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A study of the sintering reaction of mullite–ZrO_2 ceramics by positron annihilation technology

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Abstract. We measured the positron annihilation average lifetime in the sintered mullite–ZrO_2 ceramic material at different ratios A/Z and including Cr_2O_3 and at three temperature values. The experimental results show that the positron lifetime can sensitively reflect the influence of different ratios A/Z and different temperature values on the microscopic structure. According to the theory of microscopic defects and phase-change information supplied by positron lifetimes, some characteristics of the sintering reaction of the mullite–ZrO_2 ceramic are explained in this paper. The results were found to be in good agreement with those obtained using other methods.

1. Introduction

The area of mullite–ZrO_2 ceramics has received widespread attention [1, 2]. There are a variety of methods, such as electron microscopy, scanning electron microscopy, x-ray diffractometry and electron probing [1, 2], that can be used to study the material. In the last decade, positron annihilation experiments have been widely used to investigate crystal lattice defects. The speed of a positron injected into a densified material rapidly reduces during the processes of thermalisation and diffusion until the positron is eventually annihilated. According to the theory of annihilation the annihilation rate is relevant to the electron density in a material [3]. Therefore, the measurement of the positron annihilation characteristics [4] in a solid can provide information concerning the internal structure and concentration of defects. However, more than one electron state [5] is possible in any general ionic compound, including perfect crystals. There are also different positron states in different types of crystal, and there are different positron lifetimes; therefore one can investigate the transition of an ionic compound with the aid of positron annihilation technology. The purpose of work described in this paper is to try to obtain some useful information about the kinetics of the sintering reaction of mullite–ZrO_2 at various ratios $Al_2O_3/ZrO_2{\cdot}SiO_2$ (A/Z), using positron annihilation experiments.

2. Description of the experiment

Five samples with different A/Z ratios were prepared and are listed in table 1. In addition, 8% Cr_2O_3 was added to sample E. Each sample contains three groups having the sintering temperatures of 1550 °C, 1600 °C and 1650 °C respectively.

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Table 1. The A/Z ratio in the different samples.

Sample	A	B	C	D	E
A/Z	0.60	0.82	1.10	11	0.82 (8% Cr_2O_3 added)

Table 2. Porosity of samples and positron lifetime data.

Sample		Sintering temperature (°C)	Porosity (%)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	$\bar{\tau}$ (ps)
A	1	1550	20.56	34 ± 1	218 ± 1	1438 ± 20	34.2 ± 0.1	59.9 ± 1.0	273
	2	1600	16.65	85 ± 4	279 ± 3	1565 ± 28	36.9 ± 1.1	58.0 ± 1.0	227
	3	1650	0.98	80 ± 4	315 ± 3	1514 ± 28	27.6 ± 0.7	66.6 ± 0.7	320
B	1	1550	24.43	86 ± 3	248 ± 4	1559 ± 25	45.9 ± 1.5	48.9 ± 1.4	251
	2	1600	18.05	98 ± 3	269 ± 5	1590 ± 28	50.8 ± 1.6	44.0 ± 1.5	241
	3	1650	1.21	94 ± 4	320 ± 4	1526 ± 30	33.0 ± 1.0	61.2 ± 0.9	315
C	1	1550	24.43	106 ± 3	287 ± 6	1667 ± 33	58.9 ± 1.5	36.5 ± 1.4	246
	2	1600	22.85	93 ± 3	268 ± 4	1512 ± 26	48.9 ± 1.4	45.9 ± 1.3	244
	3	1650	0.93	82 ± 4	309 ± 3	1468 ± 28	31.1 ± 0.8	63.2 ± 0.7	305
D	1	1550	30.63	107 ± 3	281 ± 7	1569 ± 30	63.3 ± 1.7	31.9 ± 1.6	231
	2	1600	30.98	104 ± 2	280 ± 7	1551 ± 29	63.0 ± 1.0	32.2 ± 1.5	232
	3	1650	31.36	116 ± 2	305 ± 9	1597 ± 34	68.3 ± 1.8	27.1 ± 1.5	236
E	1	1550	20.99	118 ± 2	317 ± 3	1685 ± 33	53.9 ± 1.5	41.3 ± 1.4	272
	2	1600	17.40	124 ± 3	325 ± 5	1677 ± 30	60.6 ± 1.8	34.3 ± 1.5	275
	3	1650	3.05	128 ± 3	337 ± 4	1686 ± 32	40.9 ± 1.5	54.3 ± 1.7	316

The lifetime spectra were measured on a fast–fast coincidence system with the ORTEC 583 as the selector of energy. The time resolution (FWHM) of the system with a ^{60}Co source was 280 ps. As a positron source $^{22}NaCl$ was sealed in a Mylar foil, with a thickness of about 1 mg cm^{-2}. The measurement time was set at 7.2×10^3 s. The number of events was about 8.0×10^5. The lifetime spectra were analysed using the computer program POSITRONFIT EXTENT. Three lifetime components τ_1, τ_2, τ_3 and the corresponding intensities I_1, I_2 and I_3 (not listed in table 2) were obtained. The positron average lifetime is given by

$$\bar{\tau} = \sum_{i=1}^{3} I_i \tau_i .$$

The results of the experiments are listed in table 2.

3. Analysis and discussion

For the convenience of analysis, the relationships between the positron average lifetime and the sintering temperature are shown in figure 1.

Figure 1 shows the relationship of $\bar{\tau}$ to T in four series of samples, which have different A/Z ratios and possess the same variation trend. In the temperature interval 1550–1600 °C, it can be seen that $\bar{\tau}$ decreases gradually with the increase of temperature. The reason for this is that above 1550 °C the microstructure of the samples is changed. Al_2O_3 and $SiO_2 \cdot ZrO_2$ constitute a mixture before the reaction and form the chemical compound mullite. The remainder of the ZrO_2 and Al_2O_3 are combined in the mullite. This densifying process can cause a decrease in $\bar{\tau}$. A new phase is formed about 1600 °C [6]. We can see from table 2 that the porosities of all specimens are obviously decreased. It can be concluded that the reactions are so extreme that the increase in the number of micro-defects makes $\bar{\tau}$ increase quickly. This may be the reason for the increase in $\bar{\tau}$ in this temperature region.

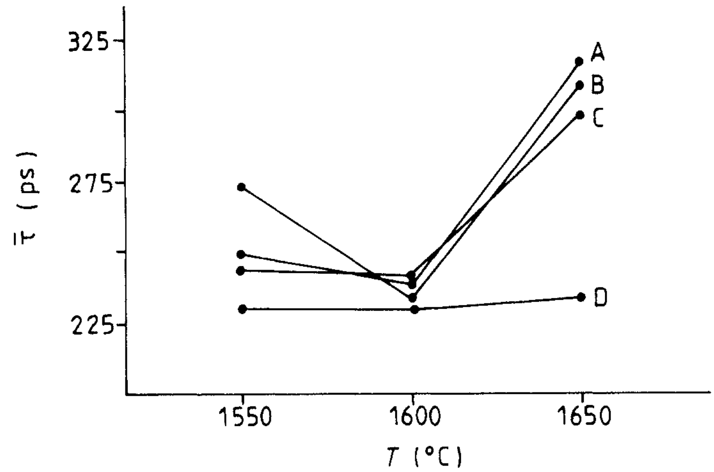

Figure 1. The relationship of $\bar{\tau}$ of each sample group to the change in temperature.

In figure 1, when the A/Z ratio is increased, the change of $\bar{\tau}$ with T is reduced. This indicates that the variation of the microstructure and the chemical reaction are weakened. The chemical equation is

$$3Al_2O_3 + 2ZrSiO_4 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2ZrO_2.$$

We suggest that the higher the A/Z ratio, the more Al_2O_3 remaining, and this remaining Al_2O_3 makes the chemical reaction slow down. Lutz [7] point out that the higher the A/Z ratio, the slower the diffusion of the new phase. Pena and Aza also proved [8] that the higher the A/Z ratio is, the higher the agglomerate temperature. Our results are in good agreement with these previous results [7, 8].

Cr_2O_3 was added to sample E, which was different from the other samples. The A/Z ratio in sample E is the same as that in sample B. It can be seen from table 2 that the average positron lifetime is increased because of the presence of Cr_2O_3. It can also be seen from the Cr-distributed pattern of sample E in figure 2 that Cr_2O_3 becomes mainly a 'corundum foundation' during the sintering process of Cr_2O_3. We consider the fact that the radii of the Cr^{3+} are different from those of the Al^{3+} to be due to the solid-solute

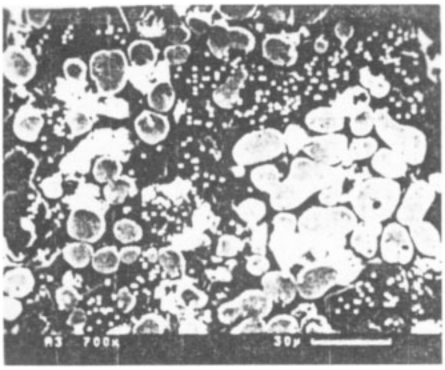

Figure 2. The Cr-distributed pattern of sample E.

state of Cr_2O_3 in Al_2O_3, which results in the crystal lattice warping, and the number of defects and $\bar{\tau}$ increasing. The experiments also show that adding Cr_2O_3 can increase the porosity and has a hindering effect on the sintering reaction.

We can see from table 2 that the higher the temperature, the lower the porosity, and the porosity at 1650 °C reaches a minimum. The lifetime at 1650 °C is higher than that at 1550 °C and 1600 °C for any group of samples with the same A/Z ratio, i.e. the samples with the minimum porosity have the maximum lifetime, which contrasts with the law obtained from the positron annihilation experiments on a normal metal. The reason for this is that the porosity in a ceramic material is macroscopic and the porosity in a metal is microscopic. There is no corresponding relation between $\bar{\tau}$ and the porosity in ceramics. The positrons are not sensitive to defects that are far larger than the atomic size.

4. Conclusions

In this paper we have studied the ceramic material mullite–ZrO_2 using positron annihilation technology. The positron lifetime can reveal the influence of the temperature on the sintering reaction and also reflects the reaction speed in the sintering process. The relationship between the different A/Z ratios and the structural phase transformation has been explained. The results obtained from the study of mullite–ZrO_2 ceramics are in good agreement with those obtained by other methods.

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