Environment's Atmosphere and Preheat Influences on ZrB₂-ZrC Nanocomposite Synthesis by MASHS

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Abstract: Mechanical Activation Assisted Self-Propagating High-Temperature Synthesis (MASHS), as an advanced method in early decades is used for synthesis of advanced engineering compounds and composites; so, preparation of ceramic composites reinforced by second phase by this process is focused in different industries because of their unique thermal, erosion, corrosion, chemical, mechanical and electrical properties. In this research the influences of type and pressure of synthesis environment and preheating of samples on synthesis characteristics and structure of produced ZrB₂-ZrC composite were surveyed. Raw materials powder were mixed stoichiometrically and ball milled for 10 hours according to $2ZrO_2+B_2O_3+C+7Mg=ZrB_2+ZrC+7MgO$ chemical equation. Then influences of type and atmosphere of synthesis environments including relative vacuum, Argon gas in atmospheric pressure and pressurized Argon gas and also preheating of samples conditions on combustion reaction, synthesized phases and achieved product structure were studied. Synthesized samples were analyzed by XRD and SEM methods for inspecting of produced phases and achieved structures. XRD patterns revealed that by changing combustion environment from relative vacuum to pressurized atmosphere, process is more controllable for producing desirable phases but from structural point of view, only preheated sample was synthesized in the form of nanocomposite.
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1. Introduction

Amongst several advantages of mechanical activation assisted self-propagating high-temperature synthesis process, the most prominent of them is using of it for synthesizing of ultra high temperature ceramics (UHTC). Some of other advantages of this process are high efficiency of energy, producing pure products, and suitable for mono phase or composite materials synthesis and densification simultaneously [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. Requisite of occurrence such a phenomenon is adequate produced heat by reaction which raises the next reactants temperature in order to initiating reaction in them. This temperature is named combustion temperature. Under ideal conditions (adiabatic), the most achieved temperature in combustion region is adiabatic combustion temperature (T_{ad}). Another limiting factor for SHS process is relevance between enthalpy-heat capacitance ratio in 298K ((H/C_p) $_{298}$) and adiabatic temperature (T_{ad}). This relationship for some compounds is shown in Figure1. The proper limit for propagating SHS process for materials with $T_{ad}\leq T_m$

could be expressed as (H/C_p) $_{298}\geq2000K$. This means when adiabatic temperature is less than product melting point, if enthalpy-heat capacitance ratio in 298K be smaller than 2000K, propagating mode does not exist and external heat source such as preheating or chemical oven (exothermic reactants mixture) must be used [2]. Also, by using preheated raw materials, according to thermodynamial equations, adiabatic temperature is raised and more activation energy is prepared for performing of the reaction [3].
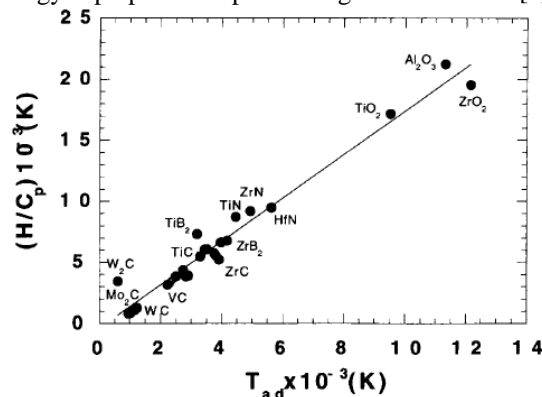

Figure1. *Enthalpy-heat capacitance ratio in 298K vs. adiabatic temperature ($T_{ad}\leq T_m$) [2]*

In some studies prerequisite for performing SHS process is production of very much heat due to reaction which must be more than H=40 kcal/mol or H=168 kJ/mol [4].

ZrB$_2$-ZrC composite unique properties such as high melting point, high strength and hardness, good toughness, low evaporation rate, chemical stability and good electrical and heat conductivity, make it suitable material for considering as a constructional component for producing high temperature and high erosive and corrosive environment resistance compounds. So, recently usage of this precious composite which produced by several kinds of process grows up increasingly. Amongst these processes, MASHS have a wide horizon for inspecting and research because of its new foundation and also from economical points of view is affordable which could produce nanocomposite structure materials [1-6].

1. Scope

In synthesis of ZrB$_2$-ZrC composite by SHS process from raw oxide materials, preparation of process activation energy from a combination between mechanical activation and preheating of reactants was studied and because of explosive mode of reaction, it was attempted to prepare a proper environment (atmosphere) for reacting of reactants in a controllable and none explosive mode.

2. Experimental procedure

In this research Zirconium dioxide (ZrO$_2$) powder (SIGMA-Aldrich, 99% purity), Boron trioxide (B$_2$O$_3$) powder (SDFCL, 99% purity), Graphite (MERCK, 99% purity), and Magnesium powder (SIGMA-Aldrich, 99% purity) were used stoichiometrically as raw materials. For reaching proper ball milled material, a planetary ball mill machine was used with 10 hours milling time, BPR=5 and 250rpm turning speed. Achieved raw material powder was pressed by a one directional press machine at 300MPa pressure. Samples were processed in a reactor with relative vacuumed (1.6*10^{-1}torr), flow of Argon gas and pressurized Argon atmosphere (1.9bar) in two main group; preheated and no preheated samples. Preheat temperature in this research is 200 °C. Products of reactor were analyzed by X-ray diffraction instrument for achieving XRD patterns. Characteristics of X-Ray instrument are: Type: Philips pw3710, 40kV, 30mA, Anode: Cobalt (λ=1.789010°A), Step size=0.02, (Time/Step) =0.5sec. Also for determination of morphology and grain size of products, only pressurized Argon gas condition synthesized samples were

sent to SEM laboratory Because of their synthesis were done under a controllable process.

3. Results and discussion

All two preheated and no preheated groups of samples were processed in reactor in order to have a controllable atmosphere for them. Because of extracting Oxygen and the other trapped gases in samples, the first step was done in 1.6*10^{-1}torr vacuum condition. Samples were synthesized in powder form and explosive mode. The source of heat for preparation of activation energy of the reaction was a radiant Tungsten filament (also for all other samples). The obtained powders from each sample were analyzed by XRD instrument and as it could be seen in Figure2 there are only ZrB$_2$ peaks and no ZrC peak.
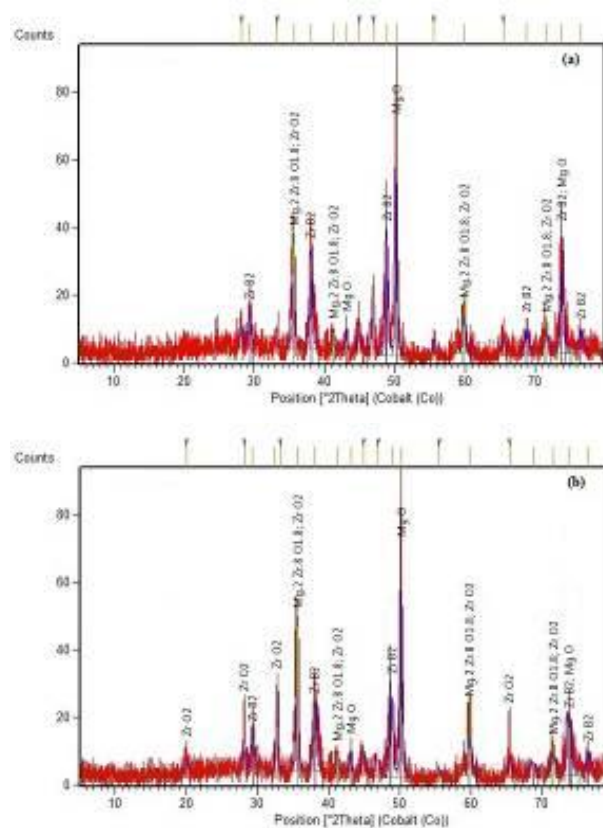

Figure2. *XRD patterns for synthesized samples in reactor under1.6*10^{-1}torr vacuum condition a) No preheated, b) Preheated [7]*

This phenomenon could be rationalized by evaporation of Magnesium because of high vapor pressure of it in high temperatures and dominant vacuumed condition. The remained reductant metallic element is used for reducing ZrO$_2$ and B$_2$O$_3$ [8, 10]. On the other hand from

thermodynamically points of view, ZrB_2 is a preferred compound for formation till ZrC and also first compound is more stable than second one. So the reduced products of this step of

process are consumed for ZrB_2 formation and because of it there is no detectable ZrC peak in XRD diagrams (Figure3).
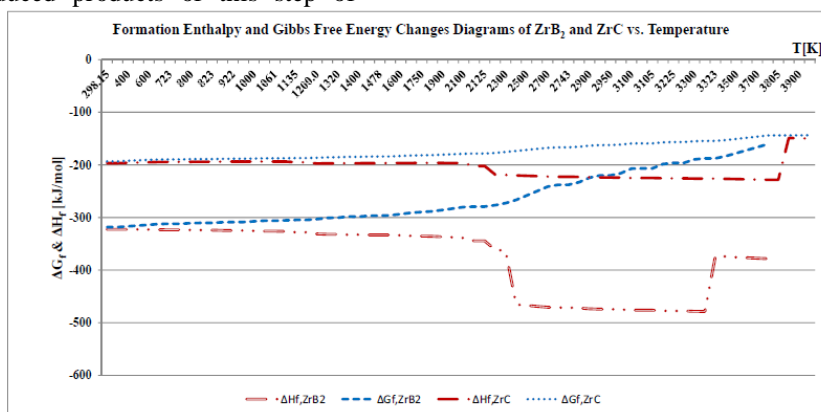

Figure3. *Formation enthalpy and Gibbs free energy for ZrB_2 and ZrC vs. temperature [9]*

In second step, samples were processed under Argon gas flow. Again products were in powder form but this time both ZrB_2 and ZrC phases have been seen in XRD diagrams (Figure4). This means there is enough reductant for formation both ZrB_2 and ZrC phases.

Figure4. *XRD patterns for synthesized samples in reactor under Argon gas flow*
a) No preheated, b) Preheated [7]
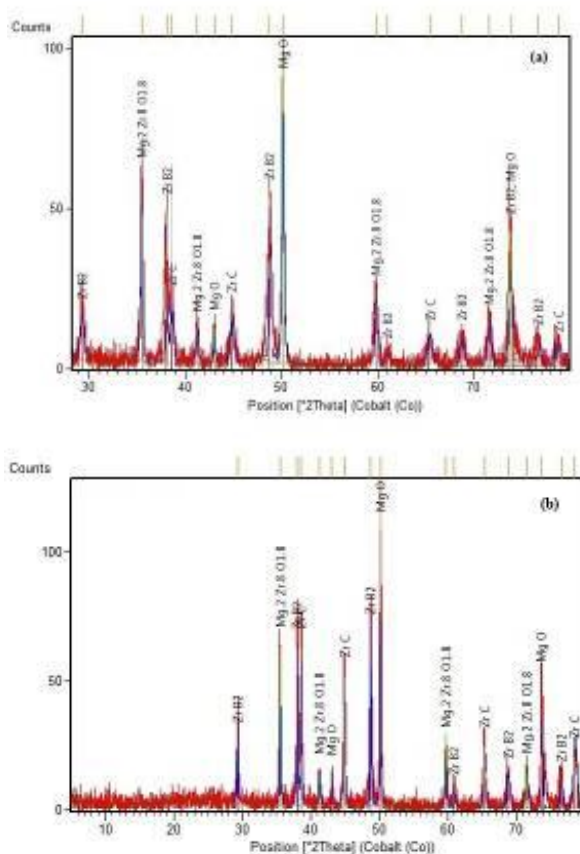
The third step was done in pressurized atmosphere condition with 1.9bar Argon pressure, because of samples explosion prevention. High vapor pressures of Magnesium and Boron trioxide in reducing environments are the main causes of this explosion [8, 10]. Vapor pressure diagrams of Magnesium and Boron trioxide are shown schematically in Figure5.
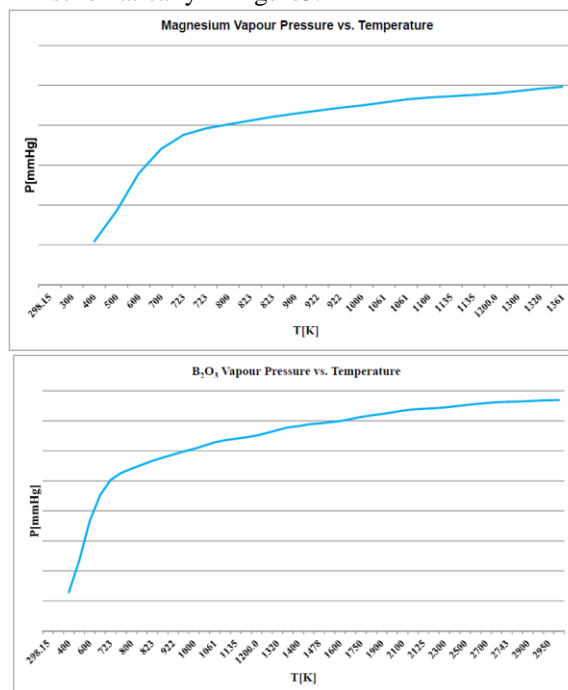

Figure5. *Schematics of Magnesium and Boron trioxide vapor pressures vs. temperature [9]*

Influence of environment's pressure on forms of products could be seen in Figure6.

***Figure6.** Samples form, a) Pressed raw material b) Synthesized without pressurized environment by inert gas (under vacuumed condition or Argon gas flow) c) Synthesized in 1.9bar Argon gas pressure*

Products of these reactions were analyzed and XRD diagrams in Figure7 show intensive peaks of ZrB2 and ZrC in diagrams.
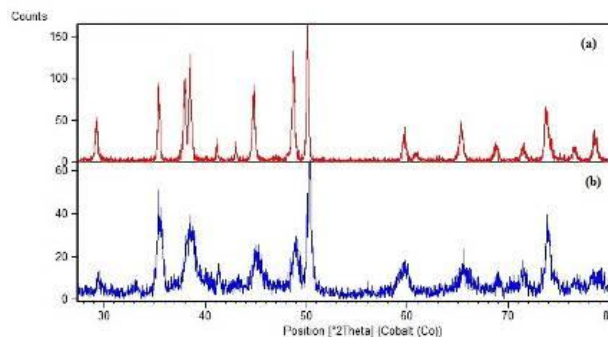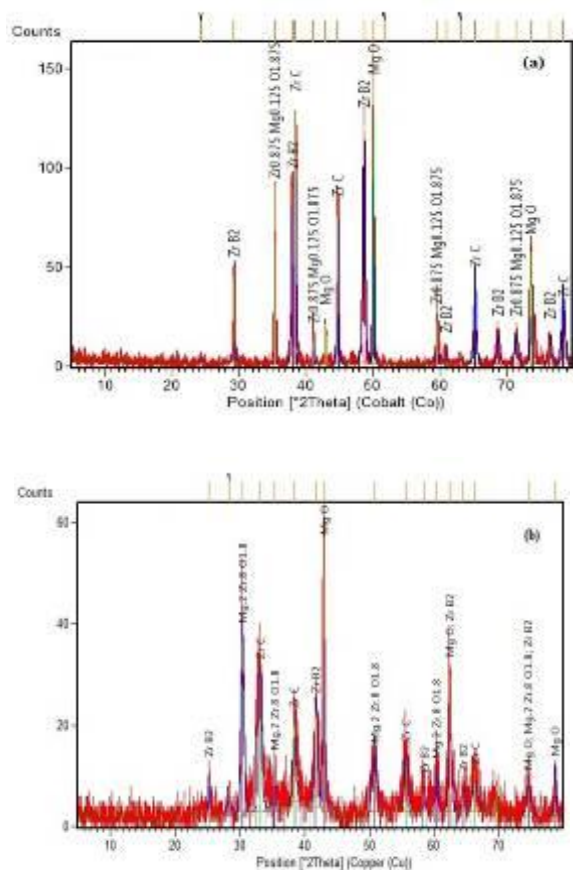

***Figure7.** XRD patterns for synthesized samples in reactor under 1.9 bar pressurizes Argon gas, a) No preheated, b) Preheated (widened peaks are evident in 200 °C preheated sample) [7]*

As could be seen in XRD diagrams (Figures2, 4&7), an oxide compound including Zirconium, Magnesium and Oxygen exist in all of them. This Magnesia stabilized Zirconia produced by dissolving of Magnesium oxide in ZrO_2 structure at high temperatures [11, 12]. This phase is produced unavoidably under this research conditions and from thermodynamical points of view, it is an abiding phase [9]. Another oxide phase is Magnesium oxide which eliminated by leaching easily.

In morphological study of produced composites in third step by SEM method, it was expected there were nano-sized particles and grains of synthesized phases, because of huge difference between products melting point (3245 °C for ZrB_2 and 3420 °C for ZrC) and ultimate combustion temperature of process i.e. 1176 °C (Figure8). According to Figure9 (a), no nano-sized grain was synthesized because in this situation, raw materials are less activated. No preheating causes to have less activation energy, so nucleation occurred less and the grains remained coarse meanwhile process. About preheated sample to 200 °C, in spite of elevated combustion temperature till 1490 °C, a desirable result was achieved. Produced grains had nano-size dimensions (Figure9 (b)).
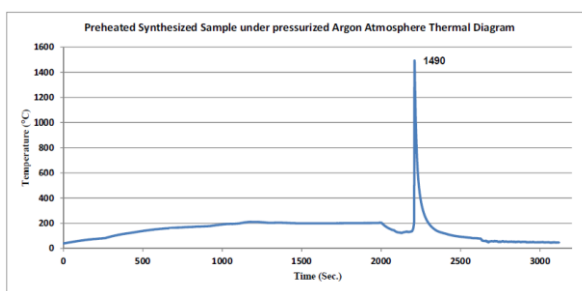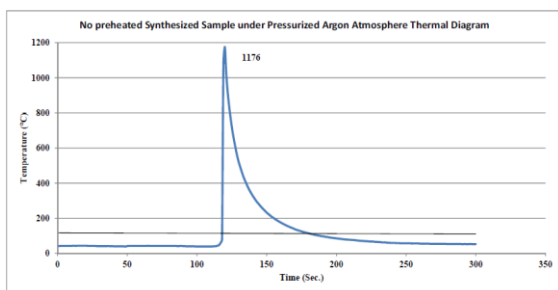
Figure8. *Thermal diagrams of synthesized samples in 1.9 bar pressurized Argon gas*
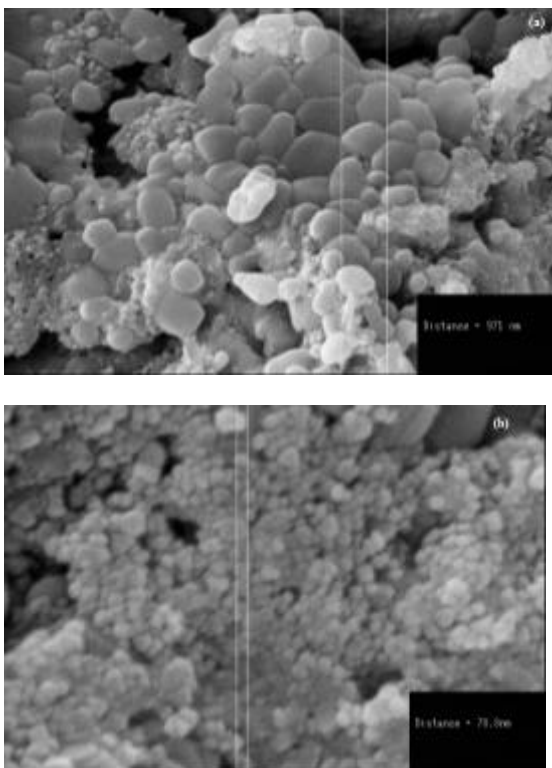

Figure9. *Morphology and grain size of a) No preheated sample and b) 200 °C preheated sample (×30,000)*

As could be seen from Figure7, results of XRD diagrams are similar and no new phase has been formed in preheated sample. According to $\Delta HT = \int_{T0}^{Tad} CpdT$ thermodynamic equation,

adiabatic temperature of reaction increased by preheating of sample and this means prepared activation energy is more than for no preheated sample, so enough activation energy is prepared for nucleation of new grains from structural defects which produced by ball milling of raw materials. Widening of peaks on Figure7 (b) validate this phenomenon.

4. Conclusion

1. Synthesis of ZrB_2-ZrC composite is not controllable under vacuumed atmosphere because some of reactants (Mg and B_2O_3) evaporated from reaction environment and reaction is done in an explosive mode without desirable composite formation.

2. Synthesis of ZrB_2-ZrC composite under Argon gas flow in preheated and no preheated condition is done in explosive mode as powder.

3. Synthesis of ZrB_2-ZrC composite under 1.9bar pressurized Argon gas condition, exits it from explosive mode and products form changed to bulk.

4. Producing of undesirable phases because of Magnesium presence meanwhile ZrB_2-ZrC synthesis from raw oxide materials under all used condition in this research is unavoidable.

5. Using preheat condition on synthesizing sample under pressurized Argon gas atmosphere, causes raised adiabatic temperature (which raised combustion temperature) and as a result, activation energy for nucleation from structural defects produced by mechanical activation and grain growth in a nano-metric scale is prepared successfully in this research.

6. As a proposal, it is suggested, new grain nucleation mechanism from defects and crystallites produced by mechanical activation in this process is studied more precisely.

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