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Effects of additive gases on radio-frequency plasma sintering of alumina

MING YUNG CHEN
Wright Research and Development Center, MLBM, Wright Patterson Air Force Base, Dayton, OH 45433, USA

D. L. JOHNSON
Northwestern University, Department of Materials Science and Engineering, 2145 Sheridan Road, Evanston, IL 60208, USA

Pure and 0.25 wt% MgO-doped alumina powder compacts were sintered using a radio-frequency induction-coupled argon plasma. The effects of additive oxygen, hydrogen, nitrogen and water were investigated by injecting varying amounts of each gas during sintering. The addition of diatomic gases or water vapour to argon gas during plasma sintering increased the temperature and sintered density of the specimens. Water vapour showed the strongest effect, followed by hydrogen, nitrogen and then oxygen. The presence of MgO dopant resulted in greater density and a lower sample temperature than those of the pure material.

1. Introduction

Previous studies [1–16] have shown that using a plasma as the heat source enables sintering to be completed in a very short time, a few seconds or minutes rather than hours, particularly when coupled with rapid pass-through sintering. Furthermore, fine grain sizes and high density have been achieved. Compared to samples sintered in a conventional furnace with the same sintering temperature, time, and atmosphere, plasma-sintered specimens have been reported to exhibit higher room-temperature mechanical strength [1].

The following observations were reported by previous investigators on rapid pass-through induction coupled argon plasma sintering of alumina rods and tubes.

1. The specimen temperature and the final density were found to increase with the translation rate through the plasma for both pure and doped specimens [7, 8]. At sufficiently high rates pure specimens could be melted.
2. The sample temperature spontaneously dropped, by as much as 800 °C, when the translation was stopped without any other changes in operating conditions [7, 8].
3. A sintered sample, upon re-entering the plasma, could never achieve a temperature as high as a green sample could; the difference was as much as 800 °C [7, 8].
4. When a green rod was passed through a low-power, low-pressure plasma such that heating was insufficient for sintering and then through the normal sintering conditions without exposure to the ambient, the specimen remained cool in argon. Sintering could be effected either by exposing the specimen to the ambient (moist air) or by adding oxygen to the argon [12].

These findings suggested that the observed heating phenomena were related to adsorbed gases on the sample, and motivated the present investigation to gain a better understanding of these effects.

2. Experimental procedure

As-received deagglomerated alumina powder with surface area of 30 $m^2 g^{-1}$ was used for all experiments. The powder was doped with 0.25 wt % MgO by adding a magnesium nitrate solution and drying prior to the binder addition. 3 wt % poly(vinyl butyral) in acetone was added as a binder. Rod specimens, 4.5 mm diameter, were isostatically pressed at 275 MPa. The binder was burned out at 650 °C in air for 2 h to increase green strength and to convert the magnesium nitrate to magnesium oxide. The rods were stored at 100 °C until sintered.

The sintering apparatus was the same as that used by Johnson and Rizzo [6]. The plasma was generated within a water-cooled 45 mm i.d. fused quartz tube, using a four-turn induction coil that was excited at 5 MHz. All experiments were performed in a flowing atmosphere with argon as the carrier gas. The flow rates of the argon carrier and the additive gases were maintained at 4.5–6.5 and 0.02–0.2 $cm^3 s^{-1}$ (STP), respectively. Water vapour additions were made by diverting a metered portion of the argon through a thermostated humidifier. The specimen was rotated at about 50 r.p.m. during sintering to enhance heating uniformity. The entire assembly was lowered through the coil at a rate of 10–60 mm min^{-1} to effect zone sintering of the specimen.

In order to study the effects of additive gases on the plasma sintering of alumina, it was necessary to reduce the amount of adsorbed gases in the specimens. This

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was done by passing the presintered specimen through a low-temperature plasma, which is defined as the cleaning plasma. The cleaning plasma power and low pressure were adjusted to minimize sintering, while at the same time causing desorption of adsorbed gases, thereby at least partially cleaning the powder particle surfaces. The doped and undoped specimens required different plasma conditions for cleaning, as well as for sintering. These conditions were obtained by varying the plate voltage of the radio frequency (r.f.) generator, argon pressure, and sample translation rate as shown in Table I.

After a specimen passed through the cleaning plasma, the plasma was extinguished, the plasma assembly was raised to withdraw the specimen from the coil, and the plasma was restarted, all the while maintaining a flowing argon atmosphere to prevent readsorption from the ambient. The power and pressure were adjusted according to the sintering conditions shown in Table I, and the specimen was sintered, with or without gas additions. Sintered densities (by Archimedes method), emission spectra, and microstructural analysis on fractured or polished surfaces were studied.

An optical spectrometer (250 mm Ebert monochromator with a stepping motor scanning drive and an electrometer) connected to a recorder was used to determine the elements present in the plasma during an experiment. Both single scans from 280–900 nm and stationary measurements at the strongest hydrogen emission line (656 nm) were made. Specimen temperatures were measured using a two colour optical pyrometer. Because the emission of the plasma interfered with the pyrometer, the plasma-quench technique employed by Kim and Johnson was used [7]. The output of the pyrometer was recorded as the plasma was quenched, and the temperature was estimated by extrapolating the resulting curve back to the moment of quench.

TABLE I Plasma conditions for cleaning and sintering

	Specimen	Plate voltage (kV)	Pressure (kPa)	Translation (mm min^{-1})
Cleaning	Pure	3.3	4.5	10
	Doped	3.0	6.7	10
Sintering	Pure	3.8	10.7	10
	Doped	3.8	13.3	40

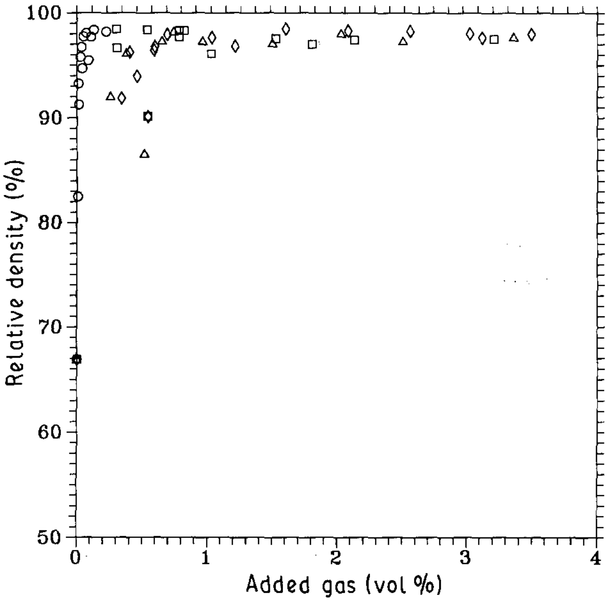

Figure 1 Relative density of pure specimens against amount of additive gas to the argon gas. All samples had already received the prior cleaning treatment. (○) H_2O, (□) H_2, (△) N_2, (◇) O_2.

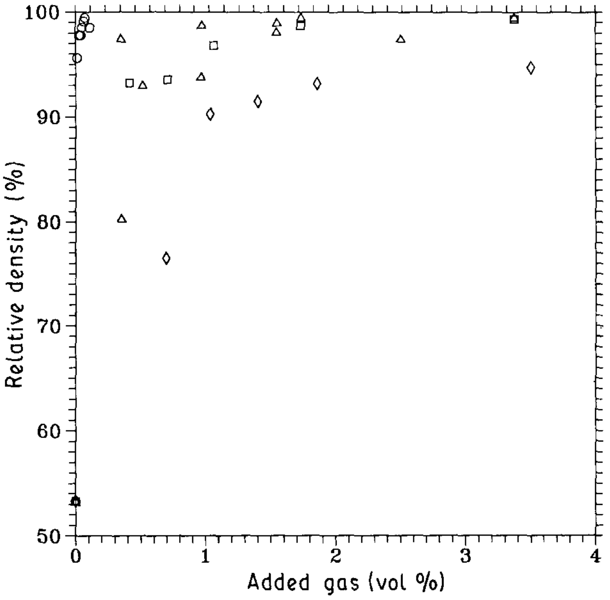

Figure 2 Relative density of MgO-doped specimen against amount of additive gas to the argon gas. All samples had already received the prior cleaning treatment. (○) H_2O, (□) H_2, (△) N_2, (◇) O_2.

3. Results

Sintered densities of rods that had been previously cleaned are displayed in Figs 1 and 2. The water vapour results are shown on an expanded scale in Fig. 3. The densities of cleaned undoped and magnesia-doped specimens sintered in pure argon were about 67% and 53%, respectively. The drastic reduction in sintering brought about by the cleaning treatment can be appreciated by noting that the densities of uncleaned rods sintered in argon without additive gases were about 96.8% and 99.5% for the undoped and magnesia-doped specimens, respectively. All of the additive gases caused significantly increased specimen temperatures and sintered density compared with the as-cleaned specimens sintered in pure argon. The diatomic additions (oxygen, nitrogen and hydrogen) gave similar results except for oxygen with the doped powder. Here the densities of the doped specimens were lower than the undoped specimens. A lower specimen temperature was seen in the oxygen addition experiments and accounts, at least in part, for the lower sintered density. The doped samples showed an increasing yellow-to-brownish colour after sintering as the amount of oxygen was increased. In contrast, all other samples remained white after sintering. There were no significant differences between densities of samples sintered with nitrogen or hydrogen additions.

The addition of water vapour had a much greater effect than the other gases on plasma sintering of alumina, as seen in Figs 1 and 2. In this case, the density increased rapidly with the addition of as little as 3×10^{-4} volume fraction of water vapour. The MgO-doped sample always reached a higher density than the pure samples with the same amount of water vapour added (Fig. 3).

Table II shows ranges of sample temperatures of pure and doped samples with hydrogen or water vapour added during sintering. It can be seen that the magnesia dopant caused a significant reduction in temperature at equal additive gas concentration compared with the undoped specimens, in agreement with previous observations [10–12], while the doped samples achieved higher densities, as observed for conventional and rapid sintering [17, 18]. The lower density of the pure specimen for the water vapour additions resulted from sintering temperatures that were higher than the optimum, which resulted in exaggerated grain growth and trapped pores. In contrast, the same temperatures, within experimental error, were achieved for both gases for the doped case, and the final densities were nearly the same. There was no evidence of trapped pores in this case.

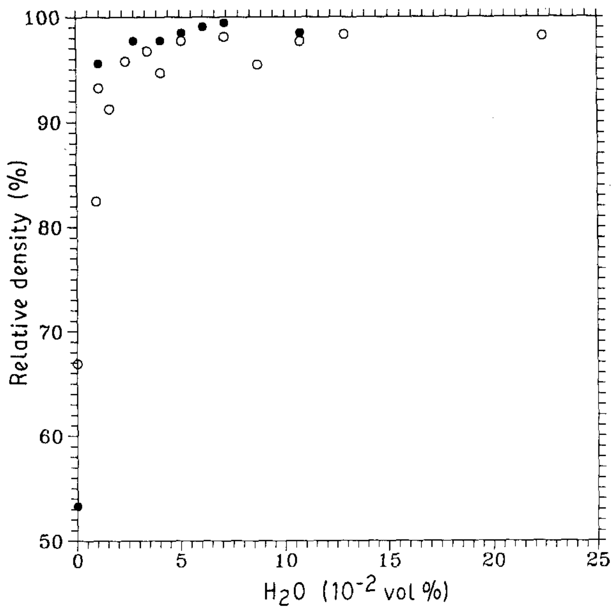

Figure 3 Relative density against amount of water vapour addition to the argon gas. All samples had already received the prior cleaning treatment. (○) Pure, (●) MgO-doped samples.

Average grain sizes for several specimens estimated from polished sections using the intercept method are listed in Table III. The grain sizes are significantly larger for the undoped material, and reached as much as 100 μm in the case of the nitrogen addition. Magnesia-doped specimens had very small grains. For both pure and doped cases, the grain size increased from the centre to the edge of the specimens, suggesting that the edge reached a higher temperature than the centre. This is due to the fact that the edges were directly heated by the hot plasma.

The major elements detected in the various plasmas by emission spectroscopy are shown in Table IV. Atmospheric and material components account for most of these. The sodium was either an impurity in

TABLE II Specimen temperature ranges observed for hydrogen and water-vapour additions

Specimen	Gas amount and type	Average density (%)	Temperature range (°C)
Pure	0.7% H_2	98.0	1640–1750
	0.05% H_2O	97.5	2025–2045
Doped	1.7% H_2	98.6	1630–1790
	0.05% H_2O	98.5	1675–1725

TABLE III Results of grain-size measurements

	Specimen no.	Gas additive	Amount added (%)	Density (%)	Grain size (μm)	Variance (%)
Pure	1	None	–	66.9	–	–
	2	H_2	0.3	96.6	2.45	6.0
	3	H_2	1.8	97.7	5.43	4.9
	4	O_2	0.3	91.9	1.45	5.1
	5	O_2	1.5	98.4	11.9	7.3
	6	N_2	0.25	92.0	0.93	5.2
	7	N_2	1.5	98.1	100.0	14.2
	8	H_2O	0.009	82.4	–	–
	9	H_2O	0.07	98.1	90.6	13.5
Doped	11	None	–	53.3	–	–
	12	H_2	0.4	92.7	0.46	5.2
	13	H_2	1.75	98.6	0.66	5.5
	14	O_2	0.65	76.5	–	–
	15	O_2	3.5	94.6	0.56	5.4
	16	N_2	0.5	93.0	0.61	4.3
	17	N_2	1.5	98.6	0.69	4.5
	18	H_2O	0.011	95.6	0.56	5.0
					0.35	4.0[a]
	19	H_2O	0.071	99.5	1.70	5.0
					1.66	5.0[a]

[a] Measured from linear intercepts.

TABLE IV Emission lines used for spectroscopic analysis

Element	Wavelength (nm)
Ar	549
Al	310
H	658
[a]H′	487
Mg	520
Na	590
N	671
O	781
S	571

[a] H′ denotes a less intense emission line

TABLE V Emission spectra intensity ratios during cleaning. The numbers given are ratios of intensity of selected spectral lines with and without a specimen present under the same pressure and power

Specimen	Ar	H	O	N	Na
Pure	1	5	4	2	–
Doped	1	7	5	[a]	[a]

[a] Species that were detected in the plasma with a specimen present but not without.

TABLE VI Emission spectra intensity ratios during sintering of cleaned pure and doped alumina in plasma containing various additive gases. The numbers given are ratios of intensity of selected spectral lines with the additive gas to the intensity in pure argon with a specimen present in both cases

Additive	Ar	H	O	N	Na	S	Al	Mg
Nitrogen								
pure	1	1	1	[a]	[a]	–	–	–
doped	1	9.5	7	5	[a]	[a]	–	[a]
Hydrogen								
pure	1	6	3	[a]	–	–	[a]	–
doped	1	8	25	2	[a]	[a]	[a]	[a]
Water								
pure	1	7	50	[a]	[a]	[a]	[a]	–
doped	0.7	7	53	1	[a]	[a]	[a]	[a]

[a] Species that were detected with the additive gas but not without.

TABLE VII Emission spectra intensity ratios during sintering of cleaned pure and doped alumina with additive gases. The numbers given are ratios of intensity of selected spectral lines with nitrogen or hydrogen to the intensity with water vapour.

Additive	Na	S	Al	Mg
Nitrogen				
pure	0.2	0.0	0.3	–
doped	1.0	2.1	0.0	7.8
Hydrogen				
pure	0.0	0.0	0.2	–
doped	0.9	1.1	0.7	3.3

the as-received alumina powder or an inadvertent contaminant. Sulphur was expected because the alumina powder had been derived from an alum. There were no silicon lines found for any cleaning or sintering conditions, suggesting that the quartz tube was cooled sufficiently well to avoid contamination.

Relative intensities for major elements detected during cleaning and sintering are listed in Tables V–VII. The intensity ratios listed are qualitative in nature, derived simply from the magnitudes of the intensity of the peaks listed in Table IV. The intensities of spectroscopic emission of sodium, sulphur, aluminium and magnesium in plasma containing nitrogen and hydrogen are compared with those in the plasmas containing water vapour in Table VII. (Intensities were normalized to the water-vapour plasma simply because all the listed elements were observed in this plasma.)

4. Discussion

It is clear that a pure argon plasma could not heat alumina from which adsorbed gases had been removed to temperatures sufficiently high to cause significant densification. It is also clear that water vapour is far more effective in increasing the sintering rate than any other gas considered in the present study. Because specimens that had been exposed to the ambient could be sintered readily in a pure argon plasma, it is obvious that the naturally occurring adsorbed gases in the specimen play a critical role in plasma sintering of alumina. It is probable that adsorbed water is the most significant factor in this regard. It is well known that active alumina powder adsorbs water molecules very readily. Outgassing of H_2O has been detected at temperatures as high as 1900 °C [19]. This water can be assumed to be attached to the powder in the presintered specimens. Another source of water can be found in the gamma phase of the starting powder [20]. The water level in the doped specimens may have been further increased through the use of a water solution of the MgO dopant.

Each of the additive gases could affect the sintering behaviour itself, or alter the nature of the plasma, or both. Because the heat for plasma sintering comes from the direct interaction between the plasma and the specimen, any variation in the plasma caused by the additive gases would imply a change in the sample heating.

Depending on the type of the gases added, they could enhance sintering by increasing the creation of defects of the rate-controlling species [21–25], by decreasing the sintering activation energy [20, 26], by affecting the behaviour of the sintering aid (MgO), or by a combination of the above mechanisms. Some of the reported work on the effect of atmospheres on the conventional sintering of alumina is consistent with results presented here, and some is not. One of several similarities is the effect of water-vapour content in the sintering atmosphere. The enhanced densification found with water vapour addition agrees with Harmer's findings [27] on the sintering of pure and MgO-doped alumina. In his results, final densities were higher for specimens sintered in a dry atmosphere than for those sintered in a wet atmosphere at 1300 °C; and the opposite results were obtained for temperature above 1500 °C. This agrees with our experiments which were carried out in the range 1600–2000 °C. The more enhanced sintering in hydrogen than in oxygen for the doped case seems to follow the suggestion that the sintering rate increased as the oxidizing power of the atmosphere decreased using a conventional sintering method [23, 26]. On the other hand, this trend was not observed for the pure specimens. The inconsistencies concerning the effects of the atmosphere may indicate that the plasma was causing other effects in addition to providing heat.

The addition of polyatomic gases can affect the plasma in at least four ways. First, the introduction of gas molecules which have larger cross-sections increases the electron-impact excitation of the vibrational energy. Molecules such as nitrogen, carbon monoxide, carbon dioxide and water have larger cross-sections than hydrogen and oxygen. As a result, an electron will excite a nitrogen, carbon monoxide, carbon dioxide or water molecule more than a hydrogen or oxygen molecule. This vibrational energy could then be given to the specimen during inelastic collisions. Secondly, the recombination at the specimen surface is another process in which energy is liberated to the specimen, and the additive gases might affect atomic and ionic recombination rates [28]. In addition, because the heat content is greater for diatomic gases than for monatomic gases at temperatures above 3000 K [29], greater heating would be observed in their presence. The third way is to increase the dissociation yield of the residual gases in the plasma. For instance, it was reported that traces of water or oxygen can enhance dissociations of hydrogen or nitrogen [28, 30, 31]. Finally, because diatomic gases have higher thermal conductivity in a plasma than monatomic gases have, these molecules in the plasma can also increase the conductive and convective heat transfer from the plasma to the specimen. Most likely, a combination of these effects explains the enhanced heating upon introduction of polyatomic gases.

Table V shows significant increases in hydrogen, oxygen, and nitrogen when raw samples were inserted into the plasma under cleaning conditions, indicating at least partial removal of adsorbed water vapour, nitrogen and, perhaps, atmospheric oxygen. The effectiveness of the cleaning condition can be appreciated by noticing the ratio of hydrogen, oxygen, and nitrogen under sintering conditions with and without the additive gas, as shown in Table VI. It is apparent that the cleaning condition for the doped specimens was not as effective as that for the pure specimens. For instance, the hydrogen and oxygen intensities were markedly enhanced in the sintering plasma with nitrogen addition for the doped specimens. This suggests that the adsorbed species were only partially removed during cleaning.

Table VII reveals that the intensity of magnesium emission in the nitrogen and hydrogen plasmas is considerably enhanced over that in the water-vapour plasma. This is probably an indication that the MgO is evaporated from the sample at a greater rate in nitrogen and hydrogen. The lower rate of MgO evaporation may be a factor in the effectiveness of water vapour as a plasma additive to enhance sintering.

The anomalous heating phenomena mentioned in Section 1 can be explained based on the finding that plasma sintering of alumina depends strongly on the presence of water vapour in the sintering atmosphere. When a pre-sintered sample is inserted into a sintering plasma without prior "cleaning" treatment, desorption of water molecules occurs. The water vapour is being continuously swept away by the flowing argon. As the translation rate is increased, fresh material is inserted into the plasma at a faster rate so that the concentration of desorbed vapour in the chamber is increased. This causes a higher sintering temperature and enhanced sintering through the mechanisms described previously.

A sintered specimen could not be reheated to the sintering temperature because its surface area is too small to carry sufficient water vapour to cause heating.

5. Conclusions

The addition of oxygen, hydrogen, nitrogen, or water vapour to argon gas during plasma sintering of plasma-cleaned specimens significantly accelerated sintering. Water vapour showed the strongest effect, followed by hydrogen, nitrogen and then oxygen. Pure argon did not heat the pure alumina (with cleaning treatment) to the sintering temperature under the power and pressure conditions of the present study.

The presence of MgO resulted in greater density, finer grain size and lower sample temperature than those of the pure material, except in the case of oxygen addition. There were essentially no differences in the final densities for the pure specimens with the addition of oxygen, nitrogen, or hydrogen.

The anomalous heating phenomena could be explained in terms of adsorbed gases, especially water vapour, on the initial alumina powders, and the water contained in the gamma alumina constituent of the starting powders.

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