

The Effect of Using Nano ZrO_2 on the Properties of W-ZrC Composite Fabricated through Reaction Sintering

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ABSTRACT

To fabricate W-ZrC composite through reaction sintering at first WC and ZrO_2 powders with molar ratio of 3-1 are ball milled, then the green body made from this mixture is sintered. Since reactivity is the main problem in sintering of micronized powders the starting ZrO_2 powder is selected in nano size to see whether the reaction improves. The XRD pattern indicates that W-ZrC composite has been formed, although some unreacted compounds still exist and some unwanted components have been created. In the case of using nano powders the amount of unreacted WC and ZrO_2 phases and unwanted W_2C phase reduces and the reaction progresses better. Additionally by using nano powders the reaction progressed and the mechanical proprieties including density, hardness, Elastic modulus and Flexural strength improved.

Keywords: W/ZrC Composite, Reaction Sintering, Tungsten Carbide, Nano Zirconium Oxide

1. Introduction

To improve low-temperature plasticity in tungsten and its strength at high temperature, making composite is an effective way. W-Cu and W-ZrC are the examples of such composites. Strength at high temperature and thermal shock resistance of those composites caused their application at high temperature environments, such as the nozzle throat of solid fuel rocket. In fact the ZrC has low coefficient of thermal expansion, high elastic modulus, good strength at high temperatures and low thermal conductivity. Also it is compatible with tungsten because they have a comparable melting point, similar coefficient of linear expansion and both have relatively high thermal conductivity. Furthermore W and ZrC exhibit little mutual solid solubility at high temperature and do not react to form other compounds. The density of zirconium carbide is almost one third of tungsten which results in a lighter composite. Consequently W and ZrC make a preferable composite [1-3].

Three way of production has been reported for fabrication of W/ZrC composites:

1) Displacive compensation of porosity (DCP): Porous WC preforms are produced by gel casting, hot isostatic

pressing or other conventional ceramic processes and then the porous preform will be exposed to molten Zr_2Cu at 1200 - 1300°C and ambient pressure. The Zr_2Cu liquid rapidly infiltrate into the preform and undergoes a displacement reaction with WC to yield dense ZrC/W composite. Among the advantages of this process are less required pressure and heat rather than hot press, possibility of making larger and more complex parts and lower cost, but being a two-stage method, retention of copper-rich phase which usually makes unwanted impurities with a low melting temperature within the composite and inability to control the exact size and porosity of the preform and therefore production of the same part are the disadvantages of this method [1-4].

2) Hot-press: This method is one of the most expensive and perhaps the most common processes used for making composites because of its simplicity. It is similar to warm sintering unless the temperature and pressure are applied simultaneously. Of all advantages that this method contains, increasing the properties of raw and sintered material such as density, strength and fatigue properties is the main one. Other advantages of this method are less grain growth, less porosity, higher strength and improving the high temperature properties. However simple

shape of made parts which needs further machining decreases the speed of the production and increases the cost. High pressure and high temperature required in this method are the main disadvantage of hot pressing [5-12].

3) Reaction sintering: It is a new method for producing W/ZrC composite in which metal powders are subjected to high temperatures, typically in an inert atmosphere or under vacuum. In this method ZrO_2 and WC powders are mixed in desired volume or mass fraction, at the presence of a suitable binder. The mixed powders then form a green body which at the next stage is heated at a temperature sufficient for the binder to be volatilized, between 400 - 600°C and then the temperature is elevated up to 1850°C to produce an oxide-reduced or partially-sintered body. The temperature of the partially sintered body is then raised to 2100°C to complete the densification [13].

In this study, the W-ZrC composite is fabricated by reaction sintering of WC and ZrO_2 Powders that are selected in micron and nano size to see the differences between the resultant composites. One objective of the present study is to investigate the changes after using the nano particles instead of micron particles. Therefore in order to compare the composites at first a sample reference is made from micron powders, then it will be compared with a composite that has been made by using nano powders. For this the volume fraction of different phases which has been formed in both composites is approximately estimated by the ratio of the integrated area of the peaks and the total XRD patterns [14] to see the efficiency of process. The densities of best obtained samples are determined using Archimedes method, according to ASTM B311 standard method. The hardness is evaluated in accordance with ASTM E10. Moreover the bending strength of the composite has been measured by bending test according to ASTM C1161 and the modulus of elasticity is measured as well, by ASTM C1419 test standard method. Also by secondary electron microscopy (SEM) and back scattered electron (BSE) the morphology of samples are studied.

2. Experimental

Commercial tungsten carbide powder ($d_{50} = 2 \mu\text{m}$, purity = 99.5%) and zirconium oxide (in two sizes $d_{50} = 75 \text{ nm}$ and $d_{50} = 1 \mu\text{m}$, purity = 99.6%) are used as raw materials. **Figure 1** shows the morphology and particle size of these starting powders.

To fabricate W/ZrC composite through reaction sintering method, at first ZrO_2 and WC powder were mixed at presence of a binder so that a precursor was formed. To produce a workpiece weighing 150 g, WC and ZrO_2 powders are mixed according to **Table 1** with optimum molar ratio of 3 - 1 [13] between WC and ZrO_2 , although

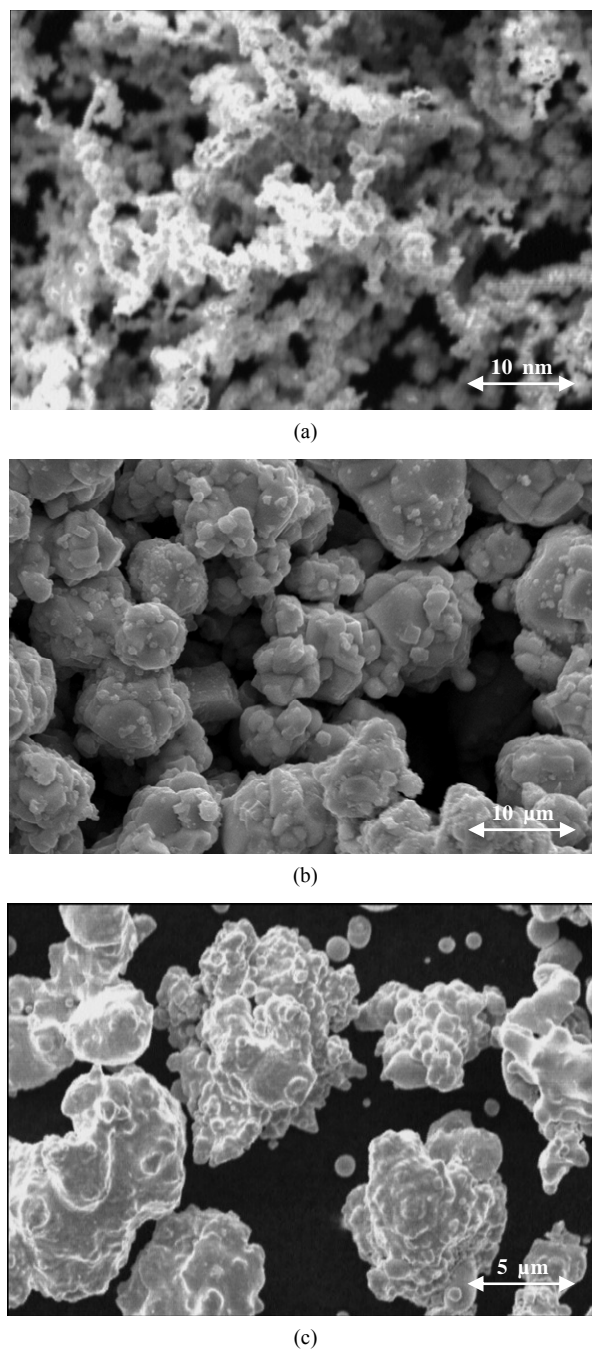


Figure 1. The morphology of a) Nano ZrO_2 , b) Micron ZrO_2 and c) WC powders.

Table 1. The amount of WC and ZrO_2 for production of a 150 g workpiece.

Code of Sample	WC to ZrO_2 molar ratio	Particle Size	WC + ZrO_2 (g)	WC (g)	ZrO_2 (g)
3W1Z-M	3:1	Micron	150	124	26
3W1Z-N	3:1	Nano	150	124	26

regarding the desired proportion of W to ZrC in composite this ratio may be different. After 6 hours mixing in alcohol media, the resulting mixture is dried 12 hours in an oven. Finally this mixture is gelcasted to make a pre-form from WC and ZrO_2 powder [15-18]. The gelcasting was done according to the steps showing in **Figure 2**, in which sodium alginate ($\text{C}_6\text{H}_7\text{NaO}_6$), sodium hexametaphosphate ($(\text{NaPO}_3)_6$), phosphate calcium ($\text{Ca}_3(\text{PO}_4)_2$) and ammonium citrate ($(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$) were used as monomers and after adding each of them mixing continues for 10 minutes. Then the mixture of WC and ZrO_2 were added slowly and finally hexane acid ($\text{C}_6\text{H}_{10}\text{O}_4$) was added as initiator, that at this stage the workpiece must be casted quickly before hardening. The mold used here is made of rubber which compared with other materials and offered the best results.

The workpiece remains 24 hours at room temperature, heated 6 hours in an oven at $50 - 60^\circ\text{C}$ to burn polymeric additives and then for calcination, it is pulled out from the mold and heated in a vacuum furnace at $600 - 700^\circ\text{C}$. The last step is sintering that usually is done at about 1500°C . **Figure 3** shows the sintering process for gel casting. The gel casted body is sintered in a vacuum furnace at 2100°C [13], according to the cycle showing in **Figure 4**.

In order to detect the type of synthesized phases and components XRD analysis with the Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) was carried out and the integrated area of the

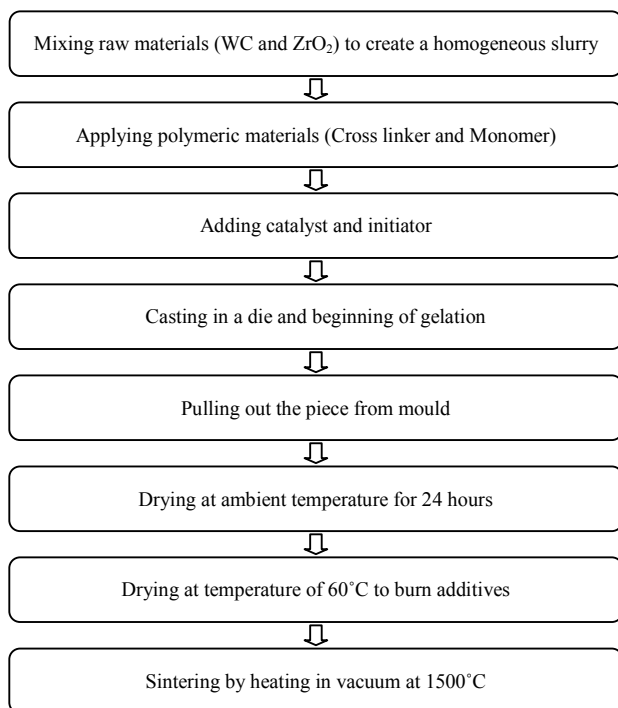


Figure 2. The steps in gel casting of WC/ ZrO_2 .

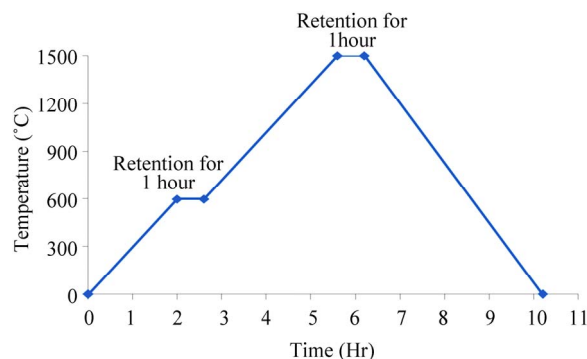


Figure 3. The sintering process of gel casting.

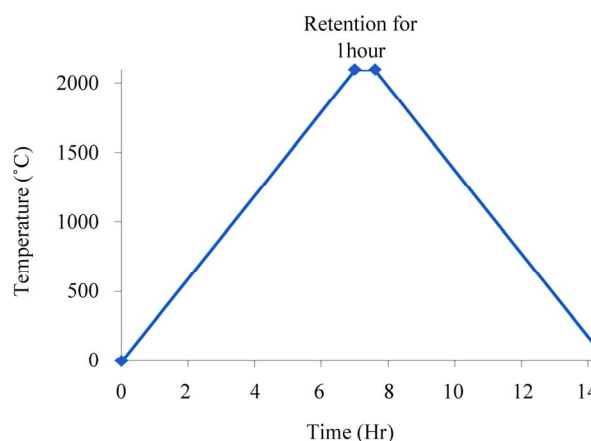


Figure 4. The sintering process of reaction sintering.

peaks were calculated to obtain the volume fraction of the phases in the composite. Additionally the microstructure of the samples was studied using scanning electron microscope. To see the differences between phases in the composites, the back scattered electron (BSE) images were studied as well as secondary electron (SE) images.

3. Results and Discussion

To control the formation of W-ZrC composite x-ray diffraction of the powders before reaction and after making the composites were analyzed to see whether the reaction is complete or not. **Figure 5** shows the XRD pattern of composite made from micron powders (3W1Z-M) and **Figure 6** shows the XRD pattern of composite made from nano powders (3W1Z-N) in which 1) is WC powder, 2) ZrO_2 powder, 3) The mixture of WC and ZrO_2 and 4) W-ZrC composite.

Figure 5 is the XRD pattern of 3W1Z-M sample, showing the peaks belong to ZrC and W phases that confirms the formation of W/ZrC composite was successful. In spite of that some WC and ZrO_2 phases are observed which illustrates that reaction between these two phases

to form W/ZrC composite was not complete. Also the W_2C phase that was formed during mixing, still exist in the composite. According to the integrated area of the peaks related to these phase and the total XRD patterns, the volume fraction of them is calculated and listed in **Table 2**.

Figure 6 is the XRD pattern of 3W1Z-N sample. In this pattern ZrC and W phases are visible that point out the formation of W/ZrC composite through reaction sintering. On the other hand some ZrO_2 phase is observed but there is no WC any more. The W_2C phase still exists in the composite. According to the integrated area of peaks in the XRD patterns, the volume fractions of these phases are shown in **Table 3**.

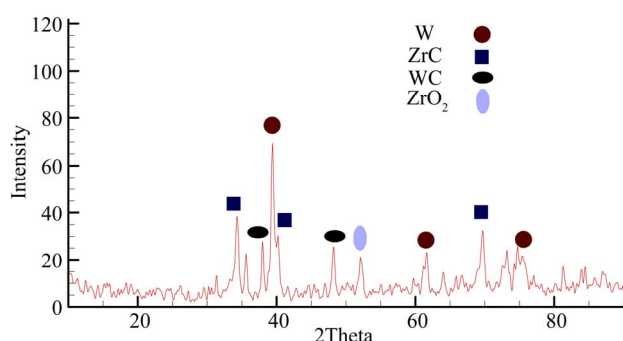


Figure 5. XRD pattern of composite fabricated by reaction sintering of micron WC/ ZrO_2 .

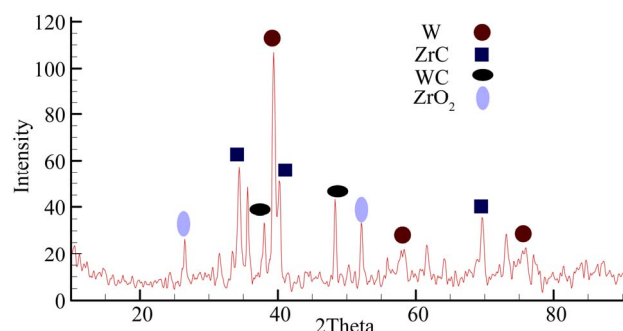


Figure 6. XRD pattern of composite fabricated by reaction sintering of nano WC/ ZrO_2 .

Table 2. The volume fraction of different phases in the 3W1Z-M Sample.

Phase	W	ZrC	ZrO_2	WC	W_2C
Vol%	40.1	19.7	10.2	9.1	20.9

Table 3. The volume fraction of different phases in the 3W1Z-N sample.

Phase	W	ZrC	ZrO_2	W_2C
Vol%	45.1	24.7	10.9	19.3

Finally by SEM micrographs the morphology of the samples is studied. **Figure 7** shows the BSE micrograph of W-ZrC composite and **Figure 8** shows the BSE micrograph in 3W1Z-N sample.

As it is clear the bright phase in back scattered electron images related to heavier elements. On the other hand in the images, the composite is made of a dark phase and a bright phase which represent zirconium carbide and tungsten respectively. To prove this EDX-line scan of both phases were studied. **Figure 9** shows the EDX-line scan of bright phase and dark phase in W/ZrC composite. Accordingly in 3W1Z-N sample the amount of W is more, that shows the reaction in nano powder improved better.

The average values for mechanical properties of the both nano and micron samples, including density, hardness, Elastic modulus and Flexural strength, are listed in

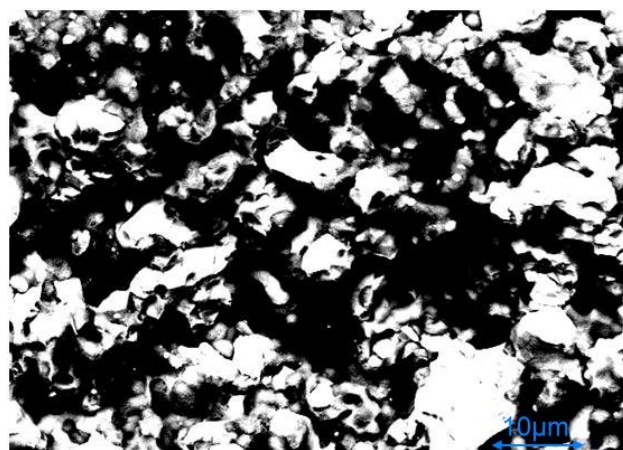


Figure 7. The BSE micrograph of W/ZrC composite prepared by reaction sintering in 3W1Z-M sample.

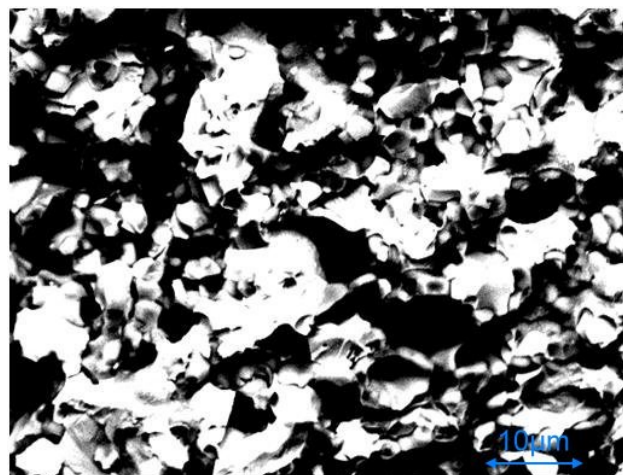


Figure 8. The BSE micrograph of W/ZrC composite prepared by reaction sintering in 3W1Z-N sample.

Table 4 Comparing to prior ZrC-W composites [2] these values for mechanical properties are acceptable. Anyway the variances might be because the reaction between ZrO₂ and WC did not go to completion and because of the effect that the un-reacted components have on the properties of the composite.

4. Conclusions

In this study the feasibility of fabricating W/ZrC composite through reaction sintering was studied and the differences of composite made from nano and micron ZrO₂ were investigated. The W/ZrC composite was produced by mixing WC and ZrO₂ powders, gel casting the mixture to produce a green body and then sintering at 2100°C. The XRD patterns and SEM images indicate that W/ZrC composite has been fabricated successfully by this method, although some extra compounds have been formed. Moreover the XRD pattern of nano sample

showed that the reaction was more successful and proceeded more effectively, with regard to ~45%W-25%ZrC in nano sample compared to ~40%W-20%ZrC in micron sample. Additionally the amount of unreacted ZrO₂ decreases and there remains no WC in nano sample. The amount of unwanted W₂C phase decreases as well. Even when some weak points, like the inefficiency of process and presence of ZrO₂ phase, were taken to consideration, the produced composites showed good mechanical properties, comparable to the composites fabricated through hot-press and other conventional methods. Anyway the composite produced by nano powders possess better properties rather than the micron one.

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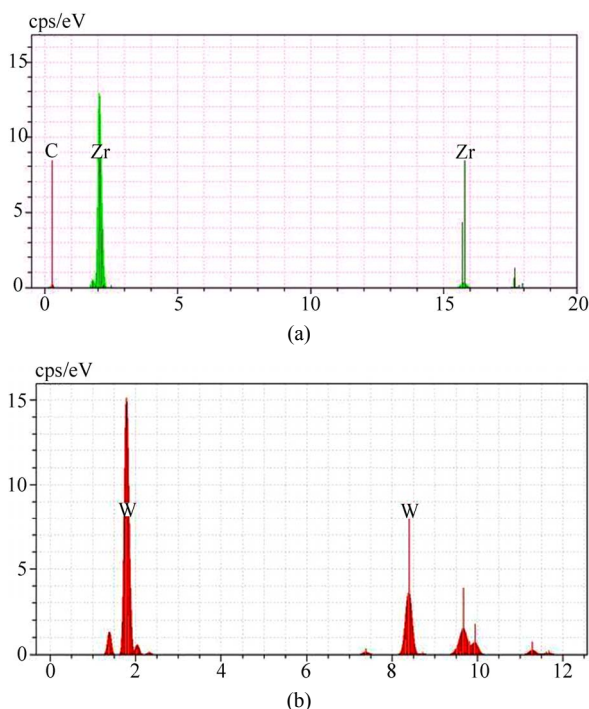


Figure 9. EDX-line scan of (a) Dark phase and (b) Bright phase in 3W1Z-N sample.

Table 4. The mechanical properties and standard deviation for made W/ZrC composites.

Sample	Density (g/cm ³)	Hardness (GPa)	Elastic modulus (GPa)	Flexural strength (MPa)
3W1Z-M	12.1	4.3	339	431
3W1Z-N	12.8	4.7	368	442

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