

Research Article

Wetting of Al₂O₃ by Molten Aluminum: The Influence of BaSO₄ Additions

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The effects of BaSO₄ additions on the wetting of alumina by molten aluminum were studied by the sessile drop technique. To study the effect of BaSO₄ decomposition (1100–1150°C), the additions were treated at two temperatures 700°C (973 K) and 1450°C (1723 K), respectively. BaSO₄ additions at low and high temperatures did not improve the nonwetting character of these compositions. However, at higher firing temperature, the formation of BA₆ (BaO•6Al₂O₃) has a nonwetting trend with increasing its content. To address the BA₆, specifically a pure BaO•6Al₂O₃ was produced and tested. It was more nonwetting than the pure alumina. After the analysis of the contact angles for the BaSO₄ and the BA₆ (BaO•6Al₂O₃), it was concluded that these additions to alumina do not inhibit wetting by molten aluminum. In fact, at the addition levels common for refractories, the wetting tendency of molten aluminum is enhanced. Alternative explanations for the effectiveness of BaSO₄ additions to alumina refractories are discussed.

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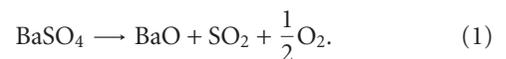
1. INTRODUCTION

The wetting of molten metals on solid ceramics such as described by the liquid/solid contact angle (ϕ) directly affects whether it is possible to use a specific ceramic for many different engineering applications. Potential uses include composites, brazed components, the bonding of ceramics with metals, and the use of ceramics as refractories to contain molten metals [1].

Molten aluminum containment during its production process has used certain chemical additives to alumina refractories starting from late 1970s. These have been suggested to decrease the wetting of the refractory by molten aluminum and thereby reduce the aluminum penetration into the monolithic refractory products. These chemical additives include zircon (ZrSiO₄), barium sulfate (BaSO₄), calcium fluoride (CaF₂), and some glass frits as well. The levels of these additions to the refractories are usually only from 0.5 to about 6 wt% [2–13].

The Handbook of Chemistry and Physics [14] reports that BaSO₄ melts at 1580°C, however prior to melting, it decomposes. The decomposition reaction occurs from about

1100°C to 1150°C:



This reaction defines two temperature regimes for the effects of BaSO₄ additions to Al₂O₃. One is below 1100°C and the other is above 1150°C, the latter after the sulfate has decomposed to the oxide, BaO.

Brosnan [2], in his review of refractory corrosion, has suggested that the BaSO₄ additives to aluminum refractories may act to provide a mechanism for the oxidation of the molten aluminum. This is important if the metal penetrates the exposed surfaces of the refractory. Oxidation could occur through reactions of the type:

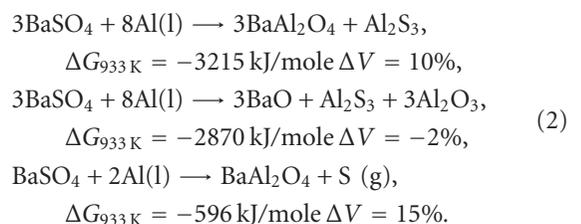


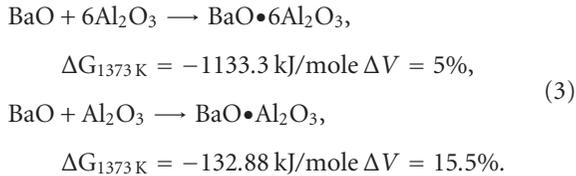
TABLE 1: Activation energies (Q) reported for (2).

Q (kJ/mol)	Sample	Atmosphere	Temperature ($^{\circ}\text{C}$)	Reference
415.8 ± 0.2	Powder	Vacuum	1124	[3]
407.6	Crystal	Vacuum	1154	
383.5 ± 8.4	Crystal	Vacuum	1147–1267	[4]
409.7	Crystal	Vacuum	1177	

These reactions suggest that BaSO_4 can react with molten Al above its melting point 660°C ($\sim 933\text{ K}$) and form stable phases like BaAl_2O_4 (spinel), BaO , Al_2S_3 , and Al_2O_3 .

At temperatures above that of the Al melting point, barium aluminates can be formed after the BaSO_4 decomposes. Although BaSO_4 is reported to melt at 1580°C , the study by L'vov and Ugolkov [3] suggests that the decomposition reaction is kinetically favorable from 1124°C (1397 K) to 1154°C (1450 K). Mohazzabi and Searcy [4] applied mass spectrometry to determine if SO_3 was present in the products of (1). They concluded that the decomposition process is correctly described by (1). Table 1 summarizes some of the kinetic results from these studies [3, 4].

The data in Table 1 suggests that the BaSO_4 decomposition occurs over the temperature range from 1124°C (1397 K) to 1267°C (1540 K). After the BaSO_4 decomposition, the barium oxide may react with alumina to form stable oxide phases. These may include the barium hexaluminate ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$) or the monoaluminate spinel ($\text{BaO}\cdot\text{Al}_2\text{O}_3$), as illustrated in the two following reactions:



As these reactions are highly exothermic, extreme care must be used during experiments to observe or to utilize these reactions.

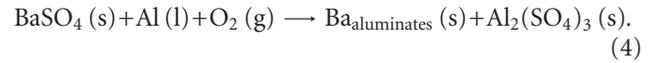
Teiken and Krietz [5] have reported that the addition of 6%- BaSO_4 reduces the penetration of molten aluminum in conventional castables and in low-cement castables. A comparison of these refractories gives the advantage in penetration resistance to the conventional castable. Teiken and Krietz also have suggested that alumina or aluminosilicate refractories are mostly improved for the lining of aluminum-melting furnaces and other refractory containers just from 980°C to 1090°C .

Afshar and Allaire [6] have also studied the additions of BaSO_4 and those of CaF_2 to aluminosilicate castable refractories to reduce their corrosion. They reported that an addition of 7%- BaSO_4 improved the corrosion resistance of refractory samples for firing temperatures at $<1000^{\circ}\text{C}$ (1273 K). For additions of CaF_2 , they reported less efficient corrosion protection after firing below 1000°C . The use of 3.5% CaF_2 actually provoked the formation of large cracks in the refractory, facilitating metal-penetration and enhancing

corrosion. These studies suggest that these additives may be limited to temperatures $<1000^{\circ}\text{C}$ (1273 K).

The addition of BaSO_4 to phosphate bonded, or phosphate-free plastics, ramming mixes, brick, mortar, or castables has been confirmed to reduce molten aluminum penetration and significantly reduces dross and molten aluminum adherence [5–9]. The principal additives effects studied by these researchers were their reactions with molten aluminum and its alloys. Investigators have also suggested that the additives may fill the voids in the refractories and inhibit penetration by reducing porosity at the interfacial contact region between molten Al and additives.

The above empirical corrosion tests were all completed at $<1090^{\circ}\text{C}$ (1363 K) in air or by ASTM guidelines with the cup test. The barium sulfate also can be affected by the partial pressure of oxygen in the presence of molten aluminum as follows:



This reaction is even more exothermic than the previous ones as they are analyzed without any oxygen (2). The Gibbs free energy changes at 1000°C (1363 K) for the formation of barium monoaluminate (BaAl_2O_4) and hexaaluminate ($\text{BaAl}_{12}\text{O}_{19}$) are -4866 kJ/mol and -6620 kJ/mol , respectively. These energies are high and are likely possible to occur in the dross zone of a refractory lining, which contains the reactants for the completion of (4).

The above observations suggest that additions of BaSO_4 to alumina refractories may have two temperature regimes of protection for these refractories. One is below the temperature of the BaSO_4 decomposition reaction at $\sim 1100^{\circ}\text{C}$ and the second is above the decomposition reaction: $>1250^{\circ}\text{C}$. From previous studies, it was confirmed that additions of compounds, such as BaSO_4 to refractories for molten aluminum containment, reduced their corrosion [5–9]. However, the mechanism of this corrosion reduction is not clear. It could be either decreased molten Al wetting of the refractory, or a pore channel blocking effect by Ba-compound formation. To address the wetting aspect of this controversy, this molten aluminum wetting study of the effects of BaSO_4 additions to an alumina was undertaken.

2. EXPERIMENTAL PROCEDURES

Consider a flat, undeformable, perfectly smooth, and chemically homogeneous solid surface in contact with a nonreactive liquid in the presence of a vapor phase. If the liquid does not completely cover the solid, the liquid surface will intersect the solid surface at a contact angle, ϕ or θ , depending on the particular angular definition. The wetting relationship of the surface tensions of the solid-vapor interface (γ_{sv}), the solid-liquid interface (γ_{sl}), and the liquid-vapor interface or surface tension (γ_{lv}) in a sessile drop configuration is usually expressed by Young equation [15]. It can be written either as

$$\cos \phi = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (5)$$

TABLE 2: Chemical analysis of the 1020 aluminum (wt%).

Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Ca	Na	Ga	others
0.15	0.20	0.02	0.03	0.12	0.001	0.005	0.003	0.01	0.006	0.003	0.013	<0.01

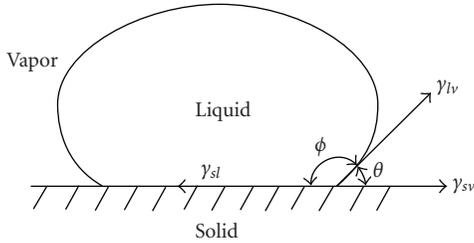


FIGURE 1: Surface energy balance and the contact angle equilibrium definition of the Young equation. Note the two different definitions of the contact angles, ϕ and θ .

or

$$\cos \theta = \frac{\gamma_{sl} - \gamma_{sv}}{\gamma_{lv}}. \quad (6)$$

Referring to Figure 1, the ϕ definition of the wetting contact angle is applied throughout this thesis. Because $\phi + \theta = \pi$, it naturally allows the interchangeable application of both definitions for the wetting angle. Some researchers use θ .

Figure 2 illustrates the definition of (5) using ϕ as the contact angle. When ϕ is equal to 180° , no wetting occurs, and the droplet sits over the solid in point contact. When ϕ is $>90^\circ$, a partial nonwetting condition prevails. Partial wetting occurs when ϕ is $<90^\circ$. However, when the contact angle is equal to 0° , it is understood that complete wetting and droplet spreading occurs over the solid surface.

2.1. Specimen preparation

The effect of BaSO_4 on the wettability of alumina by molten aluminum was studied for several Al_2O_3 - BaSO_4 compositions. One was pure alumina and other three had BaSO_4 additions at the 1, 3, and 5% levels. The specimen preparation consisted of mixing a 99.96% $0.5 \mu\text{m}$ alumina powder with 1, 3, and 5% of a 99.9% BaSO_4 ($1 \mu\text{m}$). Individual 100 g batches were prepared by ball mill mixing for 2 hours using a cylindrical container and spherical alumina balls with a ratio of balls to mix of 3 : 1. The ball-mixing fluid medium was isopropanol. A mix speed of 100 rpm was used. After mixing, the powder was dried at 70°C (343 K) for 48 hours.

The dried powder was then passed through a -325 mesh sieve ($45 \mu\text{m}$) to break up the agglomerates. The resultant powder was weighed for 5 g specimens for axial pressing of ~ 1 inch diameter discs at 150 MPa. Sintering schedules were using a heating rate of $5^\circ\text{C}/\text{min}$ to 700°C (973 K) and to 1450°C (1723 K) for one hour hold each in air.

In addition, the pure $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ phase was produced using same experimental set up and used the theoretical composition of $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ by mixing 27.6 wt%

BaSO_4 with 72.4 wt% Al_2O_3 . To produce the pure BA_6 ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$) phase, the Al_2O_3 - BaSO_4 specimens were sintered using a heating rate of $5^\circ\text{C}/\text{min}$ to 1700°C (1973 K) for one hour hold in air.

The BaSO_4 - Al_2O_3 specimens at different firing temperature were subsequently analyzed by density using the Archimedes method and by X-ray diffraction measurements (35 kV, 25 mA, and $\text{Cu}_\lambda = 0.15406 \text{ nm}$). The surfaces of all ceramic specimens prepared for the wetting studies were semipolished with an SiC # 325 mesh sandpaper to achieve a constant roughness effect.

Aluminum metal specimens were fabricated from a commercial 1020 aluminum ingot provided by Alcoa. The chemical analysis of the Al is shown in Table 2. Impurities were Si, Fe, and Mg, each at the $<0.20\%$ level. The Al test specimens were 0.5 cm diameter cylinders with a height of 0.5 cm. To minimize oxidation during the experiments, the Al specimens were first semipolished with an SiC # 400 mesh sandpaper then ultrasonically cleaned in isopropanol.

2.2. SESSILE DROP EXPERIMENTS

Sessile drop tests of the molten 1020 aluminum on the three different types of BaSO_4 - Al_2O_3 specimens were completed using a commercial sessile drop apparatus manufactured by Centorr Associates, Inc. (Suncook, NH, USA). It is schematically illustrated in Figure 3. The experiment consisted of placing the aluminum metal cylinder on the refractory substrate in the center of the furnace. After closing, the furnace was evacuated to less than 50 millitorrs. An ultrahigh purity argon ($\sim 99.999\%$) was introduced to a pressure of 1000 millitorrs. These vacuum/argon steps were repeated four times to reduce the experimental chamber oxygen level. The sessile drop experiments were then completed in the argon atmosphere to avoid any of the oxide skin effects that have been observed on Al droplets and reported by other investigators [16–25]. Measurements in the sessile drop furnace were under argon gas at ~ 1520 Torr. The partial pressures of several gas species were $P_{\text{H}_2} = 10^{-16}$, $P_{\text{H}_2\text{O}} = 10^{-19}$, $P_{\text{N}_2/\text{CO}} = 10^{-19}$, and $P_{\text{O}_2} = 10^{-17}$ Torr as determined by a gas analyzer (MKS Vision 100-B).

Heating of the test assembly was manually controlled by applying current (mA) to the heating element until the desired temperature was achieved. The actual heating profile is illustrated in Figure 4. It had isothermal temperature holds from 800°C (1073 K) to 1200°C (1473 K) at intervals of 200°C (473 K). Once the solid aluminum cylinder melted during heating, it immediately formed a droplet. A camera lens and a video monitor (black and white) connected with a VCR recorded the experiments. The droplet shape was monitored for 20 minutes at each of the holding temperatures. This length of time, ~ 20 minutes, was the same as that reported by Li [18].

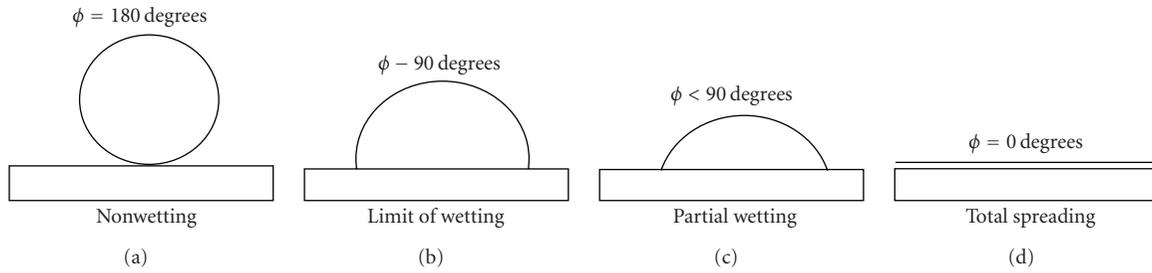


FIGURE 2: Wetting stages resulting from the interaction of a solid and a liquid.

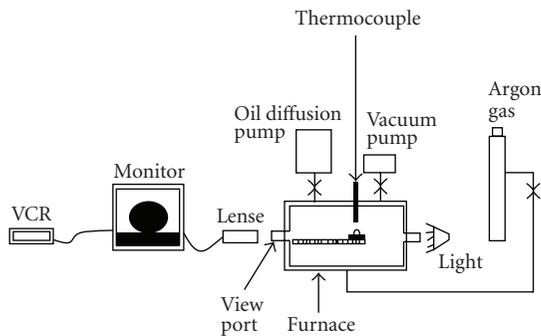


FIGURE 3: Schematic of the sessile drop apparatus.

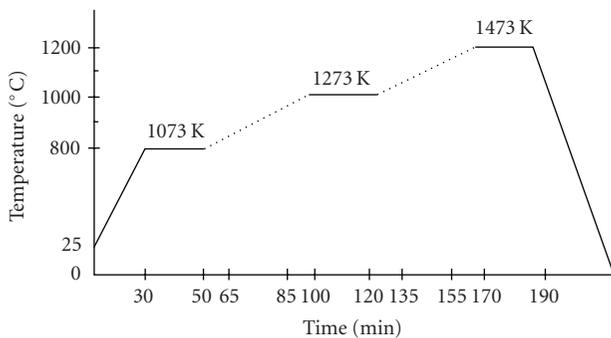
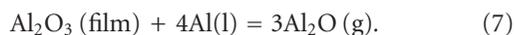


FIGURE 4: The heating schedule followed in the sessile drop measurements.

A principal difficulty when studying the wetting of the molten Al and a solid Al_2O_3 system couple is the presence of a high partial pressure of oxygen. Aluminum metal may react with oxygen at high temperatures [16–25] to form gas by the reaction:



Although this equation is not thermodynamically favorable ($\Delta G_{1173\text{K}} = 1,040.7 \text{ kJ}$), it has been reported to occur during experimental observations and by spectrographic analysis [18, 21].

Droplet shape analysis is required to accurately determine the contact angle (ϕ). Videotapes of the sessile drops were transferred to a PC by using the DFG/LC1 frame grabber with Grab and View 2.1 software. This allowed

the direct observation of individual frames at any time during the duration of the experiment. It has an efficiency reading of 0.01 second. Figure 5 illustrates a droplet and its representation. Analysis determined the droplet profiles and fitted them to theoretical shapes obtained from the solution of the Laplace equation of capillarity [22].

3. RESULTS

3.1. Wetting of the Al_2O_3 - BaSO_4 system fired at 700°C (973 K)

After firing in air at 700°C (973 K), the BaSO_4 content in the alumina was confirmed by microchemical analysis in a scanning electron microscope (SEM) using the EDS technique (35 kV and 25 mA) getting a 99.85% of reading accuracy. It was also checked by X-ray diffraction (XRD) as shown in Figure 6 (35 kV and 25 mA) using Rietveld measurements. The EDS results were for an average of five specimens. The BaSO_4 contents were found to be 0.98%, 2.97%, and 4.98%. Firing at a temperature of 700°C does not affect the BaSO_4 . The densities of the Al_2O_3 - BaSO_4 specimens fired at 700°C (973 K) are illustrated in Figure 7. Open porosity increased as the amount of BaSO_4 increased. The open porosity changed from 34.0 to 40.0%, and the density decreased from 2.4 to 1.9 g/cm^3 for 1.0 and 5.0% of BaSO_4 , respectively. These Al_2O_3 - BaSO_4 specimens were quite porous as well as the pure aluminas.

Figure 8 illustrates the Al wetting contact angles as a function of time for the Al_2O_3 - BaSO_4 specimens at 800°C (1073 K), 900°C (1173 K), and 1000°C (1273 K). These measurements were at temperatures above the sintering temperature of the mixes. The wetting of the BaSO_4 -free alumina is slightly temperature dependent. The wetting contact angles, the ϕ_0 -values at zero time, are 134° at 800°C (1073 K), 132° at 900°C (1173 K), and 128° at 1000°C (1273 K). The contact angle is $>90^\circ$ at all temperatures, a nonwetting condition as previously illustrated in Figure 2.

Additions of BaSO_4 affect the wetting contact angles (ϕ) differently at the three different temperatures. At the lowest temperature, 800°C (1073 K), the 1% addition of BaSO_4 actually decreases the contact angle to 105° , nearly 30° less than that for pure alumina. At 800°C , the 3% addition of BaSO_4 also increases the wetting tendency of the alumina by the molten aluminum. The 5% BaSO_4 addition has nearly the same contact angle profile as that for the pure alumina,

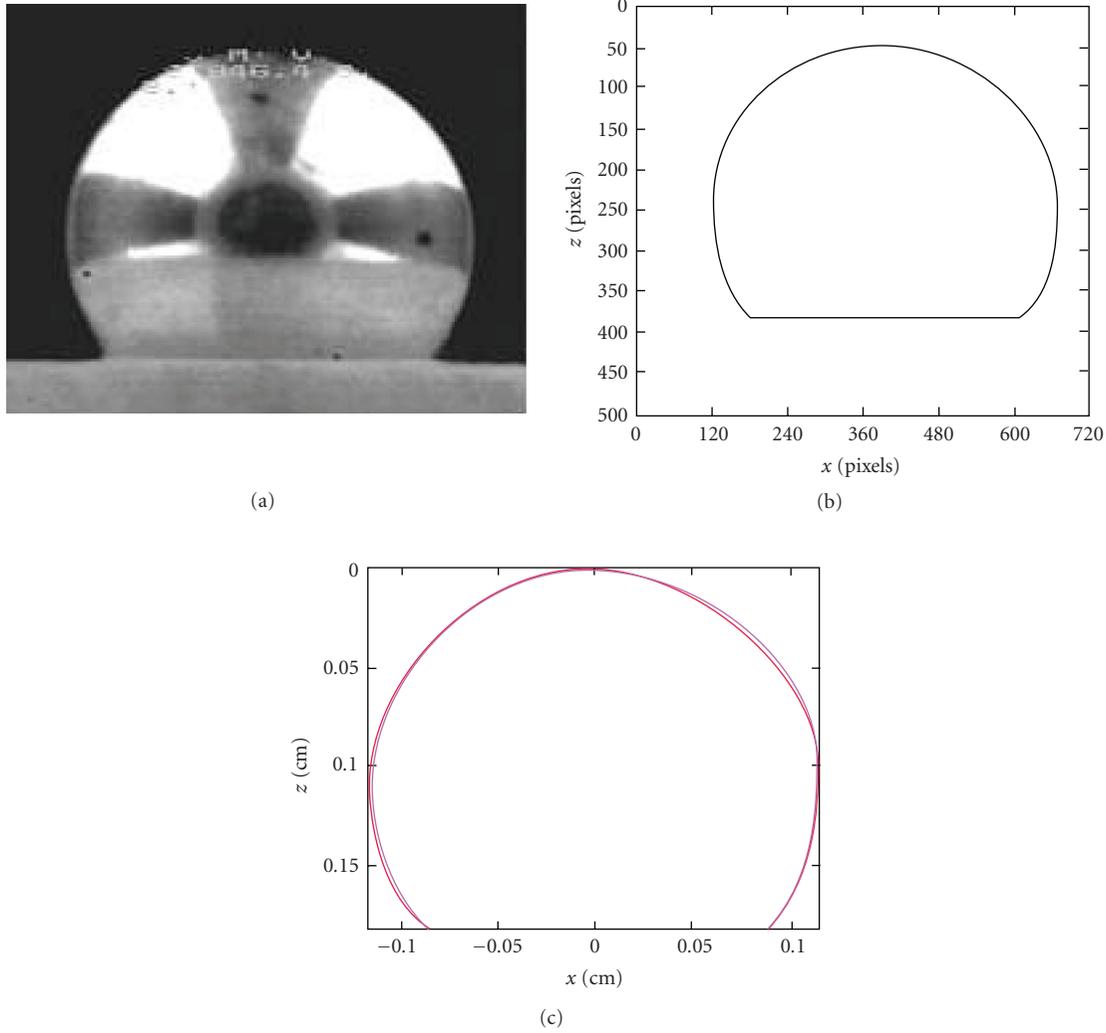


FIGURE 5: Typical droplet acquisition data to obtain the contact angle (ϕ) by image analysis and optimization of the Laplace equation of capillarity.

but the 3% addition decreases the contact angle (ϕ) from 134° to 126° .

The effects of higher temperatures on the wetting of the Al_2O_3 - BaSO_4 specimens are always that of increasing the wetting tendency. At 800°C (1073 K), only the 5% BaSO_4 addition appeared to decrease the wetting tendency of pure alumina, all the wetting contact angles decreased, but those for the BaSO_4 additions decreased more rapidly than those for pure alumina. The result is that from 900°C (1173 K) to 1000°C (1273 K), the pure alumina is more difficult to wet than the alumina with the BaSO_4 additions.

Figure 9 illustrates the contact angle (ϕ_o) as a function of temperature. These results show that by adding BaSO_4 to alumina, the wetting contact angles are less than those for pure alumina. Although the contact angles remain $>90^\circ$, their decreases indicate an increased wetting tendency with the BaSO_4 additions. The 5%- BaSO_4 specimen has a slightly larger contact angle than alumina at 800°C (1073 K).

However, at higher temperatures the contact angle becomes less than that for the pure alumina.

Variation of the ϕ_o -values with temperature can be expressed as

$$\phi_o = \phi'_o - \left(\frac{\partial \phi_o}{\partial T} \right)_t T, \quad (8)$$

where ϕ'_o is the value at zero Kelvin and the slope $(\partial \phi_o / \partial T)_t$ represents the decrease of the wetting contact angle with increasing temperature. These two parameters increase with the BaSO_4 content as illustrated in Figure 9. The BaSO_4 addition effects in alumina at temperatures from 800°C (1073 K) to 1000°C (1273 K) are generally to increase the wetting tendency by molten aluminum. However, at no times the contact angles were reduced to less than 90° . As $\phi < 90^\circ$ is the criteria for partial wetting, it must be concluded that no wetting process was observed, but the additions of BaSO_4 to Al_2O_3 increased the wetting tendency.

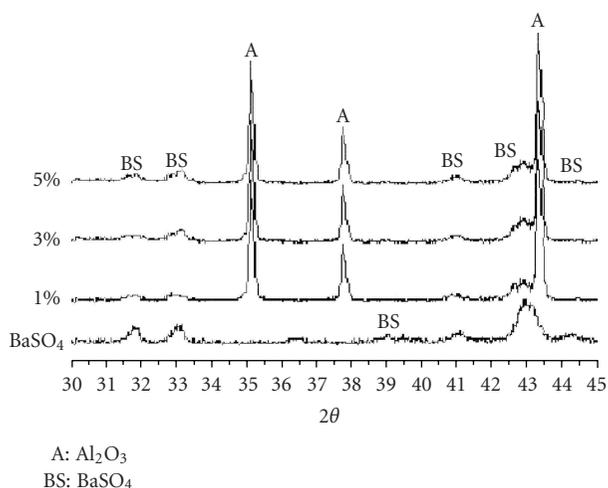


FIGURE 6: X-ray diffraction patterns of the Al₂O₃-BaSO₄ specimens fired at 700°C (973 K) for one hour. Observe that BaSO₄ is present in each sample and its intensity increases proportionally to the amount of BaSO₄ added.

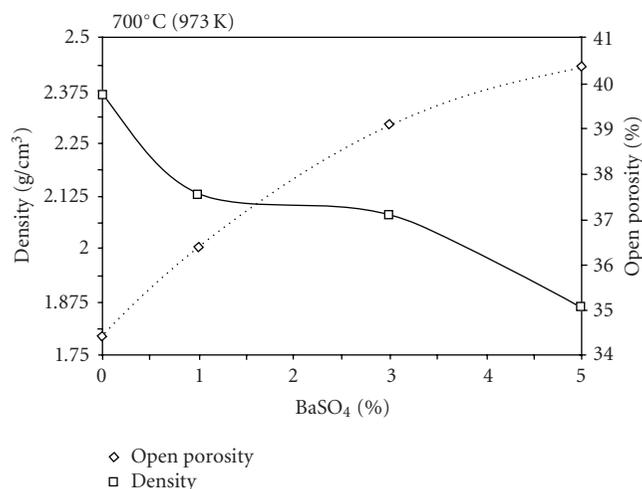


FIGURE 7: Density measurements by Archimedes method for Al₂O₃-BaSO₄ specimens at different additive amounts of BaSO₄, sintered at 700°C (973 K) for one hour.

3.2. Wetting of the Al₂O₃-BaSO₄ system after firing at 1450°C (1723 K)

After firing the Al₂O₃-BaSO₄ specimens at 1450°C, the BaO content in the alumina specimens was analyzed by microchemical analysis in an SEM (EDS) (35 kV and 25 mA) getting a 99.85% of reading accuracy and by X-ray diffraction (XRD). The EDS results represent an average value for five specimens. Only Ba, Al, and O were detected. Sulfur was absent. The amounts of BaO increased in the order of 0.64, 1.92, and 3.25% for the initial introductions of 1.0, 3.0, and 5.0% of BaSO₄. From (1), the reaction for BaSO₄ decomposition, the theoretical amounts of BaO are 0.66, 1.97, and 3.28% for additions of 1.0, 3.0, and 5.0% BaSO₄. These values are nearly the same as those

obtained by EDS microanalysis. This confirms that the BaSO₄, which was introduced to the alumina and then fired at 1450°C (1723 K), decomposed as described by (1). The BaO obtained then reacted with the Al₂O₃ to form BaO•6Al₂O₃ (3). This is confirmed by the XRD in Figure 10, where the two phases coexist. The amounts of BaO•6Al₂O₃, obtained by X-ray diffraction analysis, are of 3.10, 9.50, and 16.20%, respectively. These values are in agreement with the theoretical ones of 3.28, 9.85, and 16.42%, respectively.

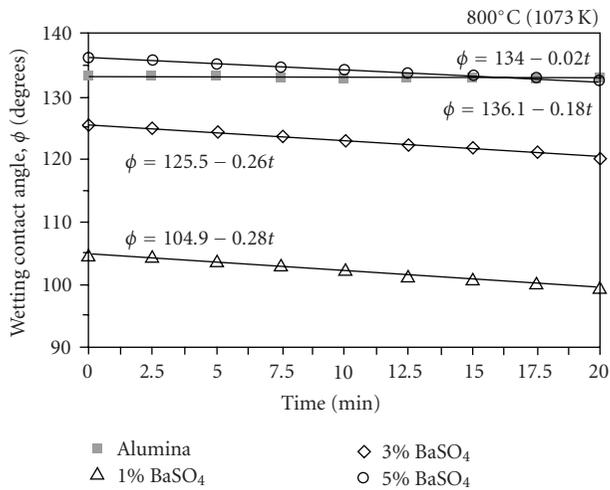
The equilibrium binary phase diagram of Al₂O₃ and BaO illustrated in Figure 11 can be used to explain the above results. It is shown that when adding BaO to Al₂O₃ the first stable compound formation is BaO•6Al₂O₃. This compound has about 20 wt% BaO and 80 wt% Al₂O₃. It is congruently melting at ~1915°C (2188 K) and it is a highly refractory material.

The Al₂O₃-BaO•6Al₂O₃ specimen densities, after firing at 1450°C/1hour (1723 K), are presented in Figure 12. The densities are much higher and the porosities are much lower than the previous series of Al₂O₃-BaSO₄ specimens. The results show an increase of porosity as the amount of BaO•6Al₂O₃ increases. The total porosity changes from 12.0% to 17.0% for the 1.0% and 5.0% additions of BaSO₄, respectively.

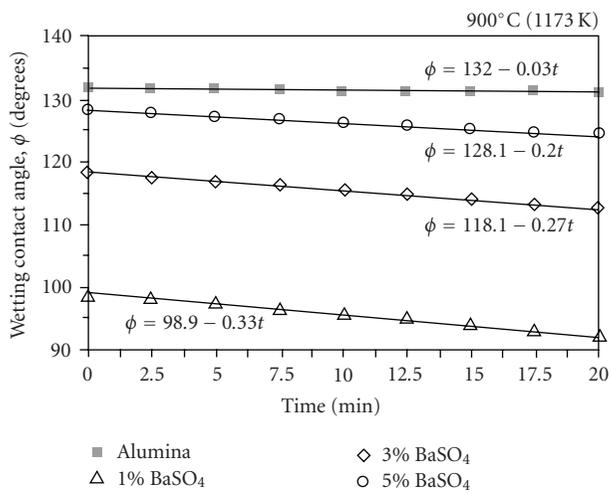
The wetting contact angle (ϕ) variations with BaO•6Al₂O₃ content and their changes with temperature are illustrated in Figure 13. Large contact angle differences are obtained from the BaSO₄ additives after firing at 1450°C. The temperature effect is evident. It normally decreases the contact angle. Figure 13 illustrates the aluminum contact angles of the Al₂O₃-BaO•6Al₂O₃ specimens at the three temperatures, 800°C (1073 K), 1000°C (1273 K), and 1200°C (1473 K). The wetting of the alumina without BaSO₄ additions after firing at 1450°C is only slightly temperature dependent. Its contact angles (ϕ_0) at $t = 0$ are 125° at 800°C, 121° at 1000°C, and 118° at 1200°C.

The BaO•6Al₂O₃ effects on the contact angles (ϕ) are similar for the three temperatures. At the lowest temperature, 800°C (1073 K), the 3.1% BaO•6Al₂O₃ decreases the wetting contact angle to 95°, about 30° less than that for the pure alumina. The addition of BaO•6Al₂O₃ has the effect of increasing the wetting tendency of the alumina by molten aluminum. At 800°C (1073 K) the 9.5% and 16.2% of BaO•6Al₂O₃ the wetting contact angles decrease to 105° and 107°, respectively. This suggests that by increasing the BaO•6Al₂O₃ phase in the microstructure the contact angles will increase toward less wetting. One can speculate that further increases of BaO•6Al₂O₃ phase content may increase the wetting contact angles beyond that obtained for the pure alumina.

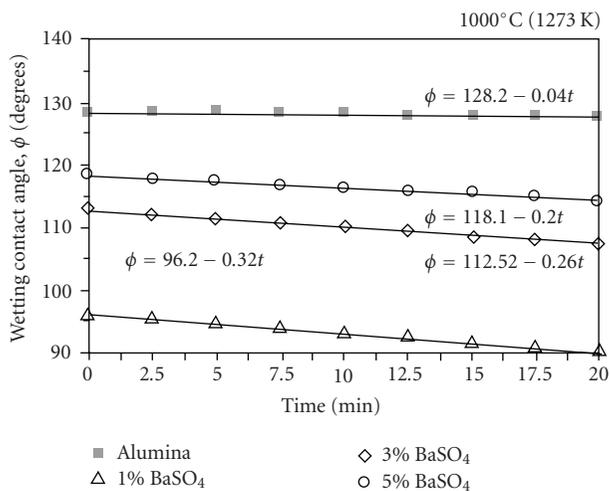
The effect of temperature decreases the wetting contact angles (ϕ) for all of the Al₂O₃-BaO•6Al₂O₃ specimens. From 800°C (1073 K) to 1200°C (1473 K) contact angles are reduced for all levels of BaO•6Al₂O₃ additions. The result is that at all three temperatures, the pure alumina is the most difficult to wet. The presence of BaO•6Al₂O₃ consistently decreases the tendency toward wetting. It must be concluded that the amounts of BaO•6Al₂O₃ additions to alumina tested at temperatures from 1000°C (1273 K) to



(a)



(b)



(c)

FIGURE 8: Wetting contact angle (ϕ) variation with time at different temperatures for the Al_2O_3 - BaSO_4 systems fired at 700°C (973 K) for one hour. The regression equations are listed on the figures.

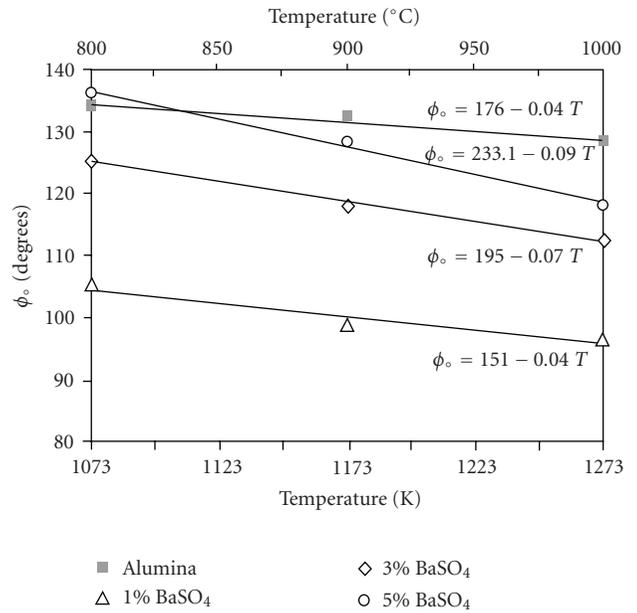


FIGURE 9: Variation of the wetting contact angle (ϕ_0) at time zero with temperature for the pure alumina and BaSO_4 additions of 1%, 3%, and 5% after firing at 700°C (973 K).

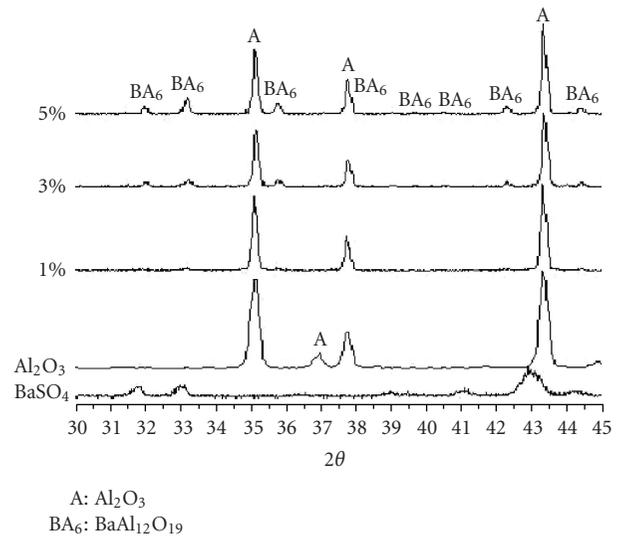


FIGURE 10: X-ray diffraction patterns of Al_2O_3 - BaSO_4 specimens fired at 1450°C (1723 K) for one hour. Observe that the BaSO_4 has decomposed and reacted with the Al_2O_3 , forming the stable $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ phase.

1200°C (1473 K) do not reduce or inhibit the wetting of pure alumina by molten aluminum. Figure 14 summarizes the effects of temperature on the wetting contact angles for the addition of $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ additions.

Figure 14 shows a linear tendency of the decrease of the wetting contact angle (ϕ_0) with temperature. This describes the effects of temperature on the contact angle variation. With $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ additions to alumina, it is observed that the contact angles are increased from those obtained with

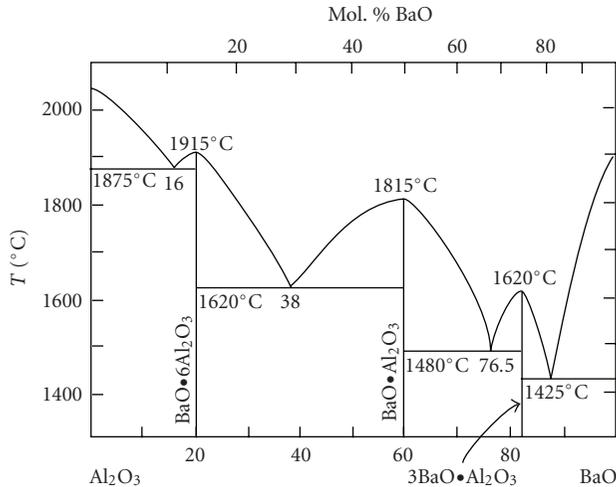


FIGURE 11: Binary phase diagram of the BaO-Al₂O₃ system [23].

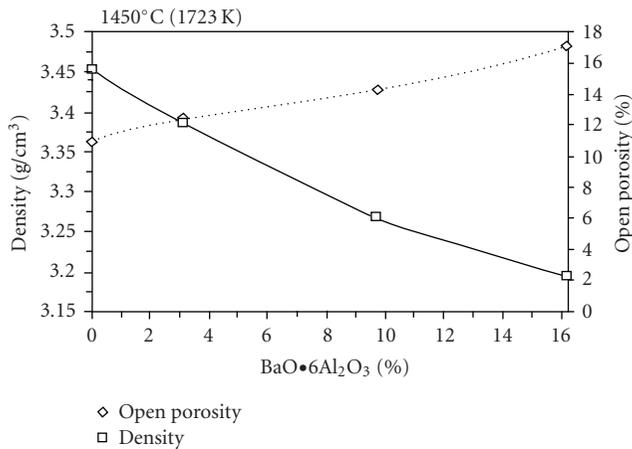


FIGURE 12: Density measurements by the Archimedes method in Al₂O₃-BaO•6Al₂O₃ specimens after firing 1450°C (1723 K) for one hour.

pure alumina. However, the resultant slopes $(\partial\phi_o/\partial T)_t$ are similar to those for the pure alumina.

The decrease of ϕ_o with increasing temperature is described by (8). It is probable that the BaO•6Al₂O₃ phase may increase the resultant contact angle of molten aluminum beyond that for pure alumina. The trend in Figure 14 certainly suggests that larger additions of AB₆ (BaO•6Al₂O₃) may achieve contact angles above from those of the pure alumina and actually decrease the wetting by molten Al.

3.3. Wetting of the pure BaO•6Al₂O₃ phase

Davis et al. [26, 27] suggest different processing routes for the synthesis of pure BaO•6Al₂O₃ and establish that this barium compound is of interest as a refractory. Barium monoaluminate BA (BaAl₂O₄) hydrates, m.p. ~1800°C (2073 K), and could be the basis of cement or grouting material. The hexaluminate BA₆ (BaO•6Al₂O₃), however, is

the more likely engineering ceramic, m.p. ~1925°C (2198 K) [26, 27].

The only study in the literature reporting properties of the barium hexaluminate BA₆ (BaO•6Al₂O₃) is that by Zawrah and Khalil [28]. They prepared the compound from both low and high purity materials by sintering at 1700°C (1973 K). The first was prepared from high purity BaSO₄ and Al₂O₃, while the second was prepared from natural minerals, Egyptian barite and Chinese bauxite. They found that by firing the pure materials at 1700°C (1973 K), a mix of BA₆ (BaO•6Al₂O₃) and Al₂O₃ was present in the microstructure. However, when firing the natural minerals at 1700°C (1973 K), a mix between BA₆ (BaO•6Al₂O₃), Al₂O₃, and BAS₂ (BaO•Al₂O₃•2SiO₂) was present in the microstructure. They identified these phases by X-ray diffraction. The X-ray diffraction results for their pure materials are in agreement with those presented in Figure 15 for the present study.

Figure 15 illustrates the reaction of the Al₂O₃-BaSO₄ specimens to form BA₆ (BaO•6Al₂O₃) as a function of the firing temperature. After firing at 1200°C (1473 K) there remains a large amount of BaSO₄ that has not reacted with the Al₂O₃. However, on firing at 1400°C (1673 K) is observed that the reaction process has initiated and as a result there is a formation of BA₆. After firing for one hour at 1700°C (1973 K), the formation of the BA₆ phase is complete.

The densities of the BA₆ (BaO•6Al₂O₃) specimens are illustrated in Figure 16. There is a reduction of open porosity as the temperature increases. The open porosity is 6.5% after firing at 1700°C (1973 K). The density is 3.97 [g/cm³]. The pure alumina fired at the same conditions had 5% open porosity and a density of 3.52 [g/cm³].

The Al wetting contact angle (ϕ) for the BA₆ phase is illustrated in Figure 17. The results for the pure alumina fired at 1700°C (1973 K) are also presented. Distinct differences with respect to the pure alumina are obtained for all of the temperatures. This result was predicted by Figures 13 and 14 that show increases of the Al contact angles proportional to the BA₆ phase content. The BA₆ phase actually increases the wetting angle trend of molten aluminum beyond that for pure alumina. The BaO•6Al₂O₃ phase is consistently more nonwetting than pure alumina.

The Al contact angles (ϕ_o) at time zero for the BA₆ phase changed from 135.3° for 800°C (1073 K) to 127.4° for 1200°C (1473 K). These ϕ_o s are above those obtained for the pure alumina of 122.7° and 115.3° at the same temperatures. These represent a nearly 10% increase of the contact angles, respectively. Figure 18 illustrates this variation of contact angle with temperature. It is observed that the BA₆ (BaO•6Al₂O₃) has larger wetting contact angle than that for the pure alumina for all temperatures. Both have similar slopes, $(\partial\phi_o/\partial T)_t$. This clearly illustrates that the pure BA₆ (BaO•6Al₂O₃) phase is less wetting to the molten aluminum than pure alumina.

3.4. The pure alumina wetting contact angle

In the assessment of the effect of BaSO₄ and BaO•6Al₂O₃ additions, the fired refractory ceramics were compared with

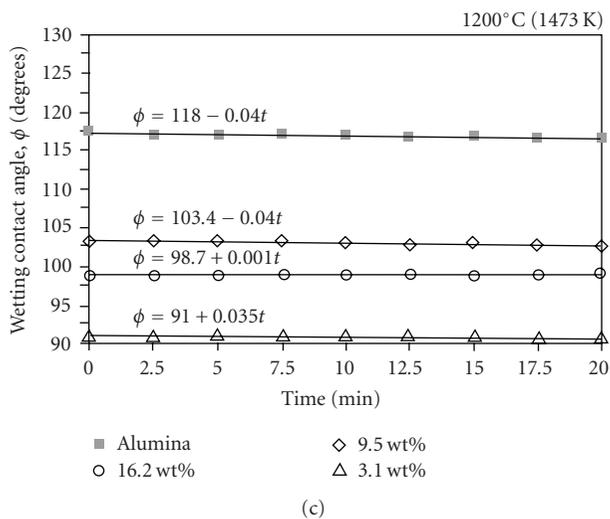
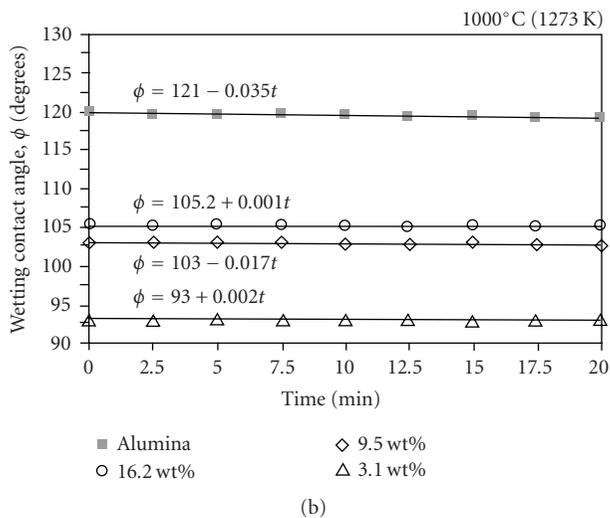
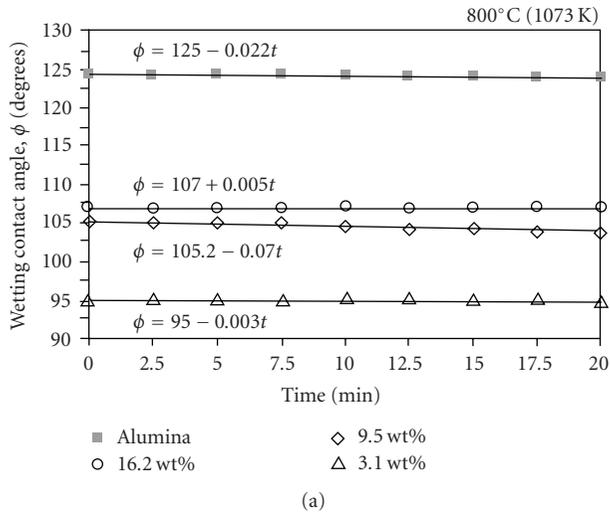


FIGURE 13: Wetting contact angle (ϕ) variation with time at different temperatures for the Al_2O_3 - $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ system fired at 1450°C (1723 K) for one hour.

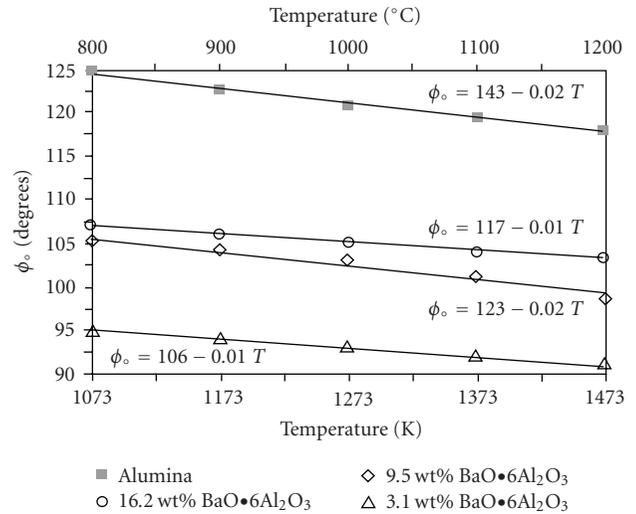


FIGURE 14: Variation of the wetting contact angle (ϕ_0) with temperature for the $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ additions to alumina and after firing at 1450°C (1723 K) for one hour.

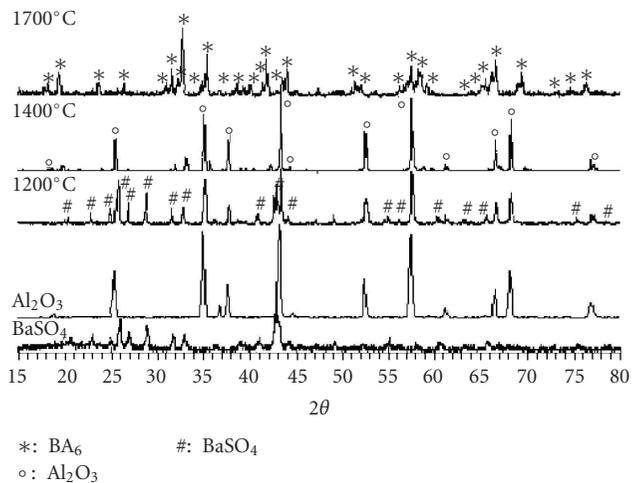


FIGURE 15: X-ray diffraction patterns of the Al_2O_3 - BaSO_4 specimens fired from 1200°C (1473 K) to 1700°C (1973 K).

the pure alumina fired under the same conditions. The contact angles of the three aluminas were presented in Figures 8, 13, and 17 at the three different temperatures. The molten aluminum wetting contact angles are different for the three different alumina firing conditions. These three different firing schedules for the pure alumina produced three different levels of porosity, 34.5%— 700°C (973 K), 11%— 1450°C (1673 K), and 5%— 1700°C (1973 K), respectively. This shows the densification process of alumina with temperature and coupled with the microstructural differences, this naturally created different surfaces roughnesses. The reason for the different contact angles for these pure aluminas is their different structural surface roughnesses [28].

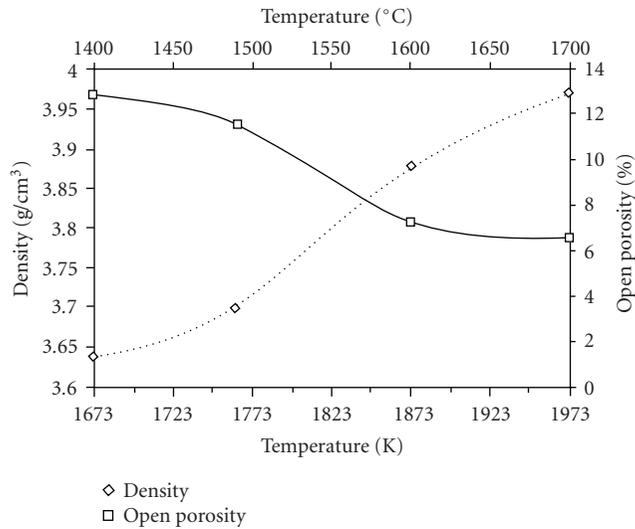


FIGURE 16: Density and open porosity variation with temperature after firing $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ at 1700°C (1973 K) for one hour.

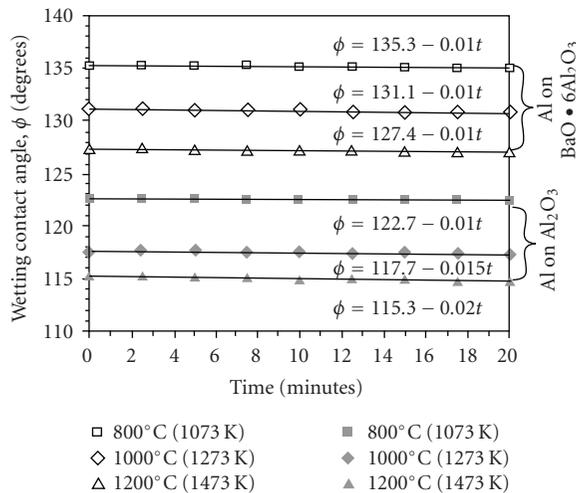


FIGURE 17: Wetting contact angle (ϕ) with time at constant temperatures. Note the Al contact angles obtained with the pure BA_6 ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$) are larger than those obtained with the pure Al_2O_3 .

4. SUMMARY AND CONCLUSIONS

The additions of BaSO_4 to alumina have two different Al wetting regimes as the firing temperature is increased to produce refractory ceramic bodies. The decomposition temperature of BaSO_4 divides these regimes. For $T < 1124^\circ\text{C}$ (1397 K) (700°C (973 K) firing was used in this study) the BaSO_4 does not decompose. It remains as the sulfate mixed with alumina. It is observed that the resultant molten Al contact angles are less for the Al_2O_3 - BaSO_4 mixtures than those obtained with the pure alumina. Specimens do not show higher contact angles than the pure alumina. The BaSO_4 does not reduce the wetting of alumina to molten

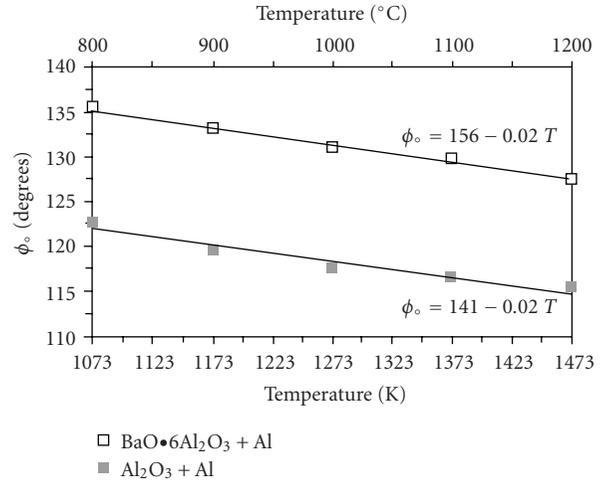


FIGURE 18: Variation of ϕ_0 with temperature for the couple systems of $\text{BaO}\cdot 6\text{Al}_2\text{O}_3/\text{Al}$ and $\text{Al}_2\text{O}_3/\text{Al}$. Note that the $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ phase is more nonwetting than pure alumina.

aluminum. In fact, the BaSO_4 reduces the wetting contact angle toward more wetting conditions.

The Al_2O_3 - BaSO_4 specimens fired at $T > 1450^\circ\text{C}$ (1723 K) cause the decomposition of the BaSO_4 (2). The reaction results in a stable compound BA_6 ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$). The amount of $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ is proportional to the content of BaO from the sulfate decomposition reaction in (1). The BA_6 ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$) amounts obtained by SEM (EDS) analysis from 1%, 3%, and 5% of BaSO_4 additions are 3.1%, 9.5%, and 16.2%. The Al wetting angles of the Al_2O_3 - $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ mixtures are decreased below that of the pure alumina. They do increase proportionally with the amount of BA_6 ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$) presents in the system. This suggests that increments of BA_6 ($\text{BaO}\cdot 6\text{Al}_2\text{O}_3$) in the system would increase the Al wetting contact angle, possibly significant at higher BA_6 phase levels.

The investigation of the wetting of the pure $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ ceramic by molten aluminum yielded wetting contact angles greater than those for pure Al_2O_3 . This indicates that $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ is less wetting toward molten aluminum than pure alumina. However, the contact angles for $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ ceramic do not approach the $\phi = 180^\circ$ mark indicative of an absolute nonwetting condition.

All of the contact angles decreased with increasing temperature. Higher temperatures promote wetting. They also might be expected to enhance refractory penetration and increased corrosion at higher temperatures.

The contact angles (ϕ) resulting from these refractory systems and 1020 Al decrease linearly with increasing temperature even in the presence of the additives. Measurements of the Al contact angles on the BaSO_4 additive containing alumina do not confirm that this additive inhibits wetting. In fact, in most cases the contact angles were reduced toward more wetting, suggesting that the BaSO_4 addition may actually promote wetting characteristics. However, BaSO_4 addition did not decrease the contact angles below 90° , the criterion for the transition from nonwetting to wetting.

One must conclude that the nonwetting theory for the improvement of aluminum refractories by BaSO₄ additions does not appear to be the correct explanation.

There remain several other alternatives for the obvious corrosion improvements of aluminum containing refractories by BaSO₄ additions. One is the formation of compounds such as BaO•6Al₂O₃ or BaO•Al₂O₃ that fill the refractory pores and channels reducing porosity and the penetration of molten aluminum. Another is the suggestion by Brosnan [2] in his review, namely, that the sulfate participates in a reaction, or a series of reactions to promote the oxidation of molten aluminum if it does penetrate the refractory structure. Both of these are viable explanations.

Finally, it must be noted that this study was for the additions of BaSO₄ and its derivative compounds on the wetting of a pure alumina by a pure aluminum metal. These results may not directly translate to the wetting of other refractories such as the different aluminosilicates and cement-containing refractories by more complex highly alloyed aluminum metal.

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