# Stabilization of Porosity in Reaction Bonded Aluminum Oxide (RBAO) by Coarsening in a Reactive Atmosphere

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**Abstract**

A coarsening treatment in an HCl containing atmosphere was performed to stabilize the porosity of $Al_2O_3/ZrO_2$ composites up to elevated temperatures. There is minimal shrinkage during the reactive coarsening treatment and the porous microstructure is stable during subsequent heat treatments. The reaction bonding of aluminum oxide (RBAO) process was used to fabricate the samples. Coarsening was investigated as a function of initial density (40-60 % TD) and coarsening temperatures (1250-1400°C). After the HCl coarsening step, samples were sintered in air to determine the effect of coarsening treatment on pore stability. Up to the temperature of the coarsening treatment no further densification is observed. Above the HCl coarsening temperature densification is significantly retarded. Thus, it is shown that the porosity in RBAO can be stabilized by heat treatment in a 10 vol % HCl containing atmosphere. During the coarsening treatment in HCl at 1300°C, 1350°C and 1400°C little densification was observed ($\Delta \rho \leq 2$ % TD) in comparison with the densities that result from sintering reaction bonded samples in air at 1350 °C ($\Delta \rho \sim 5$ to 8 % TD). Therefore, the HCl coarsening is a promising approach to adjust a desired level of porosity for high temperature applications of porous materials. It is postulated that at a given density, the coarsened materials should exhibit increased strength compared to un-coarsened materials due to increased contact area between the particles.

**Keywords:** Reaction bonding, sintering, density, coarsening.

## 1. Introduction

Many applications of ceramics require high levels on porosity. Specific examples are filters, catalysts, and electrodes for electrochemical systems (e.g. fuel cells) which require high permeability and high surface areas [1-3]. In addition, porous materials are also used as precursors to fabricate advanced metal/ceramic composites with interpenetrating networks by melt infiltration [4-5]. Finally, in oxide fiber reinforced oxide matrix ceramic matrix composites (CMCs), controlled porosity in the matrix is used to ensure weak bonding at the fiber-matrix interface, a necessary condition for high toughness and damage tolerant CMCs [6-8]. However, porosity in ceramic bodies is detrimental to their mechanical properties and therefore the optimization of porosity to get the functional properties while maintaining adequate strength is an active area of research.

Further, if these porous materials are designed for use at high temperatures, the pores must be stabilized to avoid further densification during application. Thermodynamically, the stability of highly porous microstructures is controlled by the radius of curvature at particle-particle contacts [9] and the strength is controlled by the solid-solid contact between particles [10-11]. Therefore, microstructural stabilization procedures that decrease the radius of curvature of the pores and increase contact area between particles should lead to pore stability and improved mechanical properties [12-13].

To find a treatment to stabilize porosity at high temperatures one must look at the basics of sintering. The fundamentals of sintering have been investigated since the 1950s resulting in a good understanding of the thermodynamics and kinetics of sintering. The progress and the status have been well documented in review articles and textbooks including a comprehensive review [9]. Fundamentally, the driving force for sintering is the reduction in surface area and overall surface energy of the system accomplished by both the reduction of the solid-vapor interface area (for example by pore surface smoothing) and replacement of the solid-vapor area by the lower energy solid-solid surface area. Initially, during sintering, interparticle necks form quickly, often during heat up in normal sintering cycles, by the surface diffusion or vapor phase transport of atoms from pore surface to interparticle contacts to achieve local equilibrium. Neck formation rapidly increases the elastic modulus of the porous body without significant linear shrinkage or densification [12]. These processes are collectively referred to as *coarsening processes*. At higher temperatures significant volume and grain boundary diffusion of atoms occurs from inter-particle boundaries to the interparticle necks and particle centers approach as the body begins to densify and porosity decreases. These processes are collectively called *densification processes*. Coarsening and densification compete for the available driving force from reduction in surface area. In general, and especially for the early stages of sintering, six possible combination of atom source, sink and transport paths occur (referred to as *mechanisms*). Three of these mechanisms in which the source of atoms are pore-solid surfaces do not contribute to densification but coarsen the microstructure. In the process, these mechanisms reduce the overall driving force available for further coarsening and densification (e.g. by Ashby [14]). Therefore, one logical approach to stabilize porous microstructures is to promote coarsening mechanisms.

To stabilize porosity, regimes of processing conditions must be found which promote material transport from surface sources. In their pioneering work, Readey and co-workers showed that vapor phase transport can be enhanced using reactive atmospheres, such as HCl, during sintering [15-18]. Reactive atmospheres can increase the partial pressure of the diffusing species making vapor phase transport the dominant mass transfer process. For example, in the presence of HCl, $Al_2O_3$ reacts to form gaseous aluminum chloride according to [19]:

$$Al_2O_{3\,(s)} + 6HCl_{(g)} \Leftrightarrow 2AlCl_{3(g)} + 3H_2O_{(g)}$$

while zirconia is likely to form:

$$ZrO_{2(s)} + 4HCl_{(g)} \Leftrightarrow ZrCl_{4(g)} + 2H_2O_{(g)}$$

Material transport occurs from the surface of particles to the particle-particle neck, thereby coarsening the microstructure with little or no densification [15-18]. This reactive vapor phase assisted coarsening has also been demonstrated for mullite and zirconia matrices by Haslam and Lange [20].

Reaction Bonded Aluminum Oxide (RBAO) is a zirconia toughened alumina (ZTA) that starts with a mixture of metallic aluminum, $Al_2O_3$ and $ZrO_2$ and uses a controlled oxidation of the aluminum to form the final ceramic [21-24]. The oxidation happens mostly below the melting temperature of Al in a heat treatment that avoids the uncontrolled Goldsschmidt reaction that is usually expected [25]. After reaction which is completed at 1000 $^oC$ the microstructure is characterized by the newly formed nano size alumina and the $Al_2O_3$ and $ZrO_2$ of the precursor mixture and can be sintered to full density at 1550 $^oC$ [26].

RBAO has excellent mechanical properties, green machinability due to the ductile aluminum in the grey state, and near-net shape processing due to the volume expansion of the aluminum upon oxidation. The RBAO process is also robust, allowing the use of low-cost starting materials, and easy control of green and reaction bonded densities. The processing and the properties of this material have been reported in detail elsewhere [27]. In addition, porous RBAO is a potential matrix-material for oxide fiber/oxide matrix composites [27-29]. The porous matrix results in weak interfacial bonding between the fiber and the matrix leading to debonding and fiber bridging [30]. Porous RBAO has also been investigated as substrate material for ceramic membranes [31].

Due to its attractive properties, RBAO continues to be investigated. In a recent study, near-net shaped $Al_2O_3$ porous ceramics were produced by combination of the additive manufacturing (binder jetting) and RBAO process [32]. The powder formulations were composed of stearic acid coated Al powder and dextrin coated $Al_2O_3$ powder with different volume ratios. After the binder jet printing process, the specimens were subjected to RBAO process, in which they were heat treated from room temperature to 1200 °C, in an oxidative atmosphere. The flexural strength increased about 20 % with an increase in Al volume ratio from 0.25 to 0.50. This increase had no influence on apparent porosity of 64% and averaged density of 1.35 g $cm^{-3}$ [32]. High strength porous $Al_2O_3$ ceramics were also prepared by indirect selective laser sintering and reaction bonding to form random pores with increased strength [33].

Finally, RBAO has been used to join ceramics without applying any external pressure. $Al_2O_3$ green bodies were joined with the use of an Al/ $Al_2O_3$ powder mixture as an interlayer at temperature of 1650 $^oC$ for 2 h. The joined alumina ceramics have similar strength as monolithic alumina ceramics [34].

As mentioned earlier, for many applications (e.g., CMCs and membranes), a porous body in which the porosity is stable at operating conditions is required. Given the advantages of RBAO articulated above, in this paper, we investigate the influence of dilute HCl-coarsening treatment on the densification behavior of RBAO both during the coarsening treatment and during subsequent heat treatment. We report on the effect of coarsening treatment parameters on the stabilization of porosity in reaction bonded $Al_2O_3$ /$ZrO_2$ composites at elevated temperatures. The effect of coarsening in dilute HCl is compared with coarsening in air and the effect of green density has been investigated. Finally, it should be emphasized that we have used 10 vol % HCl which is significantly safer to handle, compared to 100 % HCl, in standard laboratory and industrial conditions.

## 2. Experimental Procedure

The powder used in this investigation for reaction bonding was produced by high-speed attrition milling of Al, $Al_2O_3$ and $ZrO_2$ powders (Pearl mill PML-H/V, Draiswerke GmbH, Germany) with 1 mm Zirconia balls in ethanol (3.5 hrs. at 3,700 rpm). The compositions of starting powder compact and the reaction bonded materials used in this study are given in Table 1 and complete process flow is shown Figure 1.

After attrition milling, the powders were uniaxially cold-pressed (HYP/SK, HSV, Maschinenfabrik Velbert, Germany) in a hardened steel die with a double acting punch to form bars of approximate dimensions 6 mm x 6 mm x 43 mm. To produce compacts with different green densities, the pressure was varied from 10 MPa to 75 MPa. To further increase the density, some samples were cold-isostatically pressed (PW 200 E-KIP, Paul Weber Maschinen- und Apparatebau GmbH, Germany) for 2 minutes at pressures between 75-325 MPa. Sample densities were varied to have an additional degree of freedom to adjust the final density. Using this procedure, green samples with a broad green density range, from approximately 38 % to 65 % of the theoretical density, were produced.

The reaction bonding step converts the green powder compact to a ceramic body. In this step, the aluminum is oxidized to form new $Al_2O_3$ grains which bond the $Al_2O_3$ and $ZrO_2$ powder in the green compact. The oxidation of aluminum begins around 300 °C and is completed by 1000°C. For further details on reaction bonding cycles please see [24]. This cycle has been optimized to achieve full conversion of aluminum to alumina. It includes a 12 hrs. hold at 450°C to allow a controlled aluminum oxidation step. The maximum temperature was set to 1000°C to avoid significant densification during this step. The complete thermal profile for reaction bonding is shown in Figure 2(a).

In Figure 2(b) the effect of compaction process (combination of uniaxial and isostatic pressing) on the green density (before reaction bonding) and the reaction bonded density (i.e., density after heat treatment shown in Figure 2(a)) is shown. Note that, for this reaction bonding cycle, there is a direct almost linear correlation between the green and the reaction bonded density. It is worth noting that since the sample composition changes during reaction bonding (due to oxidation), the theoretical density of the sample increases from 3.945 g/cm$^3$ to 4.250 g/cm$^3$. In addition, the volume fraction of porosity is approximately, unchanged. This is because, due to the low temperature, there is insignificant densification in this reaction bonding cycle. Thus, this process is an effective way to make porous $Al_2O_3/ZrO_2$ composite ceramics with a broad range and controlled level of porosity (from approximately 35 % to 65 % porosity). After the reaction bonding step, the samples were cut, using a slow speed diamond saw, into bars of approximately 6x6x10 mm. These samples were used for further investigation.

For coarsening, the samples were heat treated in HCl containing atmosphere. The coarsening treatment was conducted in a tube furnace, which was evacuated and refilled with 10 vol % HCl in $N_2$ at atmospheric pressure. The system was then opened to a gas bubbler to keep the pressure constant during the heat-up. Samples were coarsened at temperatures between 1250°C and 1400°C with holds for two and four hours. To quantify the effect of the coarsening treatment on pore stability, samples were subsequently sintered in air and compared to samples with the same sintering treatment but without HCl coarsening. Sintering temperatures and times between 1250°C and 1550°C, with a heating rate $\dot{T}$ of 10 K/min, and hold times of 1, 2, 12, 48 and 50 hours were investigated.

The densities of the specimens were measured after reaction bonding, coarsening, and sintering by the Archimedes method. The procedure used is a slightly modified version of the procedure in ASTM C 20-92. Specifically, after determining the dry weight (D), the samples were immersed in boiling water for two hours followed by soaking for 12h at room temperature. To avoid damage, the samples with the highest porosity were only soaked in hot water without boiling. This was followed by the measurement of the suspended weight (S) and saturated weight (W). These three weights were used to calculate the bulk density according to ASTM C 20-92. Density measurements were also verified by the geometric method. Microstructure was characterized by examining gold coated fracture surfaces in a scanning electron microscope (JEOL 5200, JEOL, Japan). Fracture surfaces, rather than polished surfaces, were used due to the fragility of the porous samples and to allow examination of the particle-particle necks.

## 3. Results and Discussion

### 3.1 Free sintering in air

The sintering characteristics of RBAO have been studied in detail for green densities above 60 % of the theoretical density (%TD). From dilatometer studies it is known that densification of RBAO starts at 1200 °C and reaches significant densification rates above 1350 °C to 1550 °C.

In this study the intention is to stabilize a desired level of porosity at elevated temperatures and therefore a wide range of green densities was investigated. To investigate the effect of heat treatment on the stability of the porosity, the reaction bonded samples were sintered in air at 1550 °C for different times. Figure 3 shows the densification behavior of RBAO for reaction bonded densities between 39 %TD and 63 %TD. This range represents the attainable reaction bonded densities for the processing parameters used. The sample with the highest density represents the standard powder processing of RBAO and results in sintered density of 98% TD after sintering at at 1550 °C for one hour. For lower starting densities the time for densification increases significantly but does not limit the final density. Even for the lowest reaction bonded density samples (39 %TD) reached a sintered density of close to 95 %TD after sintering for 12 hrs. at 1550 °C.

### 3.2 Coarsening in HCl

Coarsening treatments were conducted in the temperature range of 1250 to 1400 °C in a 10 vol % HCl in Nitrogen atmosphere, just above the temperatures where RBAO starts densifying. Figure 4 shows the density increase in samples of different reaction bonded densified after coarsening treatment in HCl. During the coarsening treatment in HCl at 1300 °C, 1350 °C and 1400 °C (hold time 2 hours) little densification was observed ($\Delta\ \rho \leq 2$ % TD) for all samples. Increasing the coarsening time from two to four hours did not lead to further densification. For comparison, the densities that result from sintering reaction bonded samples in air at 1350 °C for 2 hours are also shown. In this case, the density increased between 5 to 8% for all the samples. These results clearly demonstrate that the presence of 10 vol % HCl prevents densification at temperatures where densification occurs in air.

These results demonstrate that different transport mechanisms dominate at these temperatures in air and in HCl containing environment. These results are in accordance with reported results in the literature. One difference is that here it has been shown this change in mechanism to occur for dilute concentrations of HCl. Based on the results in the literature, it can be inferred that in 10 vol % HCl environment, vapor transport from the surface of the particles to the neck area is the dominant transport mechanism [4, 16, 19].

**3.3 Stability of the porous structure**

To investigate the stability of the coarsened structure, a series of post-coarsening sintering experiments were conducted. Figure 5 shows densities after sintering in air, at 1550 °C and 1hour for as reaction bonded and HCl coarsened samples ($T_{HCl}$ =1300 °C and 1350 °C) as a function of the initial sample density. The HCl coarsening treatment significantly reduces the densification of RBAO. Note that the density of the un-coarsened samples increased by approximately 30% whereas the HCl coarsened samples show a significantly lower amount of densification. Independent of the initial density the final density of HCl coarsened samples is ~20 % lower than of the un-coarsened ones. Densification is also affected by the temperature at which the samples were coarsened. As expected, samples coarsened at higher temperatures were more stable and densified less than those coarsened at lower temperatures. Note that the sintering temperature is higher than the coarsening temperature. To further investigate the stability of the microstructure the sintering time was increased up to 12 hours as shown in Figure 6. These results again confirm the observation that the porosity in coarsened samples is quite stable and although the density during the high temperature heat treatment increases, the increase is significantly lower than the samples that have not been coarsened in HCl.

Figure 7 plots the densification after a HCl coarsening treatment relative to uncoarsened samples. It shows that for the samples coarsened at 1300 °C the density changes during sintering at 1550 °C is only 60 % of the uncoarsened samples. With increasing the coarsening temperature to 1350 °C this is further reduced to about 40 % of the value without HCl coarsening. This is independent of the starting density. In Figure 8, the sintered density changes of samples coarsened in dilute HCl at 1350 °C, for 2 hours, normalized by the density change of uncoarsened samples for different sintering times is plotted. The sintering treatment was at 1550 °C, for various times. These results also clearly show the stabilization of the porosity. Even under the most aggressive sintering conditions, 1550 °C for 12 hours, the relative density change for the coarsened samples is in the range of 75 to 85% of the uncoarsened samples. These results clearly show that the coarsening treatment is effective in reducing the densification even at temperatures and times significantly higher than the coarsening treatment. Therefore, it clearly indicates that the coarsening treatment reduces the driving force for sintering.

Finally, Figure 9 shows the densification behavior as a function of time for various combinations of 10 vol % HCl coarsening treatment and sintering cycles. RBAO usually reaches full density when sintered at 1550 °C for one hour. However, after the 10 vol % HCl coarsening treatment at 1300 °C, the time needed to achieve nearly full density increases significantly to 12 hours and to 50 hours after coarsening in HCl at 1400 °C. Figure 8 also shows that if the sintering temperature is equal to the coarsening temperature no densification can be observed. This was shown up to temperatures as high as 1400 °C, the maximum coarsening temperature used in this study.

From these results, it can be concluded that HCl coarsening stabilizes porous microstructures for extended times for temperatures up to the coarsening temperature. Exposure to temperatures greater than the coarsening temperature will result in densification, but at a much slower rate than for untreated samples. The densification rate has been reduced due to a reduction in the driving force for sintering (neck curvature) during the coarsening step. The coarsening and subsequent sintering behavior discussed above can be correlated with the sample microstructures shown in Figure 10. Comparing the reaction bonded (Figure 10a) and coarsened (Figure 10b) microstructures, the maximum grain size remains almost the same, however the shape of the grains changed from an angular to a more spherical shape with distinct necks. Small grains have also disappeared. After sintering in air for one hour at 1550 °C, the microstructure of the as reaction bonded samples shows a wide range of different grain and pore sizes with some agglomerates of large pores as seen in Figure 10c. The pre-coarsened sample exhibits a regular and much more homogeneous distribution of grains and pores (Figure 10d). It should be noted that the density of the sample in Figure 10d is 20 % less than that in Figure 10c due to the HCl coarsening retreatment. During coarsening large grains and neck regions grow at the expense of small grains, creating a more uniform microstructure. It should be noted that oxide ceramics undergo active corrosion in halogen-containing gases such as HCl to form gaseous corrosion products only. At high temperatures, such corrosion reactions are controlled by gaseous diffusion of the product gases away from the solid surface [19]. Thus, no chemical changes are expected in the properties of the solid phase before and after HCl and heat treatments.

## 4. Conclusions

In this study, we developed a processing approach to make $Al_2O_3/ZrO_2$ composite by reaction bonding of aluminum oxide (RBAO) with a broad range of porosity. It has also been shown that there is no change in porosity during the reaction bonding step and therefore it is possible to control the porosity of the RBAO composite. We have also investigated the effect of coarsening treatments in 10 vol % HCl containing atmospheres on the densification of RBAO $Al_2O_3/ZrO_2$ composites. It was shown that insignificant densification occurs during this treatment. Even at temperatures up to 1400 °C, the presence of HCl significantly retards the densification of the $Al_2O_3/ZrO_2$ composites for a broad range of initial densities of RBAO $Al_2O_3/ZrO_2$ composites.

The stability of the porous structures in air, was determined by investigating the sintering behavior of the coarsened samples at temperature equal to and greater than the coarsening temperature. Up to the temperature of the coarsening treatment, no densification is observed. This demonstrates the potential to stabilize porosity at temperatures where materials without the coarsening step would not show a stable porous microstructure. At temperature greater than the coarsening temperature, samples densified, but at a much slower rate than the samples that had not been coarsened. The hindered densification can be explained due to a reduction in the driving force for densification during coarsening. The coarsening treatment produced samples with larger particle-particle necks most likely by vapor phase transport. The coarsening treatment also homogenized the grain size and pore structure.

In summary, HCl coarsening is a promising approach to adjust a desired level of porosity for high temperature applications of porous materials. Such materials should also exhibit increased strength and lower strength variability compared to un-coarsened materials of similar porosity due to increased contact area between the particles and uniform microstructure. This study has also demonstrated that a dilute mixture of HCl (10 vol %) is sufficient to realize this effect. Further investigations are needed to determine the minimum level of HCl needed to observe the coarsening and stabilization effect. In addition, the strength and strength distribution of coarsened sample should be evaluated and compared to those of uncoarsened samples (at the same density).

**Declaration of competing interest**

The authors declare no competing interest.

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## List of Figures

**Figure 1:** Flow chart of the experimental research reported in this paper.

**Figure 2 (a):** The heat treatment profile to make reaction bonded aluminum oxide (RBAO).

**Figure 2 (b):** The range of densities before and after reaction bonding at 1000 °C. The density of RBAO is almost the same as the green density. Using a combination of uniaxial and cold isostatic pressing, porosities between 37 and 62 %, in reaction bonded $Al_2O_3/ZrO_2$ composites have been realized.

**Figure 3:** Sintered density of RBAO, sintered at 1550 °C for various times, as a function of sample density after reaction bonding.

**Figure 4:** Density change after heat treatment in 10 volume % HCl atmosphere, for 2 hours, at various temperatures. For comparison density change after heat treatment at 1350 °C, for 2 hours, in air is also shown. During heat treatment in dilute HCl, there is almost no change in density while there is significant densification during heat treatment in air.

**Figure 5:** Density after sintering in air, at 1550 °C for 1 hour, for reaction bonded and HCl coarsened samples (Tc =1300; 1350 °C, for 2h) as a function of the initial sample density. Densification is significantly retarded for HCl coarsened sample; the effect is more pronounced for samples coarsened at higher temperature.

**Figure 6:** Sintering in air at 1550 °C after HCl treatment at 1350 °C for different times up to 12h. For temperatures above the HCl heat treatment temperature, densification does occur, but the amount of density change is significantly lower than that of un-coarsened samples.

**Figure 7:** Normalized density changes after sintering in air at 1550 °C for 1 hour for samples coarsened in dilute HCl at 1300 °C and 1350 °C for 2 hours. The normalization is by the density change for the uncoarsened samples.

**Figure 8:** Normalized density changes after sintering in air at 1550 °C for different times for samples coarsened in dilute HCl at 1300 °C and 1350 °C for 2 hours. The normalization is by the density change for the uncoarsened samples.

**Figure 9:** Density change after heat treatment at 1550 °C and at 1400 °C for different times (up to 50 hours) for samples with different heat treatments. The results show that following a short coarsening treatment (2 hours), there is no densification (up to 50 hours) in air at temperature up to the coarsening temperature. The densification at temperature higher than the coarsening temperature is retarded for coarsened samples.

**Figure 10:** Micrographs of RBAO (40%TD initial density) with different heat treatments (a). reaction bonded, (b). 1350 °C HCl coarsened, (c). sintered in air at 1550 °C, (d). 1350 °C HCl coarsening followed by sintering in air at 1550 °C.

## List of Tables

***Table 1****: Compositions of powders used and final RBAO product*

| | RBAO C20 | | |
|---|---|---|---|
| **Sample Condition** | **Al[*] (vol %)** | **$Al_2O_3$ [+] (vol %)** | **3Y-$ZrO_2$ [♣] (vol %)** |
| Green | 45 | 35 | 20 |
| Reaction bonded | - | 82.5 | 17.5 |

[*] AS 081, Eckart-Werke GmbH, Fürth, Germany
[+] CL 3000, Alcoa Industrial Chemicals Europe, Frankfurt/Main, Germany
♣ SF-Extra, Z Tech Corporation, Bow, NH, USA ($ZrO_2$); HCStark Goslar ($Y_2O_3$)