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Effect of TiO_2 and MnO Addition on the Sintering and Corrosion Behavior of Alumina

Shahab Khamneh Asl*, **Dariush Rasouli**

Department of Materials Engineering, Faculty of Mechanics, Tabriz University, Tabriz, Iran

Email address
sshahab_kh@yahoo.con (S. K. Asl)
*Corresponding author

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Abstract

The effect of additives on the densification behavior of alumina has been investigated. Fast milling was used for the mixing of these additives in order to achieve a uniform distribution and thereafter homogeneous microstructure on sintering. Sintered density and microstructures were evaluated along with the mechanical properties. Effect of manganese oxide and titanium oxide as additives on sintering of alumina is described. Manganese oxide and titanium oxide dopants lead to achieving theoretical density. The alumina +2wt% MnO_2 or 1wt% TiO_2 system resulted in high densification giving a uniform microstructure at temperature low as 1300°C. The higher density and lower porosity of doped alumina increased the corrosion resistivity of alumina rings.

1. Introduction

The environments of offshore oil production are characteristic of aggressive conditions such as corrosion and erosion. Corrosion-erosion, primarily at gravel packs, nozzles and Christmas trees, can cause up to 15% loss in oil and gas production, even before hydrocarbons arrive at the first separator [1]. However, the deterioration rate of metal is accelerated by this phenomenon, owing to the combined effect of electrochemical etching and mechanical erosion. This combined influence, known as synergy, can result in higher metal loss rate and greater damage than erosion or corrosion alone. Therefore, the lifetime of components can be shortened remarkably by this effect [2, 3]. Moreover, owing to their high mechanical properties and machinability at low price, the carbon steels have extensively been applied in oil wel. However, in a large extent, the poor corrosion resistance of carbon steel restricts their further applications, particularly in aggressive conditions as mechanical rings. Thus, a variety of approaches, such as corrosion inhibitor method, cathodic protection and covering the coatings or films on the steels, or bulks are used to protect the carbon steels against corrosion [4]. Depositing the shielded coating onto the surface of carbon steel becomes one of the most widespread approach to decrease the corrosion rate [5, 6]. For preparing the coatings, numerous methods, such as chemical plasma spray, plasma electrolytic oxidation (PEO), sol-gel, vapor deposition (CVD), physical vapor deposition (PVD) and high velocity oxy-fuel (HVOF) spraying, could be employed [7-10] but to identify the mechanical and chemical properties of alumina coatings or bulks similar methods were applied.

A wide variety of materials, including metals, polymers and ceramics, can be sprayed onto the metal and ceramic substrates by thermal spray coating among them. This coating is built with the intent to enhance the engineering performance such as resistance to corrosion, wear or high temperature and increasing the component life [11]. The ceramic coatings are effective in various environments, where the resistance to corrosion and wear are necessary, particularly in an elevated temperature condition, whereas the other coatings could reach [12-13]. For instance, alumina and zirconia bulks and coatings are applied increasingly and widely in the area of industry to supply resistance to wear and erosion, thermal insulation and corrosion protection [14, 15]. The defects exiting in the surface of the ceramics are harmful to the corrosion resistance of the systems [16]. Defects in the surface are definitely toxic, as they provide direct pathways for corrosive electrolytes to go through the surface [2, 4].

Alumina has been sintered to ~99% of its theoretical density (TD) using small amounts of a number of additives, such as SiO_2, TiO_2, and MnO, either singly or in combination, to form liquid phases at temperatures in the range 1400_/1500°C. In addition to improving densification, the formation of liquid phase reduces the sintering temperatures below those characteristic of solid state sintering. This improves the control over grain growth and aids in tailoring the properties of the final material. Both experimentation and theory show that the sintering temperature of alumina can be lowered to 1400°C and below by using small particle sizes and certain additives like TiO_2 and/ or MnO. The general idea is that sintering is aided by the development of a liquid phase at this low temperature, due to the presence of the additives [17-20].

Additions of small amounts of TiO_2 and MnO to plain Al_2O_3 have been proven effective in attaining sintered bodies with densities ~/98% TD at temperatures as low as 1300°C [17, 18]. A phase equilibrium diagram for the Al_2O_3_ /TiO_2_/MnO is available in the literature, an analysis of the corresponding Al_2O_3_/ TiO_2_/MnO diagram (Figure 1) revealed that the formation of liquid phases can take place at temperatures as low as 1300°C, which can greatly assist in the densification of alumina to nearly TD upon sintering at the temperature range of 1500 and 1600°C. [17]

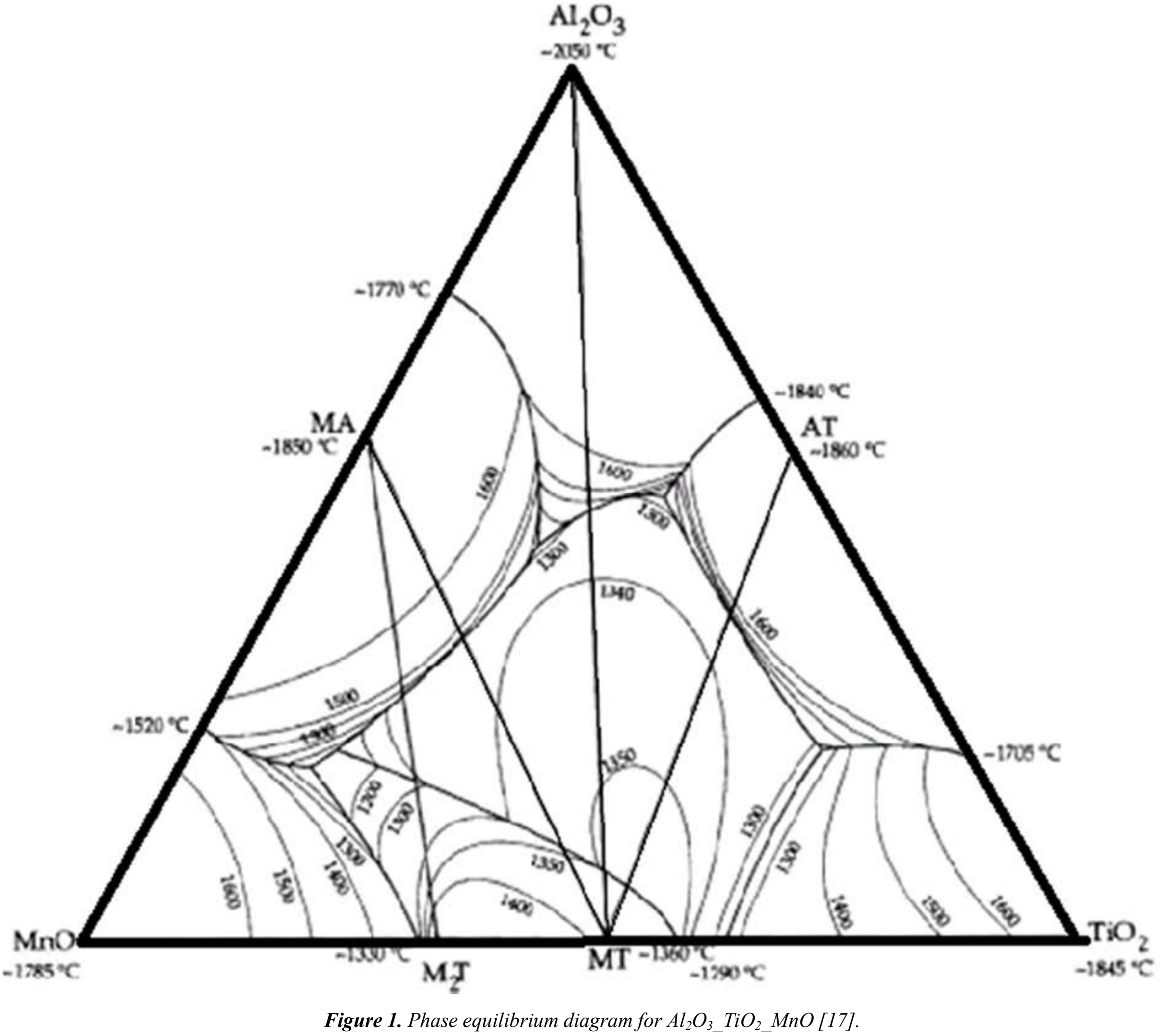

Figure 1. *Phase equilibrium diagram for Al_2O_3_TiO_2_MnO [17].*

The goal of this study is to lowering the sintering temperature of alumina with addition of small amounts of TiO_2 and MnO.

2. Experimental Procedure

2.1. Starting Materials

The starting materials were Bayer derived alumina (C999) with average particle size about 12 µm. Alumina suspensions containing 0.5–5.0 wt.%of each additive and different ratio of them were milled in a planetary mill for 1.0 h in aqueous medium in polyurethane bowl and alumina balls; 2.0 wt.% of 60:40 vol.% polyvinyl alcohol (PVA) and polyethylene glycol (PEG) in water were added as binding agents. The mixture was dried and sieved through 200 mesh to obtain soft granules, which were then pressed into pellets of 10 mm dia using a uniaxial press at a pressure of 100 MPa. The pressed samples were pre-heated to 100°C for 12 h. The density of the dried samples was about 58% of theoretical density (T.D). The compacts were sintered at various sintering temperatures. Sintered specimen densities were determined by Archimedes' method using water as the immersion medium and the average value of five samples was reported.

2.2. Sintering Conditions

The compacts were sintered under isothermal conditions in an electrically-heated furnace with $MoSi_2$ elements. The temperature was monitored and controlled by a controller with Pt-Rh thermocouples in an atmosphere of static air. The green compacts were heat treated at a rate of 5°C/min up to 600°C and then the heating rate was changed into 10°C/min till their maximum sintering temperature reached. Then the compacts were soaked for 2.0 h at that sintering temperature. The sintered compacts were cooled to room temperature at a cooling rate of 5°C/min.

2.3. Electrochemical Corrosion Test

The electrochemical corrosion test was carried out in the following steps. First, the surface of samples had the copper forconducting wires welded on subsequently; epoxy resin was insert into the samples with only 1cm^2 exposed area for surface left. Then the electrochemical corrosion tests were carried out in the three-electrode cell, where the graphite, the saturated calomel electrode (SCE) and the samples were used as the counter electrode, the reference electrode and the working electrode, respectively. Moreover, the electrolyte was consisted of the crude oil and the simulated seawater which contains 96.5 wt.%H_2O, 2.73wt% NaCl, 0.24 wt% $MgCl_2$, 0.34 wt% $MgSO_4$, 0.11 wt% $CaCl_2$ and 0.08 wt. % KCl. The immersion times were set as 3, 10, 20, 40, 60 days. The ELS spectra was collected at the open circuit potential of samples, when the signal amplitude is 10 mV rms and the frequency is in the range of 0.01 to 100000Hz. The EIS fitting software was applied to fit and interpret the EIS data. SEM was used to analyses the corroded samples after long time dip. Noted that all sets of measurements were repeated for three times to confirm the repeatability.

3. Results and Discussion

The Bayer derived alumina powder compact without addition was sintered to 98.5% of T.D. at 1650°C for 3.0 h. The doped samples reached 98–99% of T.D at the same sintering temperature of 1400°C for 2.0 h.

Figure 2 illustrates the effect of TiO_2 content on the sintered density of titania doped alumina sintered at 1450°C for 3.0 h. The green density of the alumina decreases with increasing titania content from 58 to 53% of T.D. However, when the material is sintered to 1400°C, the density increases from 81 to 98% of T.D for the concentration of 2.5 wt.% . At 1450°C, 96% of T.D is obtained for pure and 98% of T.D for 0.1 wt.%of TiO_2. At higher temperatures, the addition of titania does not elevate the sintered density.

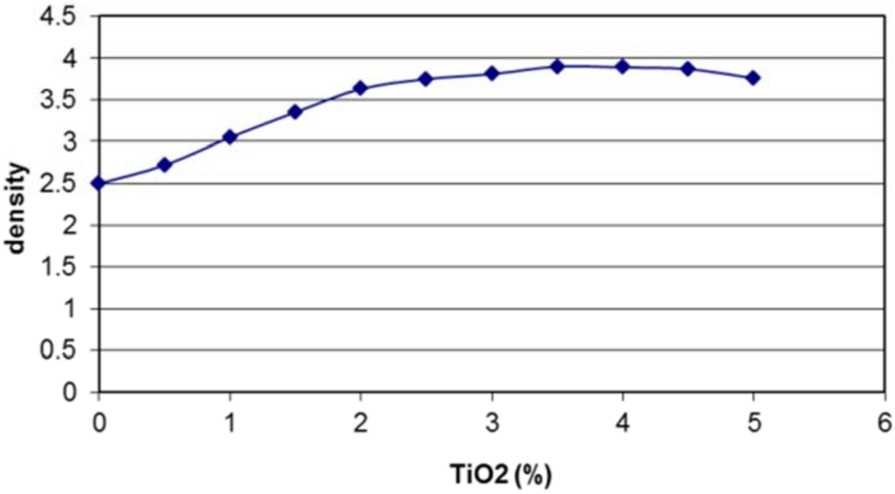

Figure 2. Effect of TiO_2 on the densification of alumina sintered at 1450°C.

Figure 3 illustrates the effect of TiO_2 and MnO contents on the sintered density of doped alumina sintered at 1450°C for 3.0 h.

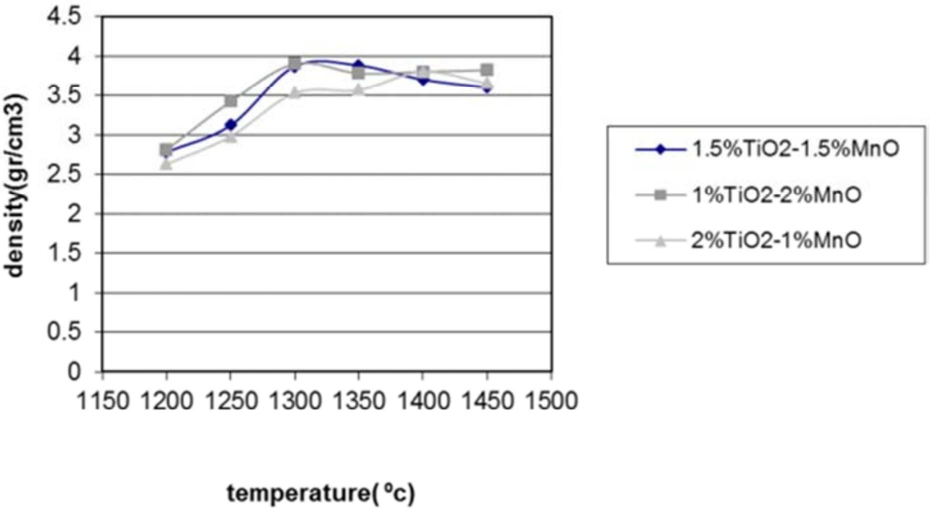

Figure 3. *Densification as a function of TiO_2/MnO ratios.*

Table 1. *$I_{corr.}$ and R_{ct} of alumina samples with or without additives in simulated seawater mixed crude oil for 60 days.*

	alumina		**TiO_2 alumina**		**MnO alumina**	
day	**$I_{corr.}$/µA**	**R_{ct}/kOhm**	**$I_{corr.}$/µA**	**R_{ct}/kOhm**	**$I_{corr.}$/µA**	**R_{ct}/kOhm**
3	0.7855	25.88	0.7422	21.524	0.7414	22.124
10	1.354	24.21	0.7584	21.333	0.7456	21.774
20	2.487	22.45	0.7699	21.277	0.7576	21.660
40	3.999	21.02	0.7991	21.119	0.7881	21.444
60	4.109	20.94	0.8588	21.111	0.7991	21.251

Electrochemical impedance spectroscopy was used to identify the corrosion resistance of the sintered samples. Nyquist spectra obtained for samples, where the samples produced through additives were immersed in the mixture of simulated seawater and crude oil. It was obvious that the EIS spectra and corrosion test results collected in Table 1 of these two additives showed a similar behavior. That indicated that these two additives possessed similar electrochemical corrosion mechanism.

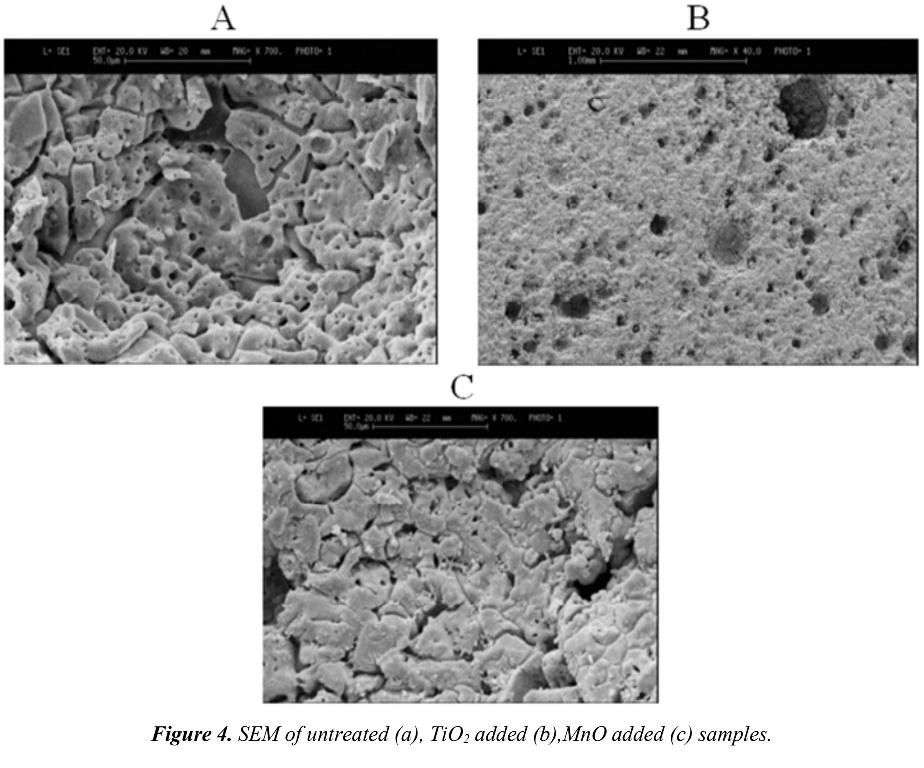

Figure 4. *SEM of untreated (a), TiO_2 added (b),MnO added (c) samples.*

The microstructures of sintered samples are shown in Figure 4. A dense microstructure exhibiting high homogeneity was obtained when doping samples. However, some pores were observed through micrograph in the shape of black spots. It is reported that such pores were induced by the semi and unmelted particles in alumina samples but by adding TiO_2 or MnO these pores reduced, there pores could be recognized by the characteristic of spherical shape. The uniform, homogeneous and free form surface cracks are observed in doped samples. To improve the corrosion stability of alumina samples, preparing a whole and relatively homogenous sample is crucial as seen in Figure 4.

4. Conclusion

The effect of additives on the densification behavior of alumina has been investigated.. Effect of manganese oxide and titanium oxide as additives on sintering of alumina is described. Manganese oxide and titanium oxide dopants lead to achieving theoretical density. The alumina with 2wt% MnO_2 or 1wt% TiO_2 systems resulted in high densification giving a uniform microstructure at temperature low as 1300°C. the electrochemical investigation indicated that doped samples have a remarkable effect on the corrosion performance, furthermore, based on the corrosion test, where the samples were placed in the mixture of the simulated seawater and crude oil for 60 days, doped samples exhibited higher corrosion stability than that untreated samples.

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