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Tungsten Carbide: A Versatile Additive to Get Trace Alkaline-earth Oxide Impurities
out of ZrB₂ based Ceramics

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Abstract

In this work, trace amounts of alkaline-earth oxide impurities (M_xO_y), M=Mg, Ca and Al, are identified from different graded ZrB₂ based ceramics. The reactions in M_xO_y-WC systems at high temperature are therefore investigated via X-Ray diffraction and element analysis, which have been further supported by thermodynamic calculations. Since M_xO_y with low melting point deteriorates the high temperature performance of ceramics, the effective role of WC on strong ZrB₂-SiC-WC ceramics is re-considered: apart from the contribution on removing of ZrO₂, WC serves as a versatile additive with capacity to remove different oxide impurities from the ceramic body.

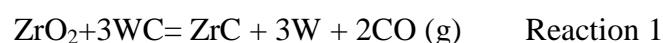
Keywords

Borides; alkaline earth; ceramics; surface oxygen impurities;

Strong ceramics are generally desired for their service at high temperature [1-3]. On the one hand, for a ceramic part with a fixed geometry, a higher strength value means that **it** could bear a greater load before fracture; on the other hand, thermal shock resistance of ceramics with a higher strength will be substantially improved, since the thermal shock parameters (R' and R'') for crack initiation are proportional to the

1 strength level with other things being equal [4]. According to the theory of Griffith's
2 fracture, at room temperature, the strength of brittle ceramics is governed by the
3 dimension of its largest defects, in terms of void, inclusion and crack et al. However,
4 these effects become less important with increasing the temperature, due to the fact
5 that some of the cracks, especially for the machine-generated ones, could be healed
6 during the high-temperature testing [5, 6]. Therefore, in absence of low melting
7 phases at the grains junctions, the strength of ceramics at higher temperature relies
8 predominantly on their intrinsic property: bonding characters, lattice structures, etc.
9 Previous research in ZrB₂-SiC ceramics shows that the effect of impurity phases plays
10 a decisive role [6].

11 The impurities could be originated from the raw powders, collected during the various
12 steps during ceramic processing, or contaminated in the environment for sintering.
13 The softening of these impurities at high temperature is an indicator for the strength
14 degradation of ceramics. In fact, adjusting the chemistry of the impurities have been
15 demonstrated to be an effective route to obtain SiC [7-8] and Si₃N₄ ceramics [9-10]
16 with better high temperature performance. Alternatively, these impurities could be
17 removed by selecting suitable additives to achieve a cleaner grain boundary. Ceramics
18 with tightened grain boundary have exhibited superior strength [7, 11-13]. Boride
19 ceramics are a class of important engineering ceramics and benchmark materials
20 liable to be affected by the oxide impurities. For instance, in ZrB₂ ceramics, oxide
21 impurities are present on the surface oxide layer of the ZrB₂ powders, which are
22 assumed to be amorphous B₂O₃ and crystalline ZrO₂ [14-15]. B₂O₃ could be
23 eliminated from the ceramic body by its evaporation in vacuum, whereas ZrO₂ has to
24 be removed chemically by its reaction with WC or other carbides through Reaction 1
25 [16].



26 Benefiting from the WC additions, strong ZrB₂-SiC-WC ceramics with clean grain

1 boundary and without any strength degradation up to 2000°C have been successfully
2 developed [11-12]. However, observations on the boride ceramics have suggested that
3 besides B₂O₃ and ZrO₂, other oxides with low melting temperature, e.g. alkaline-earth
4 oxide, have been detected in the as sintered ZrB₂ body from different research groups
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boundary and without any strength degradation up to 2000°C have been successfully developed [11-12]. However, observations on the boride ceramics have suggested that besides B₂O₃ and ZrO₂, other oxides with low melting temperature, e.g. alkaline-earth oxide, have been detected in the as sintered ZrB₂ body from different research groups *cf.* Table I. The coexistence of various oxides in ZrB₂ based ceramics implies that the mechanism for the impurity removal in ZrB₂ by WC additions (Reaction 1) is still unclear. In addition, alkaline-earth oxides have been commonly observed from the ceramic product [17] and their influence is mostly negative [18]: deterioration of the corrosion resistance to molten metals and high temperature strength are amongst the major detrimental effects. On this basis, the aim of the study is to understand the role of WC on removing the impurities in boride ceramics, to provide new insights on understanding the mechanism for strong ZrB₂-SiC-WC ceramics at higher temperatures and to seek a practical way to eliminate the alkaline-earth oxides from the ceramic body.

In order to identify the oxide impurities in ZrB₂ based ceramics properly, ZrB₂-SiC [5] and ZrB₂-ZrC ceramics [19] prepared from different ZrB₂ suppliers were chosen for a further characterization. The oxide impurities observed in ZrB₂ based ceramics have been summarized and listed in Table I. The impurities in the starting powders and sintered ceramics were mainly examined by a transmission electron microscope equipped with energy dispersive X-ray spectroscopy (EDS). Since impurities such as CaO, MgO and Al₂O₃ were identified from the EDS analysis, three powder mixtures, namely, CaO-WC, MgO-WC and Al₂O₃-WC, were prepared by mixing the corresponding oxide (M_xO_y, M refers to Al, Mg and Ca, similarly hereinafter) with WC powder (Hard alloy Co. Ltd, Zhuzhou, China, particle size <1µm) based on a molar ratio of 1:5. Although the amount of MgO in the impurity (Fig.1d, 1h and S1b) is limited, MgO-WC system was investigated since MgO is the major impurity in the boride powder synthesized by magnesiothermic reduction [20]. A larger proportion of WC was intentionally chosen in the composition because excess WC had been added

1 in ZrB₂-SiC matrix compared with corresponding oxygen levels. For example,
2 3-5vol% WC (4.0-6.6mol%) was always added in to ZrB₂ powders with a documented
3 oxygen level of <1wt% (ZrO₂ content<0.58mol%) [11-12]. 3Y-ZrO₂ balls and ethanol
4 were used as the media and the solvent for the mixing. As mixed slurry were dried
5 through rotary evaporation and then crashed and meshed into fine powders. The
6 pellets with diameter of 10mm were obtained by uniaxial dry pressing the powders at
7 ~100MPa for 30s, which were followed by heating them up at 10°C/min to 1600°C in
8 a graphite furnace. The entire heat treatment also includes an isothermal step at
9 1600°C for 0.5h and the vacuum level in the furnace during holding was maintained at
10 ~5Pa.

11 After removing the surface layers, the phase assemblage of as-mixed and 1600°C
12 treated samples was firstly determined by X-ray diffraction (XRD). The composition
13 of the samples before and after heat treatment was also analyzed by X-ray
14 fluorescence (XRF) analysis. Finally, Glow Discharge Mass Spectrometry (GDMS)
15 was employed to compare some impurity changes for the hot-pressed ZrB₂-SiC
16 ceramics with and without 5vol% WC doping.

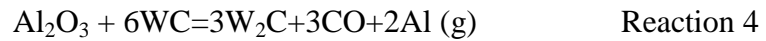
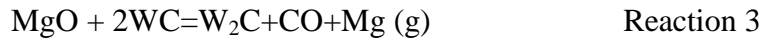
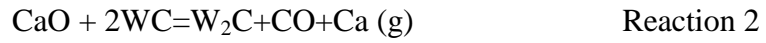
17 Independently from the implementation of boro/carbothermal reduction routes,
18 impurities could be clearly detected from the as-synthesized powder (Fig.1a, b and e,
19 f). These phases were easily recognized as they are characterized by low contrast due
20 to their high content of light elements and are generally located separately from the
21 ZrB₂ agglomerates. Similarly, amorphous phase based on Zr-Si-K-Ca-Mg-Cl-O
22 (corresponding electron diffraction pattern and EDS spectrum are shown in Fig.S1) is
23 detectable from commercial available ZrB₂ powder (H.C. Starck, Grade B), cf. Fig.1i
24 and 1j. After sintering, amorphous phase appears in the form of impurities as shown in
25 Fig 1c and 1g, which generally exist in the triple junction of the grain boundaries and
26 adjacent to one or more SiC grains, cf. Fig.1c and g. Although their composition
27 varied marginally for different samples and at different locations within the single
28 sample, they generally included Al, Mg, Ca, O, Y and occasionally contained carbon

1 and silicon, Fig.1d and 1h. These impurities are not necessarily associated with the
2 SiC phases in the as-sintered ceramics and easy to be found (Fig.1k and 1l). For
3 example, crystallized ZrO_2 covered by amorphous phase with Al-Mg-Ca-Si-O were
4 disclosed by the elemental mappings (Fig.1m) from dense ZrB_2 -ZrC ceramics. Based
5 on a summary in Table I and the above microstructure characterization, it seems that
6 the existence of these impurities in ZrB_2 ceramics is inevitable, regardless of the
7 powder source, the composition of the ceramics and even the research group who
8 handles the process to produce the ceramics.
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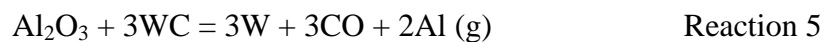
10 **Since** these alkaline-earth oxides have not been detected in ZrB_2 -SiC sample with WC
11 additions [13], their possible removals by WC **is thus probable**. The reactions in M_xO_y
12 -WC systems were investigated accordingly to address the issue. Although the peak
13 intensity of MgO and CaO is relatively weak, both of them still could be indexed from
14 the starting powder mixtures (Fig.2a). After a heat treatment at 1600°C, nevertheless,
15 the diffraction peaks of MgO and CaO disappeared while a series of peaks belong to
16 W_2C were found, together with the unconsumed WC. With regards to Al_2O_3 -WC
17 sample, no visible Al_2O_3 peaks could be seen either from the starting powder or the
18 pellet after heat treatment (Fig.2a and b). Typical peak broadening was found in a
19 separate XRD pattern collected from the starting Al_2O_3 powder only (Fig.S2),
20 indicating a finer grain size and reduced crystallinity, which can well explain its
21 absence from the XRD pattern (Fig.2a). Further indexing of the pattern suggests the
22 Al_2O_3 powder has a cubic symmetry of the γ polytype. The absence of Al_2O_3 peaks
23 after heat treatment suggests Al_2O_3 might have reacted with WC, if not, α - Al_2O_3
24 peaks would have been visible in Fig.2b. The phase transformation from γ - Al_2O_3 to
25 α - Al_2O_3 with improved crystallinity normally takes place at ~650°C and completes
26 below 1000°C, which has been well documented in the literature [21].
27

28 In order to verify some hypotheses from the XRD analysis, the composition of the
29 pellets before and after the heat treatment has been determined quantitatively by XRF
30 and the results were compared through the histogram in Fig.3. Clearly, significant
31 decrease in the concentration of MgO, CaO and Al_2O_3 has been found after heat
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1 treatment. In fact, no noticeable amount of CaO and MgO had been analyzed from the
2 treated pellets. Combing these observations with the XRD results, the following
3 reaction mechanisms might take place during the heat treatment at 1600 °C and the
4 loss of Ca, Mg and Al in vapour phase caused their reduction in Fig.3.
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19 For MgO-WC system, 2 mol of WC are sufficient to reduce 1mol of MgO in to Mg
20 (g), CO(g) and W₂C. Considering the molar ratio between WC and MgO in the
21 powder mixture was set as 5:1, excess WC is expected after the reaction which fits
22 well with the XRD analysis (Fig.2b). Similar considerations apply for the CaO-WC
23 system. In Al₂O₃-WC system, however, 6 mol of WC are required to react with 1 mole
24 of Al₂O₃ according to Reaction 4. Consequently, some WC must be further oxidized
25 into W to consume the extra Al₂O₃ and balance the equation (Reaction 5).
26 Coincidentally, a series of W peaks were found in the Al₂O₃-WC pellet after heat
27 treatment (Fig.2b), while they were not observed from MgO (CaO)-WC pellets. This
28 further supports the proposed reaction path shown above.
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45 According to the XRF results in Fig.3, various oxide impurities were present in the
46 starting MgO, CaO and Al₂O₃ powders. Interestingly, with the reduction of M_xO_y by
47 WC, the levels of these impurities also decreased. For instance, measured SiO₂, Cr₂O₃,
48 Al₂O₃ and Fe₂O₃ content in the starting MgO powder is 0.246, 0.447, 0.049 and 0.125
49 wt%, respectively, these values decreased to <0.001, <0.001, 0.03 and 0.07 wt% after
50 the heat treatment. Likewise, 0.675wt% Na₂O, 0.044wt% Al₂O₃, 0.226wt% SiO₂ and
51 0.442wt% Cr₂O₃ are present in raw CaO powder, these numbers changed to <0.001,
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1 0.087, 0.069 and 0.197 wt%. To summarize, WC also shows the potentials to reduce
2 the amount of other oxide impurities, apart from M_xO_y , from the ceramic body, e.g.
3 Cr_2O_3 , SiO_2 etc.
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6 The detailed processes for removing M_xO_y by WC could be illustrated via
7 thermodynamic calculations as displayed in Fig.4. Consistently with the experiments,
8 M_xO_y are unstable when WC is present and they are heated at high temperature in a
9 mild vacuum level (5Pa in this case). For MgO-WC and CaO-WC systems (4a and
10 4b), a significant drop of the oxide amount occurs at $\sim 1000^\circ C$ and $\sim 1200^\circ C$,
11 respectively. Meanwhile, gaseous reaction products, such as $Mg(g)$, $Ca(g)$ and $CO(g)$,
12 start to be released above that temperature. The vapours of magnesium and calcium
13 reach their maximum at $\sim 1250^\circ C$ and $\sim 1350^\circ C$, calculations also predict that W_2C is
14 the only solid product from that temperature to $2000^\circ C$ in both systems. The reactions
15 in Al_2O_3 -WC system are more complicated, but clearly, Al_2O_3 starts to react with WC
16 at $\sim 1200^\circ C$. The formation of W_2C indicates that Reaction 4 becomes favorable above
17 $\sim 1100^\circ C$, which is prior to Reaction 5, because the occurrence of W is found to be at
18 $\sim 1400^\circ C$. Although AlO_2 is predicted to be a stable phase in Al_2O_3 -WC system
19 between 1300 and $1700^\circ C$ (Fig.4c), its existence has not been observed in this work.
20 It should be noted that the reduction of these oxides is strongly related to the WC
21 additions. When WC is absent, the decomposition of MgO and CaO requires a
22 temperature over $1800^\circ C$ (Fig.3d and 3e) while no remarkable degradation was
23 calculated in Al_2O_3 up to $2000^\circ C$ under the same vacuum level. Incorporating WC in
24 to the oxide system leads to the formation of CO as a gaseous byproduct. The
25 continuous evacuation of CO (g) and M (g) out of the furnace chamber is helpful to
26 reduce the temperature at which Reactions (2)-(5) become favorable by decreasing the
27 Gibbs energy change of each reaction. Put the results from Fig.3 and Fig.4 together, it
28 has demonstrated that WC serves as a versatile additive, showing ability to get
29 different alkaline/alkaline-earth oxide impurities eliminated from the ceramic body at
30 a moderate processing conditions, e.g. temperature $< 1600^\circ C$ and a mild vacuum level
31 of $\sim 5Pa$.
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1 Since yttria and iron oxide used to be detected from ZrB₂-SiC ceramics by TEM-EDS
2 (Fig.1h and Table I), their possible reductions by the reaction with WC are also
3 considered here. As displayed in Fig.S3, although the removal of Y₂O₃ and Fe₂O₃ by
4 WC is adequately possible, fully removal of Y₂O₃ require higher temperatures
5 (>1800°C). More importantly, significant amount of Y(g) and Fe(g) vapors can only
6 be generated above 1750°C and 1600°C, while the densification of ceramics had
7 already started at that temperature. Taking into account that (1) Y and Fe atoms could
8 be incorporated in to ZrB₂ lattice below that temperature and form solid solution with
9 ZrB₂, (2) the escaping gaseous Y(g) and Fe(g) from denser ceramics is extremely
10 difficult, this implies that the **complete removal** of these impurities from ZrB₂ body by
11 WC becomes hard to achieve. The Y content obtained by GDMS in hot pressed
12 ZrB₂-SiC (ZS) and ZrB₂-SiC-WC (ZSW) ceramics (Table I) is 0.86 and 0.76 wt %,
13 showing a good consistency with the proposed.
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29 Zhang's work revealed that ZrO₂ impurity in ZrB₂ could be removed by reaction with
30 WC or B₄C, the elimination of oxide impurities has been proved to play a key role on
31 enhancing the pressureless densification of ZrB₂ ceramics [16]. However, compared
32 with WC, the removal of M_xO_y by B₄C is incomplete. Calculations (Fig.S4) show that
33 in CaO-B₄C system, the evaporation of Ca (g) is retarded by the formation of two
34 solids: CaB₆ and Ca₃B₂O₆. Remarkable amount of gaseous substance is only observed
35 when the T > 1600°C. At equilibrium, 75% of input Ca still remains in the CaO-B₄C
36 system even at an extreme condition (2000°C, 5Pa). The flexural strength of
37 ZrB₂-SiC-B₄C ceramics degraded gradually **starting** from 1300°C while
38 ZrB₂-SiC-WC ceramics exhibit even higher strength value at 1600°C compared to that
39 at room temperature [11, 23] *c.f.* Table I. Considering the softening of oxide
40 impurities above their glass transition temperature have been proposed to be
41 responsible for the strength drop of ZrB₂-SiC ceramics with a temperature increase [5],
42 the improved high temperature performance in ZSW might be attribute to the
43 synergetic oxide impurities removal effect resulted from the addition of WC.
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1 In this work, trace amounts of alkaline-earth oxide impurities, M_xO_y (M=Mg, Ca
2 and Al) were identified from various as-sintered ZrB_2 based UHTCs. The removal of
3 M_xO_y in ZrB_2 based UHTCs by WC additions has been proved. Thermodynamic
4 calculations indicated that M_xO_y could be fully reduced in to Mg, Ca or Al by suitable
5 amounts of WC under mild temperature and vacuum level, further **elimination** of
6 these metal species from the ceramic body could be realized through their evaporation,
7 hence, “clean” ZrB_2 based ceramics free of low melting point oxides could be
8 obtained. The current finding provides a reasonable explanation for understanding **the**
9 **excellent behavior** of ZrB_2 -SiC-WC ceramics at high temperature.

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22 51532009 and 51272266) and NSFC-JSPS cooperation program (No. 51611140121).
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Table and Figure captions

Table caption:

Table I Typical oxide impurities observed in ZrB_2 based ceramics from different research groups, including their processing details and the corresponding flexural strength at room temperature (RT) and 1600°C.

Figure Caption:

Fig. 1 Typical oxide impurities in ZrB_2 powders and corresponding ceramics observed by TEM: (a) (b) ZrB_2 powders with different magnifications synthesized from ZrO_2 and B_4C , (e) (f) ZrB_2 powders synthesized from ZrO_2 , B_4C and C, (i)(j) commercial ZrB_2 powder without any treatment from H.C. Starck (Grade B). Arrowed in 1c and 1g are the oxide impurities in the sintered ZrB_2 -SiC ceramics using powders from 1a and 1e, corresponding EDS spectra on the impurities phase highlighted in 1c and 1g are shown in 1d and 1h, respectively. The polished surface of ZrB_2 -10vol%ZrC ceramics is shown in Fig. 1k with corresponding Al mapping (Fig.1l). The morphology and elemental mappings of an oxide inclusion in ZrB_2 -ZrC ceramics are displayed in Fig. 1m. Processing details of these ceramics refer to reference [4, 18].

Fig.2 XRD patterns of (a) as-mixed and (b) as-treated M_xO_y -WC pellets, the treatment was performed at 1600°C for 0.5h. Unmarked peaks in Fig.2a and Fig.2b belong to WC and W_2C , respectively.

Fig. 3 The composition of (a) Al_2O_3 -WC (b) CaO-WC and (c) MgO-WC pellets before and after heat treatment measured by XRF.

Fig. 4 Molar content of the equilibrium products calculated by the reactions between 5mol WC and 1mol M_xO_y as a function of the temperature at a vacuum level of 5Pa. (a) MgO-WC, (b) CaO-WC and (c) Al_2O_3 -WC. The calculations on M_xO_y only

without WC additions are shown in 4d-4f for a comparison.

Figure captions in the Supplementary

Fig.S1 The electron diffraction pattern (a) and EDS spectrum (b) of impurity phases in the commercial ZrB_2 powder purchased from H.C. Starck (marked in 1i and 1j).

Fig.S2 The XRD pattern of raw Al_2O_3 powder, all the peaks could be indexed to γ type.

Fig.S3 Equilibrium products predicted in 5mol WC-1mol Y_2O_3 and 5mol WC-1mol Fe_2O_3 . The calculation parameters are the same as that in Fig.4.

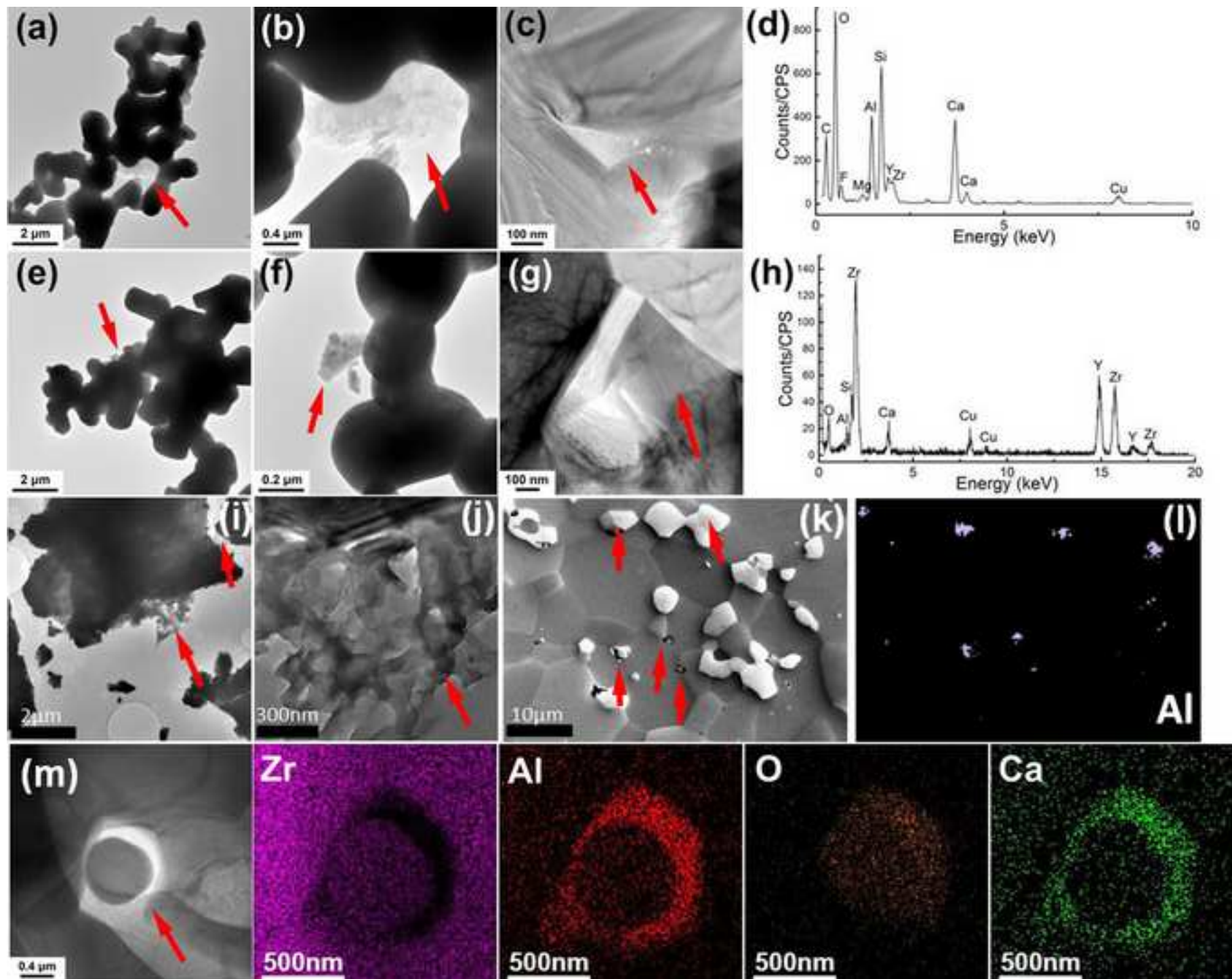
Fig.S4 Equilibrium products predicted in 5mol B_4C -1mol CaO . The calculation parameters are the same as used in Fig.4. The change of some gaseous substance, e.g. $BO_x(g)$, was not plotted in this figure for simplicity.

Table I Typical oxide impurities observed in ZrB₂ based ceramics from different research groups, including their processing details and the corresponding flexural strength at room temperature (RT) and 1600°C.

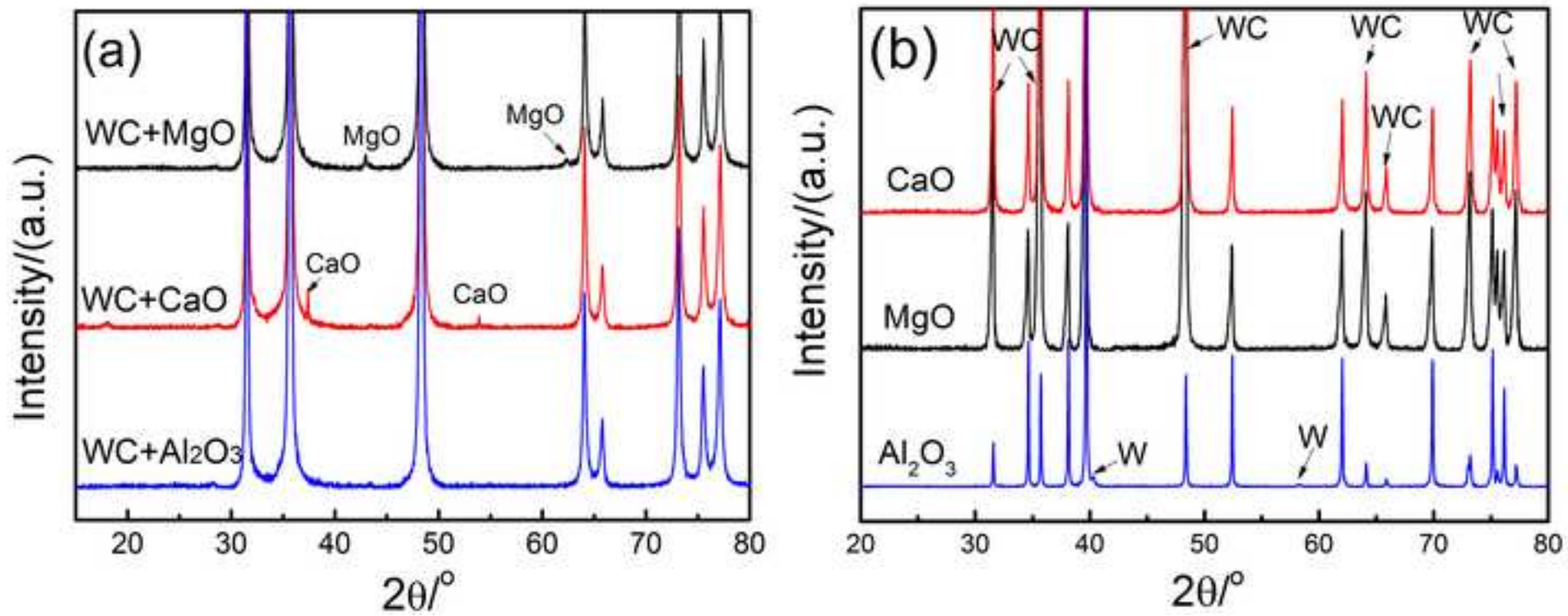
Research Group	ZrB ₂ Starting Powder	Composition	Sintering parameters	Oxide morphology	Composition of the impurity	3pt-flexural strength /MPa	
						RT	1600°C
SIC-CAS [5]	Self-made ZrO ₂ +B ₄ C	ZrB ₂ -20vol%SiC	Hot-pressing 1900°C	Facet	Ca-Al-Si-Mg-Y-C-O and hBN	546±55	460±31
SIC-CAS [6]	Self-made ZrO ₂ +B ₄ C+C	ZrB ₂ -20vol%SiC	Hot-pressing 1900°C	Facet	Zr-Al-Si-Y-Ca-O and hBN	671±19	471±32
Missouri S &T [19]	Grade B ZrB ₂ , H.C. Starck	ZrB ₂ -10vol%ZrC	Hot-pressing 1900°C	Spherical	ZrO ₂ and Zr-Al-Si-Ca-O	596 ± 111*	378 ± 32*
University of Arizona [22]	Grade B ZrB ₂ , H.C. Starck	ZrB ₂ +0.25wt%B ₄ C	Spark Plasma Sintering (SPS) at 1900°C	Spherical and facet	Ca-O-N-C, Ca-Fe-Y-Al-Ag-O and Fe-Co-O	660 ± 68	N/A
Missouri S &T [23]	Grade B ZrB ₂ , H.C. Starck	ZrB ₂ -20vol%SiC-5vol%B ₄ C	Hot-pressing 1900°C	Wet by the GB	Ca, Y, Al, Fe, Ni, and U, O	695 ± 69*	569 ± 56*
SIC-CAS [11,13]	Self-made ZrO ₂ +B ₄ C	ZrB ₂ -20vol%SiC-5vol%WC	Hot-pressing 1900°C	Not found	Not found	546±21	675±33

*Values were measured by four-point flexural test.

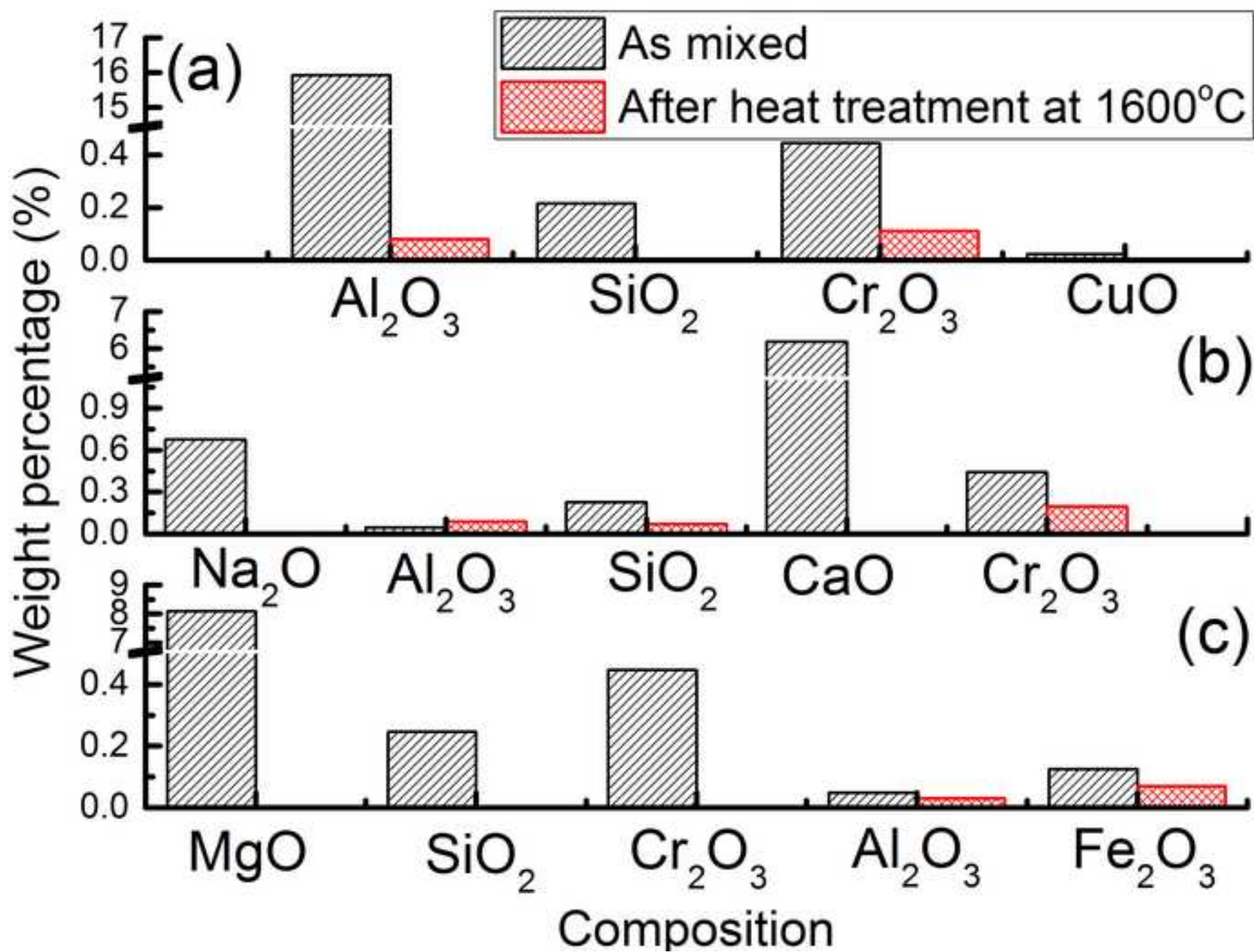
Figure(1)
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Figure(2)
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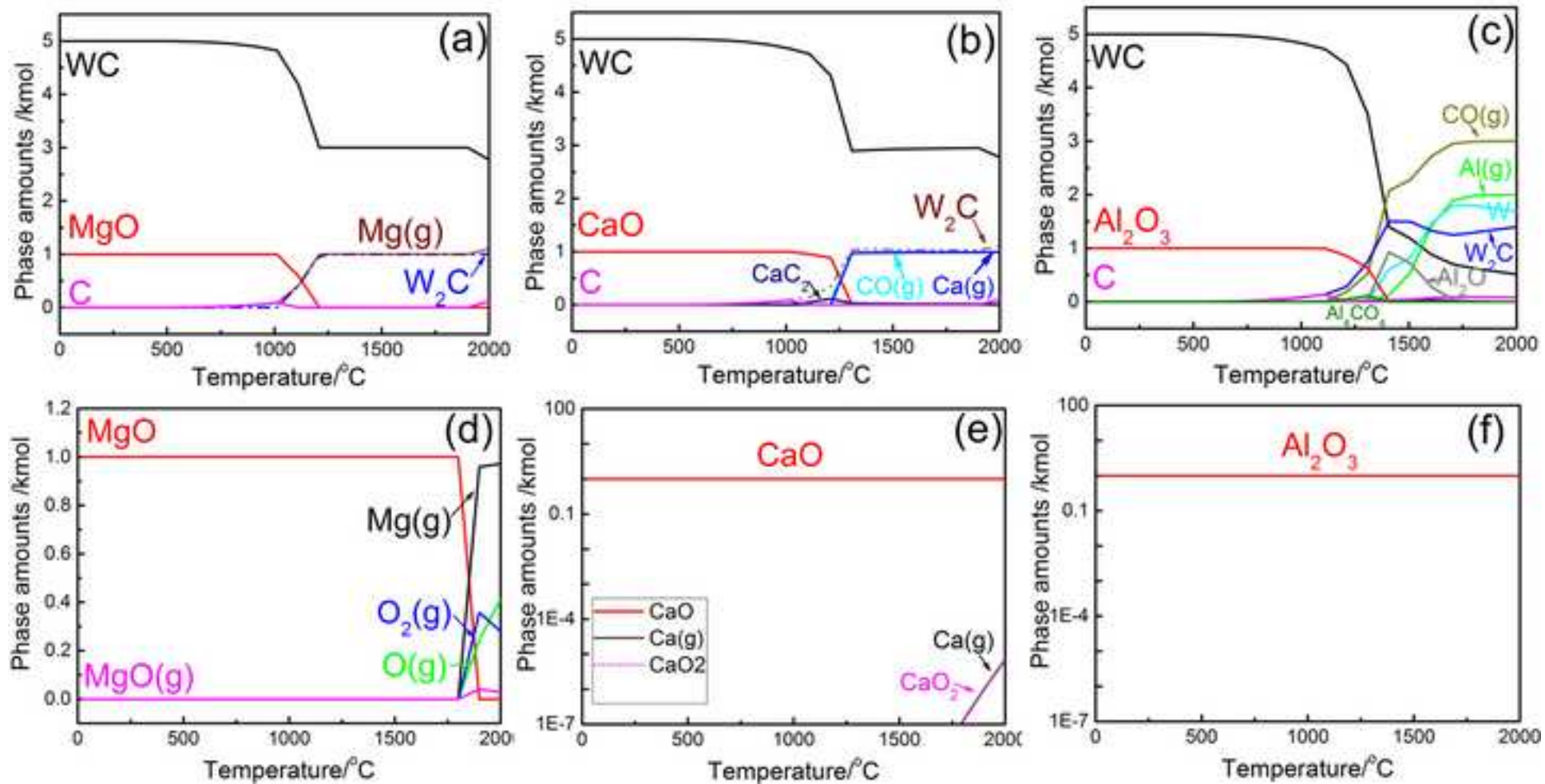


Figure(3)
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Figure(4)

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Supplementary Material Figure S1

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