The Fabrication of W/ZrC Composite through Reaction Sintering

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Abstract
Considering the problems and high cost related to graphite parts, the tendency to use composite materials such as W/ZrC as a suitable substitute has been noticed. In this study the W-ZrC composites fabricated by in situ reaction sintering of two precursors were compared, 1- The conventional WC and ZrO_2 which are ball milled with established molar ratio of 3-1 for 12 hours, gelcasted to form a green body and then undergo a pressure less sintering cycle, 2-A new and innovative way in which for the first time $ZrSiO_4$ was used instead of ZrO_2, and by testing different molar ratio between WC and $ZrSiO_4$ it was understood that the optimum ratio is 3-1 once again.
Keywords: *W/ZrC composite, Reaction Sintering, Mechanical property, $ZrSiO_4$.*

1. Introduction
Composites comprised of a refractory metal as matrix and carbides as the reinforcement have interesting combination of chemical, thermal and mechanical properties. For instance, W and ZrC often coupled to make composite because ZrC is compatible with tungsten from several point of view [1]. The important application of W/ZrC composite materials is in the missile nozzle and aircraft engine parts, fuselage, nose, attack edge, etc. Some of the properties of W and ZrC which make them suitable to make composite is presented in table 1. Beside they exhibit little mutual solid solubility at high temperature (less than 7% mol at 2800˚C) and do not react to form other compounds [2-4].

Table 1 Properties of W and ZrC [2-4]

	Melting point (˚C)	linear expansion coefficient (/˚C)	Thermal conductivity (W/m-k)	Density (g/cm³)
W	3422	4.5×10^6	105	19.3
ZrC	3420	4×106	40	6.63

ZrC/W composite possess higher wear resistance, creep resistance and hardness rather than pure refractory metals and shows better fracture toughness (K_1C), which demonstrates higher resistance than pure carbides. As a result, this composite is used in many industries like aerospace, aircraft, automotive, energy, material processing and defense industry. Also is used in many applications such as rocket nozzles, leading edges, combustion chambers and exhaust flaps [1-2].

Three ways of production have been reported for fabrication of W/ZrC composites. 1-DCP (Displacive compensation of porosity), a porous WC preforms will be exposed to molten Zr_2Cu at 1200-1300˚C and ambient pressure, then the Zr_2Cu liquid infiltrate into it and ZrC and W will form in conclusion [1-5]. 2-Hot press, the elemental ZrC and W powders are mixed and then will be subjected to heat and pressure at the same time [6]. 3-Reaction sintering, ZrO_2 and WC powders in designed volume or mass fraction are subjected to high temperature and after that will be formed into a green body which then is heated in an inert gas atmosphere to produce ZrC and W [7, 8]. Also in a new way, deployed by the authors, the $ZrSiO_4$ has been used instead of ZrO_2 to make the composite through reaction sintering, because $ZrSiO_4$ is more abundant and much cheaper than ZrO_2, so by using $ZrSiO_4$ the cost of production decrease considerably.

In this study at first the W-ZrC composite is fabricated by reaction sintering of micron and nano WC/ZrO_2, and then fabricated through reaction sintering of $ZrSiO_4$/WC, in which the powders are blended with different molar ratio to understand the optimum ratio and are selected in micron and nano size to see the differences between the resultant composites. The volume fraction of different phases in the composites is approximately estimated by the ratio of the integrated area of the peaks and the total XRD patterns to see the efficiency of process [9]. The density is determined using Archimedes method, according to ASTM B311 [10] standard method. The hardness is evaluated in accordance with ASTM E10 [11]. Moreover, the bending strength of the composite has been measured by bending test according to ASTM C1161 [12] and the Modulus of Elasticity is measured as well, by ASTM C1419 [13] test standard method. Also, by secondary electron microscopy (SEM) and back scattered electron (BSE) the morphology of samples is studied.

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2. Experimental

To produce W-ZrC composite through reaction sintering, a preform, conventionally made from the mixture of ZrO_2 and WC is sintered, but here for the first time $ZrSiO_4$ was used instead of ZrO_2 to fabricate the composite. The perform can be made by any conventional ceramic forming method, like normal mechanical pressing or isostatic pressing, however for the first time a low-toxic gel casting system is used to form the green body made from WC/ZrO_2 or WC/$ZrSiO_4$, to evaluate the process and use the results for next studies. As a consequence the process is studied for two different precursors:

2.1 Reaction sintering of WC and ZrO_2

ZrO_2 and WC powder are mixed at presence of a binder so that a precursor is formed. According to the results obtained in a study [14] the optimum ratio between WC and ZrO_2 powder is 3-1, so to produce a work piece weighing 150g with molar ratio of 3-1, 126gr WC and 26gr ZrO_2 powders are mixed, however regarding the desired proportion of W to ZrC in composite this ratio may be different. Mixing is conducted in alcohol media and then after 6 hours mixing, the resulting mixture is dried in an oven for 12 hours. Finally this mixture is gelcasted to form a green body, in which sodium alginate ($C_6H_7NaO_6$), a natural polymer is used as monomer [15-17]. Hence at first 19.41wt% of ceramic powder (here is 150g WC/ZrO_2) distilled water and 0.34wt% of ceramic powder, sodium alginate are mixed for at least half an hour. After this period 0.11wt% of ceramic powder, hexametaphosphate (($NaPO_3)_6$) is added as collator and mixing continues for more 10 minutes. Then 0.21wt% of ceramic powder, diphosphatecalcium ($Ca_3(PO_4)_2$) is added to the mixture and mixing continues for another 10 minutes. Finally 0.19wt% of ceramic powder, ammonium citrate (($NH_4)_3C_6H_5O_7$) is added as dispersant in the same way and mixing continues 10 minutes. At this stage the WC and $ZrSiO_4$ powders are added to the slurry slowly and finally the initiator, hexane acid ($C_6H_{10}O_4$), is added which immediately after adding it the composition starts gelation. Due to this fact it is necessary to be casted quickly before hardening. The amount of initiator added to the composition is 0.15wt% of ceramic powder. The mold used here is made of rubber which offers the best results compared with other materials that have been used.

After casting the workpiece remains 24 hours at room temperature and then heated 6 hours in an oven at 50-60˚C to burn polymeric additives. Then for calcinations, the workpiece is pulled out from the mold and heated in a vacuum furnace at 600-700˚C. A low heating rate (2-3˚C/min) is selected in order to prevent the samples from cracking.

The last step is sintering that usually is done under the melting point of ceramic powder which here is about 1500˚C, so the workpiece is kept for 1 hour at this temperature. Fig.2. shows the steps in gel casting of ZrO_2/WC.

After gel casting the reaction sintering is conducted according to the cycle showing in Fig.3. In this process the gelcasted body is sintered in a vacuum furnace at 2100˚C [8].

2.2 Reaction sintering of WC and $ZrSiO_4$

Commercial WC powder (99.6% purity and $d_{50}=2\mu m$) and $ZrSiO_4$ powder (in two sizes $d_{50}=75nm$ with 99.3% purity and $d_{50}=2\mu m$ with 99.5% purity) are used as raw materials (Fig.1.).
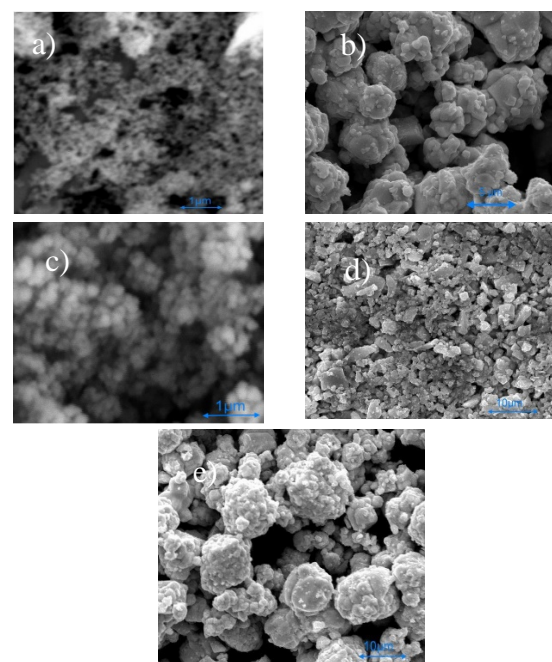

Fig.1. The morphology and particle size of a) nano ZrO2, b) micron ZrO2 c) nano ZrSiO4, d) micron ZrSiO4 and e) WC powder.

To fabricate W/ZrC composite, at first $ZrSiO_4$ and WC powders are mixed at presence of a binder so that a precursor is formed. Since the optimal ratio between WC and $ZrSiO_4$ is not clear, the test is done for molar ratio of 1-1, 2-1, 3-1 and 4-1 according to table 2.

Mixing is conducted in alcohol media to avoid oxidation, and then after 6 hours mixing the resulting mixture is dried in an oven for 12 hours. Finally this mixture is gel casted according to the above mentioned steps (Fig.2), to form a green body. In this way it is expected that the composite forms according to equation (1).
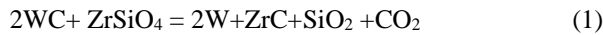
$$2WC + ZrSiO_4 = 2W + ZrC + SiO_2 + CO_2 \qquad (1)$$

Table 2 The amount of WC and $ZrSiO_4$ for production of a 100 or 170g workpiece

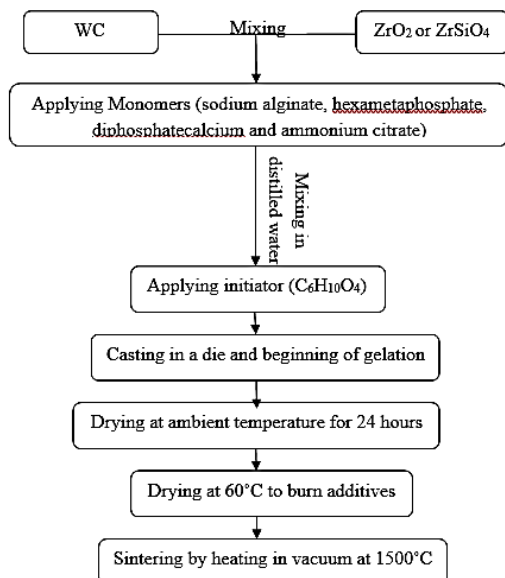| Sample	WC to ZrSio4	Size	Whole Charge (g)	WC (g)	ZrSiO4(g)
1W1Z-M	1 : 1	Micron	100	51.56	48.54
2W1Z-M	1 : 2	Micron	100	69.3	30.7
3W1Z-M	1 : 3	Micron	170	129.58	40.42
4W1Z-M	1 : 4	Micron	100	81.06	18.94
1W1Z-N	1 : 1	Nano	100	51.56	48.54
2W1Z-N	1 : 2	Nano	100	69.3	30.7
3W1Z-N	1 : 3	Nano	170	129.58	40.42
4W1Z-N	1 : 4	Nano	100	81.06	18.94

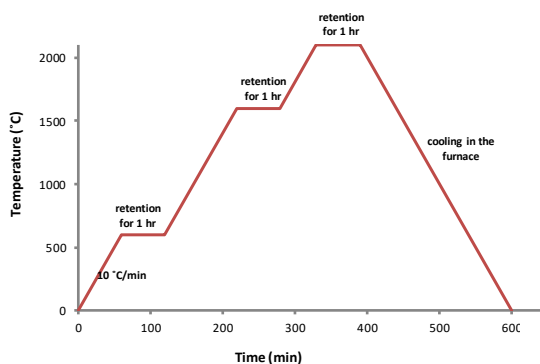**Fig. 2.** The steps in gel casting of WC/ZrO_2 or $WC/ZrSiO_4$.

Fig. 3. The sintering process of reaction sintering.

In order to detect the type of synthesized phases and components XRD analysis with the Cu Kα radiation (λ=1.54˚A) was carried out and the integrated area of the peaks were calculated to obtain the volume fraction of the phases in the composite [10]. Additionally the microstructures of the samples were studied using scanning electron microscope. To see the differences between phases in fabricated composites, the back scattered electron (BSE) images were studied as well as secondary electron (SE) images.

3. Results and Discussion

3.1 Reaction sintered WC/ZrO_2

To control the formation of W-ZrC composite x-ray diffractions of the reactants before and after sintering were analyzed to see whether the reaction was complete or not. Fig.4. shows the XRD pattern of reaction sintered WC/ZrO_2 made from micron powders (W-MZr) and nano powders (W-NZr) in which a) is WC, b) Micron ZrO_2 and c) Nano ZrO_2 powders, and d) and e) are the W-ZrC composite made from 3W1Z-M and 3W1Z-N samples.

The peaks in XRD pattern of powders in Fig.4a, b and c show only WC and ZrO_2 which are seen distinctly in the images. Fig.4d shows the XRD pattern of 3W1Z-M, and Fig.4e is the XRD pattern of 3W1Z-N sample. In these patterns ZrC and W phases are visible that point out the formation of W/ZrC composite through reaction sintering. 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. In order to know how the reaction has been progressed and the amount of composite produced via the sintering, the percentage of phases observed in XRD pattern of the composite will be calculated. According to the integrated area of the peaks related to these phases and the total XRD patterns, the volume fraction of the phases are calculated approximately [19]. According to integrated area of peaks in the XRD patterns, the volume fraction of different phases in the WC/ZrO_2 reaction sintered samples are shown in table 3.

Table 3 The volume fraction of different phases in the reaction sintered $WC/ZrO2$.

Sample	W	ZrC	ZrO$_2$	WC	W$_2$C
W-MZr	38.9	18.3	10.2	11.1	21.5
W-NZr	43.7	23.3	12.2	-	20.8

Table 4 The comparison of mechanical properties in reaction sintered WC/ZrO2 and WC/ZrSiO4 with experimental results presented in articles

Sample	Density(g/cm³)	Hardness(GPa)	Elastic modulus(GPa)	Flexural strength(MPa)
W-MZr	11.8	4.2	327	439
SD	0.5	21.3	10.6	17.1
W-NZr	12.5	4.4	359	471
SD	0.8	22.9	8.1	13.5
3W1Z-M	11.1	3.9	314	423
SD	1.1	30.4	11.7	9.8
3W1Z-N	11.6	4.1	332	421
SD	0.9	27.6	9.2	12.4
W/ZrC	13.9 [3, 5]	5.77 [3, 5]	430 [6]	705 [3, 5]

The average values for mechanical properties of the both nano and micron composites, including density, hardness, Elastic modulus and Flexural strength, are listed in table 4. Comparing to prior ZrC-W composites [8] these values for mechanical properties are acceptable.
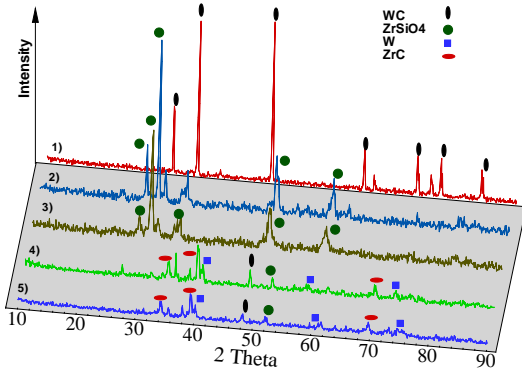

Fig.4. XRD patterns in reaction sintered WC/ZrO2, a)WC powder, b)Micron ZrO2 powder, c) Nano ZrO2 powder and made composite from d) 3W1Z-M sample and e) 3W1Z-N

3.2 Reaction sintered WC/ZrSiO₄

Fig.5. shows the XRD patterns of reaction sintered WC/ZrSiO₄ made from micron powders with molar ratio between WC and ZrSiO₄ equal to 1-1, 2-1, 3-1 and 4-1, respectively and Fig.6. show the XRD patterns of composite made from nano powders with the same molar ratio. Accordingly Fig.5 and Fig.6 a and b are related to the XRD pattern of starting powders, which obviously show WC and ZrSiO₄. Fig.5c-f and 6c-f are the made composite from the mentioned mixtures, which clearly shows the existence of W and ZrC peaks, thus the formation of W/ZrC composite. Nevertheless still there are some unreacted phases (WC and ZrSiO₄) and some extra phases (W₃O, ZrO₂, ZrO, SiC, SiO₂ and W₂C).
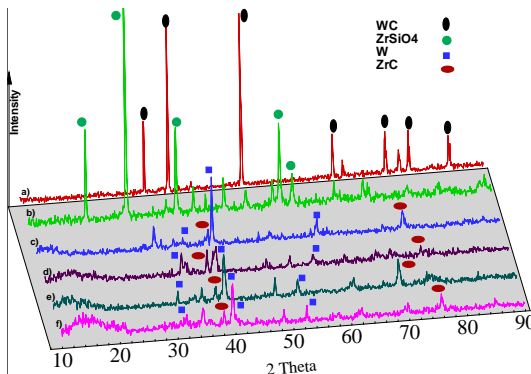

Fig.5. XRD patterns in reaction sintered WC/ZrSiO4, a)WC, b)ZrSiO4 powders and the W-MZr composite made from c)1W1Z, d)2W1Z, e)3W1Z and f)4W1Z samples.
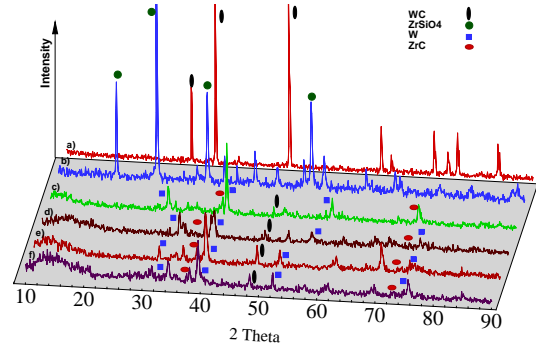

Fig.6. XRD patterns in reaction sintered WC/ZrSiO4, a)WC, b) Nano ZrSiO4 powders and the W-NZr composite made from c)1W1Z, d)2W1Z, e)3W1Z and f)4W1Z samples.

For composite samples obtained from mixing ZrSiO₄ micron and WC with molar ratio of 1-1 (1W1Z-M), 2-1 (2W1Z-M), 3-1 (3W1Z-M) and 4-1 (4W1Z-M) and also for composite made from mixing WC and nano ZrSiO₄ with molar ratio of 1-1 (1W1Z-N), 2-1 (2W1Z-N), 3-1 (3W1Z-N) and 4-1 (4W1Zr-N), an approximation in volume fraction of all phases is shown in table 5. As is shown the result of all nano samples is better than micron.

Table 5 The volume fraction of different phases in the reaction sintered WC/ZrSiO4.

Sample	W	ZrC	ZrSiO₄	WC	W₃O	ZrO₂	ZrO	SiC	SiO₂	W₂C
1W1Z-M	31.82	15.02	13.27	11.33	-	10.36	-	-	3.1	15.1
2W1Z-M	44.64	16.75	18.56	-	11.08	5.17	-	-	3.8	-
3W1Z-M	47.14	18.23	13.3	8.15	9.1	-	-	-	4.08	-
4W1Z-M	37.37	18.04	16.35	-	12.5	11.74	-	-	4	-
1W1Z-N	32.89	15.28	11.95	10.44	-	9.33	9.19	-	10.92	-
2W1Z-N	45.78	22.45	8.5	-	-	-	9.7	10.41	3.16	-
3W1Z-N	51.44	22.97	6.5	-	7.4	4.59	-	-	7.1	-
4W1Z-N	43.98	15.9	17.01	-	19.07	-	-	-	4.04	-

Of all samples the best result was obtained for reaction sintered WC/ZrO₂ in W-NZr sample, that Fig.7. shows the SEM and BSE micrograph of this sample. Also Fig.8. shows the SEM image of reaction sintered WC/ZrSiO₄ for 3W1Z-N sample and the BSE image of fracture surface in it. The lack of grain boundary is noticeable in this picture, as if the liquid-state sintering has happened for this sample. According to the feature of back scattered electron images, the bright phase is related to heavier elements, because heavier elements reflect more light, so the dominant bright phase relates to W and dark phase to ZrC.
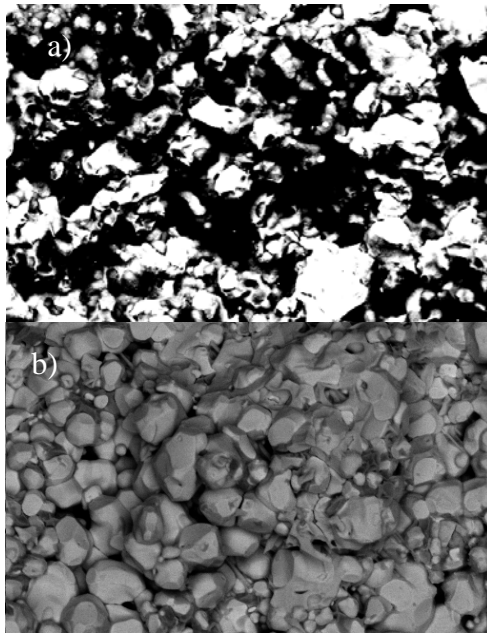
Fig.7. The a) SEM and b) BSE images of reaction sintered WC/ZrO2 in W-NZr sample.
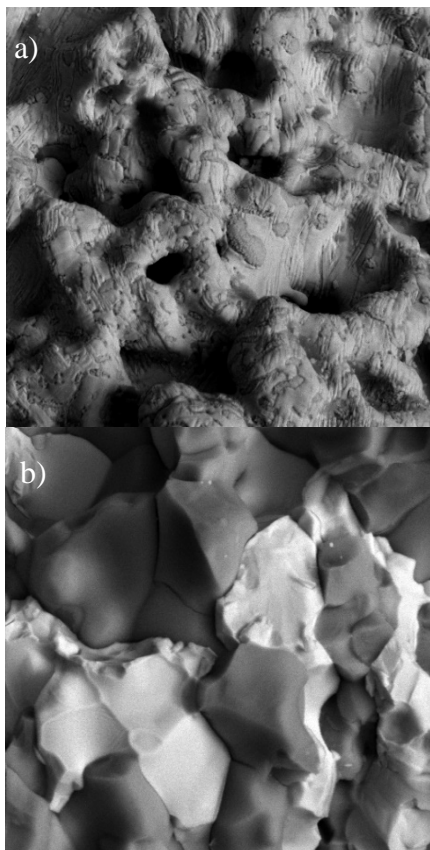

Fig.8. a) The SEM image of reaction sintered WC/ZrSiO4 for 3W1Z-N sample b) The BSE image of fracture surface in 3W1Z-N sample.

The assessed values of mechanical properties, including density, hardness, Elastic modulus and Flexural strength, in these two samples have been compared with the data which have been accessed in some studies and as you see in table 4, comparing to prior ZrC-W composites these values for mechanical properties are acceptable. The evaluated properties are better in reaction sintered WC/ZrO_2 tether than $WC/ZrSiO_4$ and in nano samples rather than micron one.

It is necessary to state that the samples made for mechanical tests failed prematurely, which might be because of the effect of un-reacted components on the properties of composite, however compounds with low melting point can cause crack healing at elevated temperatures as well.

Regarding the cost considerations, reaction sintering of $WC/ZrSiO_4$ is a much cheaper process, because of the cheap apparatus needed and the price of raw materials. It seems that by optimizing the process parameters, like the temperature and time of keeping at this temperature which can be studied in future works, $ZrSiO_4$ is a valuable substitution for ZrO_2, in production of W/ZrC composite through reaction sintering.

4. Concluding Remarks

The XRD patterns and SEM images of W/ZrC composite made from reaction sintering of ZrO_2/WC and $ZrSiO_4/WC$, pointed out the successful fabrication of W/ZrC composite by this method, however the reaction between $ZrO_2/ZrSiO_4$ and WC did not go to completion and some extra compounds have been formed and some phases remained unreacted. Although the resultant composites were highly impure, the mechanical properties were not far from what is expected for the composite. The formed phases showed deviation from what is expected, which might be as a result of deficiency in the process.

As for nano samples the reaction was more successful and proceeded more effectively because the amount of unreacted WC and $ZrSiO_4$ reduced. The optimum ratio between WC and $ZrSiO_4$ was obtained 3-1 for both nano and micron samples.

Because of the price of raw materials, reaction sintering of $WC/ZrSiO_4$ was a cheaper process, despite the evaluated properties were better in reaction sintered WC/ZrO_2.

Even when some weak points, like the inefficiency of process, were taken to consideration the produced composites showed good mechanical properties, comparable to the composites fabricated through hot-press and other conventional methods.

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