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The acidic/basic effects on preparation of zirconia powders from molten salts

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The influences of the acidity/basicity on the phase composition and the crystallite size of zirconia powders prepared in the $NaNO_3/KNO_3$ system was investigated by adding Lux–Flood bases ($NaNO_2/KNO_2$, Na_2O_2 and Na_2CO_3) to the system. It was found that the reaction occurred at lower temperatures in the system containing bases than in the pure $NaNO_3/KNO_3$ system. The phase composition of the tetragonal zirconia yielded varies with the concentration of the bases contained in the $NaNO_3/KNO_3$ melt. When the base concentration is above a certain value, 100% tetragonal phase can be produced. The crystallite size of the tetragonal phase decreases with increasing base concentration, i.e. basicity, in the melt. The crystallite size, was found to decrease in the order of added bases in the molten $NaNO_3/KNO_3$ system: $Na_2O_2 > Na_2CO_3 > NaNO_2/KNO_2$. The strength of the basicity of the commonly used molten nitrate and nitrite systems was found to decrease in the order: $NaNO_2/KNO_2 > LiNO_3/KNO_3 > NaNO_3/KNO_3$ and $NaNO_3$. It appears that the acidity/basicity of a melt plays a very important role in the phase composition and crystallite size during the precipitation of zirconia from molten salts.

1. Introduction

It is well known that the monoclinic structure of zirconia is stable below 1100 °C and the tetragonal phase above 1200 °C. However, the tetragonal form may be stabilized at lower temperatures under certain conditions. The retention of the metastable tetragonal phase has been explained by a number of investigators [1–5], but the actual mechanism still remains obscure.

Davis [6] reported, in the preparation of zirconia powders from aqueous solutions, that the precursor solution pH results in the formation of the tetragonal or the monoclinic phase after calcining the materials at 400–600 °C. Recently, the pH influence on phase composition and crystallite size has been investigated in different precursor materials [7–9]. It was suggested by Jada and Peletis [10] that the solution chemistry plays a key role in controlling phase formation, polymorphic phase transformation and polycrystalline growth.

In recent years, it has been reported that zirconia powders can be prepared in molten nitrates and nitrites [11, 12]. Kerridge [13] studied the reactivity of zirconium (IV) sulphate in the molten $LiNO_3/KNO_3$ eutectic. It was found that the zirconium (IV) reacted as Lux–Flood acid and the reaction took place at lower temperatures when bases (Na_2O_2, Na_2O and NaOH) existed in the melt, but, unfortunately, the properties of the precipitated powders and relations between the properties of the precipitated powders and the solution chemistry were not stated. More recently, the authors investigated the reactions of zirconium (IV) sulphate in molten $NaNO_3/KNO_3$ and $NaNO_2/KNO_2$ eutectics [14] and found that the powders produced in the above two systems were different both in crystallite size and crystal structure. The structure of powders precipitated in nitrates was a mixture of the monoclinic and tetragonal phases and the crystallite size was larger than that produced from nitrites. However, only the tetragonal phase was present when powders were prepared from nitrites. The reaction kinetics and mechanism were shown to be different and it was proposed that the acidic/basic differences of the two systems resulted in the differences in the reaction mechanisms and in the properties of the powders, e.g. structure and crystallite size.

Therefore, it is of interest to carry out a more definitive investigation of the influence of acidity/basicity (by adding bases, such as $NaNO_2/KNO_2$, Na_2CO_3 and Na_2O_2) on the reactions and properties of zirconia powders precipitated in the molten $NaNO_3/KNO_3$ system, which is a more acidic melt than the $NaNO_2/KNO_2$ [15] melt. This may result in a better understanding of the chemistry of molten nitrates, effects of the adding bases, factors determining the metastable tetragonal phase, and further control of the properties of the powders produced.

2. Experimental procedure

Zirconium (IV) sulphate hydrated was dehydrated by heating gradually to 350 °C for 2 h. Dry $NaNO_3$, KNO_3, $NaNO_2$ and KNO_2 were dried at around 180 °C for 24 h. The eutectics were prepared by mixing 50 mol % $NaNO_3$/50 mol % KNO_3, and 65 mol %

$NaNO_2$/35 mol % KNO_2, respectively. Other bases were used directly from the bottles. The chemicals were mixed and fully ground in a mortar before heating for the reactions.

A Steram G70 thermobalance was employed to investigate the reaction through weight loss produced by gas evolution. The measurements were performed in an alumina crucible open to the air with a few hundred milligrams of sample in it. Blank runs indicated an approximately zero weight loss in the range of 200–600 °C. There was also no weight loss when heating nitrites or nitrates alone below 550 °C, demonstrating that the salts were dry and there was no decomposition of either melt below 550 °C. The preparation of the zirconia powders was carried out in a Pyrex tube.

The zirconia powders were extracted from the cooled salt by dissolving the melt in distilled water followed by vacuum filtration. A Philips (PW-1050) diffractometer with CuK_α radiation was employed for phase, phase composition and crystallite size analysis. The ratio of peak intensities $[I(1\,1\,1)_T/I(1\,1\,1)_T + I(1\,1\,\bar{1})_M + I(1\,1\,1)_M]$ was used to estimate the volume fraction of the tetragonal phase [16] and the mean crystallite size was determined by Scherer's method [17].

3. Results and discussion

Thermogravimetric analysis results of anhydrous $Zr(SO_4)_2$ in the molten $NaNO_3$–KNO_3 eutectic melt and the melt containing different Lux–Flood bases of Na_2O_2 and Na_2CO_3 are shown in Fig. 1. The overall reaction between $Zr(SO_4)_2$ and $NaNO_3$–KNO_3 has been found to be [14]

$$Zr(SO_4)_2 + 4NO_3^- \rightarrow ZrO_2 + 2SO_4^{2-} + 4NO_2 + O_2 \qquad (1)$$

It can be seen from Fig. 1 that both the starting and finishing temperatures of the reactions are lowered by the addition of Lux–Flood bases to the $NaNO_3$–KNO_3 melt, which is consistent with the results obtained from the $LiNO_3$–KNO_3 system [13]. The reaction of $Zr(SO_4)_2$ with the pure $NaNO_3$–KNO_3 melt took place at over 200 °C and finished at about 450 °C, with two overlapping stages. It was accompanied by evolution of brown NO_2 gas and formation of a white powder. Whereas, in the melt containing Na_2O_2, $Zr(SO_4)_2$ began to react at about 130 °C with evolution of gas and precipitation of a white powder. A further reaction commenced at approximately 260 °C and finished at about 380 °C with evolution of more gas. In the melt containing Na_2CO_3, the reaction occurred in three main stages with the first one starting at about 100 °C, the second 200 °C and the third 300 °C, finishing at about 400 °C. Both the lower starting and finishing temperatures in the melts with bases are probably because of the reaction of Na_2O_2 and the ionization of CO_3^{2-} in the melt, i.e.

$$Na_2O_2 \rightarrow Na_2O + \tfrac{1}{2}O_2 \qquad (2)$$

Na_2O can further ionize

$$Na_2O \rightarrow 2Na^+ + O^{2-} \qquad (3)$$

and

$$CO_3^{2-} \rightarrow CO_2 + O^{2-} \qquad (4)$$

The release of oxygen and the oxide ions to the melt can lower the reaction temperature of Equation 1, for example, by the reaction between Zr^{4+} and O^{2-}

$$Zr^{4+} + 2O^{2-} \rightarrow ZrO_2 \qquad (5)$$

The X-ray diffraction (XRD) profiles of the powders produced from the $NaNO_3$/ KNO_3 melt at 450 °C for 90 min containing various quantities of $NaNO_2$/ KNO_2 eutectic are illustrated in Fig. 2. From the peak height and width, it can be seen that the phase composition and crystallite size vary with the concentration of $NaNO_2$/KNO_2 in the melt. The XRD results of zirconia powders prepared from the $NaNO_3$/ KNO_3 eutectic with different concentrations of Na_2O_2 and Na_2CO_3 show a similar trend.

Fig. 3 demonstrates that all the fractions of the tetragonal zirconia obtained from the ratios of peak height $[I(1\,1\,1)_T/I(1\,1\,1)_T + I(1\,1\,\bar{1})_M + I(1\,1\,1)_M]$ have a similar trend with the concentrations of different added bases. Firstly, it can be seen that the tetragonal fractions increase when small quantities of bases exist in the melt. Then the fractions decrease with further

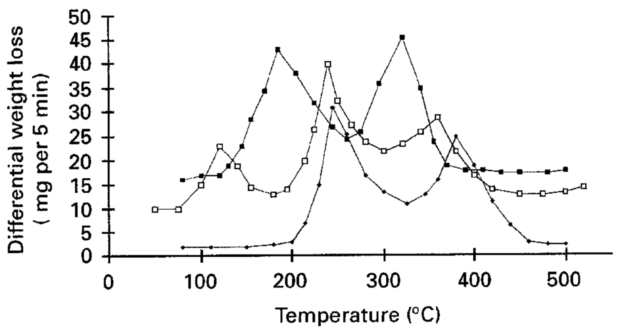

Figure 1 The reaction of $Zr(SO_4)_2$ in the $NaNO_3$–KNO_3 melt and the melt containing Lux–Flood bases. Series 1: $Zr(SO_4)_2$ (5 mol %) + $NaNO_3$–KNO_3; Series 2: $Zr(SO_4)_2$ (5 mol %) + $NaNO_3$–KNO_3 + Na_2CO_3 (20 mol %); Series 3: $Zr(SO_4)_2$ (5 mol %) + $NaNO_3$–KNO_3 + Na_2O_2 (20 mol %). ◆ Series 1; □ Series 2; ■ Series 3.

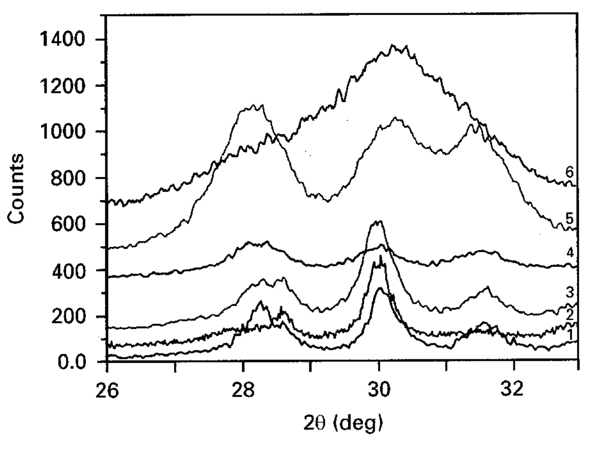

Figure 2 XRD patterns of ZrO_2 prepared in $NaNO_3$/KNO_3 containing $NaNO_2$/KNO_2 Concentrations of $NaNO_2$/KNO_2 (mol %): 1:0, 2:5, 3:10, 4:20, 5:30, 6:40.

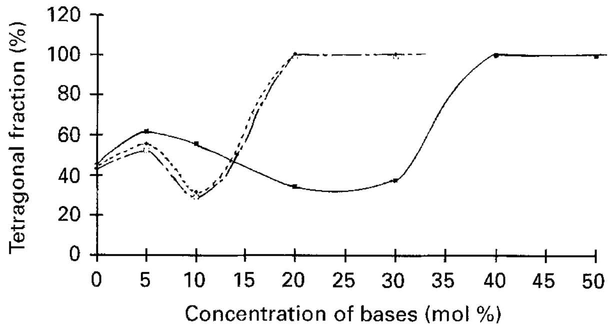

Figure 3 Fractions of tetragonal ZrO_2 prepared from $NaNO_3$–KNO_3 containing added Lux–Flood bases. ■ $NaNO_2$–KNO_2; □ Na_2CO_3; ◆ Na_2O_2.

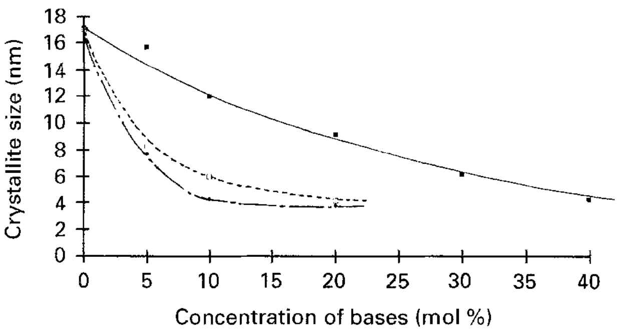

Figure 4 Crystallite sizes of ZrO_2 produced from $NaNO_3$/KNO_3 containing added Lux–Flood bases. ■ $NaNO_2$–KNO_2; □ Na_2CO_3; ◆ Na_2O_2.

increase of base concentrations. After the base concentration reaches a certain amount, the fractions increase again abruptly to 100% tetragonal structure, and then remain there after the base concentration increases further. The fractions produced in the melt containing Na_2CO_3 are slightly lower than that containing Na_2O_2 when the concentration is lower than 20 mol %. The minimum concentration of $NaNO_2$/KNO_2 in $NaNO_3$/KNO_3 at which 100% tetragonal phase can be obtained, however, is approximately 40 mol %, whereas the quantities of Na_2O_2 and Na_2CO_3 are both about 20 mol %. This means that the presence of Na_2O_2 or Na_2CO_3 has more effect on the phase composition of zirconia which is precipitated in the melt than does $NaNO_2$/KNO_2.

On the other hand, as shown in Fig. 4, the trend of the crystallite sizes, obtained from the tetragonal peak (1 1 1) width, is much more simple than that shown in Fig. 3, which decrease with the increase of the base concentrations, i.e. decrease with the increase of basicity of the melt. If the relationship is true, it can be deduced that the sequence of the basicity by comparing the crystallite size at the same concentration of the different added bases in Fig. 3 is

$$Na_2O_2 > Na_2CO_3 \gg NaNO_2/KNO_2$$

From this point of view, the relationship between the crystallite size and the basicity of a melt could be extended as a criterion to judge the basic strength of various molten salts or melts containing bases, although the definitive Lux–Flood acidity of $-\,p[O^{2-}]$ in molten salts has not been established due to the fact that the ionisation data of $[O^{2-}]$ are lacking. Table I lists the phase and crystallite size of ZrO_2 powders precipitated in presently commonly used nitrate and nitrite melts. It can be seen that the powders produced in nitrate systems are all a mixture of monoclinic and tetragonal phases, but their crystallite sizes are different. By using the above criteria, the following series of basicity can be deduced, $NaNO_2/KNO_2 > LiNO_3/KNO_3 > NaNO_3/KNO_3$ and $NaNO_3$.

TABLE I Phase and crystallite size prepared in different melts (450 °C, 90 min)

Melt	$LiNO_3$/ KNO_3	$NaNO_3$/ KNO_3	$NaNO_3$	$NaNO_2$/ KNO_2
Phase	m + t[a]	m + t	m + t	t
Crystallite size (nm)	11.4	17.0	17.1	4.7

[a] m, monoclinic; t, tetragonal.

In summary, the acidity/basicity of the molten salts plays a very important role in determining the phase composition and crystallite size during the process of the preparation of ZrO_2 powders from molten nitrates and nitrites. The relationship between the phase composition and crystallite size and the general acidic data $p[O^{2-}]$ cannot be established at the present stage, however, because of the lack of the ionisation data of Lux–Flood bases in molten salts. It is possible to precipitate pure tetragonal or a mixture of the monoclinic and tetragonal zirconia with desired crystallite size by controlling the acidity/basicity of a melt.

4. Conclusion

The addition of Lux–Flood bases to the $NaNO_3$–KNO_3 system can lower the reaction temperatures when using $Zr(SO_4)_2$ as the starting material to prepare zirconia powders.

The proportion of tetragonal zirconia produced changes with the acidity/basicity of the $NaNO_3$–KNO_3 system. When the acidity/basicity reaches a certain level, 100% tetragonal phase can be produced.

The crystallite size of the zirconia powder precipitated decreases with increasing basicity of the $NaNO_3$–KNO_3 system. By applying this relationship to the various bases and molten salts, the following basic sequence is deduced according to the crystallite size of zirconia powders produced under same conditions, i.e., for Lux–Flood bases $Na_2O_2 > Na_2CO_3 > NaNO_2/KNO_2$, and the commonly used molten nitrate and nitrite systems $NaNO_2/KNO_2 > LiNO_3/KNO_3 > NaNO_3/KNO_3$ and $NaNO_3$.

Because the acidity/basicity of a melt has effects in determining the reaction, phase composition and crystallite size of the zirconia powders precipitated, it can be said that the quantitative understanding of the role of acidity/basicity of a melt plays a very important part in controlling the properties of zirconia powders produced from molten salts.

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