

Feasibility Study of Metallic Reductant Element Replacement by Mechanical Activation Process in ZrB₂-ZrC Composite Synthesis from Raw Oxide Materials by SHS

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Abstract: Because of many advantages of self-propagating high-temperature synthesis, this method is used increasingly for advanced compounds and composite materials production. ZrB₂-ZrC composite has unique characteristics, so its synthesis with the least undesirable phases is an important problem for producing this composite. In this research, synthesis of this composite by metallic element as a reductant agent by SHS is done successfully, but elimination of undesirable compounds are costly and difficult. In order to prevent creating these compounds, replacement of metallic element by MASHS process, thermodynamically and practically points of view were studied. According to used mechanical activation conditions, synthesis of desirable composite was not occurred. For this process replacement, the initiating activation energy subject was discussed for achieved results.

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1. Introduction

ZrB₂-ZrC composite has unique properties such as high melting point, high strength and hardness, good toughness, low evaporation rate, chemical stability and good electrical and heat conductivity, so because of them, this composite is candidate as a constructional component for producing high temperature, erosive and corrosive environments resistance compounds [1,2]. Other used processes for preparing this composite is hot pressing (HP), spark plasma sintering (SPS), reactive hot pressing (RHP) and pressureless sintering (PS) [1].

Foundation of SHS process is based on exothermic reactions which after starting the reaction by sufficient energy, it continues spontaneously to consume reactants for producing of products. Amounts of produced heat are important, because next raw materials need to it for starting their reaction. This heat leads in combustion temperature [3]. The most important SHS process advantage is using of it for producing UHTC¹ materials. Other advantages of this process are high energy efficiency, producing pure products, suitable for single phase or composite compounds synthesis and simultaneously densification of them. Recently this process is

modified practically by mechanical (used for this research), chemical, preheated and electromagnetism activation [4].

According to these characteristics for SHS process and our own accord composite, it should be expected that ceramics which is prepared by ZrB₂ and ZrC and mentioned process have an excellent potentials for preparing heat resistance structures. For this purpose, preparing ZrB₂-ZrC composites with fine structure and without impurities and undesirable phases are very important [5].

For initiating of some SHS reactions, chemical oven is used as producers of extreme needed heat. These ovens selected in such way that before starting the main reaction in furnace or reaction chamber, materials of oven react and produce sufficient heat for starting the main reaction and then it will be continued by itself [6].

1. Scope

In synthesis of ZrB₂-ZrC composite by SHS process and Magnesium as a reductant and heat preparatory agent, undesirable phases produced by this metal compounds are unavoidable; so, this research is aimed to prevent producing them by

¹ Ultra High Temperature Ceramics

changing the process to MASHS² and eliminating of Magnesium from reactants.

2. Experimental procedure

Zirconium dioxide (ZrO₂) powder (SIGMA-Aldrich, 99% purity), Boron trioxide (B₂O₃) powder (SDFCL, 99% purity), Graphite (MERCK, 99% purity), and Magnesium powder (SIGMA-Aldrich, 99% purity) were mixed and ball milled stoichiometrically for 15 minute (as 0 hour ball milled sample and only mixture) for Magnesium included samples and 15 minute (as 0 hour ball milled), 3, 6 and 10 hours for Magnesium free samples in BPR=15 and 300rpm condition by ball mill machine. Prepared powders were pressed by one directional pressing machine in 300MPa compression condition. Samples were processed in an electrical resistance furnace under Argon inert gas flow at 850 °C, 950 °C and 1050 °C synthesis temperatures. Magnesium free samples processed in 1050 °C were processed for second time by chemical oven. Products of

furnace were analyzed by X-ray diffraction instrument for achieving XRD patterns. Characteristics of X-ray instrument are: Type: Philips pw3710, 40kV, 30mA, Anode: Cobalt ($\lambda=1.789010^{\circ}\text{A}$), Step size=0.02, (Time/Step)=0.5sec.

3. Results and discussion

3.1. Magnesium included chemical reaction (1): $2\text{ZrO}_2 + \text{B}_2\text{O}_3 + \text{C} + 7\text{Mg} = \text{ZrB}_2 + \text{ZrC} + 7\text{MgO}$

These three samples were processed under 850 °C, 950 °C and 1050 °C and Argon flow controlled atmosphere condition and all three samples were synthesized severely in a short time as powder. Explosion mode of synthesis is attributed to vaporization of B₂O₃ under reducing condition [7, 8, and 10]. It is obvious from Figure1 that desirable ZrB₂ and ZrC phases are synthesized in 850 °C furnace temperature. This sample received the least activation energy in this group. Undesirable phases including Magnesium are detected in products which influence on synthesized composite characteristics and removing of them are costly and difficult.

² Mechanical Activation Assisted Self-Propagating High-Temperature Synthesis

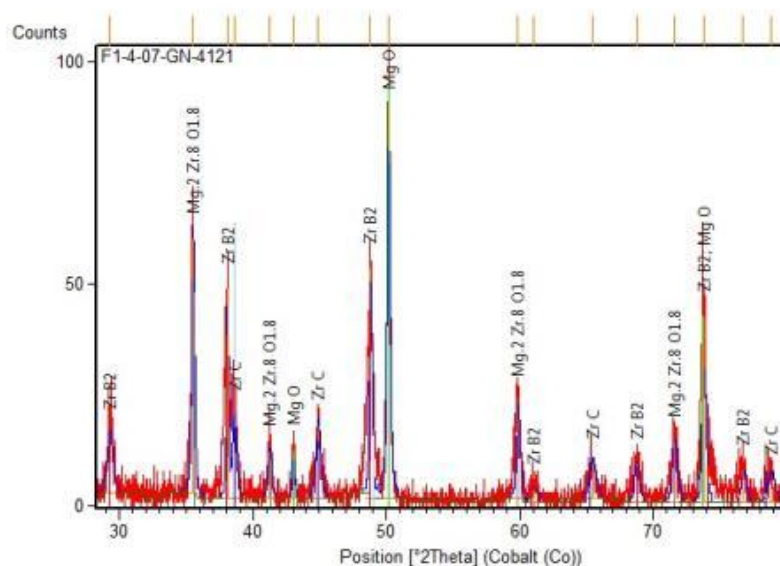


Figure1. XRD pattern for 850 °C processed sample (equation No.1) [9]
(By product peaks are obvious)

Thermodynamically study of reaction (1) showed if activation energy is prepared, the reaction will be initiated and continued spontaneously. Heat

generating (exothermic) and abiding of this reaction could be seen in Figure2 [10].

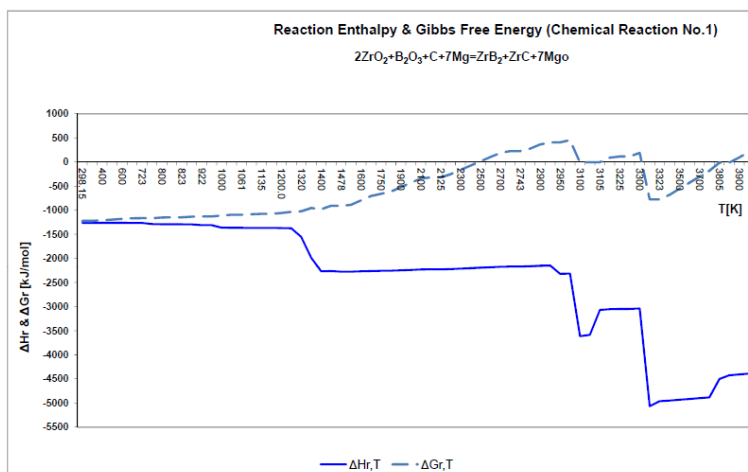


Figure2. Enthalpy and Gibbs free energy of reaction No.1 vs. temperature [10]

The products of reaction (1) are more stable than its reactants (Figure3). This means that under definite condition for synthesis of this reaction, difference between products and reactants energy located in

minus energy regions, so needed heat for continuing the reaction is prepared and from other sight of view, Gibbs free energy shows good situation for stability of the products [10].

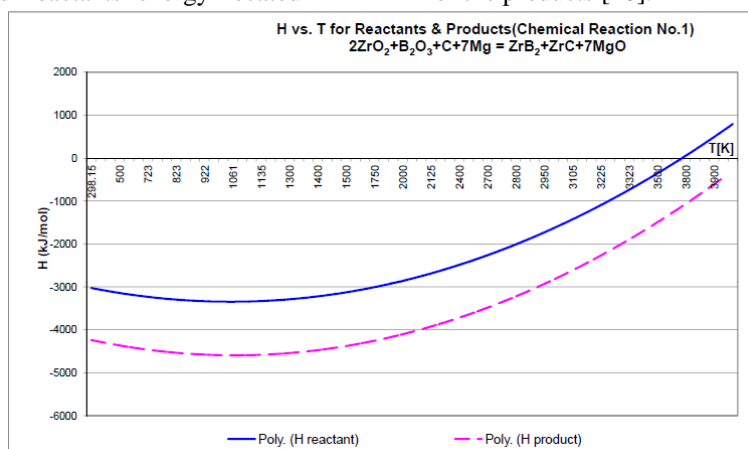


Figure3. Diagram of enthalpy for reactants and products for reaction No.1 vs. temperature [10]

3.2. Magnesium free chemical reaction (2): $4\text{ZrO}_2 + 2\text{B}_2\text{O}_3 + 9\text{C} = 2\text{ZrB}_2 + 2\text{ZrC} + 7\text{CO}_2$

For reaching to boundary condition of thermal and minimum mechanical activation needed for initiating synthesis of reaction (2), samples were entered in controlled atmosphere furnace from the least received thermal and mechanical activation energy, i.e. 0 hour ball milled and 850 °C furnace temperature without chemical oven, to the most encountered energy, i.e. 10 hours ball milled, 1050 °C furnace temperature and chemical oven accompanied. Used chemical oven composition was Mo+1.4Si+0.6Al, which reacts suddenly and

creates very much thermal shock. According to this procedure, there are 16 samples. Chemical oven is used only for four samples which processed at 1050 °C condition. None of processed sample of this group showed ostensibility changes that implicated to synthesis occurrence. So, only the last item of each milling class i.e. 0, 3, 6 and 10 hours ball milled samples which exposed to 1050 °C accompanied by chemical oven (maximum received thermal shock in each class) were analyzed by X-ray diffraction method (Figure4).

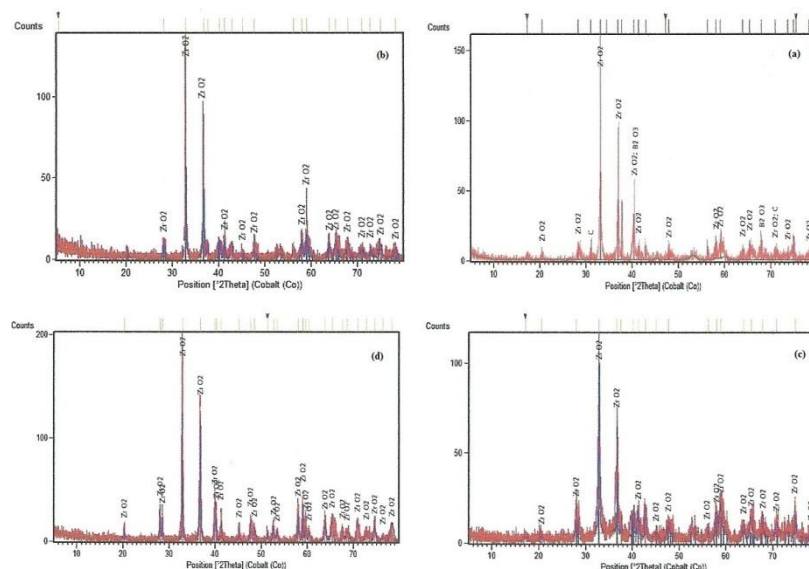


Figure4. XRD patterns for 1050 °C processed samples accompanied by chemical oven (equation No.2) Ball milled for a) 0hr, b) 3hrs, c) 6hrs and d) 10hrs [9]

As could be seen, no ZrB_2 or ZrC pick observed in XRD patterns. In Figure5 ZrB_2 and ZrC enthalpy and

Gibbs free energy of formation indicated that synthesis of them is exothermic and abiding [10].

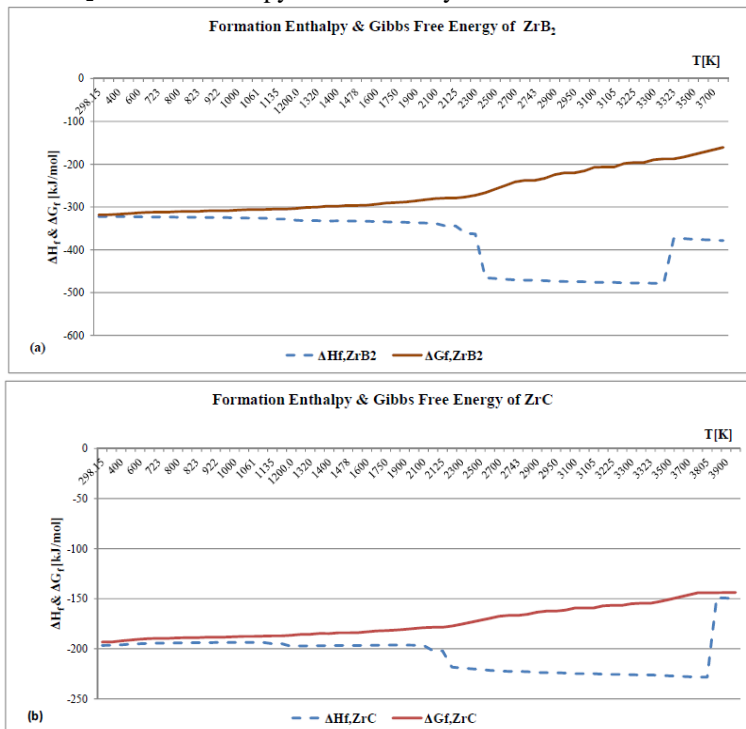


Figure5. Diagram of Formation enthalpy and Gibbs free energy vs. temperature for a) ZrB_2 & b) ZrC [10]

So, according to chemical reaction (2) and thermodynamical data, products are stable if they synthesized, but by observing Figure4 (d) even by applying the most mechanical activation and thermal excitation, none of ZrB_2 and ZrC phases synthesized. So, reason must be tracked in whole of reaction. By

elicitation thermodynamical data for chemical equation (2), it was cleared enthalpy and Gibbs free energy of reaction has positive quantities of energy till 3000 °C (roughly) which means no reaction in desire direction will be occurred (Figure6) [10].

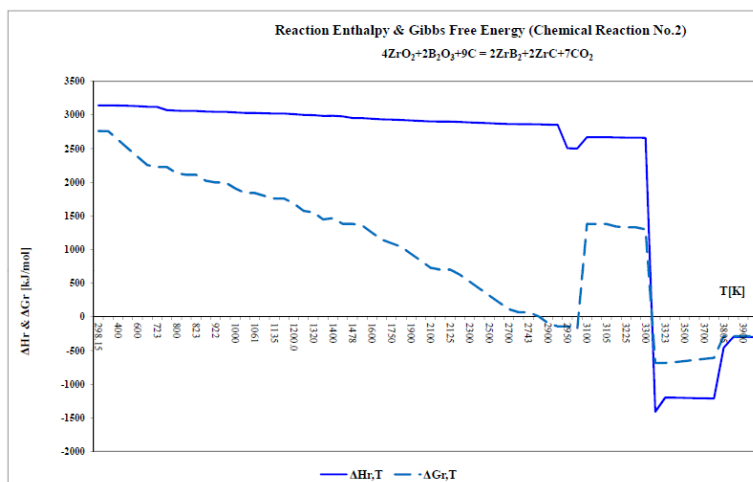


Figure6. Enthalpy and Gibbs free energy of reaction No.2 vs. temperature [10]

Also, according to enthalpy changes diagram of products and reactants vs. temperature, abiding of

reactants in comparison of products are cleared until 3400 °C roughly (Figure7) [10].

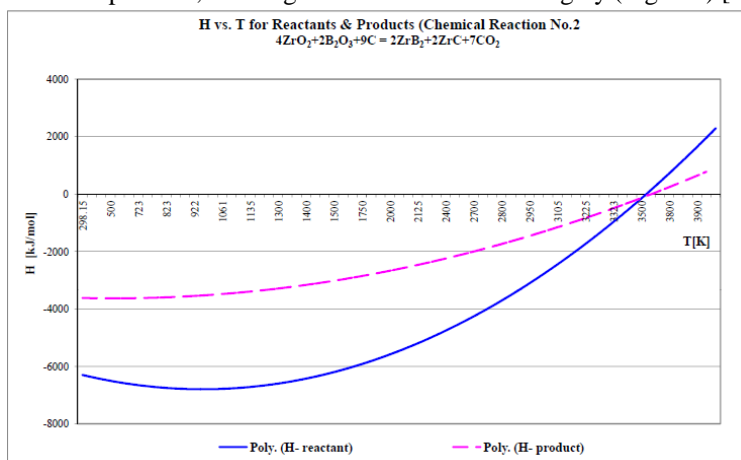


Figure7. Diagram of enthalpy for reactants and products for reaction No.2 vs. temperature [10]

Because difference of these two diagrams is located in minus regions, there is no tendency to reaction occurrence in desire direction. Trend of alterations in high temperatures are in such way that products (ZrB₂ and ZrC) are more stable against reactants, but this time in positive regions.

According to achieved results and thermodynamical analysis, reaction occurrence in desire way is very much endothermic and need to very high abiding activation energy, so that 10 hours mechanical activation in mentioned conditions and using of chemical oven in 1050 °C furnace temperature could not initiate and continued the reaction. So, using of metallic reductant element for promoting the reaction and achieving ZrB₂ and ZrC compounds with surveyed conditions in this research is unavoidable.

4. Conclusion

1. In presence of Magnesium as a reductant element, summation of reactants enthalpy in equation (1) is more than summation enthalpy of products, even without activation of raw materials.
2. ZrB₂-ZrC composite synthesis from raw oxide materials in presence of metallic reductant element has lowered activation energy, so initiating and continuing of reaction is available.
3. Producing of undesirable phases because of presence of Magnesium meanwhile ZrB₂-ZrC synthesis from raw oxide materials is unavoidable.

4. Summation of reactants enthalpy in equation (2) is less than summation of products enthalpy (in inactivated situation).
 5. In spite of exothermic formation and abiding of products in equation (2), activation energy for initiating and continuing of reaction was not prepared by mechanically activated raw oxide materials according to this research condition, even using chemical oven in the highest furnace temperature (1050 °C).
 6. For achieving the scope of this research, it is suggested thermodynamic of raw material activation in SHS process and also other methods of activation being studied.
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