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Influence of corrosion and mechanical loads on advanced ceramic components

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Abstract

Advanced oxide ceramics are prospective materials for severe application conditions, including corrosion, particularly, in oxygen-rich environments, combined with the action of mechanical loads. The corrosion behavior and mechanical strength decrease of oxide ceramics, such as high alumina, alumina–mullite and zirconia-based ceramics, were studied in water steam supercritical conditions (elevated temperatures and pressures). The strength decrease under the action of the studied aggressive environment is mostly dealt with the glassy phase dissolution and intergranular corrosion for alumina–mullite and high alumina ceramics, while degradation of zirconia-based ceramics is also dealt with the phase transformation. The influence of structure defects related to processing of the ceramics on corrosion is considered.

Keywords: C. Corrosion; C. Strength; D. Al_2O_3; D. ZrO_2

1. Introduction

Advanced ceramics are highly prospective engineering materials for severe application conditions, including corrosion, particularly, in oxygen-rich environments, combined with the action of mechanical, thermal and electrical loads [1–6]. However, the degradation of non-oxide advanced ceramics occurs rather fast in wet oxygen-rich atmospheres at elevated temperatures due to their oxidation [3,6–10]. In opposite, oxide ceramics have a high potential in these situations. Among a variety of applications, where the mentioned conditions may exist, these materials can be successfully used in energy generation, nuclear power plants and reactors, mineral, mining, oil&gas and chemical processing. In particular, special types of oxide ceramics are strong to corrosive attacks in harsh environments such as high-temperature water steam at elevated pressures and acidic and basic aqueous solutions of high concentrations, especially if the action of corrosive agents occurs at mechanical, thermal and electrical loads.

For example, these severe conditions take place in nuclear power plant and reactors where high-temperature and high-pressure steam is used as the heat processing source. Electrical insulators (e.g. feedthroughs for electrical cables installation, structural and electrical insulating components in nuclear reactors and others), as well as valve and mechanical seals, made of alumina and alumina–mullite ceramics are successfully used there due to high mechanical and electrical strength, corrosion and radiation resistance [1,2,5,11–14]. As another example, water steam of high temperatures and pressures is also used in oil processing; steam injection is a common method of extracting of heavy oil. This method is considered as an enhanced oil recovery method, and it is used as the main process of thermal stimulation of oil reservoirs. It includes "cycle steam stimulation" and "steam flooding" where steam is injected into a well for a certain period of time to heat the oil in the surrounding reservoir to the conditions when oil flows. The steam-assisted gravity drainage (SAGD) is one of the "advanced" oil recovery methods, particularly used in oil sands in Canada, where the conditions are even more severe for the processing equipment components due to the combination of corrosion, abrasion, erosion, mechanical and thermal loads. It is clear

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that only advanced materials can survive in these conditions with minimal degradation, and oxide ceramics based on alumina and zirconia may be very good candidates for manufacturing of different valves, seats, mechanical seals, bearings, pistons, impellers, lining for pump volutes, nozzles, turbo drill components and many others [15,16]. Severe corrosion conditions also take place in the "modified" Claus sulphur recovery units in oil&gas and chemical processing where "water-wall" boilers are used utilizing high-velocity oxygen-rich air as the oxidant and where steam and acids at high temperatures attack the structural components and lining. High alumina ceramics is one of the mostly used materials in these units.

In general, during exposure of ceramics in corrosive environment or, moreover, under joint attack of corrosive and abrasive–erosive environment, the bonds between grains in polycrystalline ceramics become weaker. In some cases, it is accompanied by the formation of micro-cracks, which then propagate to the visual cracking, and by the leaching of the material from the surface. This weakening, of course, depends on the kind of corrosive–erosive medium and service conditions, and it results in the strength reduction of ceramics.

At the development and manufacturing of advanced ceramic materials and components designated for the service in corrosive environment and structural and wear protection applications, many factors have to be taken into consideration. They include the design of the components and general assembling into devices; the features of their applications, such as mechanical, thermal and electrical loads and how these loads are applied, duration of their actions; types and compositions of corrosive and abrasive media, their parameters, e.g. temperature and pressure of corrosive media, hardness and size of particles of abrasive media, flow velocity, duration and cycling, etc. Also the manufacturing features and capability of the ceramics have to be taken into account, e.g. ability to produce particular shapes and sizes, ceramic microstructure, capability to joint ceramic materials and components with other components of the devices.

The information related to the influence of corrosion in water steam environments on mechanical properties of oxide ceramics is limited; particularly, with minimal amounts of recent publications. In this paper, the features of the corrosion of advanced engineering ceramics, mainly alumina- and zirconia-based materials, in water steam of "supercritical" parameters (elevated pressures and temperatures) used in some industrial applications are considered and summarized based on the extensive studies conducted during the years. The influence of these corrosive environments on the mechanical strength and joint action of corrosion and mechanical loads was evaluated as the studied materials have to serve under mechanical loads. Some technological factors affecting reliability, mechanical properties and corrosion resistance of ceramics were reviewed. Many factors affecting corrosion process of ceramics in water steam environments, including when mechanical loads are also the part of the service conditions, may be spread out for the integrity of ceramics and corrosion situations in other environments.

2. Features of the water steam as the corrosive media

Water steam being at high temperatures and pressures (200–400 °C and 4–40 MPa, respectively) is a highly corrosive environment, and the corrosion process in these conditions may be very strong when the exposure occurs during a long period of time. Basically, water molecules have the–O–H bonds with the length of about 0.1 nm and the hydrogen bonds H…O- with the length of about 0.176 nm. The "aggressiveness" of the water steam is dealt with the fact that, at high temperatures and pressures, hydrogen bonds between molecules of water are weakened and broken, and it results in significant decrease of viscosity and surface tension of water and increase of its penetration into the pores of solid bodies. At these severe conditions, water partially dissociates to hydrogen and hydroxyl ions:

$$H_2O \rightarrow H^+ + OH^- \text{ and } 2\,H_2O \rightarrow H_3O^+ + OH^-$$

The constant of dissociation and, hence, the activity and reaction ability of the hydrogen and hydroxyl ions in the gaseous phase are increased with the increase of temperature and pressure. The influence of temperature increase may be expressed by the van't Hoff equation $d(lnK)/dT = -U/RT^2$, where K—constant of water dissociation, T—temperature, R—universal gaseous constant, U—heat of dissociation. The pressure increase also results in the destruction of the bonds in the water structure and hence promotes the activity of the formed ions. The pressure dependence may be expressed as $(dlnK_x/dP)_T = \Delta V/RT$, where ΔV—partial molar volume, x—mole fraction, P—pressure. These ions have very small sizes, and, because of this, they can easy penetrate through micro-pores of the ceramic surface and the grain boundaries and defects of the ceramic structure destroying the grains after a long exposure. Due to the small sizes of these ions, their penetration into the crystalline lattice of the surface grains may take place. The interaction of metal oxide with water steam, in general, occurs through the formation of hydroxide:

$$Me_xO_y + H_2O \rightarrow Me(OH)_z$$

$$Me(OH)_z \rightarrow Me(OH)^+_{z-1} + OH^- \rightarrow Me(OH)^+_{z\text{-}2} + 2OH^- \rightarrow \text{ finally to } Me^{Z+}$$

$$Me(OH)_z \rightarrow HMeO_z^- + H^+$$

In some cases, the "impurities" to water steam make this environment even more "aggressive".

Generally, the most corrosion resistant ceramic materials usually have microcrystalline structures formed by the thermodynamically stable phases with minimal amounts of a glassy phase and impurities and with zero open porosity. If the ceramics consist of different oxides, the interaction with water steam or with the products of its dissociation will occur preferentially through the "weakest" oxides with less covalent bonds [5].

3. Experimental

Influence of structural and compositional features of advanced ceramics on their mechanical behavior during corrosive actions was considered for the materials with different phase compositions and structures. The following materials were studied: high alumina ceramics contained 99.5–99.8 wt% of Al_2O_3 (with a MgO dopant) denoted as A995–A998, high alumina ceramics with the Al_2O_3 contents of 97–98 wt% doped by the additives from CaO–B_2O_3–SiO_2 and CaO–MgO–(B_2O_3)–SiO_2 systems denoted as A97–A98, alumina–mullite ceramics (CM), yttria partially stabilized zirconia (Y-PSZ) ceramics, zirconia–alumina (ZA) and alumina–zirconia (AZ) ceramics (the major component was zirconia or alumina, respectively). The processing of these materials, as well as their structures and physical properties, were described elsewhere [12,15,16]. Commercially supplied starting materials were used for ceramic processing; however, the materials with lower impurity levels were selected. Alumina ceramics had quite uniform microcrystalline structures with average corundum grain sizes from 2–3 μm to 5–10 μm (depending on composition and processing) with minimal contents of secondary crystalline phases and a glassy phase. Alumina–mullite ceramics (CM) contained corundum grains (major phase) with small amounts of the mullite phase, which were bonded by the earth-alkali oxide–silicate glassy phase. Zirconia-based ceramics did not contain a glassy phase; their microstructures were uniform with grain size ranging from 0.5–2 μm for zirconia to 0.5–4 μm for alumina–zirconia ceramics.

The ceramic samples-bars were manufactured by different methods; e.g. slip casting, uniaxial and isostatic pressing, extrusion and low pressure injection molding. Also ceramic tubular samples (inside diameter of 10 mm) with a bottom (cup-like shapes, height 50 mm) with different wall thickness (3–10 mm) were manufactured by slip casting and low pressure injection molding. The established manufacturing procedures (including forming and firing) were used for the samples preparation, which provided formation of dense ceramics (water absorption below 0.02%). In some cases, grain size of the ceramics has been "purposefully" modified applying specific firing conditions and by modification of the ceramic preparation process (e.g. by milling technique).

The ceramic samples were exposed in water steam at elevated temperatures and pressures (200–370 °C and 4–30 MPa) with different testing duration (up to several thousand hours). The exposure was conducted in an autoclave using a Teflon cell placed into titanium housing; a special device was used for samples insertion and holding where their possible "maximal" surface was exposed to the corrosive media. The weight and mechanical strength (standard 3-point bending) changes were used for evaluation of corrosion resistance. Microstructure was examined using optical and scanning electron (SEM) microscopes. Depth of corrosion was examined also using optical microscopy.

4. Influence of water steam on structure and mechanical properties of ceramics

This section describes the test results obtained for alumina and alumina–mullite ceramics; the results of the studies with zirconia-based ceramics are described separately in the related section of the paper. Testing of alumina and alumina–mullite ceramics contained a glassy phase in water steam at different conditions showed that a glassy phase is leached first as the weakest ingredient. The alkali and alkali–earth oxides, as well as silica, interacted with water resulting in their hydrolysis with consequent leaching. After testing of alumina–mullite ceramics at 4 MPa and 250 °C for 300 h, the content of mullite became lower but the content of corundum grew up. The SiO_2 content dropped from ~23% to ~17%. I.e., mullite partially decomposed for Al_2O_3 and SiO_2 due to the interaction with water steam, and the formed SiO_2 partially hydrolysed and leached out.

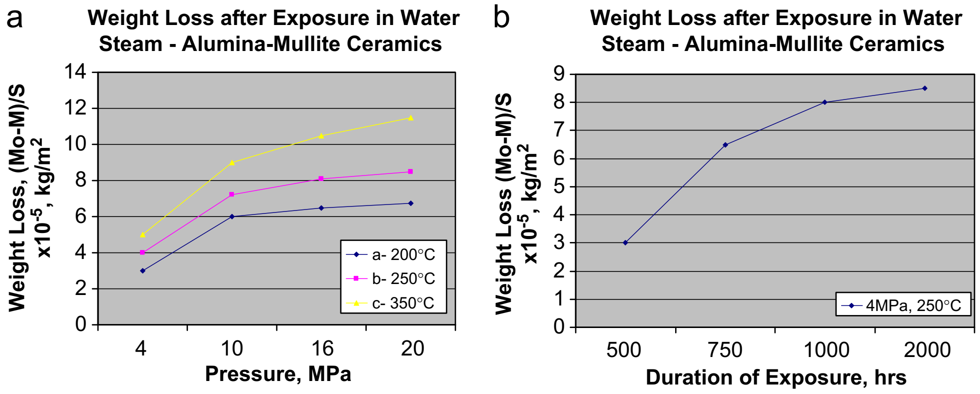

Fig. 1. Weight loss of Alumina–Mullite samples after exposure in water steam. (a) influence of pressure and temperature (300 h). (b) influence of exposure (250 °C, 4 MPa).

Water absorption and porosity increased and density decreased after the exposure that is accompanied by the weight loss of the samples (Fig. 1). Mechanical strength of alumina–mullite ceramics (CM) decreased with the pressure and temperature increase (Fig. 2). Thus, after 480 h (20 days), when pressure increased from 4 to 10 and then to 16 MPa (at 250 °C), strength dropped by 25–35% and then to 50%, respectively; and, with increase of duration, strength continued dropping but slower. Not linear strength reduction may be explained by the formation of the protective film on the surface of the samples.

The corrosion studies of alumina ceramics with different contents of the major crystalline phase (corundum) in water steam conditions showed the selective dissolution and leaching of the oxides from the grain-boundary phase, first of all, alkali and alkali-earth oxides such as Na, K, Ca, Mg, as well as SiO_2, and this behavior well corresponds with the earlier studies [1,2,5,14,17,18]. The ions of these oxides have the highest mobility due to their valence and small sizes and the ability to react with OH- ions with a hydroxide formation. It was clear noted that the materials with greater contents of a glassy phase and with the mentioned oxides experienced greater corrosion. It is noted that the alumina ceramics with two or more earth–alkali oxides had better corrosion resistance than the ceramics with only one earth–alkali oxide; similarly, the alumina ceramics with the borosilicate glassy phase had higher corrosion resistance than the ceramics with a silicate glassy phase (of course, Al_2O_3 was also the part of a glassy phase) [5]. It can be explained by the "neutralizing" effect of the action of the oxides with different ionic radii; the presence of two glassy-forming oxides, such as Si and B, also promotes the corrosion resistance because the transport ability of the Me^+ and Me^{2+} is more difficult in the B–O than in the Si–O structures due to shorter and stronger B–O bonds and stronger "positioning" of Me-ions in these structures. The corrosion of high alumina ceramics with the Al_2O_3 contents of higher than 99.5% with no or with minimal amounts of a glassy phase (that may occur due to the presence of impurities in starting alumina) is mostly dealt with leaching of these impurities. Also the corrosion of this type of alumina ceramics in water steam is dealt with the partial hydrolysis of MgO from the spinel phase (MgO is the effective additive to alumina to prevent the grain growth), although spinel, as the bonding phase, provides better material integrity in corrosion environments comparing with a glassy phase. "Pure" alumina ceramics without glassy phase with minimum admixtures usually performed better in this corrosive environment [1,2,5], and the materials with 3 N, and moreover, 4 N purity demonstrated superior corrosion resistance [14]. The hydrothermal corrosion of these "pure" alumina materials occurs with the formation of boehmite AlOOH and then, at longer exposure, with some other Al–O–H products, e.g. diaspore, at the grain-boundary area [1,2,5,14]. The possibility of Al_2O_3 hydration and the formation of the hydration products in the Al_2O_3-H_2O system depending on pH of the medium were considered in details in [19–21].

The results of the corrosion studies of alumina ceramics with different Al_2O_3 contents and glassy phase in water steam of supercritical parameters at some conditions are presented in Table 1 and Fig. 3. The tested materials had ~97-97.5% of Al_2O_3 (A975) with a CaO–B_2O_3–SiO_2-based glassy phase, ~98% of Al_2O_3 (A98) with a CaO–MgO–SiO_2-based glassy phase with a presence of small amounts of anorthite, and ~99.6% of Al_2O_3 (A996) and ~99.8% of Al_2O_3 (A998), when the corundum grains were bonded by tiny grains of spinel with practically absence of a glassy phase. The testing was conducted at temperatures 250–370 °C and pressures 4–30 MPa. These results are generally in the correspondence with the earlier published data. The alumina materials, which practically do not have a glassy phase (e.g. A996–A998), perform significantly better in the severe corrosive environments, and, as more severe the corrosive conditions, the benefit of the use of these high alumina ceramics without glassy phase in these corrosive conditions, e.g. smaller change of mechanical properties, becomes more noticeable. It is important to mark that higher corrosion resistance of the ceramics A996 and A998 is attained not only due to higher Al_2O_3 contents but also because of the spinel crystalline phase is more corrosion resistant than the silicate-based glassy phase.

The influence of the action of water steam (310 °C and 10 MPa) for high alumina ceramics based on corundum

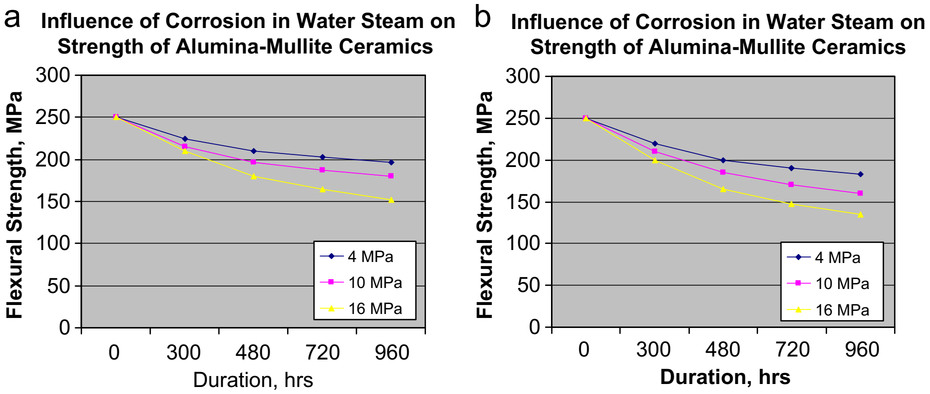

Fig. 2. Influence of corrosion in water steam on strength of Alumina–Mullite ceramics. (a) pressure 4–16 MPa, 200 °C; (b) pressure 4–16 MPa, 250 °C.

Table 1
The results of corrosion studies of high-alumina ceramics in water steam.

Material	Temperature, °C	Pressure, MPa	Weight loss ΔM/S, kg/m^2	Flexural strength loss, σ/σ_0
A975	250	4	0.0005	0.73
A98	250	4	0.0005	0.7
A996	250	4	0.0001	0.89
A998	250	4	0	0.985
A975	350	10	0.008	0.68
A98	350	10	0.009	0.65
A996	350	10	0.0002	0.83
A998	350	10	0.0001	0.95
A975	350	17	0.001	0.6
A98	350	17	0.002	0.56
A996	350	17	0.0002	0.78
A998	350	17	0.0002	0.9
A975	370	30	0.0016	0.44
A98	370	30	0.002	0.4
A996	370	30	0.001	0.72
A998	370	30	0.0006	0.8

ΔM—weight loss, S—surface area of the samples, σ—flexural strength after testing, σ_0—original flexural strength (350, 320, 320 and 300 MPa for A975, A98, A996 and A998, respectively) after 960–1000 h.

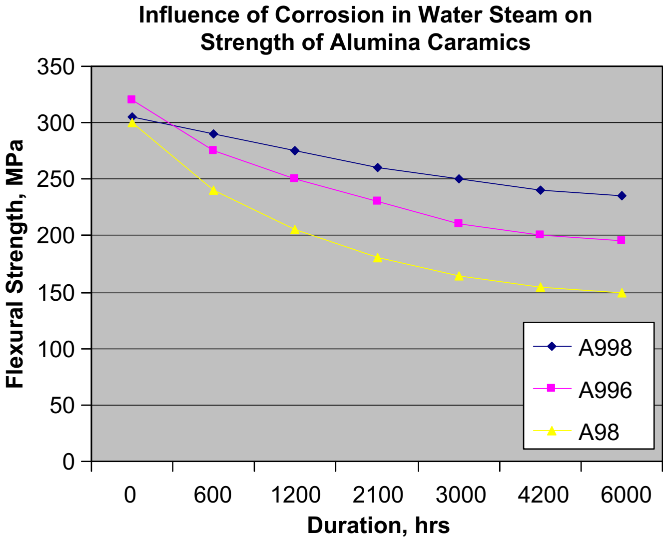

Fig. 3. Influence of corrosion in water steam on strength of high-Alumina ceramics.(temperature 310 °C, pressure 10 MPa).

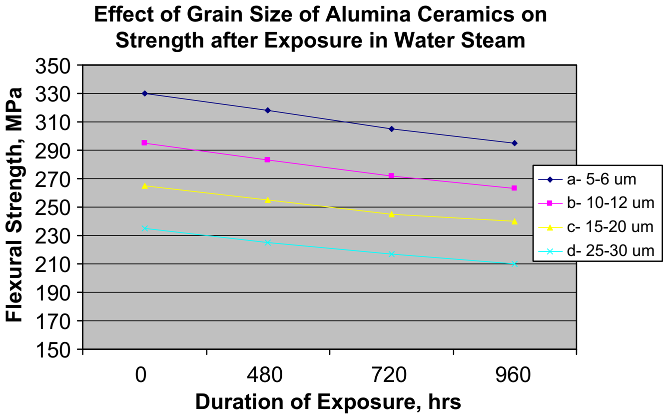

Fig. 4. Effect of grain size of high-Alumina ceramics on strength and corrosion resistance to water steam (temperature 310 °C, pressure 10 MPa).

grains bonded by small amounts of spinel phase and practically without glassy phase (A998 and A996) and alumina ceramics based on corundum grains bonded by the CaO–MgO–SiO$_2$-based glassy phase (A98) is shown on Fig. 3. It is clear that the ceramics with minimal contents of a glassy phase and impurities have smaller strength drops at corrosion. The action of corrosion is slow down with time that may be dealt with the formation of the protection layer occurred on the surface of the samples. The strength decrease is accompanied by the samples weight.

Some experiments were conducted with high alumina ceramics with ~99.6% of Al$_2$O$_3$ with practically zero contents of a glassy phase with different grain sizes. This type of alumina ceramics was selected for this testing to avoid the influence of the presence of a glassy phase; as noted above, if the ceramics contain "sufficient" amounts of silicate-based glassy phase, this glassy phase is leached faster with a higher rate of destroying. The difference in grain sizes was purposefully created modifying the ceramic processing, including varying the milling process and firing (e.g. temperature and soak) conditions. The grain size of ceramics has some effect on the corrosion resistance. It can be seen from Fig. 4 that corrosion resistance in the steam decreases with the grain size increase, but the grain size has a higher effect on mechanical strength in general than on corrosion resistance.

The example of the degradation of high-alumina ceramics (Al$_2$O$_3$ is 99.6% and greater) with relatively large grain sizes in terms of their microstructural parameters after long exposure in water steam of supercritical conditions (310 °C, 10 MPa) is shown in Table 2. The grain size

Table 2
Change of microstructure of high-alumina ceramics after exposure in water steam.

Material	Testing time, hrs	Grain size, μm	Refractive index for corundum	Refractive index for intergranular phase +/−0.003
A996 LPIM	0	6–10	*Np* 1.760; *Ng* 1.767	1.646
	4,000	5–8	*Np* 1.760; *Ng* 1.767	1.661
	6,000	3–6	*Np* 1.760; *Ng* 1.767	1.670
A998 LPIM	0	10–15	*Np* 1.760; *Ng* 1.767	1.583
	4,000	8–12	*Np* 1.760; *Ng* 1.767	1.563
	6,000	7–8	*Np* 1.760; *Ng* 1.767	1.546
A996 HP	0	4–8	*Np* 1.754; *Ng* 1.760	1.624
	6,000	4–8	*Np* 1.754; *Ng* 1.760	1.618
	10,000	3–6	*Np* 1.754; *Ng* 1.760	1.607
	12,000	2–4	*Np* 1.754; *Ng* 1.760	1.596

decreased after 4,000–6,000 h of exposure. As expected, the refractive index of corundum remained the same after the testing. However, the refractive index of the intergranular phase (glassy phase and tiny grains of spinel) changed that indicated to the corrosion through the grain boundaries.

The tested samples were manufactured through low pressure injection molding (LPIM) to the fully dense state (water absorption of after sintering was $<0.02\%$), and generally they demonstrated a high level of corrosion resistance. However, the samples of alumina ceramics similar to A996 by composition but manufactured through hot pressing (HP) did not have the grain size change after the testing in similar conditions after 6,000 h, and valuable grain size decrease ($\sim$1.5–2 times) was observed after 12,000 h [1,2]. Higher corrosion resistance of hot-pressed ceramics in comparison with pressureless-sintered may be explained by more homogeneous structure and fewer micro-defects dealt with occasional processing deviations.

In general, strength of ceramics depends on the grain size [22]. In accordance with a general theory of strength of polycrystalline materials [23–25], the effect of a grain size (d) on mechanical strength (σ) may be expressed as

$$\sigma = \sigma_0 + kd^{-n} \tag{1}$$

where σ_0 is resistance to the dislocation movement, n is coefficient ($n = 0.25$–0.5).

With respect to the noted, it is important that the cracking with the strength reduction occurs if the grain size is greater than some critical value, and strength is defined by not only the general grain size but also by the presence of the grains, which sizes are greater than the average, i.e. by the grain size distribution and structure homogeneity.

Accordingly, it may be accepted that the grain size of microcrystalline alumina ceramics changes during the exposure in strong corrosive and corrosive–erosive environment (e.g. in the steam at high pressures and temperatures and some others). In this case, strength of ceramics may be proportional to the amounts of the grains, which are involved in the corrosion process. In this case, the following expression may be proposed:

$$\sigma_1/\sigma_0 = M_1/M_0; \sigma_1/\sigma_2 = M_1/M_2 \tag{2}$$

where σ_0, σ_1, σ_2—mechanical strength of ceramic samples before and after testing in corrosive or corrosive and wear environments during the time t_1 and t_2; M_0, M_1, M_2—amount of grains in 1 g of the ceramics before and after testing with duration of t_1 and t_2.

If the values of depth of the grain destruction under corrosion (or under joint action of corrosion and wear) with duration of t_1 and t_2 are h_1 and h_2, respectively, and assuming that the grains are isometric with the side a, the ratio (2) may be written as:

$$\begin{aligned} &\sigma_1/\sigma_0 = M_1/M_0 = (a-2h_1)^3/a^3; \\ &\sigma_2/\sigma_0 = M_2/M_0 = (a-2h_2)^3/a^3; \\ &\sigma_1/\sigma_2 = M_1/M_2 = (a-2h_1)^3/(a-2h_2)^3 \end{aligned} \tag{3}$$

Assuming that alumina ceramics A997 consisting of about 99.7% of Al_2O_3 have an average grain size of 4 μm (actual range of 3–5 μm in accordance with microstructural analysis) and the depth of interaction with highly corrosive media, such as steam at high pressures and temperatures, is 0.1 μm after exposure of time t, the change of mechanical strength may be expressed as:

$$\Delta = \sigma_1/\sigma_0 = (a-2h_1)^3/a^3 = (4-2\times 0.1)^3/4^3 = 0.857 \tag{4}$$

If the ratio of geometric axis (n) of corundum grains is not 1 (can be assumes as 1.5), the change of mechanical strength after exposure with duration of t may be as:

$$\begin{aligned} \Delta^* &= \sigma_1/\sigma_0 = M_1/M_0 = (a-2h_1)^2(b-2h_1)/a^2b \\ &= (a-2h_1)^2(a-2h_1n)/a^3 = 0.835 \end{aligned} \tag{5}$$

Assuming that flexural strength of alumina ceramics A997 is 350 MPa, strength of this ceramics after exposure in the corrosive environment, when the depth of corrosion is only 0.1 μm, will be $350\times 0.835 = 292$ MPa. This type of the ceramic behavior can be taken into account at the consideration of the service conditions.

At the first stage of the water steam corrosion of high alumina ceramics in supercritical conditions, the weakening of the bonds between grains and the "damage" of the grain boundaries occurs, then intergranular corrosion in a higher extent takes place, which may be observed under microscope. Pores appear on the grain boundaries, and their amounts and size increase with increase of steam pressure and exposure in aggressive conditions; it is accompanied by the samples weight decrease. It can be assumed that the corrosion process followed by the grain boundary diffusion of the products of corrosion may lead to compressive stress occurrence due to the increase of volume in the intergranular areas. This stress occurrence, in turn, will lead to the local slow crack growth and to the mechanical properties decrease. Then, with continuation of the corrosion process and the crack propagation, the tensile stresses, which are more "dangerous" for ceramics, may occur that results in the further decrease of mechanical properties.

The exposure time in corrosive environments affects the corrosion of ceramics in a high extent in the beginning of the corrosion process. The corrosion for many ceramic materials has parabolic curve behaviour [1,2,7]. In the beginning of the process, the weight loss increases with the exposure, but then the corrosion rate (e.g. weight loss) decreases, and finally, starting from the certain time, it practically does not change (e.g. see Figs. 1–3). It is dealt with the formation of the protective film on the surface of ceramic bodies [1,2,5]. This protective film (formed as the product of the interaction of ceramics with corrosive media) inhibits the diffusion of the corrosive media (e.g. H^+, H_3O^+ and OH^-) to the ceramic surface. The thickness of the protective film (δ) may be defined from the equation:

$$d\delta/dt = kSD/\delta \quad \text{or} \quad \delta = (2kSDt)^{1/2} \tag{6}$$

where t—duration of the process, S—surface of the solid phase (ceramic samples) undergone by a corrosion process, D—diffusion coefficient, k—constant dealt with chemical potential of the particles diffusing through the film.

The value of k that may be considered as the constant of reaction rate, may be determined, with some approximation, from the equation

$$k = (2.3/t)lg(100/100-\Delta) \tag{7}$$

where Δ is the loss of weight (%) of the sample during corrosion

However, the positive influence of the forming protective film on the corrosion behavior is correct if the products of corrosion are not removed from the system by the corrosive media or, moreover, at the joint action of corrosive and abrasive media. If the corrosion occurs in the dynamic mode, and the products of corrosion are removed by the corrosive medium flow or by some other mechanical forces, and the forming protective film cannot remain on the surface of ceramic components, the dissolution of ceramics occurs constantly.

When a corrosive medium interacts with ceramics in a dynamic regime (e.g. when the medium flow contacts on the ceramic surface with a constant rate, and the concentration of the "active" ingredients in the medium practically is not changed), the rate of corrosion will depend on the change concentration (A) of the substance in the ceramic material. The constant of the process rate may be expressed as

$$K = (1/t)ln(A/A_0-x) \text{ or } Kt = ln(A/A_0-x) \tag{8}$$

where A_0 is the starting concentration of the "substance" (ceramics), x is a decrease of concentration of the "substance" during time t.

Using a known expression $K{=}K_0\ exp(-E/RT)$, the relation may be written as

$$ln(A/A_0-x) = K_0 t exp(-E/RT) \tag{9}$$

The influence of corrosion in dynamic regimes on ceramics, e.g. the speed of corrosive media flows, with the mechanical properties evaluation requires dedicated studies.

5. Structural defects, which may affect corrosion resistance

Stressed conditions of the ceramic structure (internal stresses) affect the corrosion resistance of the ceramics and mechanical strength reduction, and the external action (mechanical loads, thermal stresses) also affect the corrosion process. The stressed state of ceramic materials is defined by the non-homogeneity of the structure, presence of the internal defects, presence of the stress concentrators dealt with the product design and with the processing, the junction of a ceramic body with some other components of the total product (e.g. with metallic components). Some of the origins of the stressed state, in particular dealt with structure and processing, will be discussed below. The stressed state of ceramics leads the reduction of its thermodynamic stability; the Me–O bonds become weakened and the Me^{n+} ion can leave its position at the crystalline lattice easier that results in corrosion enhance and material degradation. The mechanical load applied during the corrosive medium action facilitates the deformation of the crystalline lattice resulting in the higher extent of non-homogeneity and internal defects occurrence. The stressed state and stress conditions are dangerous not only because of they increase the corrosion process in general but because they lead the transition of the corrosion from "even" to "local". The local corrosion results in evolution of the local degradation and crack formation.

In the case of action of thermal gradients on ceramic products, corrosion and micro-cracking and related stresses σ are enhanced in accordance with the expression:

$$\sigma = k_S(T_{max}-T_{min}) \tag{10}$$

where k_S is the coefficient dealt with elastic and thermophysical properties of ceramics, and $(T_{max}-T_{min})$ is the temperature difference on the wall of a ceramic product.

This micro-stressing issue becomes more dangerous if the aggressive action of the medium occurs during the service in a cycling regime; the cycling loading may have as mechanical and/or thermal nature. During the cycling, tensile stresses may occur in the first half of the cycle, and then these tensile stresses may be reduced or even may be transferred to compression in the second half of the cycle. This change of the stress is accompanied by the friction of interior surfaces of the cracks and by the mechanical destruction of the protective films, which may form during corrosion. This effect promotes further destruction when fresh portions of the corrosive or abrasive medium penetrate into the micro-cracks. The corrosive products may be accumulated in the cracks preventing the closure of the cracks and facilitating mechanical destruction. The destruction under corrosion or under corrosion and wear at the cycling (cavitation is a good example) occurs in two stages: the formation of the crack and its propagation to the critical value with consequent fast destruction. The first stage is defined by the appearance of dislocation and vacancies with increase of non-homogeneity of the material but without breakage of the atomic and ionic bonds. Then the formation of sub-micron- and micro-cracks occurs during propagation and coalescence of the dislocation and vacancies. The second stage starts when one of microcracks is transformed into a ‘‘large’’ crack.

Ceramic materials and products, in general, have some level of non-homogeneity and stressed state due to their structural features, stress conditions dealt with manufacturing deviations and gradients of stresses on the surface and in the middle of the products (e.g. related to forming methods and firing), as well as some geometric non-homogeneity and stresses dealt with the product design. All these irregularities affect the behaviour of ceramics under corrosive conditions because the destruction under these conditions starts from the weak areas [26]. As mentioned, the corrosion action creates additional stresses and increases non-homogeneity. Mechanical loads enhance the action of corrosion and destruction of ceramic components. The danger of the influence of stress conditions on corrosion resistance of ceramics is not only in the increase of ‘‘general’’ corrosion and degradation, but in the change of their ‘‘nature’’ resulting in transformation of the rather evenly distributed corrosion process to the local. It is obvious that the chemical interaction between the ceramic surface and the corrosive environment starts from the crack surface, to be more precise, from the crack tips. In this case, the stresses intensify the destruction of ceramics, and the micro-cracking is the most dangerous issue. This micro-cracking is enhanced due to the absorption processes, which decrease the resistance of materials to deformation and destruction, called as the absorptional effect of the strength decreasing (Rebinder's effect) [27,28]. This formation of new surfaces is facilitated by the ‘‘wedging’’ action of the surfactants of corrosive media and by the forming products of the corrosion processes. The schematic of the stress occurrence associated with corrosion is shown in Fig. 5.

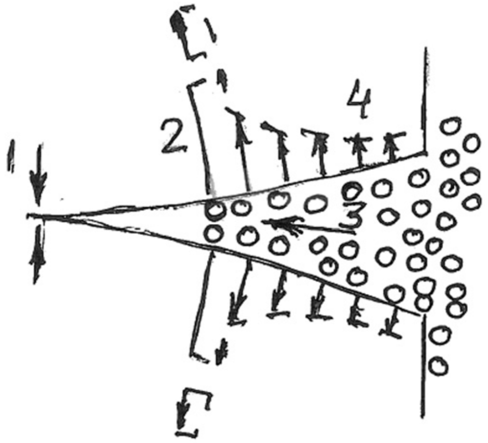

Fig. 5. Schematic of the crack formation associated with Corrosion. 1—directions of adhesion forces; 2, 4—directions of the wedging forces; 3—direction of the corrosive media and wetting actions.

Generally, the presence of internal or external defects and non-homogeneity of the ceramic structure negatively affect the reliability and mechanical properties of ceramics [29–32]. Briefly, the following factors dealt with the ceramic processing influence on structural defects, reliability of ceramics and their corrosion resistance. They include

(a) Surface defects, e.g. macro- and micro-cracks, open porosity
(b) Inclusions
(c) Voids and internal pores
(d) Internal micro-cracks and flaws
(e) Homogeneity
(f) Grain size and grain size distribution
(g) Presence of secondary crystalline phases
(h) Bonding phase (e.g. glassy phase) distribution

The surface cracks on ceramic components may occur due to deviations or imperfect procedure of the mechanical treatment (grinding) process conducted after firing (e.g. improper installation of the ceramic components into the grinding fixture, too fast grinding, improper cooling of the ceramic components, and some others). Also the surface cracks or defects may be dealt with the issues of the firing cycle, in particular, with the phase transformation (if it takes place in the ceramic composition) or with the cooling step, when the tensile-compression stresses may occur in a ceramic body. These residual stresses and related surface (and internal) micro-cracks may be noticeable especially for the large size ceramic components when rapid densification occurs on the outer area of the ceramic body while the inner area is not fully dense yet. Open porosity is associated with underfiring of ceramics.

The presence of inclusions may be dealt with occasional contaminations of ceramics; in the case of the appropriate control of the staring materials and at the batch preparation, this issue happens very seldom in industrial manufacturing. The presence of the inclusions results in the stress formation due to the differences in thermal expansions of the "main" ceramic matrix and the inclusions. It should be noted that the ceramics with lower contents of impurities that is important for corrosion resistance generally have lower sinterability. Because of this, higher requirements for the starting powders quality and homogeneity providing by the forming technique should be maintained to reach high density and uniform microcrystalline structures.

Internal voids and pores formation may be associated with the ceramic processing deviations, e.g. in forming (shaping) and firing (for instance, when the sintering is not fully completed or due to pore or flaw coalescence; also void coarsening may occur for the compacts, which originally had elevated porosity in the green body and when sintering takes place through the evaporation-condensation mechanism). The formation of these defects, in a high extent, may be dealt with the type of the forming process because each forming process brings the own features of the defects and densification. The features of the forming process and associated defects and their influence on corrosion resistance of ceramics will be considered below.

Internal micro-cracks and flaws may occur due to different reasons dealt with the irregularities of the forming, drying and firing steps. The forming-related stresses may occur due to the issues with the die design, distribution of the applied pressures, demolding step (ejection of the ceramic body), and, importantly, due to the irregularities in the powder compaction, including non-uniformity of packing density and particle orientation, and the presence of the large agglomerates and some others. For example, Roosen and Bowen [31] demonstrated that colloidal processing techniques using narrow-sized well-dispersed powders provided higher microstructural homogeneity of ceramics that was superior comparing to dry pressed materials. Seidel et al. [32] noted the difference in mechanical strength of ceramics depending on the forming process. Thus, they mentioned that the strength of alumina ceramics was lower in the case of pressed (CIP) samples in comparison with slip cast samples; the strength reduction is dealt with the presence of hard agglomerates in the pressed samples and elevated amounts of the internal flaws and pores, as well as with larger grains. Krell et al. [33] pointed out that not simply green density dominates the performance of ceramics (densification and strength), but the microstructural homogeneity of green samples (i.e., the absence of flaws) is more important, and wet-shaping techniques with sufficient dispersion are the most promising to reduce the flaws and non-homogeneity. The drying stresses and related cracks are associated with inappropriate drying conditions when the moisture is removed too fast from the outer area, especially in the beginning of the drying cycle. They also may appear when the drying occurs not from all ceramic component surfaces or with significantly different rates (e.g. the hollow cylindrical bodies starts drying faster from the outer surface area than from the inner surface area). The micro-cracks associated with firing may be dealt with the phase transformation (if this effect occurs in ceramic compositions), with probability of the gaseous phase formation during intermediate or latest steps of the firing (or when the firing profile does not accommodate the gaseous phase removal at the right conditions), tensile-compression stresses related to differentiations in densification and shrinkage of the outer and inner zones of the ceramic body, issues dealt with the firing cycle and some others. Some of the mentioned issues may result in the local structure coarsening that also results in the micro-crack formation. The problems, which occur at the steps before firing, may be accumulated with the problems occurring during firing.

Corrosion and material destruction occur in the highest extent at the tip of the micro-cracks. Steam or liquid, especially acting under elevated pressures and temperatures, penetrating to the defects create the highest mechanical impact, e.g. "wedging" pressure, at the narrowest area of the defects, and the narrowest area is the tip of the crack or flaw. The wedging pressure of the corrosive media is mostly directed to the tip of the defect, the occurring stresses may achieve rather high values, and they lead to further mechanical destruction of the ceramic material. The formed products of the corrosion accumulated at the tip of micro-cracks act with the same direction also create "wedging" and the further micro-crack growth.

The influence of the grain size and grain size distribution on corrosion resistance is not clear understood. Usually the impurities, which are generally leached out first at the corrosive medium action, are concentrated on the grain junctions, and it is more possible in the case of large size grains, especially when the grain size distribution is not very even and narrow. Similar situation occurs with the micro-defects and micro-stresses. It may happen when the mixing/milling process is not optimized. Another possibility of the formation of uneven grain size distribution and elevated grain growth and, hence, possible accumulation of the micro-defects and inclusion is uneven firing conditions (e.g., uneven gas flow in the kiln, large distance between the heating sources, accumulation of the heat at some kiln areas, too long soak time, especially coupled with improper kiln design). The weight effect may be remarkable for the large size products. The effect of the grain size on the corrosion in water steam and strength reduction was shown above for high alumina ceramics (Fig. 4).

6. Influence of the manufacturing process on the ceramic reliability and corrosion resistance

As mentioned earlier, the occurrence of different defects and presence of porosity may be associated with the features of manufacturing process. Among all the manufacturing steps, from raw materials preparation to final machining, the forming process is the most influential with respect to structure formation and mechanical properties. It is difficult to maintain absolutely defect-free processing in the real industrial environment, especially at mass-production. For example, in the case of slip casting or gel casting, if dispersion at the slurry preparation is not appropriate, the compaction of the green body is lower that automatically results in the lower firing densification (elevated closed porosity). The coarsening at the spray drying powder preparation and consequent dry pressing (uniaxial or isostatic) results in the internal stress formation, while uneven pore distribution and local grain coarsening during firing result in elevated closed porosity and micro-crack formation. Inappropriate dispersion and elevated binder content at the injection molding may result in the stress and crack formation associated with the binder burnout. Inappropriate extrusion die design and/or lower vacuuming may be the causes of the stress formation and elevated porosity of the extruded components, especially if they are manufactured from the clay-free ceramic compositions. These examples demonstrate the importance of the ceramic processing quality and control to manufacture ceramic components without defects with uniform microstructure, with high reliability, mechanical properties and corrosion resistance under severe environments.

Purity of ceramics that is defined by the purity of starting materials and by the processing affects significantly the water steam corrosion resistance. Oda and Yoshio [14] clearly demonstrated that 3N- and moreover 4N-purity alumina ceramics performed significantly better than 2N-purity ceramics, i.e. high purity starting powders should be used to maintain high corrosion resistance. However, commercial powders usually do not have so high level of purity, and the manufacturers have to use the available materials selecting “reasonable” purity. Of course, regarding alumina ceramics, only commercially produced “low soda” alumina powders should be used. Milling and slip preparation have to be conducted in the equipment with highly wear resistant ceramic lining and grinding media. As a simple example, high alumina ceramics A997 prepared from the commercial “super-ground” alumina powders through the slip preparation in the steel-lined attritor had a higher level of degradation than the same ceramics but prepared through the slip preparation in the alumina-lined attritor despite the slip preparation cycle in the attritors was only about 30 min.

Below is the comparison of the mechanical properties and corrosion resistance for some advanced ceramics manufactured by different methods. The studies were conducted for oxide-based ceramic materials, such as alumina ceramics A996, A98 and A975 and alumina–mullite ceramics (CM), which were described above. The ceramic samples-bars were manufactured by different methods; e.g. slip casting, uniaxial and isostatic pressing and low-pressure injection molding were used for alumina ceramics A996, A98 and A975, and extrusion, uniaxial pressing and low-pressure injection molding were used for alumina–mullite CM ceramics. All ceramic samples tested were dense with water absorption below 0.02%. The ceramic samples were exposed in water steam at elevated temperature and pressure (200–250 °C and 10 MPa) with different testing duration. Of course, alumina–mullite ceramic samples were tested during a shorter period of time due to their faster degradation that is dealt with a higher content of a glassy phase.

The influence of the processing method on the mechanical strength decrease under corrosion in the water steam environment can be seen from Figs. 6 and 7. The graphs demonstrated the reduction of strength under corrosion at 10 MPa pressure. It is clear that, at more severe testing conditions, e.g. at higher pressures and temperatures of the steam, the difference in the degradation would be even higher. From the alumina–mullite and alumina ceramic samples made by different forming methods, the samples made by pressing showed a higher extent of degradation due to corrosion, and their degradation started earlier. Although all samples made by different processing methods did not have open porosity, lower performance of the pressed samples (in comparison with the samples made by other forming methods) may be explained by their lower homogeneity, the presence of flaws, elevated agglomerates and elevated closed porosity in the structure of original samples. Water steam penetrates easier to the materials with more surface and internal defects with a higher extent of the formation of the corrosion products wedging the defects, and it leads to the elevated properties degradation. Comparing the behavior of alumina A996 ceramics made by slip caring and low pressure injection molding, the lower strength values of the injection molded samples are dealt with not with their lower homogeneity and the presence of flaws but with larger corundum grain sizes due to coarser alumina starting materials used. The behavior of the strength decrease with corrosion is about the same for slip cast and injection molded samples.

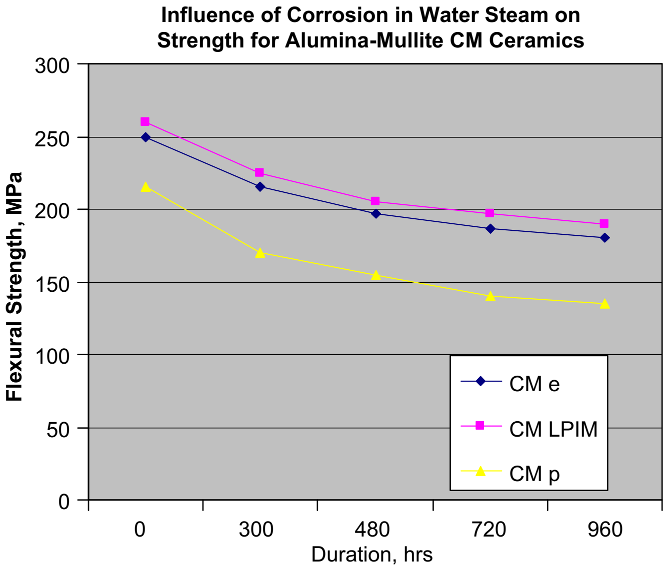

Fig. 6. Influence of corrosion in water steam on strength of Alumina–Mullite ceramics made by extrusion (e), Low Pressure Injection Molding (LPIM), Uniaxial pressing (p). Testing conditions: temperature 200 °C, pressure 10 MPa.

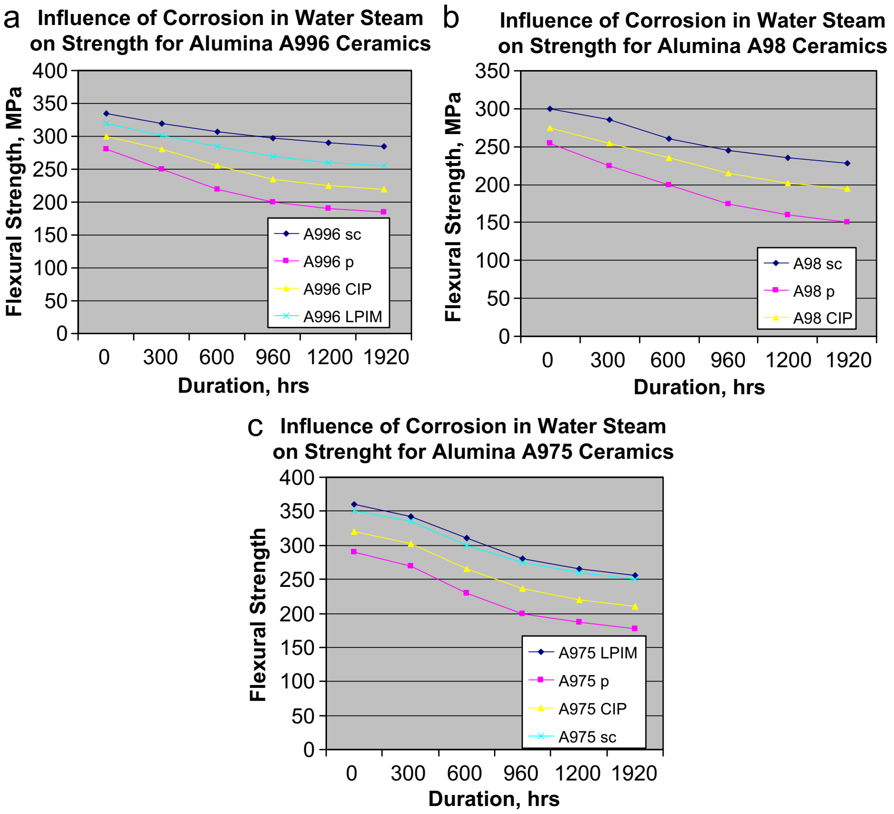

Fig. 7. Influence of corrosion in water steam on strength of Alumina ceramics A996, A98 and A975 made by slip casting (sc), Low Pressure Injection Molding (LPIM), Uniaxial (p) and Cold Isostatic Pressing (CIP). Testing conditions: temperature 250 °C, pressure 10 MPa.

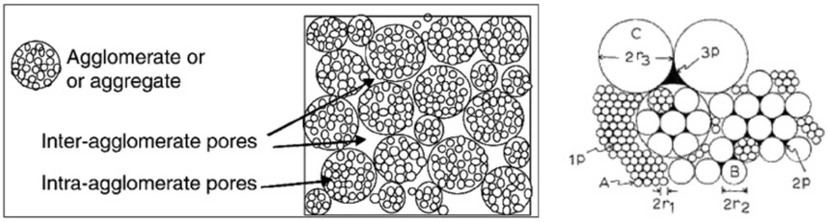

Fig. 8. Schematic of agglomerated (aggregated) powders.

While in the case of casting, extrusion, and LPIM, the formation of green ceramic bodies is attained through compaction of submicron or submicron–micron particles, the formation of the samples made by pressing is occurred through the compaction of the larger agglomerates (50–150 μm), obtained through spray drying or granulation, which consist of smaller agglomerates with sufficient amounts of pores, despite submicron primary particles prepared at the milling process (Fig. 8, adopted from Dr. P. Bowen). It has to be noted that spray dried granules usually have a "donut"-like shape, and the compaction of these aggregates has additional challenge to attain high density and minimal internal defects. The compaction of the rather large agglomerated powders at pressing is focused on the destruction of these "large" agglomerates, which may be rather hard, and on the elimination of the pores to reach high green density with minimal flaws and non-homogeneity that is quite challenging. Comparing porosity of pressed and slip cast materials, it can be noted, that, in a green body, the slip cast materials have a uni-modal pore size distribution (pore size of 0.1–0.2 μm), while the pressed materials have a bi-modal pore size distribution (pore size of 0.1–0.5 and 5–12 μm), and the samples made by CIP have smaller sizes of the "macro-pores" (3-8 μm) with a shorter peak and narrower distribution in comparison with the uniaxially pressed samples due to significantly higher pressures applied at CIP. The extruded and low pressure injection molded samples also have a uni-modal pore size distribution, but the pore sizes are some larger and the distribution is wider in comparison with the slip cast samples due to the necessity to use higher amounts of the binder. It is not related to the extruded CM samples because this ceramics contains a sufficient amount of the clay component, and the temporary organic binder is not required for the extrusion process. The pore size distributions in the fired bodies made by different forming methods have a similar trend. However, the finest pores disappear first at sintering, and if the pressed samples had "macro-pores" with elevated sizes, they may remain after sintering with a possible pore growth due to the pore coalescence that leads to the structure non-homogeneity. An additional issue related to the uniaxial pressing technology is dealt with the difference in particles orientation and related difference in shrinkage with respect to parallel or perpendicular to the pressing direction. This issue that is usually observed by manufacturing ceramic specialists was confirmed by Tanaka et al. [34] demonstrated, applying the confocal scanning laser fluorescent microscopy studies for alumina ceramics, that the shrinkage is ~15% higher in the direction parallel to pressing. The difference in the fired shrinkage and associated deformation and stressing, which lead to the flaws occurrence, have negative influence on strength of ceramics and their faster degradation under severe corrosive environments. It is obvious that these occurred stresses are greater for the bigger size products. Comparing uniaxial and isostatic pressing, isostatic pressing provides a higher compaction of ceramic bodies due to higher and 3-D applied pressures and, therefore, less possible internal flaws and defects, and, as a result, a lower extent of mechanical degradation under corrosive environments. The sintering of the green bodies with elevated amounts of agglomerates and with lower homogeneity is more difficult [35] that results in the presence of elevated amounts of the mentioned defects, which reduce mechanical strength and corrosion resistance. In practice, these ceramic bodies (which often have lower green densities) require a longer soak and/or a slightly higher temperature to attain high fired densities that may result in the grain growth.

The effect of the forming method is not exact the same for the materials of different compositions (e.g. the Al_2O_3 contents and the presence of a glassy phase have some influence). The difference in the corrosion behavior for alumina ceramics A975, depending on the forming method, is some less than for high alumina ceramics A997 with a minimal amount of a glassy phase. It may be explained that, despite the formation of some flaws and elevated closed porosity in the pressed green samples, a glassy phase fills some of these defects "improving" the samples homogeneity after firing, and a negative influence of the forming defects becomes less (although the difference between the samples made by different methods can be seen). In the case of alumina-mullite ceramics, the amount of a glassy phase is sufficient, and its distribution is less uniform in the case of pressed samples. When the corrosion occurs through the glassy phase, a lack of homogeneity affects the corrosion behavior and related strength reduction. The use of hot pressing, as mentioned above, provides minimization of closed porosity and grain growth; as a result, the hot-pressed high-alumina ceramics with an Al_2O_3 content of ~99.6–99.7% demonstrated not only the highest homogeneity and original mechanical strength, but also the lowest reduction of mechanical properties after the corrosion in the water steam even after more than 6000 h of exposure.

Post-firing machining (grinding) of ceramics may promote corrosion resistance because, in the case of the smooth surface, the contact between the corrosive media and ceramics, as well as the possibility to accumulate the chemically active substances and to remain the residual products of corrosion on the ceramic surface, are reduced. In addition, this operational step reduces the micro-defects associated with the stresses occurred at the firing (e.g. tensile-compression stresses on the surface occurred at the cooling stage). However, grinding has to be conducted very gently to avoid the grinding-related stress occurrence. Green state machining (before firing) also promotes the removal of the surface non-homogeneity and the stressed area occurred due to the forming process. For example, some stresses may occur due to the surface difference in slip cast samples (e.g. at the outer area provided by a plaster mold) or in pressed samples (e.g. at the outer area provided by a press-die when stresses may occur due to the friction and/or the spring-back effect). In the case of green machining, the stresses related to firing (cooling) also may be reduced because one of the possible issues related to the "forming issue" is lowered. The corrosion resistance tests conducted with "as-prepared" and with green-machined (~0.5–0.8 mm surface removal) ceramic slip cast and pressed bars demonstrated that mechanical strength of the green-machined samples, both before and after exposure in the corrosive environment, was higher by approximately 10–12%. The difference in strength after the corrosive action was especially noted after relatively short exposure (~600 h in a water steam) because, at this time, corrosion occurs only from the surface.

The ceramic component design optimization may reduce the non-homogeneity and the stress occurrence at the manufacturing. For example, the designs with uniform thicknesses, absence or minimization of the sharp corners and edges, the designs creating smooth media flows and some other features provide the integrity increase at the service at highly corrosive conditions where mechanical loads take place.

7. Features of corrosion and mechanical destruction of zirconia-based ceramics

Zirconia ceramics did not demonstrate very high corrosion resistance in water steam of supercritical conditions in comparison with high alumina ceramics. The older studies conducted by F. Kharitonov et al. [1,2] with CaO-stabilized zirconia ceramics showed that, at relatively low water steam parameters (4 MPa, 250 °C), the properties of the ceramics remained almost on the original level after 300 h, and they changed remarkably after 1000 h. However, at more severe conditions (350–370 °C and 10–20 and, moreover, 30 MPa), water absorption and mechanical properties changed significantly already after 300 h (flexural strength dropped for ~20% and more) with further degradation with time. The properties decrease was related to the phase transformation and diffusion and leaching of Ca^{2+}. Partial destabilization of zirconia in water steam and related volumetric changes are accompanied by the porosity increase that, in turns, promotes the diffusion of the Ca^{2+} ions from the stabilized to destabilized areas. This material transformation was accompanied by cracking of the samples. The crack formation creates more surfaces for the aggressive medium penetration and corrosion increase. Due to the phase transformation and Ca^{2+} leaching, the formation of $ZrO(OH)_2.mH_2O$ also started. Corrosion occurred through the grain boundaries.

Partially Y_2O_3-stabilized zirconia ceramics were destroyed in the water steam environments in the less extent; however, the corrosion process was also remarkable. Two major theories explained the degradation of Y-TZP ceramics in water at elevated temperatures. In accordance with F. Lange et al. [36], water leaches a sufficient amount of Y, and the surface tetragonal grains transform into the monoclinic phase, and the content of the monoclinic phase grows with time that is accompanied with a crack formation. In accordance with M. Yoshimura et al. [37,38], the formation of zirconium and yttrium hydroxides at the surface acts as the stress concentrator sites, and the formed hydroxides migrates into the crystalline lattice of the ceramics. The stressed site defects, in turn, act as the sites for nucleation of the monoclinic phase (*m*-phase), and the transformation of the tetragonal phase to monoclinic results in the micro- and macro-cracking. In accordance with M. Yoshimura et al., the leaching of Y does not occur. However, the later studies [39–43] showed the Y-leaching. As well, the experiments conducted by Ho and Wei [39] and R.A. Kanel and J.H. Adair [40] with Y-TZP powders at room temperature showed the leaching of Y. Although Ho and Wei [39] considered that the Y dissolution is not the controlling factor leading to the *m*-phase formation, the Y dissolution causes the local phase instability. At more extreme conditions (e.g. at higher pressures and temperatures as considered at the present paper), the Y-leaching may be expected. The leaching is accompanied by the reaction with OH^- with the formation of the hydroxides that results in the friable structure of the material resulting in the degradation. We think that, due to the tetragonal-to-monoclinic (*t*-to-*m*) phase transformation and migration of Y at the initial stages of corrosion and hydrolysis, further crack formation and material destabilization may occur.

The mechanism of the destruction of the Zr–O–Zr bonds with water may be presented, in accordance with Sato and Shimada [41], as the formation of the bonds H–O in the ZrO_2 surface when H from water starts connecting with O from ZrO_2 and consequent breakage of the Zr-O bonds. As a result, the Zr–O–H bonds are formed. It is logically to expect similar bond formation between the Y–O–Y bonds with water, especially taking into account that water in the supercritical conditions dissociates for the H^+ or H_3O^+ and OH^- ions. The interaction between these ions and Y_2O_3 and the breakage of the Y–O bonds may occur in the greater extent to compare with ZrO_2 due to less "covalentness" of the bonds in Y_2O_3. This interaction may be occurred as presented at the schematic (Fig. 9).

The corrosion of zirconia ceramics and related degradation dealt with the continuous *t*-to-*m* phase transformation and associated cracking result in the strength decrease. For example, in accordance with the studies conducted by Drummond [44], zirconia ceramic samples lost the strength from about 890 MPa to about 550 MPa, i.e. more than 30%, after their exposure in the water steam at 230 °C for 400 h.

Our studies with 3Y–PSZ (slip cast and pressed) confirmed the problems associated with degradation and cracking of the ceramic samples after exposure in water steam (10–12 MPa, 250–350 °C). After first 300 h, the samples almost did not lose their strength, but after 600 h the cracks on the surface became really visible, and the strength decrease became notable; then strength dropped significantly (Fig. 10). The *t*-to-*m* phase transformation occurs only from the surface of the samples, and if to machine the surface of the samples, which were under the action of the corrosive environment less than 350–400 h, the strength may be on the original level. The increase of steam temperature and pressure results in the increase of the corrosion rate of zirconia ceramics. It is dealt with a higher extent of the *t*-to-*m* transformation and

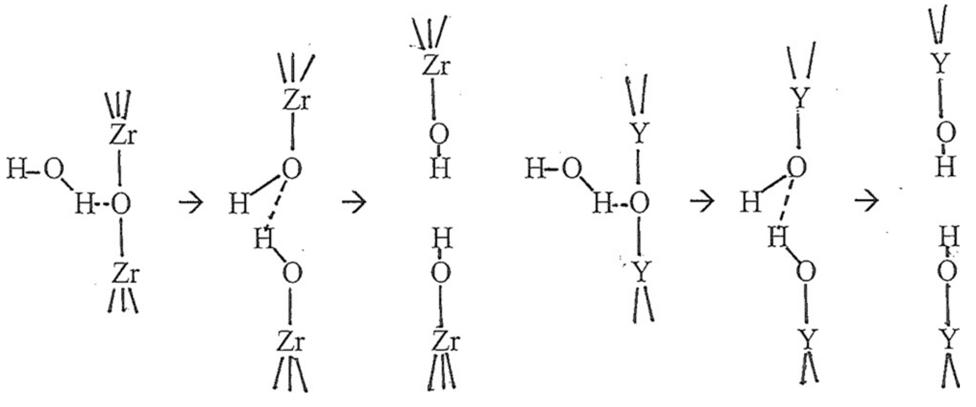

Fig. 9. Schematic of interaction of ZrO_2 and Y_2O_3 with water steam (similar to Sato and Shimada [41]).

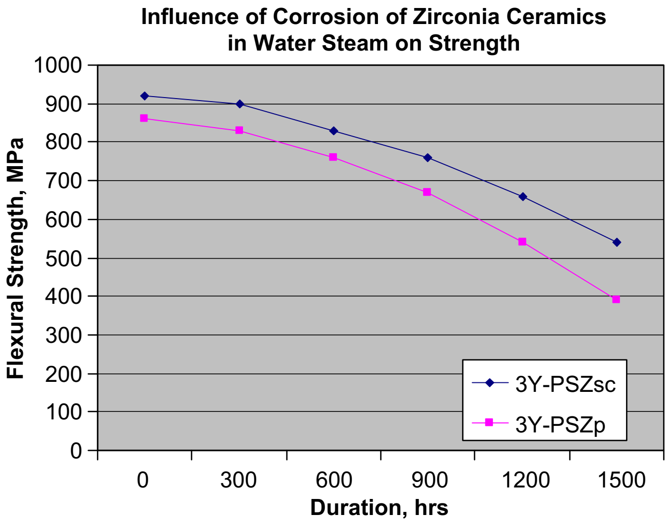

Fig. 10. Influence of corrosion in water steam on strength of Zirconia ceramics made by slip casting (sc) and uniaxial pressing (p). Testing conditions: temperature 350 °C, pressure 12 MPa.

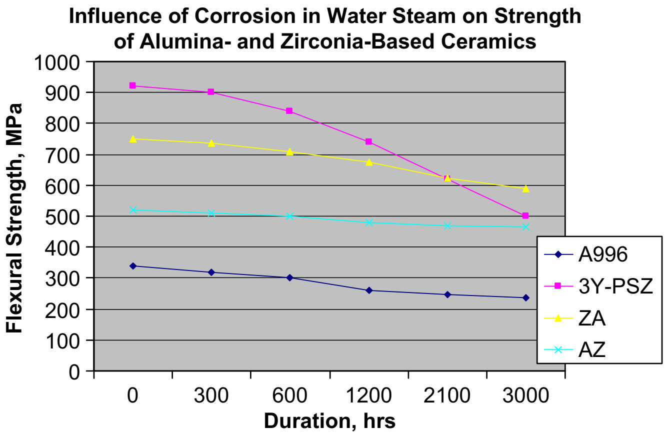

Fig. 11. Influence of corrosion in water steam on strength of some Alumina- and Zirconia-based ceramics (Alumina A996, $3Y_2O_3$—Partially Stabilized Zirconia, Zirconia–Alumina ZA and Alumina–Zirconia AZ), all slip cast samples. Testing conditions: temperature 250 °C, pressure 10 MPa.

a higher rate of the hydrolysis of Y_2O_3 and ZrO_2 with possible formation of the friable Y- and Zr-hydroxides on the grain boundaries, which occur not only on the surface of the samples but deeper. As it was shown by Ho and Wei [39] conducted the studies with 3Y–TZP powders, the amount of the monoclinic phase increases exponentially with increasing aging time and temperature. The influence of the forming method on the structure, properties and corrosion resistance studied for alumina ceramics (considered above) is fair for zirconia ceramics. Similarly to alumina ceramics, zirconia ceramic samples made by slip casting demonstrated a lower level of degradation in comparison with pressed samples that can be explained by more homogeneous microstructure, lower internal porosity and flaws.

It was also noted that, additionally to the facilitation of the *t*-to-*m* phase transformation at the long action of the water steam at elevated temperatures and pressures, some trend of the uneven zirconia grain growth or less structure homogeneity may be observed. It means that, at these conditions, some grains become smaller, but some grains enlarge. It may be dealt with the possible formation of friable hydroxides on the grain surfaces and with volume change and cracking occurrence, which create the "room" for the grains re-orientation. It was difficult to quantify this loss of the homogeneity, it was general observation. The occurred loss of homogeneity also leads to the loss of mechanical properties of the ceramics.

Opposite to zirconia ceramics, zirconia-alumina (ZA) and alumina-zirconia (AZ) ceramics consisted of alumina and Y_2O_3-partially stabilized zirconia (the major phase is zirconia or corundum, respectively) demonstrated lower extents of the strength decrease under similar conditions (Fig. 11), and hence higher corrosion resistance. It is especially seen for AZ ceramics contained the alumina matrix. These data have a good correlation with the results obtained by Thompson and Rawlings [45] for zirconia toughened alumina ceramics tested in hydrochloric acid. The increase of corrosion resistance of AZ and ZA ceramics can be dealt with the protection of the tetragonal zirconia phase by alumina grains and with the absence of the glassy phase and impurities, which are leached first from the grain boundary area. As noted, slower *t*-to-*m* transformation and retarded related crack formation are observed. No crack formation for the AZ ceramics was observed after testing at more than 3,000 h.

8. Influence of wall thickness of cylindrical samples on integrity and strength at corrosion

Ceramic components have to work, in many cases, under the joint action of mechanical tensile forces and corrosion, and the behavior of the components is important to predict their integrity and service cycle. In this case, the chemical interaction between the aggressive media and ceramics increases; less force is required to break the ceramics. In order to increase the integrity and service life of ceramic components, a wall thickness may be increased to "compensate" the corrosion. However, this is fair if corrosion occurs only from the surface. In the cases of the conditions when corrosion may occur not only from the surface but also through the volume, as in the case of water steam, the increase of thickness may lead to intensifying of corrosion in the material, and the service cycle will not be enhanced. This was confirmed by the testing of alumina ceramic samples with different sizes at the considering conditions. The influence of the sample size on the change of mechanical properties at corrosion may be in a good agreement with the statistical theory of strength of brittle materials. Based on this theory applying the Weibull analysis [46], it can be written:

$$\sigma_1/\sigma_2 = (V_2/V_1)^{1/m} \quad (11)$$

where σ_1 and σ_2 are the failure breaking stresses of the material at their volumes of V_1 and V_2, m is the constant of the material characterizing its structural homogeneity.

This formula may be modified for the strength (σ) depending on volume (V) as

$$\sigma = A/V^{1/m} \text{ or } lg(\sigma) = lg(A) - (1/m)lg(V) \tag{12}$$

where A is a constant.

The graphical expression of the dependence of $\sigma = f(V)$ in the logarithmic axes will give a straight line.

The influence of corrosion resistance of alumina-mullite, alumina (A997) and alumina-zirconia ceramics under tensile forces was studied for the samples with a tubular shape with a bottom (cups). A wall thickness of the components varied from 3 to 10 mm. The tests were conducted in water steam of temperature 250 °C and pressure 4–17 MPa during 300 h. Tangential tensile stress (θ_t) was calculated using a formula:

$$\theta_t = P({R_1}^2 + {R_2}^2)/({R_1}^2 - {R_2}^2) \tag{13}$$

where P—pressure of steam inside the tubular sample, R_1 and R_2—outside and inside radii, respectively.

The accuracy of the tensile stress calculation is reduced when the material is subjected by the corrosion, particularly it is dealt with deviations of the inside dimensions (e.g. R_2) of the samples due to corrosion.

As expected, corrosion occurred more intensively for corundum-mullite ceramics in comparison with high alumina and alumina–zirconia ceramics due to leaching of the silicate-based glassy and crystalline phases and partial transformation and decomposition of mullite. In all cases, the depth of corrosion increases with the increase of pressure of the steam, and the corrosion is higher for the thicker wall of the sample (Fig. 12).

The constant of the corrosion rate (K) was defined in accordance with a formula:

$$K = (\Delta h/h)t^{0.5}, \tag{14}$$

where Δh—depth of corrosion, h—wall thickness of a sample, t—duration of testing

The obtained results of the study of the corrosion process kinetics showed that, at 250 °C, the constant of the corrosion process is proportional linearly to the steam pressure up to ~10 MPa, but then, at higher pressures, this dependence changes. With the increase of the wall thickness, the slope of the line $K = f(P)$ decreases, but this slope has a minimal change at the wall thickness of 8–10 mm (Fig. 13).

At the same pressure, temperature and duration, corrosion increases with increase of a wall thickness, although mechanical stresses decrease. The increase of corrosion with a wall thickness may be explained by the point that the concentration of the water steam changes from the inside wall to the outside wall of the tubular sample being at pressure, and, as a thicker wall, the concentration of the diffusing steam changes smoother, i.e. the concentration of the steam is higher at the same depth when a wall thickness is higher. Also, in the case of greater wall thickness, there is higher possibility of the processing defects (pores, flaws, etc.) occurrence, which negatively affect mechanical strength and corrosion resistance. At the same wall thickness, the depth of corrosion changes depending on the tensions in the wall of the sample. This change has a linear character, and it depends on the pressure of the corrosive media.

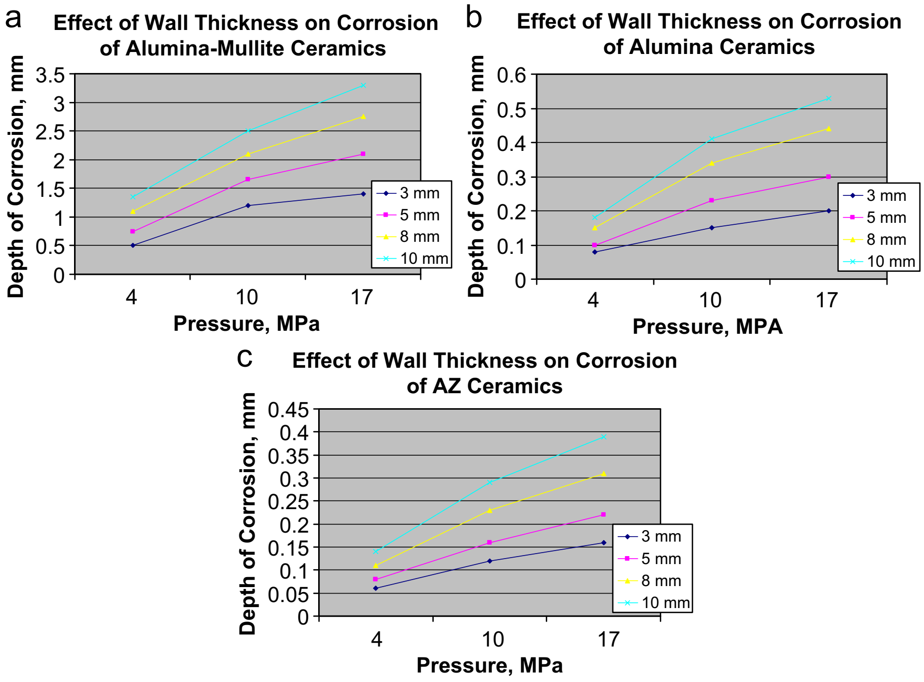

Fig. 12. Effect of wall thickness of Alumina–Mullite (a), Alumina (b) and Alumina–Zirconia (c) Ceramic samples on corrosion in water steam. Testing conditions: temperature 250 °C, pressure 4–17 MPa, duration 300 h. Wall thickness—3, 5, 8 and 10 mm.

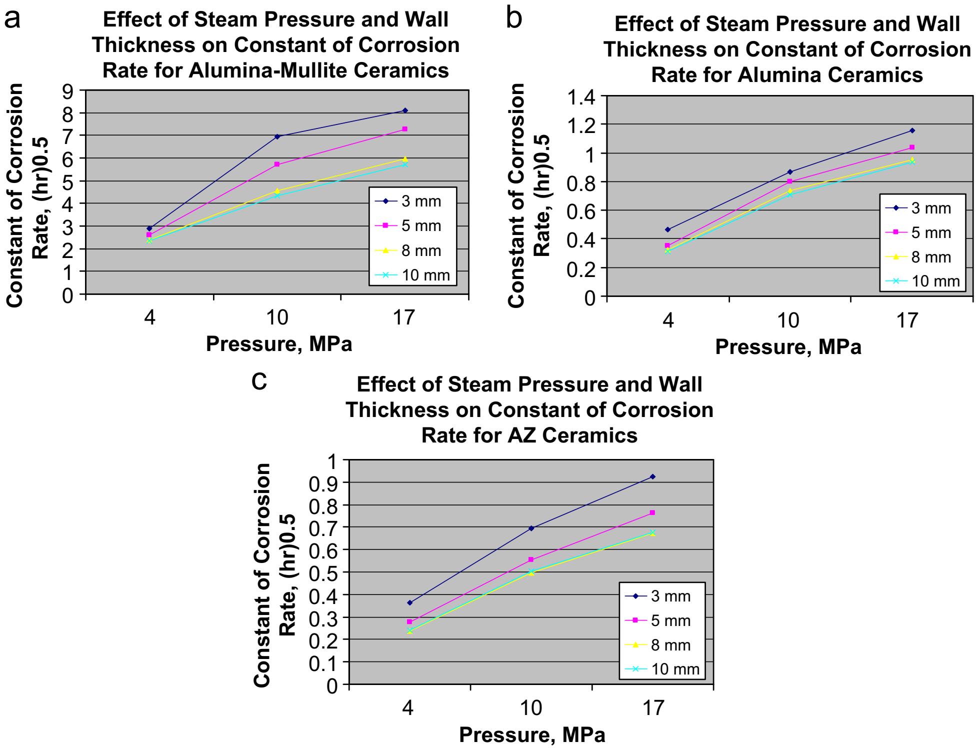

Fig. 13. Effect of steam pressure and wall thickness of Alumina–Mullite (a), Alumina (b) and Alumina–Zirconia (c) Ceramic samples on constant of corrosion rate. Testing conditions: temperature 250 °C, pressure 4–17 MPa, duration 300 h Wall thickness—3, 5, 8 and 10 mm.

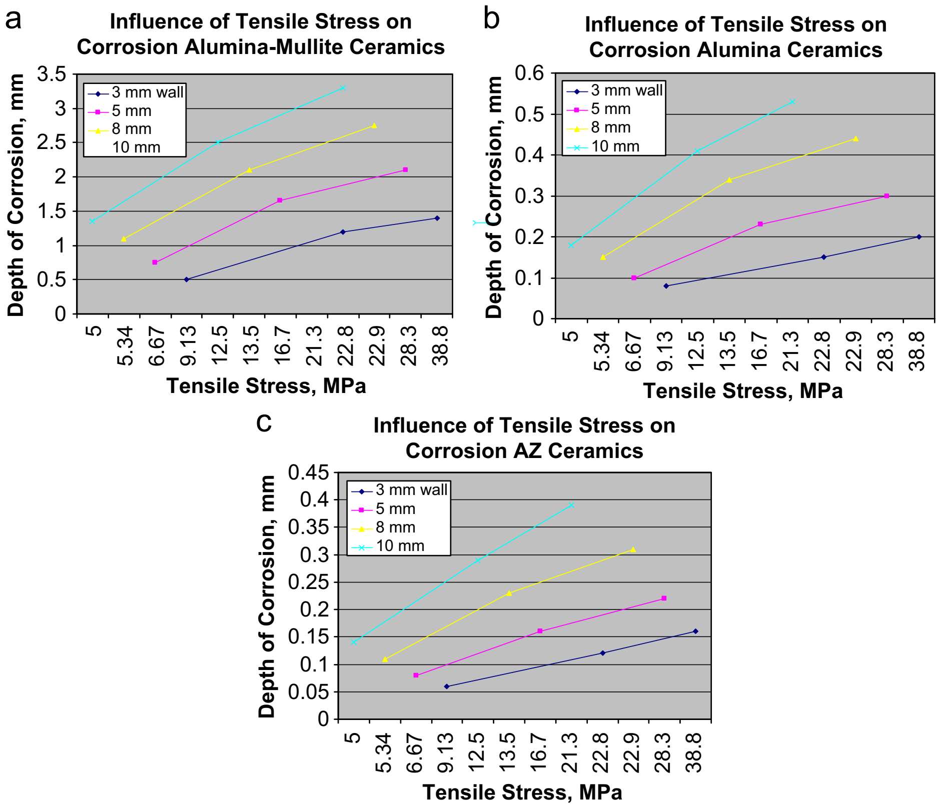

Fig. 14. Effect of tensile stress on corrosion for different wall thickness for alumina–mullite (a), Alumina (b) and Alumina–Zirconia (c) Ceramics. Testing conditions: temperature 250 °C, pressure 4–17 MPa, duration 300 h. Wall thickness—3, 5, 8 and 10 mm.

With some assumption, at relatively low stresses, the empirical equation connecting the depth of corrosion with the calculated tensile stresses in the wall of tubular samples, based on the obtained graph (Fig. 14), may written, as

$$\Delta h = K_1 \theta_t \tag{15}$$

At the higher pressures (over 10 MPa) and related tensile stresses, the slopes at the graphs (Figs. 12–14) become lower with more parabolic behavior.

Real ceramic components may contain different stress concentrators dealt with manufacturing, design and application features. These stress concentrators (from the macro-level) will affect both mechanical behavior of the components at the application conditions and the ability of the ceramic components to withstand corrosion and wear. The microstructure features of the ceramics, including grain shapes and sizes, stresses occurred between grains of different crystalline phases, internal porosity (i.e. from the micro-level) will also affect mechanical behavior and corrosion and wear resistance and their joint influence.

9. Some industrial results with water-steam resistant products

Change of properties, e.g. mechanical strength, of oxide ceramics after exposure in highly corrosive environments, such as water steam of supercritical parameters, of course, depends on actual testing conditions, and it is difficult to make a direct comparison between the data obtained in different conditions, especially to compare with the data from other researchers. However, the major principles of the influence of corrosion in water steam on mechanical properties may be used for the materials selection and consideration of their behavior in extreme environments. High alumina ceramics with Al_2O_3 contents of greater than 99.5 wt% and a microcrystalline structure with practically no glassy phase were successfully used as the structural elements and electrical insulators in the nuclear reactors under the action of water steam (Fig. 15a), as mentioned earlier. These ceramic components also demonstrated high radiation resistance in actual application conditions [2,12,13]. This type of alumina ceramics was also successfully used in the oil and gas and power generation applications when water steam, mechanical loads and wear took place (Fig. 15b), as well as for manufacturing of boiler protection tubes (ferrules). Y-PSZ and AZ ceramics with high mechanical properties (strength, hardness, fracture toughness) was used for manufacturing of the components for the oil&gas applications, including for the equipment in the SAGD process (AZ ceramics) (Fig. 15c-e); the AZ components had rather large dimensions, e.g. ~100–250 mm diameter, ~8–15 mm wall thickness and

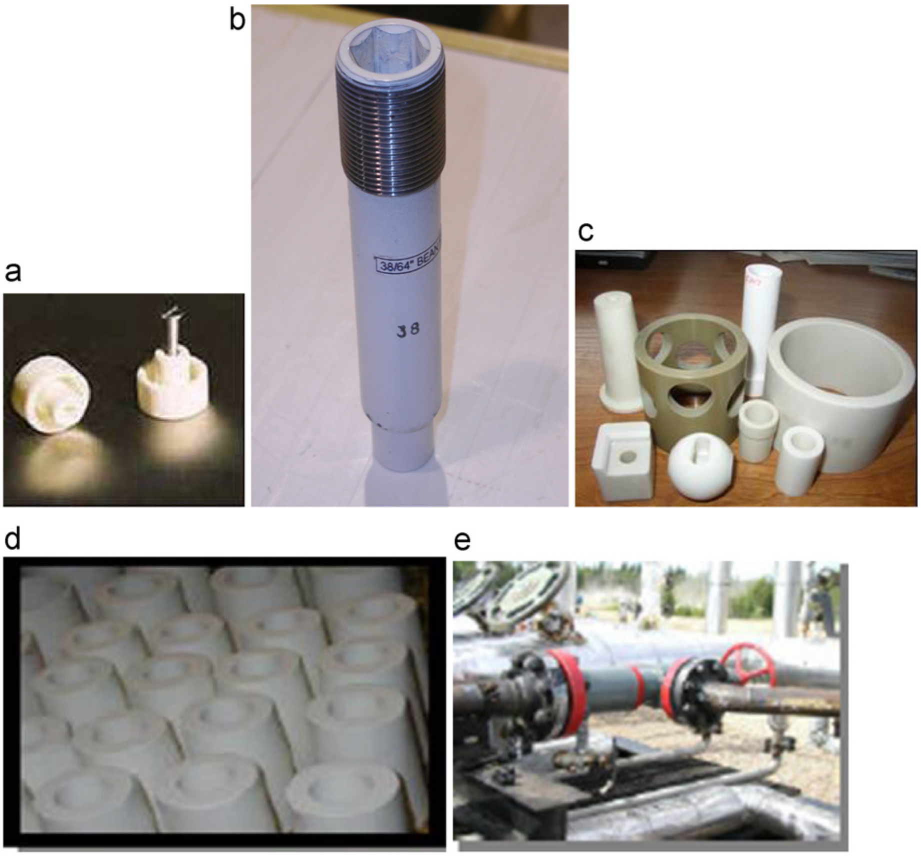

Fig. 15. Corrosion resistant Alumina (a, b), Zirconia (c) and Alumina–Zirconia (d) Ceramic components and piping system for SAGD equipped with Alumina–Zirconia ceramic components (e).

~100–300 mm height (Fig. 15d). These components were successfully employed for more than 2 years working in severe abrasive, erosive, corrosive and cavitation conditions [16,47]. The zirconia, alumina-zirconia and high-alumina ceramics also demonstrated high performance as the bearings, components of the valve systems (e.g. flow control systems) and some others, where they had to work at elevated pressures, frictions and steam corrosive media. The ceramic components were manufactured using the technologies provided a rather high level of homogeneity and microcrystalline structures with low impurity levels, which could be obtained from the commercially available starting powders, with minimization of the contaminations related to the ceramic processing.

When ceramic components have to work under mechanical loads in conjunction with wear and corrosion, specific properties of ceramics, such as brittleness and relatively not superior flexural and tensile strength, which are basically lower than for steels and hard alloys, have to be taken into account. Because of this, at the ceramic component design, the compressive loads need to be dominated over the tensile loads. Strengthening of the components may be attained not by a simple increase of the wall thickness of the components, but by particular designing, preliminary creating of compression stressed conditions, special surface treatment, coatings with particular coefficient of thermal expansion, as well as by selection of the most reliable materials, which can withstand the most severe application conditions and which may be installed to the most critical position of the devices. For example, special conical nozzles designated for the work under the action of water steam of supercritical parameters in the oil&gas applications were designed using high alumina ceramics but the "final" cone where the steam pressure achieved the maximal values (i.e. with the most critical conditions) was made of alumina-zirconia ceramics. This design provided higher integrity in comparison with the design based on the cones made of the only alumina ceramics.

10. Conclusion

Under the action of water steam of "supercritical" conditions (at elevated temperatures and pressures), the intergranular corrosion occurs in advanced oxide ceramics with weakening of the bonds between the grains that leads to the friable texture and to decrease of mechanical properties. It was confirmed that highly dense alumina ceramics and alumina-zirconia ceramics have high corrosion resistance in water steam at "supercritical" conditions. The highest level of corrosion resistance and minimal mechanical degradation, including under the joint actions of corrosion and mechanical loads, are inherent to the materials with minimal contents of impurities and a glassy phase and with microcrystalline structures obtained by the technology providing a minimal extent of non-homogeneity and internal micro-defects. High-alumina ceramics with Al_2O_3 contents of greater than 99.5 wt% can be successfully used as the structural elements and electrical insulators in the nuclear reactors, as well as in oil and gas and power generation applications, under the action of water steam. Alumina–Zirconia ceramics can be successfully used in the SAGD process and other extreme applications for the extended time where corrosion and high mechanical loads are applied as alumina grains preserve the Zirconia phase from the corrosion-related phase transformation and associated rather lower mechanical properties degradation.

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