterización del Tántalo antes de la reacción de síntesis y esto demuestra la presencia de boro en estado líquido. El mejor de los materiales preparados posee un valor del modulo de Young de 571 GPa, una dureza Vicker de 20.7 GPa (HV1) y resistencia a la fractura de 4.7 MPa $m^{1/2}$.

Introduction

The progress in advanced industries requires new, perfect materials. There is a demand for materials able to work at very high temperatures or in particularly aggressive environments. This demand opens many new opportunities and it provides a challenge for scientists to obtain new durable materials. The materials of the future should have a high hardness, resistance to oxidation and to thermal shock, chemical stability, good strength and, what is most important for these applications, it should have a high melting point and Young's modulus. Only several elements and compounds in the world have a melting point of above 3000 °C [1]. These are mainly borides, carbides and nitrides of the transition metals from IV, V and VI group of the periodic table (like Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W). These ceramic materials have the hardness of above 20 GPa, the Young's modulus of about 500 GPa and additionally metal-like properties (electrical and thermal conductivity). All these characteristics make these materials attractive among the conventional ceramics. Tantalum diboride (TaB_2) is a material which is rather unexplored due to the low availability of raw materials and due to problems with its densification [2]. The main properties of this material are: the density of 12.60 g/cm^3, the melting point at 3200 °C and Vickers hardness of above 20 GPa [3]. Most ceramic materials, before sintering, must be prepared by the various forming methods such as pressing, powder injection molding, direct coagulation casting and others [4]. A single-phase TaB_2 is usually obtained in a few technological stages: pressureless synthesis, milling of the reaction products and finally sintering processes. The reactions can occur directly through the synthesis of the metal with boron (1) or through the reduction of its oxide (2) [3,5].

$$Ta + 2B \rightarrow TaB_2 \quad (1)$$

$$Ta_2O_5 + B_4C + 4C \rightarrow 2TaB_2 + \text{gases} \quad (2)$$

Due to its properties, tantalum diboride often occurs in other ceramic materials, for example according to the reactions [6–9]:

$$2Ta + B_4C + Si \rightarrow 2TaB_2 + SiC \quad (3)$$

$$4TaC + B_4C \rightarrow 2TaC + 2TaB_2 + 3C \quad (4)$$

$$TaC + B_4C + 3Ta \rightarrow 2TaB_2 + 2TaC \quad (5)$$

$$2TaCl_5 + 5MgB_2 \rightarrow 2TaB_2 + 5MgCl_2 + 6B \quad (6)$$

Zhang et al. [3] obtained a single-phase tantalum diboride material from TaB_2 powder using Hot Pressing method. The powder was synthesized by the reduction of Ta_2O_5 using B_4C and graphite (2) in an alumina furnace. The material obtained had the following properties: Young's modulus – 551 GPa, Vickers' hardness – 25.6 GPa (HV0.5), flexure strength – 555 MPa, and fracture toughness – 4.5 MPa $m^{1/2}$.

Musa et al. [10] reported that the consolidation of TaB_2 during RSPS (Reactive Spark Plasma Sintering) processes is significantly improved (up to ~96% of apparent density) when the pressure applied is increased from 20 MPa to 60 MPa immediately after the synthesis reaction. The mechanical properties of the materials obtained in this study were consistent with the values reported by Zhang.

Licheri et al. [11] described two processes of obtaining monolithic tantalum diboride: (i) from precursors through Self-propagating High-temperature Synthesis followed by SPS (SHS-SPS) and (ii) directly by means of Reactive Spark Plasma Sintering (RSPS). The study showed a dual distribution of mean grain size, along with almost no residual porosity for the materials from RSPS processes and with diffused trapped porosity for TaB_2/SHS-SPS which had corrupted the mechanical and oxidation performances.

In the study presented in this paper, the SPS/FAST (Spark Plasma Sintering/Field Assisted Sintering Technique) method was chosen for densification processes. This method was chosen because it enables a precise setting and control of heating rate, pressure and temperature, including high sintering temperatures. SPS/FAST also provides other technological and economical advantages in comparison to conventional sintering methods [12]. These advantages include: lowering the sintering temperature necessary to obtain fully dense materials, shorter holding time, a wide range of heating rates, the elimination of the forming step. Additionally, the application of pressure and pulse electric current which is flowing through the particles in SPS/FAST processes, makes it possible to obtain materials from powders which are difficult to sinter [13]. Moreover, when used for reactive sintering, the SPS/FAST method allows for the synthesis and the sintering to occur during one process. The consolidation of refractory ceramic powders in relatively lower conditions, combined with the elimination/reduction of some technological steps