On the role of carbon in the carbochlorination of refractory oxides

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Abstract

The two reaction stages of the carbochlorination of ZrO_2 that we have recently reported were investigated by thermogravimetric measurements and characterized by following the morphological evolution of the solids by scanning electronic microscopy (SEM).

Chlorine atoms are proposed as reaction intermediates in both reaction stages. Evidence of a catalytic-like action of carbon by the dissociation of chlorine gas is observed in the initial stage, and the occurrence of the O_2–C reaction is inferred in the second stage.

INTRODUCTION

The carbochlorination of some metal oxides is a very important step in the industrial production of pure metals. Mineral oxides such as zirconia and titania can be transformed into metals by a process which can be briefly described in three steps. In the first one, which is known as the carbochlorination step, at temperatures ranging between 750 and 950°C, the oxide in the presence of carbon reacts with chlorine to give the corresponding metal chloride. The metal is then obtained by reduction of the metal chloride by magnesium or sodium. Finally, the metallic sponge is purified by vacuum distillation at high temperature.

Bergholm [1] was the first to show clearly that direct contact between the solid reactants is not necessary for chlorination of a metal oxide in the presence of carbon. Later, Barin and Schuler [2] also verified that the kinetic effect of carbon occurs even though contact between carbon and oxide particles does not take place. According to these results, carbochlorination occurs by means of at least one gaseous intermediate. Phosgene [3], chlorine atoms (Cl·) [2, 4] and oxychlorides [5] have been

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proposed as reaction intermediates, although such species have not been detected during the reaction. From different publications [2, 4, 6] Cl$\cdot$ is the most probable species. First, Barin and Schuler [2] have shown that the kinetic effect of carbon in the chlorination of TiO_2 vanishes when the distance between carbon and oxide is greater than the mean free path of Cl$\cdot$. Secondly, the formation of chlorine atoms in the gas phase when carbon is exposed to a chlorine atmosphere at temperatures below 1000°C has been verified [6]. Finally, the formation of the gaseous products O_2, CO and CO_2 agrees very well with a mechanism involving Cl$\cdot$ [4].

It is known [7-9] that the study of the evolution of the structure and shape of solids during a solid-gas reaction plays an outstanding role in the understanding of the reaction mechanisms. However, too few studies of this kind have been carried out in carbochlorination systems. Various authors [2, 3, 10, 11] have indicated that the reaction of carbochlorination takes place uniformly over the whole surface of the oxide particles without increasing porosity. These coincident observations have been made for briquettes of several minerals such as zircon and loparite [3], for briquettes of TiO_2 [11], for ZrO_2 compacts [10] and for TiO_2 tablets [2]. On the other hand, this uniform chemical reaction on the surface oxide has not been observed [12] in the carbochlorination of fly ash particles. In this case the particles underwent a vigorous erosive action, clearly localized near to C particles. The authors, Ishii et al. [12], have proposed that C in a contact state promotes the reaction on fly ash.

Chlorination of ZrO_2 and carbon powder mixtures has been studied in our laboratory [4, 13]. The reaction can be represented by [4, 8, 10]

$$ZrO_2(s) + 2Cl_2(g) + 2C(s) \rightarrow ZrCl_4(g) + 2CO(g)$$
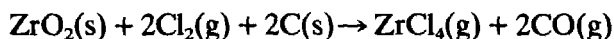
In recent work [13] we have briefly shown that this reaction involves two well differentiated reaction stages. The initial one shows a high reaction rate for a short time, whereas the later one is characterized by a reaction rate several orders of magnitude slower than the initial one. Transition from one reaction stage to another is very sudden and irreversible. This behaviour in the reaction rate has not been reported for other carbochlorination systems. However, there are examples in the literature [8] of solid-gas reactions that show sudden changes in their reaction rate. These changes are called instabilities [8]. To understand the background of the instability in the carbochlorination of ZrO_2 we undertook a study of the morphological changes of ZrO_2-C mixtures that occurred in each reaction stage. The aim of this work is to discuss the origin of this instability and to show that it can arise from a true change in the reaction mechanism.

EXPERIMENTAL

The samples used in this study were prepared by mixing ZrO_2 powder (Koch-Light Laboratories) and carbon powder obtained by thermal

decomposition of sucrose (Mallinckrodt Chemical Works). Both powders were characterized by scanning electron microscopy (SEM) (Philips SEM 515). The carbochlorination of ZrO_2 was studied using a thermo-gravimetric analyzer (TGA) described elsewhere [13]. Briefly, this TGA was developed on the basis of a Cahn 2000 electrobalance suitable for working with corrosive atmospheres, coupled to a gas blending system. Data acquisition was effected at intervals of 0.1 s using an interface connected to an IBM PC/XT computer. Our TGA allows us to detect mass changes within $\pm 5 \mu g$ while operating at 1100°C under a flowrate of 9 l h^{-1} (NTP).

The thermogravimetric procedure was as follows. Each sample of around 10 mg, placed in a quartz crucible, was heated at 950°C for 2 h under a flowing Ar atmosphere. Then Cl_2 was injected into the reactor at a given flow rate, reaching a pCl_2 of 490 Torr, and the mass changes and time were recorded. When a given reaction degree was reached, the chlorine flow was cut off, the reaction stopped and the sample was cooled at room temperature within the reactor under flowing Ar. Studies were performed [14] adjusting the experimental conditions in such a manner that the reaction occurred almost exclusively by means of one of the stages mentioned above.

Thermogravimetric measurements were corrected by apparent mass changes [13]. Corrected data allowed computation of the reaction degree, which is defined as $\alpha = [M_i - M_t]/M_i$, where M_i is the initial ZrO_2 mass and M_t is the mass of unreacted ZrO_2 at time t.

A small fraction of each sample removed from the TGA was then examined by SEM, and the morphological changes were correlated with each stage of reaction.

RESULTS

Thermogravimetry

The reaction degree (α) as a function of time corresponding to the reaction of a ZrO_2–C mixture with Cl_2 is plotted in Fig. 1. The α vs. t curve shows first a fast increase in α followed by a sharp change, after which α increases more slowly. The strong discontinuity in the α vs. t curve defines the two reaction stages indicated earlier. In the first one, α exhibits a linear dependence on time, whereas in the second one it shows a parabolic dependence. The first stage (fast stage) takes place during the first seconds, whereas the following stage (slow stage) occurs until full chlorination of the oxide is achieved.

Figure 2 shows the reaction degree α as a function of time for other experiments. Curve a shows the reaction occurring by means of the fast stage. When the reaction becomes very slow the second stage predomin-ates over the first. At this point ($\alpha \approx 0.6$) the reaction was stopped and
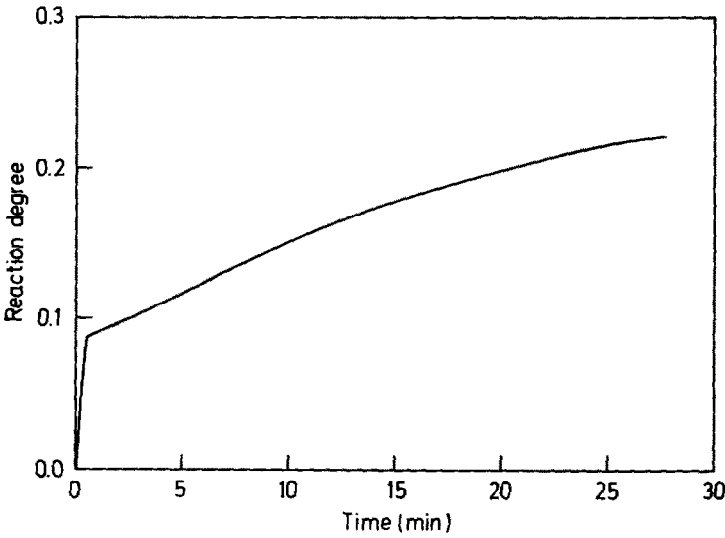
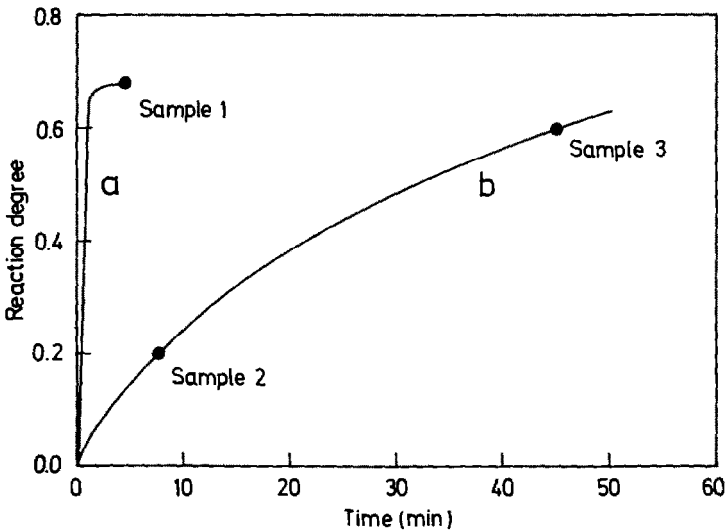Fig. 1. Reaction degree α vs. time, showing the two reaction stages.

Fig. 2. Reaction degree α vs. time: curve a, fast stage; curve b, slow stage.

the sample, which we called sample 1, was later analyzed by SEM. Curve b shows typical behaviour for the slow stage. Two samples were chlorinated under these conditions. The reactions were stopped when the reaction degree reached by the respective samples was $\alpha \approx 0.2$ and $\alpha \approx 0.6$. We called these sample 2 and sample 3 respectively.
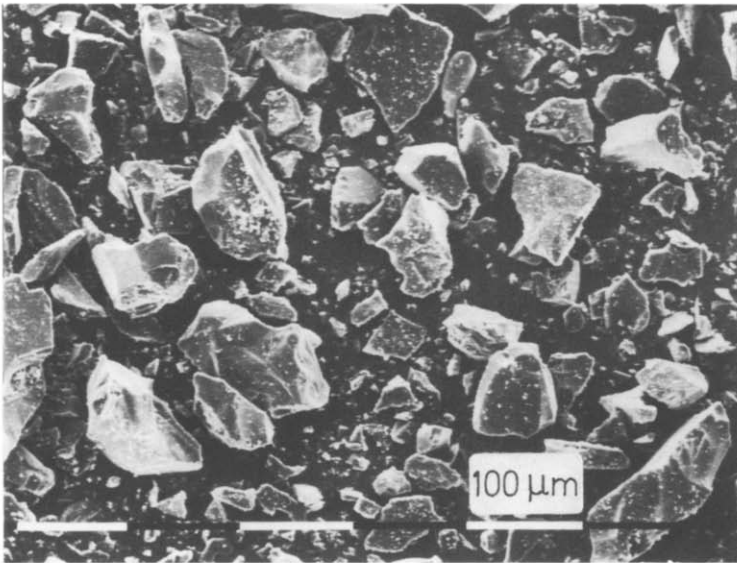
Characterization by SEM

Starting powder

Figure 3a shows the starting ZrO_2 powder, which is composed of particles of spheroidal shape with sizes smaller than 40 μm, which have a
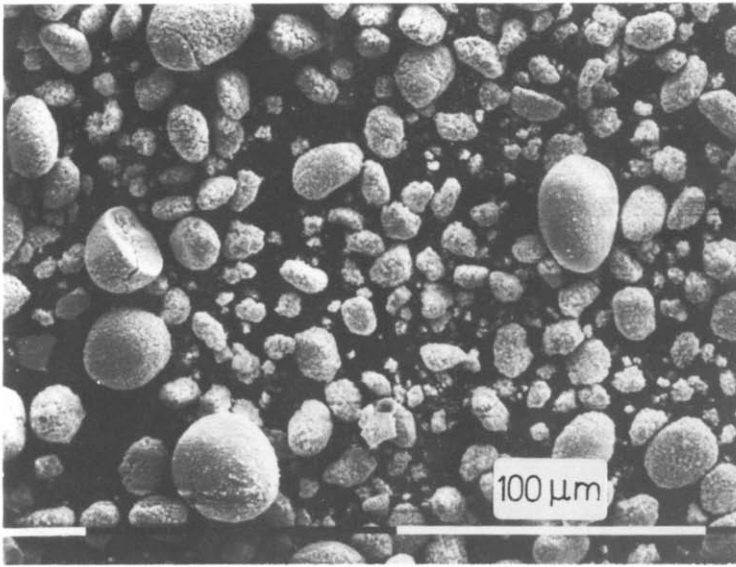
(a)

(b)

Fig. 3. Starting ZrO_2 powder (a), and starting carbon powder (b).

rough surface and no porosity. We wish to emphasize that some particles show cracks in their structure.

The starting carbon powder (Fig. 3b) is composed of particles smaller that $200\ \mu$m with sharp edges and stepped surfaces.

In both cases the particle size distribution is broad and there are many particles smaller than $1\ \mu$m.

Sample 1

Figure 4a clearly shows the interaction between ZrO_2 and carbon particles in sample 1. The carbon particle seems to be stuck into the ZrO_2 particle, which has undergone a strong chemical attack in the region closest to the carbon surface. This strong interaction with the carbon particle is markedly localized, because the rest of the ZrO_2 surface is similar to that of the starting powder. On the other hand, carbon has not
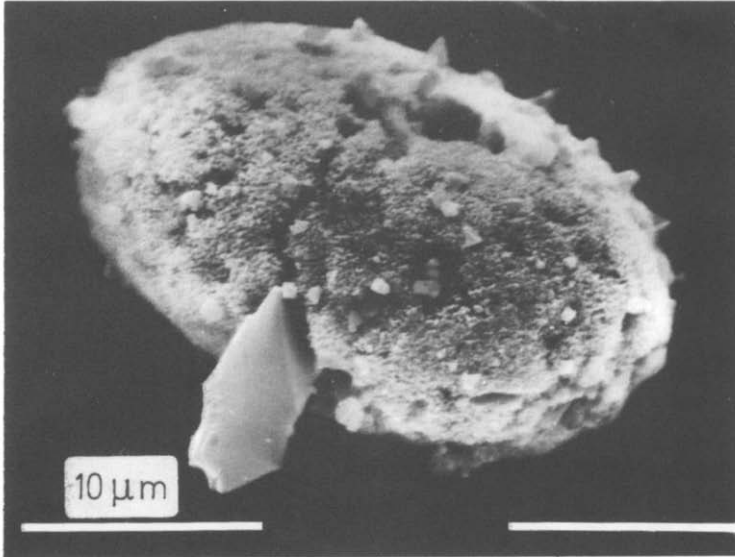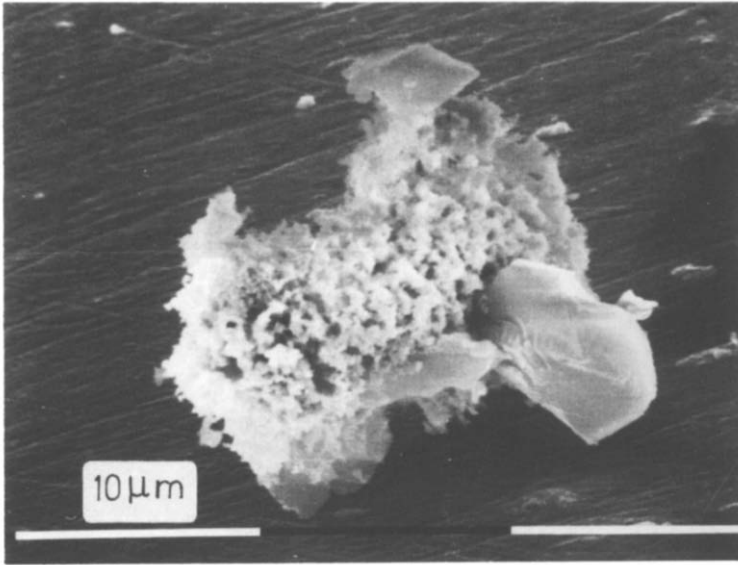

(a)
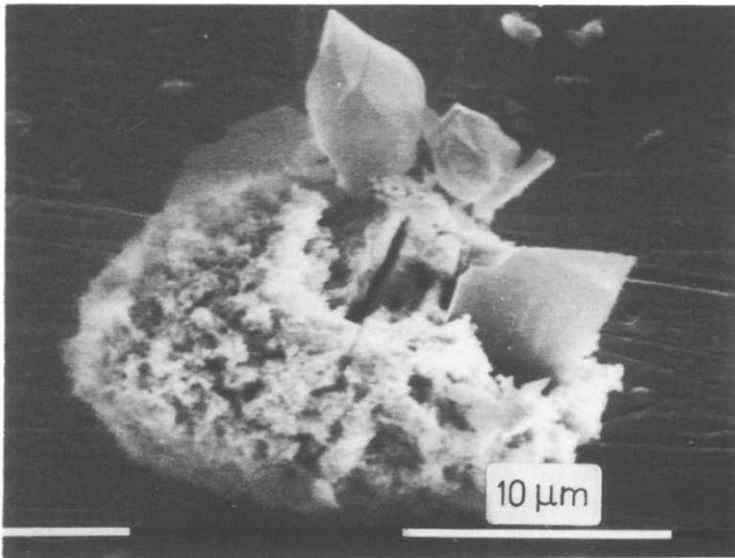
(b)

Fig. 4. Interaction between ZrO_2 and carbon for sample 1 (see text).

(c)

Fig. 4 (continued)

undergone a chemical reaction of the same magnitude as the ZrO_2 particle.

The characteristics above mentioned are also observed in Figs. 4b and 4c. These figures also show that the carbon particles have penetrated the ZrO_2 particle, showing an interaction which is characteristic for most of the particles of sample 1. It is observed that, in a similar way to that seen
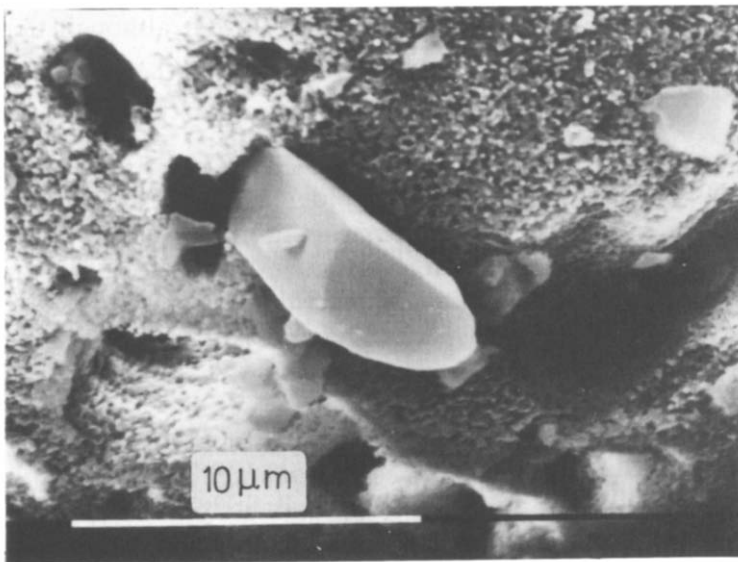
(a)

Fig. 5. Details of ZrO_2–C interaction for sample 1 (see text).
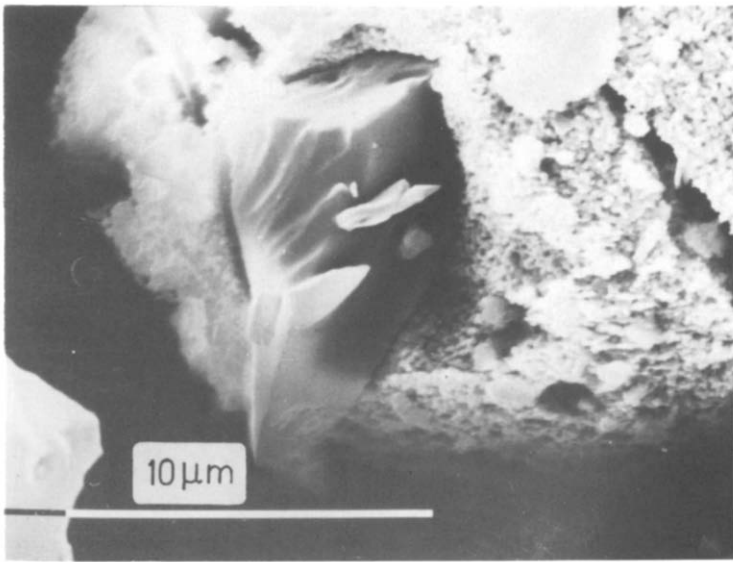
(b)

Fig. 5 (continued)

in Fig. 4a, the carbon particles have not suffered appreciable corrosion on the surface, at least not to the same degree as the ZrO_2 particles. However, an appreciable difference between the ZrO_2 particle shown in Fig. 4a and those of Figs. 4b and 4c is found. The last two have undergone, in addition to the strong interaction with carbon, uniform attack over the rest of their surface.

Figures 5a and 5b show further details of other ZrO_2 particles penetrated by carbon particles. It is important to note that although the carbon particles are very close to the ZrO_2 surface they do not seem to be touching it.

Sample 2

Sample 2 (see Fig. 6) shows that the morphology of the particles does not change appreciably. However, further examination shows the existence of cracks on the surface of some carbon particles (see Fig. 6). None of the ZrO_2 particles show localized chemical reaction.

Sample 3

In contrast with the effects observed for sample 2, sample 3 shows an appreciable corrosion effect. The carbon particles have undergone strong attack (see Fig. 7). These particles show regions of local corrosion with cavities of circular shape. Several holes (approximately 10–15 μm in diameter) separated by a smooth surface without appreciable chemical attack are observed. Some of these cavities are also made up of other smaller cavities. Large cracks and channellings are observed along the
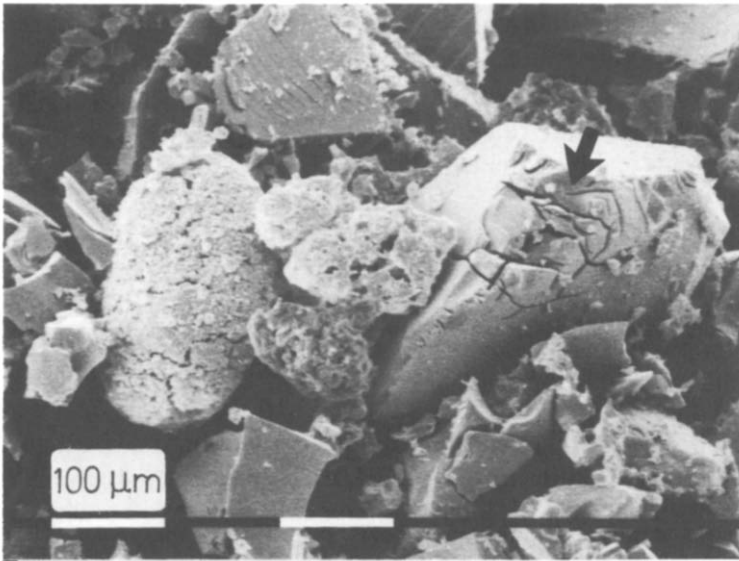
Fig. 6. Sample 2. Arrow indicates cracks on a carbon particle.
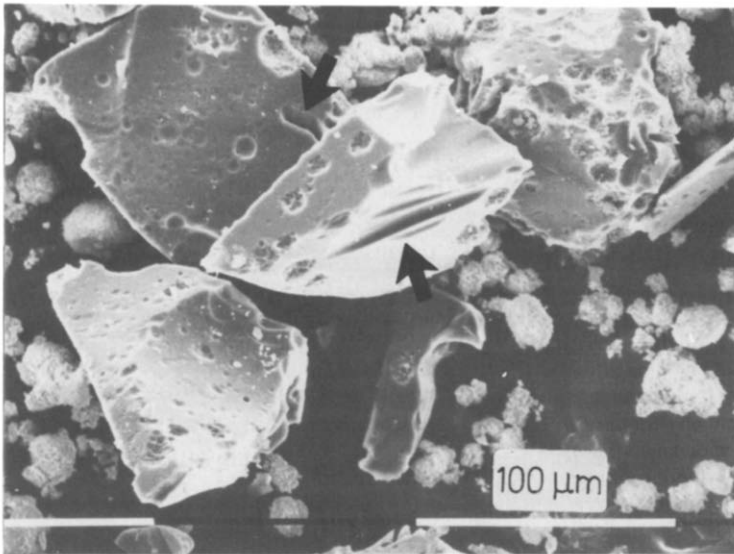
Fig. 7. Sample 3. Cavities on carbon particle surface. Arrows indicate some channelling.

surface carbon particles. On the other hand, the morphology of the ZrO_2 particles does not show notable changes in relation to the starting powder. This lack of morphological changes was observed for all ZrO_2 particles.

DISCUSSION

From Figs. 1 and 2 it is obvious that the reaction rate $(d\alpha/dt)$ is constant in the first stage and decreases continuously in the second one. This

change in the behaviour of the reaction rate indicates a change in the controlling regime (Fig. 1). Therefore we are interested in determining whether this transition is due to different intrinsic reaction mechanisms or to a change in some elemental reaction steps. As is well known, these elemental steps in solid–gas systems can be of both physical and chemical nature. We found in a detailed kinetic study [15] that the determining step of the fast stage is gas diffusion and that the determining step in the slow stage is of a chemical nature. Therefore, from an initial analysis, we might explain the instability observed by considering a change in the controlling elemental reaction step without involving a change in the intrinsic mechanism. However, this possibility is unlikely because the reaction goes from diffusional control to a chemical one, which is contrary to the behaviour of most of the solid–gas systems where the gas diffusion plays a dominant role in controlling the rate at the end of the reaction. In view of this fact it is very difficult to interpret the change shown in Fig. 1 without accounting for a change in the intrinsic reaction mechanism. Thus we will now discuss the evidence that supports a change in the reaction mechanism.

Morphological changes during the fast stage

The penetration of the ZrO_2 particles by carbon particles (Figs. 4 and 5) is a novel effect. Obviously this effect is not due to a mechanical process associated with the ZrO_2–C sample preparation, i.e. mixing and compacting. The effect is strictly due to the chemical reaction. Literature on this subject indicates that only the results demonstrated by Ishii et al. [12] could be considered somewhat similar to our observations. We think that both the penetration of carbon particles in the ZrO_2 and the results of Ishii et al. could be associated with the catalytic effect that carbon has on the dissociation of Cl_2 to form chlorine atoms in the gas phase [6]. From our results, this hypothesis is based on the fact that, first, the carbon particle surface is very close to the ZrO_2 particle surface but not touching it (Fig. 5). Secondly, the surface of these carbon particles (Figs. 4 and 5) has not suffered an appreciable attack, at least not to the same degree as the ZrO_2 particles. These two observations are in agreement with the fact that chlorine atoms can easily react with ZrO_2 [4] to produce $ZrCl_4(g)$ and $O_2(g)$, and with the fact that carbon does not lose mass in the Cl_2–C reaction [6]. Therefore the chemical attack suffered by the ZrO_2 particle could not be due to a reaction directly with carbon.

Since chlorine atoms are very reactive species, only ZrO_2 particles very close to the carbon particles can suffer chemical attack. This could explain the localized effect of the carbon particles on ZrO_2, which is clearly shown in Figs. 4 and 5. Moreover, this possibility is supported by the work of Barin and Schuler [2]. According to these authors, chlorine atoms reached

the oxide surface whenever the distance between particles of ZrO_2 and carbon was not greater than their mean free path. Under our experimental conditions this mean free path is around $1 \mu m$. Figures 4 and 5 show that the localized effect of carbon on the ZrO_2 particles does not occur at distances shorter than $1 \mu m$.

It is important to note that the carbon particles have penetrated into the oxide by their sharp edges (see Fig. 4). One reason for this could be the fact that the reactive sites for chlorine dissociation are not uniformly distributed in carbon [16, 17]. These sites could be localized in either dislocations or structural irregularities [17, 18], generating catalytic activity on the sharp tips or edges of the carbon particles.

Thus we can imagine the process by means of a simple picture: in the sample, a ZrO_2 particle is surrounded by carbon particles, which produce chlorine atoms by interaction with Cl_2. These atoms only react with ZrO_2 particles that are within their mean free path. Oxygen and $ZrCl_4$ diffuse away from the reaction site. Then the reaction progresses into the oxide in places related to the relative position and shape of neighbouring carbon particles. As the reaction occurs, the effect is that carbon particles either below or above the ZrO_2 particle penetrate into it by gravity.

In addition to the localized attack, there is also observed in Figs 4b and 4c a strong and uniform reaction over the whole ZrO_2 surface. These ZrO_2 particles show a high reaction degree. The chemical attack seems to occur at the grain boundary. Obviously this uniform reaction on the ZrO_2 particle surface cannot be explained by a mechanism based on chlorine atoms. In solid–gas systems a reaction on the whole surface is typical when the reacting gas is homogeneously distributed through the gaseous phase. This suggests that a stable species and not a reactive species such as a chlorine atom intervenes in this last attack and contributes to $ZrCl_4$ formation. Because Cl_2 is ineffective as a chlorination agent [19] and CO does not contribute appreciably to the overall chlorination of the oxide [4] it is not evident what constitutes this stable species.

Morphological changes during the slow stage

The principal feature of the slow stage is that carbon undergoes a vigorous chemical attack whereas ZrO_2 does not show differences from the starting powder. Figure 6 shows that penetration of carbon particles into ZrO_2 has not occurred but small cracks in some carbon particles can be observed. Considering that the reaction times for samples 1 and 2 are similar, we conclude that penetration of ZrO_2 by carbon is a phenomenon that corresponds only to the fast reaction stage and not to the reaction time. Therefore the morphological changes in each reaction stage are due only to different interactions between the particles. Thus we are in the presence of two reaction mechanisms. In the following we shall discuss the

morphological changes of ZrO_2 and carbon particles during this reaction stage.

Zirconia particles

Lack of morphological changes in ZrO_2 particles is also observed in sample 3, which has a high reaction degree, namely $\alpha \approx 0.6$. Thus, we infer that ZrO_2 particles have reacted uniformly without appreciable changes both in shape and in the external surface. The reaction interface seems only to be in their external surfaces because, within their original cracks, ZrO_2 particles have not developed porosity. Therefore the internal surface is not involved during the slow stage. This is a typical characteristic of a gas–solid reaction in which the surface reaction is faster than gas diffusion into the cracks [20]. Understanding of this observation might be based on a reaction of ZrO_2 with a very reactive reaction intermediate homogeneously distributed through the gaseous phase. Another interpretation of the lack of evident morphological changes in the ZrO_2 particles might also arise in the intergranular separation of the oxide in the presence of Cl_2. This was observed [19] in the same ZrO_2 powder as that used in this work. This intergranular separation might lead to a continuous removal of the surface to generate a fresh surface. As a result, reaction effects on the ZrO_2 particle surface would not be appreciable.

Carbon particles

Cracks observed in the carbon in sample 2 (Fig. 6) might be the origin of the channellings that are seen in sample 3 (Fig. 7). Cavities are also observed in this last sample. Similar effects on the carbon surface have been observed in other reaction systems [21, 22]. Cracks and channellings very similar to those of samples 2 and 3 have been found both in the O_3–C reaction [21] and in the O_2–graphite reaction [22] respectively. Channellings and pits have also been observed [23, 24] when O_2 reacts with C in the presence of metals or metal oxides and when the O_2–C reaction occurs in the presence of Cl_2 [25]. This comparison suggests that, in our system, the mass loss of carbon particles would probably be due to the reaction with O_2 to produce CO and CO_2 [4]. This possibility is consistent with recent work [4] in which the formation of O_2 was detected during the carbochlorination of ZrO_2. As a result, the O_2–C reaction in the presence of $ZrCl_4$ and Cl_2 in the gas phase might be the reason for channelling and cracks.

Assumption that the O_2–C reaction occurs in this reaction stage suggests a reaction intermediate: the chlorine atom. However, in this slow stage the formation of chlorine atoms can occur by another mechanism. We inferred this from the size and shape of the carbon cavities and the separation between them (Fig. 7). These cavities seem to be created by the effect of ZrO_2 particles resting on the carbon particles. Thus this

localized chemical attack might account for a reaction intermediate formed in the contact zone between the two types of particle. This feature coincides with information obtained by other researchers [26, 27], who indicated that Cl_2 molecules can readily dissociate upon chemisorption on a carbon surface. According to this evidence, chlorine atoms might be mobile on the carbon surface and react with ZrO_2 to produce $ZrCl_4$ and O_2. Then the principal quantity of O_2 would react with the nearest surface carbon, forming cavities, and the rest might react with carbon to form channelling and cracks.

Therefore we conclude that the transition from the first to the second stage can be interpreted in terms of a change in the formation mechanism of chlorine atoms.

CONCLUSIONS

We conclude that, in the carbochlorination of ZrO_2, both reaction stages involve chlorine atoms as intermediates. However, the mechanism associated with each stage appears to be different. In the fast stage carbon catalyzes chlorine atom formation in the gaseous phase, whereas in the slow stage chlorine atoms are adsorbed on the carbon surface.

The step-controlling change might be associated with the removal of reactive sites of carbon either by chemical reaction with oxygen or by poisoning with other reaction products. More work will be performed in order to elucidate this point and other characteristics related to each reaction stage.

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