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Thermal interaction between some oxides and zircon as a material for diesel engines filter

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Abstract

This study investigates the high temperature chemical resistance of zircon, $ZrSiO_4$, against Na_2O, $CaCO_3$, PbO, ZnO, Fe_2O_3, V_2O_5 and CeO_2. It was observed that lead and sodium oxides react with zircon only at 700 and 850 °C respectively, while the others do not react over the temperature range examined. Surprisingly, if V_2O_5 and PbO are present at the same time, the reaction of PbO is inhibited and zircon does not suffer degradation. On the other hand, the ternary mixture V_2O_5–PbO–Na_2O reacts slightly with zircon, the reaction was confirmed by XRD after thermal treatment of the mixtures at 650 °C and by FTIR after thermal treatment at 700 °C revealing the formation of lead silicates and lead zirconates. Not all the reactions between zircon and the other oxides are destructive and suggest that zircon is a suitable material for the production of diesel ceramic filters.

Keywords: C. Corrosion; C. Lifetime; E. Thermal applications; $ZrSiO_4$

1. Introduction

The durability of materials intended as filters for diesel engines has long been under investigation by two different approaches. The first aims to understand the degradation mechanisms of α-cordierite ($Mg_2Al_4Si_5O_{18}$) [1–10], the material currently used for filter production. The second considers the properties of cordierite and compares them with those of other ceramic materials (SiC, $3Al_2O_32SiO_2$, Al_2O_3, TiO_2, ZrO_2, etc.) that could be potential substitutes [11–15].

Unfortunately, literature data show these substitutes to be unsatisfactory and it appears that only mullite shows a resistance superior to cordierite against thermochemical aggression of some oxides from diesel soot [12,15]. Nevertheless the useful life of mullite is limited because, although reactions start at higher temperatures (700 °C instead of 500 °C) than cordierite, they proceed at faster rates above 900 °C [15].

Following the second approach, we have examined the high temperature chemical inertness of zircon, a commonly occurring mineral, which has high decomposition (>1600 °C) and melting temperatures (2550 °C), a low thermal expansion coefficient ($\alpha = 4.1 \times 10^{-6}\ {}^{\circ}C^{-1}$) and high chemical inertness both at low and high temperatures [16–19]. The literature does not report papers or patents concerning zircon as a potential candidate for the production of filters for diesel engines. It seems therefore interesting to study how zircon behaves in an oxidizing environment.

In this paper, we have investigated the chemical inertness of zircon against PbO, NaO, Fe_2O_3, $CaCO_3$, ZnO, V_2O_5 and CeO_2.

Diesel soot contains several oxides such as PbO, Na_2O, Fe_2O_3, $CaCO_3$, ZnO, V_2O_5 and CeO_2. In particular PbO comes from gasoline or from lubricant oils used in diesel engines; Na_2O derives from NaCl used as antifrost material on roads; Fe_2O_3 is due to the oxidation of metallic particles produced by engine wear; Ca and Zn are used as additives for lubricant oils as organometallic compounds, and transform to $CaCO_3$ or ZnO during combustion; V_2O_5 and CeO_2 are often introduced as catalysts in diesel refining. All such oxides can be present in diesel particulate, mostly at the same time. They could react with the ceramic support at high temperature contributing to the filter degradation during the regeneration processes in use. Mixtures of zircon and such oxides, treated at high temperature, can be used to simulate conditions in a diesel engine.

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The goal of this work is to test zircon inertness in the presence of these oxides, singly or in mixtures, to evaluate if zircon could be a candidate for production of ceramic filters. In this regard it is however cautious to point out that natural $ZrSiO_4$ is notably impure and often radioactive; neither natural or synthetic zircon are easy to sinter without thermal decomposition occurring. These factors, coupled with the poor commercial availability of synthetic $ZrSiO_4$ may inhibit its use.

2. Experimental procedure

The experimental procedure followed investigations of the high temperature chemical reactivity of zircon reported elsewhere [6–8,12–15] and consists of the preparation of powder mixtures of zircon and the oxide under study (wt. ratio 1/1) by wet mechanical mixing (4 h) using zirconia milling spheres (3Y-TZP, TOSOH) high density polyethylene vessels with isopropanol as the dispersing fluid. After homogenization, slurries were oven-dried at 80 °C, crushed and powders were pressed at 200 MPa into cylindrical specimens of 200 mg. In the present research, a series of pellets was prepared for each composition and each sample was submitted to one thermal treatment only. Thermal treatments were performed by a single step heating (heating rate of 10 °C/min) up to the maximum temperature followed by air-quenching at room temperature. Maximum temperature values ranged from 400 to 1000 °C with steps of 50 °C.

After thermal treatment, pellets were gently ground into powders using an agate mortar and examined by FTIR (Nicolet Magna-IR 550, Omnic deconvolutor with 4 cm^{-1} resolution) and XRD (Inel XRG 3000, with Co radiation and acquisition time of 30 min).

Elementary chemical analyses were done on a Spectro Mass 2000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). They were performed on starting and final mixtures that displayed reaction after thermal treatment at 1000 °C, i.e. in the cases where the greatest changes were expected.

Starting materials were commercial powders of $ZrSiO_4$ (average particle size 10 μm), PbO, V_2O_5, ZnO and Na_2CO_3 (all Aldrich 99%), CeO_2 (Aldrich 98%), $CaCO_3$ and Fe_2O_3 (Fisher 99%). Other mixtures containing zircon and more than one oxide, i.e. $ZrSiO_4/PbO+V_2O_5$ (wt. ratio 1/0.5+0.5) or $ZrSiO_4/PbO+V_2O_5+Na_2CO_3$ (wt. ratio 1/0.33+0.33+0.33), were also prepared and thermally treated following the procedure already described to test for synergistic effects.

3. Results and discussion

Table 1 reports the temperatures at which zircon reacts with various single oxides and compares these values with literature data [6,8,14] obtained from cordierite and the same oxides used in the present research. Temperatures reported correspond to the lowest values where XRD and FTIR analyses show formation of new phases. The new crystalline phases and their approximate quantity (low (<10 vol.%), medium (>10 and <40 vol.%) or high (>40 vol.%), as a function of temperature, were determined by XRD and reported in Table 2. A more quantitative determination of the amounts of the new phases is, in our opinion, not really relevant since their presence is sufficient to cause macroscopic changes in the microstructure of the material leading to degradation; as a consequence we consider the identification of a new phase as more important than its precise amount. For sake of brevity we do not show XRD spectra, but summarize results in Tables 1 and 2.

Some data in Table 1 seem to disagree, since XRD and FTIR analyses indicate different starting temperatures for the reaction. This can be explained by considering that the FTIR analysis acquires nanoscale information and may therefore show the emergence of the initial amorphous compounds that often precede the formation of crystalline phases.

According to results shown in Table 1, zircon is not attacked by single oxides ZnO, Fe_2O_3 and CeO_2, nor by $CaCO_3$ and V_2O_5; it reacts with PbO and Na_2CO_3, but the reaction starts at a higher temperature and with less destructive effects than with cordierite. As reported in a previous paper [6], cordierite is completely transformed into other phases at 800 °C after reaction with Na_2CO_3, or at 900 °C with PbO under similar test conditions. Since powders of zircon have average grain sizes of 10 μm whereas those of cordierite were prepared by coarse mortar grinding of sintered materials, it may be reasonably assumed that starting zircon powders have finer particle size distributions than cordierite. Homogenization is likely to produce the same effects on both

Table 1
Temperatures (°C) of starting reaction of zircon and cordierite in mixtures with various oxides or carbonates

Added material(s)	XRD		FTIR	
	Zircon	Cordierite[a]	Zircon	Cordierite[a]
Na_2CO_3	850	500	850	600
$CaCO_3$	nr	900	nr	900
PbO	700	600	700	550
Fe_2O_3	nr	nr	nr	nr
ZnO	nr	nr	nr	nr
V_2O_5	nr	800	nr	750
CeO_2	nr	nr	nr	nr
$PbO+V_2O_5$	nr	nd	nr	nd
$Na_2CO_3+PbO+V_2O_5$	700	nd	650	nd

(nr = no attack up to 1000 °C; nd = data not available); detected by XRD and FTIR analysis of the thermal treated samples.

[a] Ref. [6].

products and is therefore not really important. Since fine particles are expected to be more reactive than coarser ones, it might be argued that zircon is less reactive than cordierite.

Table 2 also shows that zircon is widely present at 1000 °C both in the presence of PbO, Na_2CO_3 and with a mixture of the two.

We now consider mixtures of PbO–$ZrSiO_4$. We may assume that in the ternary system ZrO_2–PbO–SiO_2 a liquid phase is present, under equilibrium conditions, at a temperature lower than that of pure PbO (890 °C) (for example in the binary system PbO–SiO_2 [20] a liquid phase is stable down to 720 °C). In Table 2 we see that some $PbZrO_3$ is already detected, under dynamic conditions, at 700 °C. We may conclude that solid state diffusion cannot be excluded as a possible initial mechanism of reaction between PbO and zircon leading to the formation of $PbZrO_3$, but that reaction proceeds slowly since the quantity of $ZrSiO_4$ is still high after thermal treatment at 1000 °C. Only after melting occurs does the residual PbO decrease while the amount of $PbZrO_3$ increases. As already stated above, after treatment at 700 °C, some peaks due to the presence of $PbZrO_3$ emerge from the background together with those of zircon in the X-ray diffraction patterns. The same powders, treated at 1000 °C, revealed the presence of $PbSiO_3$ and zircon, whereas the presence of $PbZrO_3$ was not documented. It is clear that, under our testing conditions, $PbZrO_3$ is not stable at high temperatures; it decreases above 900 °C accompanied by a rapid increase of $PbSiO_3$. This fact seems to be in conflict with literature data [21] showing $PbZrO_3$ stable up to 1570 °C. Nevertheless it must be considered that in our experiment, $PbZrO_3$ can further react with zircon to form $PbSiO_3$ and this seems to be the most probable course of reaction. A comparison of the elementary analyses carried out on the starting and the final products after thermal treatment at 1000 °C indicates that all changes are lower that 0.5%, hence no significant ovaporation occurred.

The reaction between sodium carbonate and zircon occurs after the sodium carbonate melts, implying a solid–liquid interaction. This reaction leads to formation of a new crystalline phase, Na_2ZrO_3, whose amount increases at increasing temperatures. The growth rate of this phase remains low, the amount of zircon remaining high at 1000 °C. A comparison of the elementary analyses carried out on the starting and the final products after thermal treatment at 1000 °C indicates that all changes are less than 1.5%.

X-ray diffraction patterns of powders containing the mixture PbO–V_2O_5–$ZrSiO_4$, treated at temperatures above 700 °C, showed only the strong peaks of zircon while the background line revealed a significant amount of amorphous phase derived from the rapid cooling of a liquid. This ternary mixture appears to consist of a vitreous phase containing PbO and V_2O_5 in which the crystalline zircon remains unreacted. The phase diagrams PbO–V_2O_5 show the presence of an eutectic liquid phase at 482 °C [22,23]. It is therefore reasonable to assume the presence of liquid in the ternary mixture PbO–V_2O_5–$ZrSiO_4$ during all thermal treatments at temperatures above 800 °C. The shifting of temperatures toward higher values with respect to the phase diagrams is obviously due to the non-equilibrium conditions of our experiments. It is interesting to note that the presence of V_2O_5 inhibits PbO from attacking zircon. This unexpected result was evidenced by the FTIR spectra (Fig. 1), that also showed that at 700 °C (curve b), the characteristic bands of V_2O_5 and PbO disappear, giving rise to an amorphous phase highlighted by the diffusion enhancement of the whole spectrum. At the same time, the characteristic FTIR absorption bands of zircon remain visible. The same result can be observed after treatment at 1000 °C (curve c). A comparison of the elementary analyses carried out on the starting and the final products after thermal treatment at 1000 °C indicates that the change in Zr is 2.4% whereas that in Pb is 1.9%.

Table 2
Results from XRD data: main crystalline phases as function of temperature (°C)

Added material(s)	700	750	800	850	900	950	1000
Na_2CO_3	$ZrSiO_4$ (h) Na_2CO_3 (h)	$ZrSiO_4$ (h) Na_2CO_3 (h)	$ZrSiO_4$ (h) Na_2CO_3 (h)	Na_2ZrO_3 (l) $ZrSiO_4$ (h) Na_2CO_3 (h)	Na_2ZrO_3 (m) $ZrSiO_4$ (h) Na_2CO_3 (h)	Na_2ZrO_3 (m) $ZrSiO_4$ (h) Na_2CO_3 (h)	Na_2ZrO_3 (h) $ZrSiO_4$ (h) Na_2CO_3 (m)
PbO	$PbZrO_3$ (l) $ZrSiO_4$ (h) PbO (h)	$PbZrO_3$ (l) $ZrSiO_4$ (h) PbO (h)	$PbZrO_3$ (m) $ZrSiO_4$ (h) PbO (h)	$PbZrO_3$ (m) $ZrSiO_4$ (h) PbO (h)	$PbZrO_3$ (m) $ZrSiO_4$ (h) PbO (h)	$PbZrO_3$ (l) PbSiO3 (l) $ZrSiO_4$ (h) PbO (m)	$PbZrO_3$ (l) PbSiO3 (h) $ZrSiO_4$ (m) PbO (l)
Na_2CO_3 + PbO + V_2O_5	$PbZrO_3$ (l) $ZrSiO_4$ (h) Na_2CO_3 (m) PbO (m) V_2O_5 (m)	$PbZrO_3$ (m) $ZrSiO_4$ (h) Na_2CO_3 (m) PbO (l) V_2O_5 (m)	$PbZrO_3$ (h) $ZrSiO_4$ (h) Na_2CO_3 (m) PbO (l) V_2O_5 (l)	$PbZrO_3$ (h) $ZrSiO_4$ (h) Na_2CO_3 (l) V_2O_5 (l)	$PbZrO_3$ (h) $ZrSiO_4$ (h) Na_2CO_3 (l) V_2O_5 (l)	$PbZrO_3$ (m) $PbSiO_3$ (l) $ZrSiO_4$ (h) Na_2CO_3 (l) V_2O_5 (l)	$PbZrO_3$ (m) $PbSiO_3$ (m) $ZrSiO_4$ (h) Na_2CO_3 (l) V_2O_5 (m)

Approximate quantity: l = low (< 10 vol.%), m = medium (> 10, but < 40 vol.%), h = high (> 40 vol.%).

Table 2 also gives information on the development of thermochemical reactions in a quaternary mixture of $PbO–V_2O_5–Na_2CO_3–ZrSiO_4$.

The appearance of $PbZrO_3$ and $PbSiO_3$ (Table 2) suggests that in the presence of PbO, V_2O_5 and Na_2CO_3, the reaction might follow a path similar to that observed in the presence of PbO alone although in a more complicated reacting system. First, the presence of liquid is expected at a lower temperature than in the previous cases. In fact, all relevant phase diagrams: $PbO–V_2O_5$, $PbO–Na_2O$ and $Na_2O–V_2O_5$ show the presence of a liquid phase at low temperatures [21–25]. In particular the $PbO–Na_2O$ phase diagram allows for a liquid phase at 300 °C. The mixture containing these three oxides is expected, under equilibrium conditions, to melt at a very low temperature. Under the assumption that liquid phase in present also under dynamic conditions, it follows that the reaction between zircon and the ternary mixtures need not involve solid state diffusion. Spectra reported in Fig. 2, where the crystal

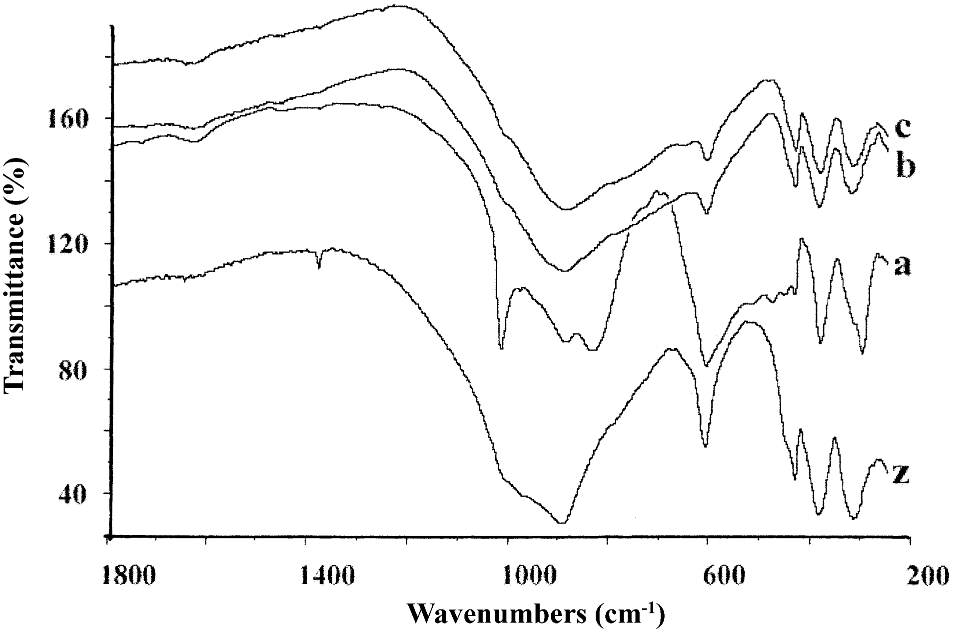

Fig. 1. FTIR spectra of pure $ZrSiO_4$ (curve z) and its mixtures with $V_2O_5 + PbO$. Curve a = as milled; curve b = after thermal treatment at 700 °C; curve c = after thermal treatment at 1000 °C.

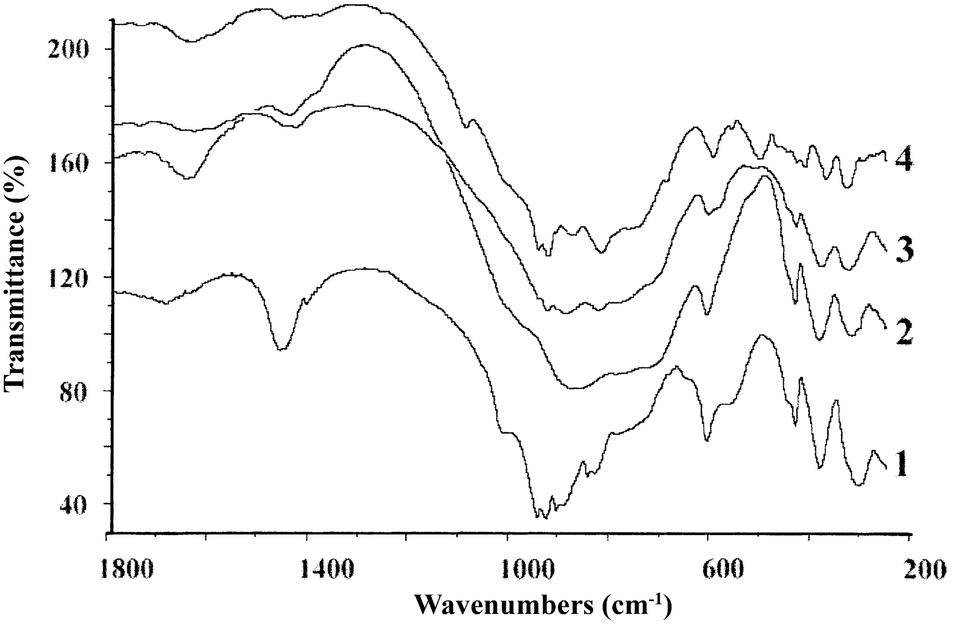

Fig. 2. FTIR spectra of mixtures of $ZrSiO_4$ with $V_2O_5 + PbO + Na_2CO_3$. Curve 1 = as milled; curve 2 = after thermal treatment at 700 °C; curve 3 = after thermal treatment at 800 °C; curve 4 = after thermal treatment at 1000 °C.

structures of PbO, V_2O_5 and Na_2CO_3 have completely disappeared at 700 °C, confirm the previous hypothesis. In particular, the FTIR spectrum of the mixture heated to 700 °C (Fig. 2, curve 2) shows a high content of amorphous phase, which is the consequence of the rapid solidification of a liquid. The amount of amorphous phase decreases as the temperature rises (Fig. 2, curve 3) because large quantities of liquid are consumed in the reaction leading to the formation of the crystalline $PbZrO_3$. Consumption of liquid phase proceeds at higher temperature leading to the formation of $PbSiO_3$ (Fig. 2, curve 4). The presence of Na_2CO_3 seems to reduce the inhibiting effect of V_2O_5 on PbO; it makes the liquid phase more aggressive and consequently the amount of $PbSiO_3$ grows at high temperature.

FTIR analysis has shown that zircon degradation is always associated with the development of a disordered amorphous silica. The spectra show a marked diffusion around the SiO_4^{4-} absorption zones. This is in agreement with the glassmaking tendencies of Na and Pb: XRD analysis shows formation of crystalline silicates of lead and sodium to be retarded or absent. A comparison of the elementary analyses carried out on the starting and the final products after thermal treatment at 1000 °C indicates that the greatest change is 1.3% in Pb.

4. Concluding remarks

Data acquired in the present study are a first step in testing zirconium silicate as a possible candidate material in the production of diesel engine filters since it stands up well, relative to cordierite, to thermochemical attack from many oxides in an oxidative environment. As a first approach to the problem, we have approximated the diesel environment to the oxidative air environment and operated under dynamic conditions (10 °C/min), thus focusing attention on short-time chemical reactivity. Under these circumstances we have seen that zircon inertness is significantly higher than that of other materials. In particular it performs better than cordierite, currently in production as a material for diesel vehicle filter.

Of course, other studies (currently in progress) such as sintering and thermal fatigue performances are also required before any conclusive assumptions can be made about the use of zircon in this application. Further possible investigations may concern also the behavior of zircon and other oxides under locally reducing conditions since the filter is required to remove mainly carbon particulates.

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