

High-temperature phase relations of ZrN–ZrO₂–Y₂O₃ ternary system

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Abstract: Zirconium nitride (ZrN) ceramics were prepared via hot pressed sintering (HP) at 1750 °C in N₂ atmosphere with ZrO₂–Y₂O₃ as sintering additive. X-ray diffraction was applied to analyze the phase composition of the as-prepared ceramics to study the high temperature phase relation in ZrN–ZrO₂–Y₂O₃ ternary system and establish ZrN–ZrO₂–Y₂O₃ ternary phase diagrams. The results show that ZrN and tetragonal ZrO₂ (t-ZrO₂) solid solution, face-centered cubic ZrO₂ (c-ZrO₂) solid solution, body-centered cubic Y₂O₃ (c-Y₂O₃) solid solution coexist in the system of ZrN–ZrO₂–Y₂O₃.

Keywords: high temperature phase relations; zirconium nitride (ZrN); ternary system; X-ray diffraction

1 Introduction

Zirconium nitride (ZrN) is a kind of transition-metal nitride and has been considered for use as an inert matrix fuel (IMF) or as advanced fuel particle coatings due to its high thermal conductivity, low neutron capture cross section, and chemical compatibility with existing fuel cycle technology [1]. In addition, due to the strong covalent Zr–N bonding, high melting temperature (2952 °C), low creep rate, high hardness (22.7±1.7 GPa), fine chemical stability, thermal shock resistance, and erosion resistance, ZrN has potential applications in wear-resistance coatings, high temperature refractories, gas turbine combustion chamber, aerospace industry fields, etc. [2–6]. Correspondingly, increasing interest works have been conducted recently focused on assessing thermo-physical properties of ZrN and mixed phases of actinide nitrides dispersed in ZrN [7–10].

However, it is very difficult to prepare the high-density bulk ZrN samples. It is necessary to add some non-oxides and rare earth oxides (such as Si₃N₄–Y₂O₃) or oxides and rare earth oxides (such as ZrO₂–Y₂O₃) as sintering additives in order to obtain a dense bulk material [11,12]. Lu *et al.* [13] reported the role of Si₃N₄–Y₂O₃ sintering additive in the ZrN–Si₃N₄–Y₂O₃ ternary system. Stubican *et al.* [14,15] found that there are three kinds of solid solutions of ZrO₂ and Y₂O₃ coexisting in the ZrO₂–Y₂O₃ binary system at 1750 °C, including tetragonal ZrO₂ solid solution (t-ZrO₂ SS), face-centered cubic ZrO₂ solid solution (c-ZrO₂ SS), and body-centered cubic Y₂O₃ solid solution (c-Y₂O₃ SS). Furthermore, Y₄Zr₃O₁₂ will form when the mole ratio of ZrO₂:Y₂O₃ is 3:2 at 1250 °C.

To our knowledge, phase relationship of ZrN–ZrO₂–Y₂O₃ ternary system at high temperatures has been rarely reported up to now. Therefore, in this paper, ZrO₂–Y₂O₃ was chosen as sintering additive to prepare ZrN ceramics. High temperature phase relation of ZrN–ZrO₂–Y₂O₃ ternary system was studied and ZrN–ZrO₂–Y₂O₃ ternary phase diagram was established.

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2 Experimental

The raw materials used in the present study include ZrN (> 99.9%, $D_{50} = 0.8 \mu\text{m}$, Beijing Deke Daojin), ZrO_2 (> 99.99%, $D_{50} = 0.2\text{--}0.4 \mu\text{m}$, Aladdin Reagent Co., Ltd.), and Y_2O_3 (> 99.99%, Ruike Rare Earth Metallurgy Research Institute).

The powders of ZrN, ZrO_2 , and Y_2O_3 were mixed with different ratios, and ground to uniform distribution in agate mortar with the additive of absolute ethyl alcohol until absolute ethyl alcohol dried completely. The mixed powders were then sieved and filled in graphite mould. Sintering process was performed with a hot-pressing furnace (ZTY-50-23, Shanghai Chen Rong Electric Furnace Co., Ltd.) in N_2 atmosphere under pressure of 1.1–1.9 MPa at 1750 °C for 1 h.

The phase compositions of the as-prepared ceramics were analyzed by X-ray diffraction (SHIMADZU-6000) with Cu $\text{K}\alpha$ as diffractive target at a scanning speed of 4 (°)/min with a 2θ range from 10° to 75°.

3 Results and discussion

XRD pattern of ZrN– ZrO_2 binary subsystem fabricated at 1750 °C under N_2 atmosphere is shown in Fig. 1. It can be seen that ZrN and ZrO_2 can exist independently. This means that no reaction between ZrN and ZrO_2 occurs and no new phase generates. The as-prepared sample is compact, indicating that ZrO_2 can prompt the densification of ZrN.

Figure 2 shows the XRD pattern of the as-prepared sample in ZrN– Y_2O_3 binary subsystem with the molar ratio of $\text{ZrN}:\text{Y}_2\text{O}_3 = 1:1$. Again no reaction between ZrN and Y_2O_3 is observed (as showing later in Table 1, points 5, 6, and 7) and no new phase appears.

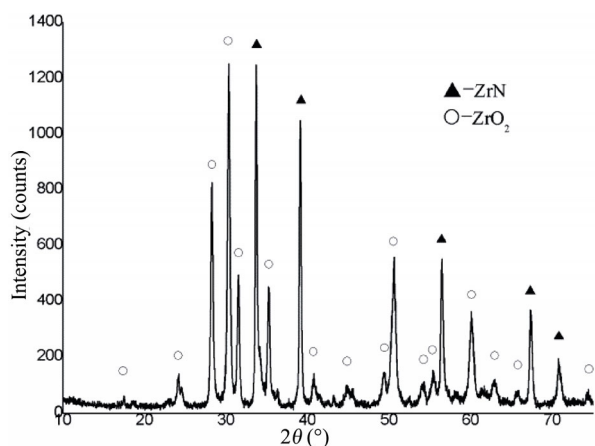


Fig. 1 XRD pattern of the sample with $\text{ZrN}:\text{ZrO}_2 = 1:1$.

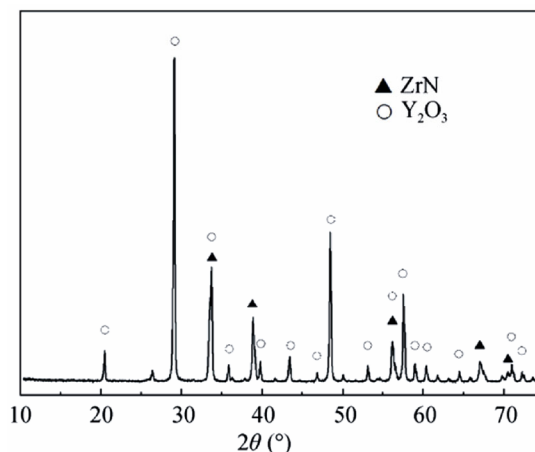


Fig. 2 XRD pattern of the sample with $\text{ZrN}:\text{Y}_2\text{O}_3 = 1:1$.

Table 1 Phase compositions of the HPed samples of $\text{ZrN}\text{--}\text{ZrO}_2\text{--}\text{Y}_2\text{O}_3$ at 1750 °C

Composition point	Mole ratio			Phase compositions
	ZrN	ZrO_2	Y_2O_3	
0	1	1	0	ZrN + ZrO_2
1	4	5.4	0.6	ZrN + c- ZrO_2 SS
2	3	1	1	ZrN + c- ZrO_2 SS
3	4	3	3	ZrN + c- ZrO_2 SS
4	4	1.2	4.8	ZrN + c- Y_2O_3 SS
5	3	0	1	ZrN + Y_2O_3
6	1	0	1	ZrN + Y_2O_3
7	1	0	3	ZrN + Y_2O_3

By the way, it is noted that a special metallic luster of ZrN is observed on the surface of the as-prepared $\text{ZrN}\text{--}\text{Y}_2\text{O}_3$ ceramic, implying that the additive of Y_2O_3 can prompt the sintering of ZrN. The reason is that a small quantity of ZrO_2 existing on the surface of ZrN can react with Y_2O_3 to form t- ZrO_2 solid solution at low temperature [15] which will fill in the phase interface of $\text{ZrN}\text{--}\text{Y}_2\text{O}_3$. Moreover, due to the existence of the small amount of ZrO_2 on the surface of ZrN in the $\text{ZrN}\text{--}\text{Y}_2\text{O}_3$ binary system, the binary system can be extended to $\text{ZrN}\text{--}\text{ZrO}_2\text{--}\text{Y}_2\text{O}_3$ ternary system and, during sintering, the densification of ZrN ceramics is promoted significantly.

In the $\text{ZrO}_2\text{--}\text{Y}_2\text{O}_3$ binary phase diagram [15], there exist three kinds of solid solutions of ZrO_2 and Y_2O_3 at the isothermal line of 1750 °C, including tetragonal ZrO_2 solid solution (t- ZrO_2 SS), face-centered cubic ZrO_2 solid solution (c- ZrO_2 SS), and body-centered cubic Y_2O_3 solid solution (c- Y_2O_3 SS). To study the effect of $\text{ZrO}_2\text{--}\text{Y}_2\text{O}_3$ as additive on the stability of ZrN, four component points, points 1–4 in Fig. 3, near the

phase boundary lines of (t-ZrO₂ SS + c-ZrO₂ SS) and c-ZrO₂ SS, c-ZrO₂ SS and (c-ZrO₂ SS + c-Y₂O₃ SS), (c-ZrO₂ SS + c-Y₂O₃ SS) and c-Y₂O₃ SS, were chosen. The corresponding molar ratios of Y₂O₃ are 10%, 50%, 50%, and 80%, respectively. The XRD patterns of the four as-prepared ceramics are respectively shown in Figs. 4–7.

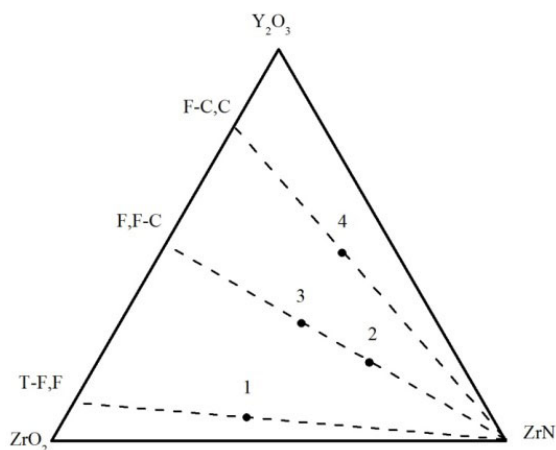


Fig. 3 Phase diagram of ZrN–ZrO₂–Y₂O₃ ternary system.

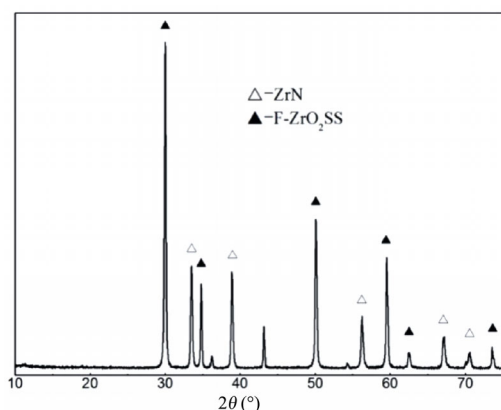


Fig. 4 XRD pattern of the sample with ZrN:ZrO₂:Y₂O₃ = 4:5.4:0.6.

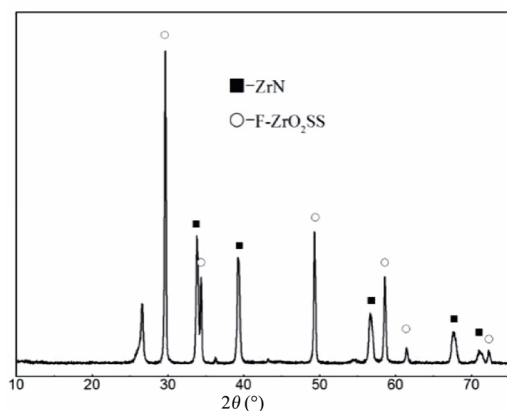


Fig. 5 XRD pattern of the sample with ZrN:ZrO₂:Y₂O₃ = 3:1:1.

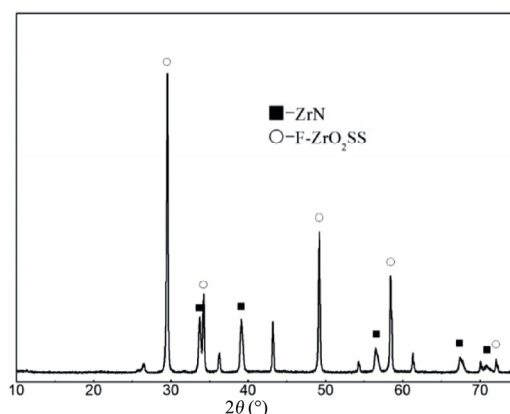


Fig. 6 XRD pattern of the sample with ZrN:ZrO₂:Y₂O₃ = 4:3:3.

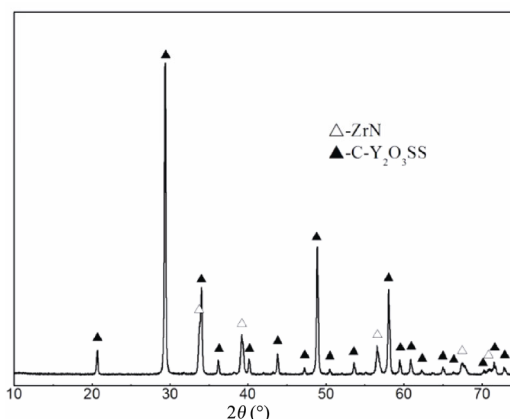


Fig. 7 XRD pattern of the sample with ZrN:ZrO₂:Y₂O₃ = 4:1.2:4.8.

As can be seen in Figs. 4–7, ZrN is extremely stable at high temperatures and can coexist with c-ZrO₂ SS and/or c-Y₂O₃ SS in the system of ZrN–ZrO₂–Y₂O₃. Based on the results shown in Figs. 4–7, ZrN–ZrO₂–Y₂O₃ ternary phase diagram can be established and the results are shown in Fig. 8. Phase compositions of the as-hot-pressed ZrN ceramics, with different molar ratios of ZrN:ZrO₂:Y₂O₃, are listed in Table 1.

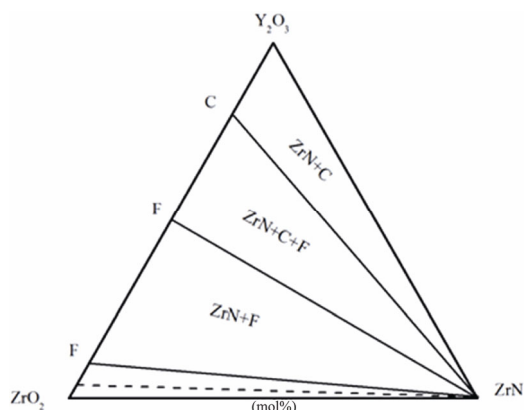


Fig. 8 Phase diagram of ZrN–ZrO₂–Y₂O₃ ternary system at 1750 °C.

4 Conclusions

In this work, the effect of ZrO_2 - Y_2O_3 as additive on the stability of ZrN was investigated and the phase diagram of ZrN-ZrO₂-Y₂O₃ ternary system at 1750 °C was established. It was shown that the thermo-physical properties of ZrN are very stable in N₂ atmosphere. ZrN does not react with ZrO₂ and/or Y₂O₃ to form new phases. In the system of ZrN-ZrO₂-Y₂O₃, ZrN can coexist with t-ZrO₂ SS, c-ZrO₂ SS, and c-Y₂O₃ SS at 1750 °C.

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