

Hard-skin development during binder removal from Al₂O₃-based green ceramic bodies

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A paraffin-based binder system was developed for low-pressure injection molding of very fine (0.4 μm) average particle size alumina ceramic bodies. Complex chemical reactions take place, during the process of binder removal, when the ceramic parts are fired in air. The effects of these chemical reactions become more pronounced at about 250°C, giving rise to a hard-skin and promoting cracks in the bodies with large cross-sections. The surface hardening occurs only when the bodies are fired in an oxygen-rich atmosphere. The hardness at the surface of the ceramic bodies fired in air at 250°C varies from about 0.4 to 1.2 GPa, depending on binder composition. Upon increasing temperature, the surface hardness decreases monotonically to more conventional values. Infrared absorption spectroscopy was used to study the debinding process and the chemical mechanism behind the hard-skin development in ceramic bodies fired in air. The experimental evidence suggests that cross-linkage between long carbon chains present in the binder and its interaction with the alumina powder surface is responsible for the high surface hardness observed in parts fired in air at 250°C. © 2002 Kluwer Academic Publishers

1. Introduction

Low-pressure injection molding (LPIM), or hot-molding of ceramics, was first performed by Gribovski many years ago [1]. This process has many advantages compared to its high-pressure counterpart. In fact, LPIM involves significantly lower manufacturing cost for dies and less die wears, as it makes use of lower molding pressures and temperatures. LPIM also imply in shorter debinding times, at lower temperatures [1–3]. These advantages over high-pressure injection molding and other forming methods make LPIM interesting for near-net-shape forming of complex shape ceramic parts in the range of 100 to 10000 units [2–4]. However, LPIM usage has been limited mainly by the difficult process of binder removal. Moreover, even nowadays several aspects important for LPIM are only poorly understood [5].

Paraffin wax is commonly employed as the main binder component for LPIM because of its wide range of molecular size and low viscosity at moderate temperatures [6]. Other waxes that can be added to the binder mixture are polyethylene wax and carnauba wax. Carnauba wax has low melting temperature, varying between 80–87°C [6, 7]. It is a brittle, hard vegetable wax which forms a thin layer on the blossoms, leaves and fruits of carnauba palm (*Copernicia cerifera*) [8–10].

Carnauba wax acts as both a lubricant and an internal mold release [6, 7]. Its chemical composition has high percentage (up to 80–90%) of esters, along with free alcohol (3%), carboxylic acids (4%) and other minor components [8, 11].

Other components are commonly added to the binder mixture to promote modification of the aluminum oxide surface. A mixture with very low viscosity can be obtained adding surfactants, which help to make stable the dispersion of fine ceramic particles in the binder [2]. This is achieved by the reaction of carboxylic acid (in our case, stearic and oleic acids) molecules with surface hydroxyl groups [1, 2], thus enhancing the wetting of binder on the powder surface. The ceramic powder plus binder mixture used for low-pressure injection molding should be optimized for high fluidity while keeping the ceramic content as high as possible.

The debinding from green ceramic bodies is the key factor for the successful manufacturing of ceramic parts by low-pressure injection molding. The binder system must be removed from the molded parts before densification and sintering. The binder is usually constituted by various organic ingredients, that have different melting points and viscosities and behave differently during thermal decomposition. The debinding is the most critical step in ceramic production

(particularly for LPIM ceramic parts), a difficult operation that can take weeks [12] and had been a major obstacle for the economic success of LPIM. The process of binder removal from green ceramic bodies is not just a problem of capillary flux in a porous medium. Complex chemical reactions take place between the organic binder components, and between them and the ceramic particles surface, making it very difficult to describe the concurrent reactions and the whole debinding process in detail. The difficulties are even greater when dealing with the debinding of large cross-section parts made with submicrometer-sized ceramic powder. Indeed, during the past years a great deal of effort has been devoted to the study of the debinding process, specially in what is concerned to the reduction of debinding time [12, 13]. In spite of that, ceramic injection molding is still more an art than a science [14].

According to Majewska-Glabus *et al.* [6, 7], the debinding process can be described as a sequence of stages. At relatively low temperatures, low melting point binders soften, melt and begin to flow out of the sample, aided by capillary forces introduced by the presence of wick powders. During this stage of debinding, the formation of small interconnected pore channels in the interior of the ceramic body takes place. As temperature increases, the binder begins to decompose and vaporize, and the rate of binder removal is limited by the diffusion of the organic vapor. At this stage it is necessary to control the rate of gas formation in order to avoid the formation of cracks and bubbles in the ceramic parts.

At higher temperatures, only small amounts of binder remain at the contact points between particles. Carbonaceous residues result from dehydration, dehydrogenation and cross-linking of the remaining binders components. These residues are eventually removed during sintering process.

The analysis of decomposition pathways for pure binders without interaction with the ceramic powder is satisfactory only for the initial stages of thermal degradation [15]. The ceramic powder has an important role in the debinding and may enhance the process of thermal decomposition or react directly with the binder. Many factors related to the ceramic powder may affect the binder degradation, including the number of hydroxyl groups present at the particle surface, percentage of free water, the quantity of adsorbed oxygen and impurities on the powder surface [13].

Among the various issues related to LPIM that deserve further studies are the sequence of chemical processes that take place during the debinding under oxidative conditions, and the interfacial chemistry of the binder/powder system at high temperatures [13, 14]. Accordingly, in this context, the study of the debinding process is very important because it is a critical step and has a central role in LPIM. In this paper we will explore some peculiarities observed during debinding in air of alumina green bodies, made with submicrometer-sized powder, particularly the development of a hard-skin at about 250°C and its effect on the quality of the ceramic part after sintering.

2. Experimental procedure

2.1. Materials

The ceramic powder used in this work was submicrometer-sized alumina (Al_2O_3) A-1000SG (Alcoa), with specific surface area of $9 \text{ m}^2/\text{g}$, 99.9% purity and mean particle size of $0.4 \mu\text{m}$. The Al_2O_3 powder was dried for 3 hours at 150°C before use. The major binder component was paraffin wax (120/125-3 Petrobras-BR) with melting point between 49–52°C. Others components were added in minor proportion to the binder mixture, including oleic and stearic acid (Synth-BR), polyethylene wax (Ipiranga Petroquímica -BR) and carnauba wax (type III).

2.2. Methods

The machine used for LPIM was a Peltsman MIGL-33. The mixture for LPIM was prepared directly in the LPIM machine, with 86 wt% of alumina and 14 wt% of binders (75% paraffin, 10% carnauba, 10% polyethylene wax, 5% oleic and stearic acid). In order to guarantee good homogeneity, the mixture was mixed for 20 hours at 90°C before injection.

The powder plus binder mixture was injected into the mold at 90°C and 400 kPa of pressure, keeping the pressure applied during 12 seconds. The ceramic pieces molded for the debinding experiments were bricks with dimensions of $10 \times 34 \times 63 \text{ mm}$.

For the debinding, several furnace temperature ramps and dwell times were tested in order to find the better conditions under which one could obtain pre-sintered ceramic bodies free of defects. The ceramic injection-molded bricks were subjected to debinding immersed into alumina powder, up to a temperature of 250°C. Above this temperature, the bodies were fired in air. Fig. 1 illustrates some of the furnace programmed ramps and dwells tested for this work. The powder bed consisted of the same alumina employed to make the ceramic bodies and provides a physical support to the ceramic bodies, preventing major distortions during debinding. Despite the same particle size, the powder bed also promoted capillary binder extraction, confirming previous observations made by Wright and Evans [5, 16]. The debinding of large cross-section ceramic bodies made from very fine average particle

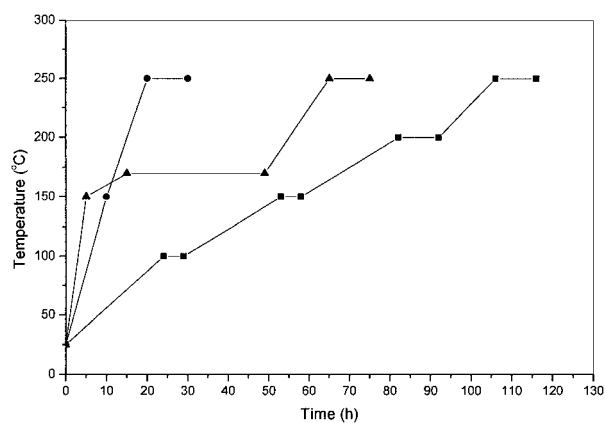


Figure 1 Temperature-time diagrams for binder removal from (●) thin ceramic parts and (▲) and (■) for large ceramic parts.

size alumina powder can take over 110 hours. Thin section pieces can be fired in a fraction of this time (30 hours). The sintering proceed at 1600°C during 2 hours, in air.

Hardness indentation tests were performed with a Shimadzu microdurometer, equipped with a Vickers tip, under loads ranging from 0.49 N to 1.96 N for 15 s. Transmittance and diffuse reflectance infrared spectroscopy (DRIFTS) analysis were performed on a Bomem MB-100. Scanning electron microscopy (SEM) images and semiquantitative energy-dispersive x-ray fluorescence spectroscopy (EDS) analysis of carbon content in the ceramic bodies were made in a JEOL JSM-5800 scanning electron microscope.

3. Results and discussion

The ceramic parts with large cross-section developed cracks and defects even when the debinding proceeded with very long times. It was observed that the ceramic pieces developed a brown coating above about 200°C, when the debinding was done in air. However, this brown coating does not appears when the debinding was made under vacuum or in an inert atmosphere. Fig. 2 shows the contrast between a green ceramic piece and one fired at 250°C, in air. While the former have a rather homogeneous aspect along all its surface, the latter displays a black-brown surface with intersecting cracks, that constitutes preferential pathways through which the binder can leave the sample. The surface color of the ceramic parts fired in air varies from light-brown to black, depending on the debinding conditions.

These observations suggest that the brown coating formed in bricks fired in air could be the result of some kind of oxidative degradation of the binder components. This conclusion is supported by the fact that only a thin layer becomes brown, indicating that this process is limited by oxygen diffusion through the ceramic body [5, 17].

Fig. 3 shows the hardness measured at the surface of ceramic parts made with different binder mixtures, after firing at increasing temperatures. In this figure it can be seen that the ceramic bodies fired under oxidative

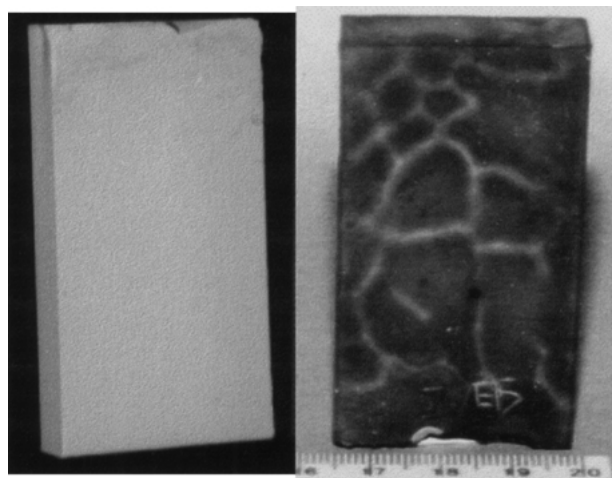


Figure 2 Green ceramic brick (left) and ceramic body fired with wicking (right), in air, at 250°C.

conditions develop a hard-skin at about 250°C. The hardness increase occurs concomitantly with the appearance of the black-brown coating on the ceramic parts.

The components of the binder mixture are mainly hydrocarbons, carboxylic acids and esters. Carnauba wax is a hard wax and, in principle, its diffusion to the sample surface could be responsible for the hard-skin development. To test this hypothesis, several experiments were performed with ceramic parts made with an increasing content of carnauba wax added to the binder mixture. In fact, the surface hardness of ceramic bodies fired in air at 250°C increases as more carnauba wax is added to the binder. However, the same hardness was obtained in ceramic parts made using a single-component binder, consisting exclusively of stearic acid, as it is shown in Fig. 3. This surface hardening is not observed when the binder consists exclusively of paraffin or when the ceramic parts are fired under vacuum or inert atmosphere. This set of observations leads us to the conclusion that one key factor for the development of a hard-skin during oxidative debinding of the ceramic bodies is the presence, in the binder mixture, of organic groups (particularly carboxylic acids and esters) that could bind chemically with the alumina surface. In fact, FTIR spectra of mixtures of alumina powder and binders containing carboxylic acids clearly show a distinct peak at about 1560 cm^{-1} indicating the formation of carboxylate salts. These salts result from the reaction of COOH groups present in the binder with hydroxyl groups from the alumina powder surface [5, 18]. This issue will be discussed in more detail further on in this paper, along with other results obtained by FTIR analysis.

The brown skin formed on the surface of the ceramic parts during debinding in air is very hard, at least when compared to the hardness measured in the rest of the sample. To quantify the hardness rate decay from sample's surface, hardness indentation tests were made along the normal to the surface of a sample fired in air at 250°C. The hardness depth-profile is well described by a complementary error function, as illustrated in Fig. 4. The same mathematical expression accounts for the oxygen concentration profile resulting from diffusion of oxygen from the atmosphere through the ceramic body [5]. This observation suggests again that the process responsible by the hardness increase of the sample surface is limited by oxygen diffusion.

A semiquantitative determination of the carbon content depth-profile was made by energy-dispersive x-ray fluorescence spectroscopy (EDS). The results obtained for a sample fired at 250°C, in air, are shown in Fig. 4. It can be seen that the carbon content depth-profile resembles that of Vickers hardness, suggesting a correlation between surface hardening and increase of carbon content at the surface of ceramic parts fired under oxidative conditions. The main difference between the two data sets in Fig. 4 is their skin-depth, which is smaller for the carbon content profile. The increase in carbon content at the sample surface can be ascribed to the flow of binder from the sample inner part and also to the carbon-rich products resulting from binder oxidative degradation. These products can react mutually, leading to the

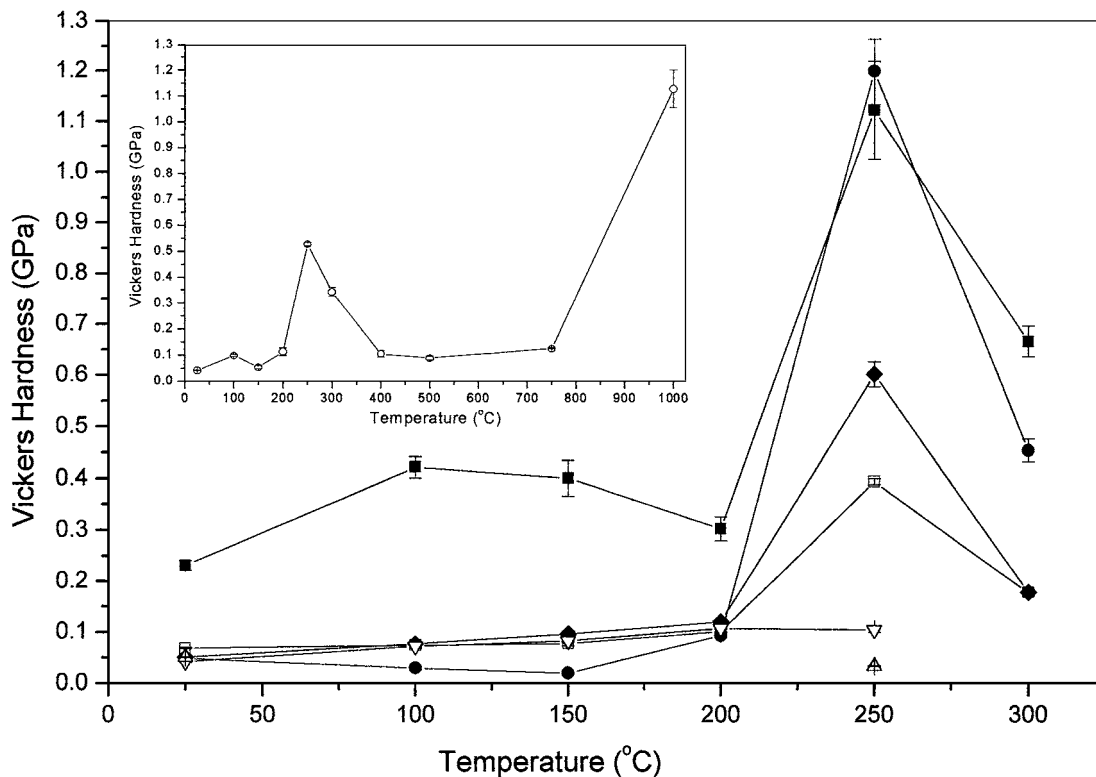


Figure 3 Dependence with firing temperature of Vickers hardness measured at the surface of alumina ceramic bodies prepared with different binders. (□) Conventional binder mixture (see text for details) without carnauba; (◆) with 1 wt% carnauba; (■) only carnauba (15 wt%); (●) only stearic acid (15 wt%); (▽) parts made with the conventional binder mixture, fired under vacuum and (Δ) in argon. The inset shows the firing temperature dependence of Vickers hardness at the surface of a ceramic part fired in air up to 1000°C.

formation of higher molecular weight compounds, possibly with a cross-linked structure [12].

Fig. 5 shows SEM images of some representative samples, including the surface and interior of a sample fired at 250°C in air, and also the inner part of a green ceramic. As can be seen in Fig. 5b, the aspect of the surface of the sample fired at 250°C in air is very similar to that of the green ceramics (Fig. 5a). For the sample fired at 250°C, the binder seems to be more concentrated at the surface, forming large agglomerates (Fig. 5b), in contrast with the almost dispersed ceramic particles found in sample's interior (Fig. 5c). In fact, the general aspect of sample's interior, as seen in Fig. 5c, is

very similar to that observed in samples fired at 500°C, when the binder was almost completely removed.

The black-brown, carbon-rich residue at sample's surface fired in air, indicates that the binder components have been subjected to incomplete pyrolysis. The hard-skin thus formed can lead to a differential contraction of the body surface, that shrinks relative to sample's interior, generating mechanical stresses that ultimately result in the development of cracks. This hard-skin may also be less permeable to the diffusion of the products from binder degradation, hampering the debinding and promoting the retention of gas bubbles. The increased carbon content at the sample surface, as shown in Fig. 4, reinforces this possibility.

One of the most studied processes of hydrocarbon oxidative degradation is that of polyethylene, which is very similar to paraffin and polyethylene wax. Under high temperature, short chain hydrocarbons simply evaporate, while long straight carbon chains oxidize to hydroperoxides, which further decompose forming aldehydes, ketones and alcohols [12, 13, 19, 20]. Under oxidative conditions, these products can oxidize once again, forming carboxylic acids, esters and lactones. Therefore, the oxidative debinding of ceramic parts can form hydroperoxides and increases the content of carboxylic acids and esters in the binder mixture, in a process that is limited by oxygen diffusion through the sample. These acids and esters can further react with hydroxyl groups, present in the alumina surface (Lewis acid-base reaction), thus forming aluminocarboxylates. The salt formation at the ceramic surface constitutes a bridge between the organic binder and

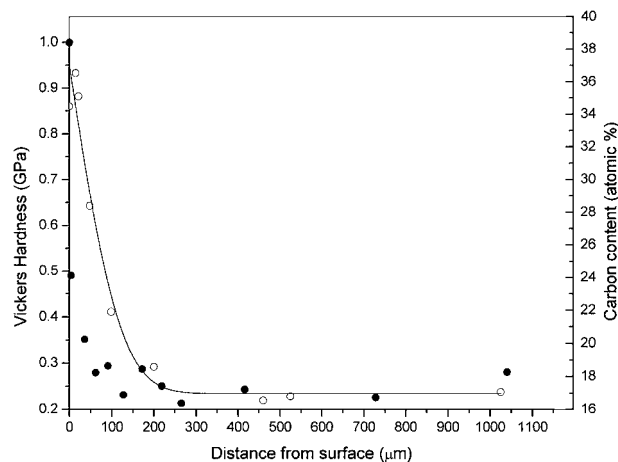


Figure 4 Hardness depth-profile (○), and carbon atomic percentage (●) in an injection molded ceramic after burnout at 250°C.

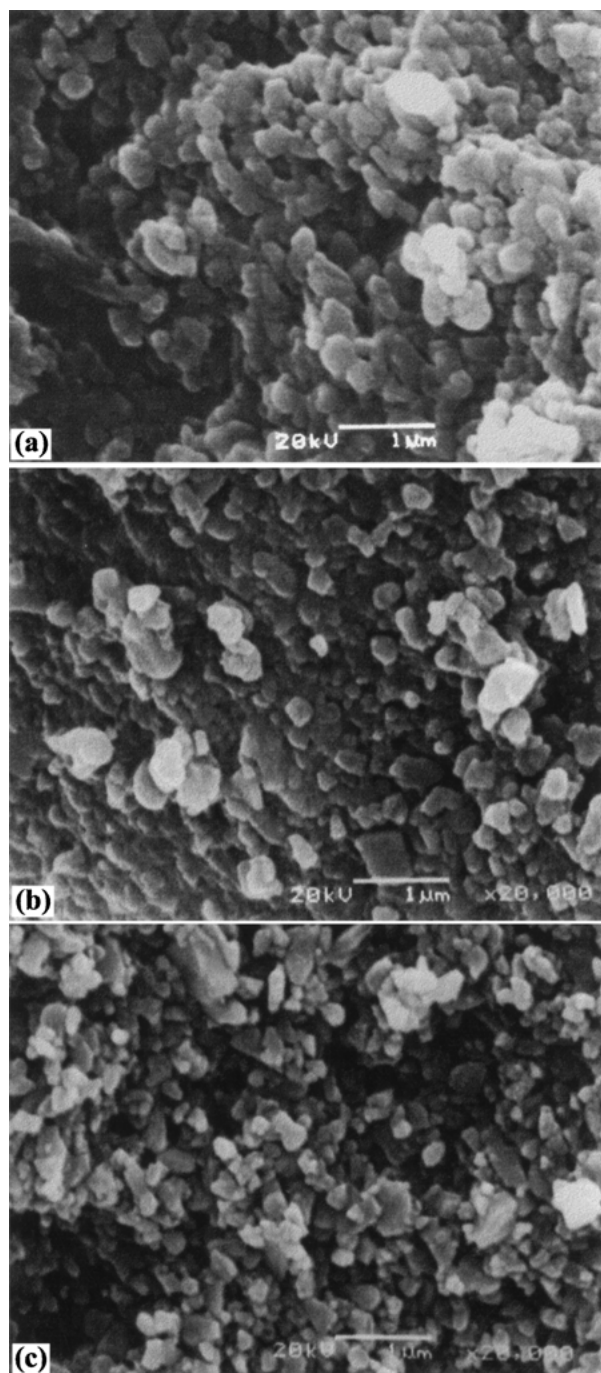


Figure 5 Back-scattered electron SEM images of a section of a (a) green ceramic, and of the (b) surface, and (c) interior of a large-cross section ceramic part fired in air at 250°C.

the alumina particles. The intermediate hydroperoxides formed during binder oxidative degradation or better the secondary radicals resulting from its thermal degradation, could also promote cross-linking reactions between long hydrocarbon chains [19], leading to the formation of a hardened organic matrix.

Fig. 6 shows the transmittance infrared spectra of the binder mixture and that of a green ceramic, obtained from samples dispersed in KBr pellets. Compared to the spectrum of the binder mixture, the infrared spectrum of the green ceramics (alumina plus binder) shows a large band at around 3500 cm^{-1} , due to the hydroxyl groups present in the alumina surface. More important, the spectrum of the green ceramics also shows the com-

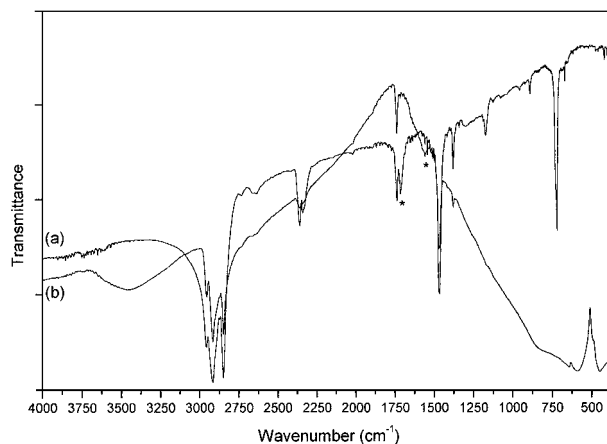


Figure 6 Infrared transmittance spectra of the (a) binder mixture and (b) green body (alumina and binder). The asterisk marks some peaks discussed in the text.

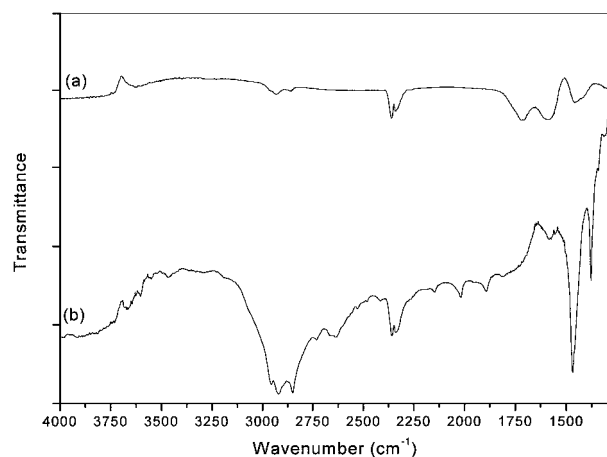


Figure 7 Diffuse reflectance infrared Fourier-transform spectra (DRIFTS) of ceramic parts made exclusively of alumina and paraffin as binder, fired at (a) 250°C in air and (b) pristine sample at room temperature.

plete disappearance of the acid group ($\text{C}=\text{O}$) peak at 1715 cm^{-1} and the development of a new peak at about 1560 cm^{-1} . As already commented before, the latter peak can be assigned to the carboxylate salt formed by the chemical reaction between the hydroxyl groups at the alumina surface and the carboxylic acids present in the binder mixture [5, 18]. The disappearance of the acid group peak and the development of the carboxylate peak in the FTIR spectrum Fig. 6b are thus linked effects.

Many features in the infrared spectrum of the binder mixture can be ascribed to its main component, paraffin. Accordingly, the spectrum in Fig. 6 shows the C–H stretching vibrations among 2800–2900 cm^{-1} , the methylene group ($-\text{CH}_2-$) bending mode at 1450 cm^{-1} , the methyl group ($-\text{CH}_3-$) bending mode at 1375 cm^{-1} and C–H out-of-plane bending vibrations at 900–690 cm^{-1} [21].

The diffuse reflectance Fourier-transform infrared spectrum (DRIFTS) of an alumina green ceramic part, made exclusively with paraffin as binder, is compared in Fig. 7 to the spectrum of the same ceramics fired at 250°C in air. Similar results were obtained for all binder compositions studied in this work. The spectrum of the

sample fired in air shows a great reduction in the intensity of the C—H stretching peaks centered at 2875 cm^{-1} . The reduction of the intensity of the infrared peaks assigned to C—H vibrations can be an indicative of binder degradation and possibly of increasing cross-linking between carbon chains [21]. The infrared spectrum of the fired sample shows a peak at about 1715 cm^{-1} which can be assigned to C=O stretching vibrations, arising mainly from carboxylic acids and esters resulting from the oxidative degradation of paraffin. The sample fired in air also shows the carboxylate peak, now at around 1590 cm^{-1} . This peak appears with increased intensity in the infrared spectra taken from the surface of ceramic pieces fired above 200°C .

According to Trunec and Cihlár, thermal degradation of hydrocarbons requires high activation energies ($150\text{--}200\text{ kJ/mol}$), while oxidative degradation, autocatalysed by hydroperoxide formation, can proceed at lower temperatures [12, 22]. Also, according to those authors, the products of oxidative debinding can react mutually, forming cross-linked structures [12]. In fact, the burnout in air of the binder mixture, without alumina powder, results in a black product similar to rubber, indicating that cross-linkage between carbon chains occurred during binder oxidative degradation. The hardness measured for the residue of binder degradation is, however, much lower than that measured for the surface of ceramic bodies fired under the same conditions.

Our observations suggest that the oxidative degradation that occurs at the surface of the ceramic parts is responsible for the hard-skin development. This process has a peak efficiency at about 250°C and possibly involves cross-linkage between long carbon chains, promoted by the products formed under oxidative conditions. The high hardness measured at the surface of ceramic parts fired in air at 250°C (of about $0.4\text{--}1.2\text{ GPa}$, depending on binder composition) is only surpassed at about 1000°C , when the ceramics begin the early stages of sintering (see the inset of Fig. 3).

The oxidative degradation is important to accelerate the debinding process because only wicking is usually not efficient enough for binder removal from large ceramic parts made with submicrometer-sized alumina powder. However, the hard-skin on the surface shrinks differently from the interior of the ceramic parts, resulting in the appearance of cracks. Therefore, it is necessary to develop a suitable furnace program to prevent hard-skin development. This is accomplished by firing the bodies in a long dwell at 170°C (34 hours) [5, 23], as it is illustrated in Fig. 1. At this temperature, the rate of binder removal is already high enough, while the rate of binder oxidation is very limited. Ceramic parts fired under such conditions were obtained free of cracks and bubbles and resulted in high density, free of defects bodies after sintering. The other alternatives to avoid the formation of the hard-skin are debinding under vacuum or inert atmosphere, which are more complicated and time consuming.

Ceramic parts made with binder consisting exclusively of paraffin do not develop the hard-skin, because the products resulting from paraffin oxidative

degradation are short-chain organic acids. On the other hand, binder mixtures containing long-chain organic components, which are able to react with the hydroxyl groups at the alumina powder surface, lead to the formation of a hard-skin when the ceramic parts are fired under oxidative conditions. Under such conditions, the products formed during binder oxidative degradation can lead to the formation of a long-range, cross-linked organic matrix [12]. This organic matrix interacts with the alumina powder via a Lewis acid-base reaction, with the formation of carboxylate salts, as evidenced in our DRIFTS results. The bridging of the ceramic particles to the carbon-enriched, cross-linked organic matrix, by means of the formation of aluminocarboxylates, thus results in the brown hard-skin observed in our experiments. This surface-hardening effect in alumina green ceramics fired under oxidative conditions reveals once more the complex interplay between the concurrent chemical reactions that take place during the stage of debinding [12, 15, 22]. The exact mechanism behind these concurrent chemical reactions, involving binder components and the surface of the ceramic particles (including the possibility of a catalytic effect of the oxide surface on the hard-skin development [15]), deserves further exploration and should be the subject of more detailed studies.

4. Conclusions

In this paper we performed a series of experiments with the aim of studying the origin and the nature of a brown hard-skin formed during oxidative debinding of ceramic bodies made with submicrometer-sized alumina powder.

According to our observations, the sudden increase in the surface hardness of parts fired in air at 250°C , can be ascribed to chemical reactions of binder components between themselves and with the alumina surface. At this temperature, the light fractions of the binder already evaporated, remaining only the heavy fractions constituted by long chain carbon compounds. The role played by the atmospheric oxygen in the process of hard-skin formation is twofold. First, under oxidative conditions, hydrocarbons (that are the major components in the binder mixture) can decompose, through the intermediate formation of hydroperoxide, to carboxylic acids and esters, thus enhancing the wettability of the binder to the alumina powder surface. This occurs by means of the formation of carboxylate salts, which bring together the organic binder and the ceramic powder. Secondly, the products formed during binder oxidative degradation promote cross-linking between the remaining long carbon chains. The ceramic particles already tightly bonded to the organic matrix through carboxylate formation, thus become trapped in a binder of increased rigidity due to cross-linkage between carbon chains. The binding of the organic components to the alumina surface and the cross-linking between long carbon chain in the organic matrix, both lead to the surface increased hardness in the ceramic parts fired in air.

To prevent the deleterious effects of the hard-skin development on the quality of presintered ceramic parts while keeping the advantages of firing ceramic parts in

air, a long furnace dwell at 170°C was employed, by means of which large cross-section ceramic parts made of very fine average particle size alumina powder were obtained free of defects.

It is noteworthy that the hardness measured at the surface of ceramic parts fired in air at 250°C only is surpassed at the early stages of sintering, at about 1000°C. The hard-skin development described in this paper constitutes an interesting effect that results from the complex chemistry involved in the process of binder extraction from green ceramic bodies.

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