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The water vapor hot gas corrosion of MGC materials with Al_2O_3 as a phase constituent in a combustion atmosphere

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Abstract

The hot gas corrosion behavior of two melt grown composite materials (Al_2O_3/YAG and Al_2O_3/GAP) in comparison with alumina and sapphire was investigated. The tests were performed in a high temperature burner rig at 1450 °C, a total pressure of 1 atm with a water vapor partial pressure of 0.28 atm, a gas flow velocity of 100 m/s and exposure times for up to 450 h.

In comparison to sapphire, alumina showed comparable corrosion rates and similar corrosion traces on the corroded surface.

The Al_2O_3/YAG and Al_2O_3/GAP melt grown composite materials were subject to degradation due to the corrosion attack of the alumina phase. This was the consequence of the formation and evaporation of volatile hydroxides (e.g., $Al(OH)_3$). In comparison to polycrystalline alumina the YAG or GAP showed a higher corrosion stability, which causes the formation of a porous YAG or GAP surface layer with increasing corrosion time. For short corrosion times, the porous YAG or GAP surface layer led to a small corrosion protection of the material. After longer corrosion times a switch to linear corrosion kinetics was observed due to spalling of the porous corrosion layer. The corrosion rates for long exposure times were comparable to bulk alumina or sapphire. In principle the regarded polycrystalline and single crystalline materials showed the same corrosion behavior.

Keywords: Corrosion; MGC; Al_2O_3; YAG

1. Introduction

The goals for future generations of gas turbine engines are to increase the thermal efficiency and at the same time to decrease the emissions of the turbine plant. This can be achieved by an increase of the hot gas inlet temperature and by lower amounts of cooling air for the turbine components, resulting in higher material temperatures. The directionally solidified oxide eutectic composites (melt grown composites) with alumina as a phase constituent are regarded as a promising material group for the use as parts in the hot gas path of future gas turbines. [1–3] These materials show a unique microstructure, where different single crystalline phases like Al_2O_3 (sapphire) with $Y_3Al_5O_{12}$ (YAG) or Al_2O_3 with $GdAlO_3$ (GAP) are entangled with each other, resulting in a three dimensional network without grain boundaries. In comparison with polycrystalline oxide materials, the melt grown composite (MGC) materials show superior high temperature mechanical behavior like high temperature strength and creep resistance. For this reason and due to their naturally given stability to oxidation, the materials are interesting for the use in the hot section of gas turbines.

The water vapor hot gas corrosion can be a life limiting problem for the long time use of non-oxide and oxide materials in a gas turbine atmosphere. Common structural ceramics like Si_3N_4, SiC, Al_2O_3 and $Al_6Si_2O_{13}$ mullite showed insufficient stability in high velocity combustion environments. Especially the water vapor in the combustion gas attacks the ceramic surface by the formation and evaporation of Si-hydroxides[4–8] (SiC, Si_3N_4, mullite) and Al-hydroxides (Al_2O_3).[8–10] In combination with high gas flow velocities and long exposure times (a service interval period is around 10.000 h), a high corrosion recession and the loss of shape and functionality of the components is proposed.[7–9,11] Therefore, the development of environmental barrier coatings (EBC) is subject of numerous researches.

Up to now, there is little knowledge about the water vapor corrosion stability of melt grown composite materials with alumina as a phase constituent. Prior studies with a very low gas flow velocity or with short corrosion times indi-

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cated a high corrosion stability of the MGC material.[3,12–14] To evaluate the potential for a future use of such materials in real gas turbines, long time corrosion tests under gas turbine simulating environments with high gas flow velocities are needed. In the present study, the hot gas corrosion stability of two melt grown composite materials in comparison to alumina and sapphire is presented.

2. Experimental

The corrosion behavior of two melt grown ceramic materials (Al_2O_3/YAG and Al_2O_3/GAP eutectic composite), alumina and sapphire was investigated. The MGC materials were supplied from Ube Industries Ltd., Japan. The sapphire was supplied from GWI Sapphire, Germany. Dense polycrystalline alumina (AKP50 Sumitomo Chemical Tokyo/Japan) was fabricated by sintering at 1300 °C in air atmosphere. The sample shape for corrosion testing is a rod with dimensions of 3.4 mm in diameter and 36 mm in length (polished surface quality).

The corrosion tests were performed in a high temperature burner rig. The burner rig consisted of a combustor with a following test section. Natural gas (mainly CH_4) was used as fuel for the combustor. To obtain a higher water vapor partial pressure in the combustion gas, water vapor was introduced separately to the air/fuel gas stream using an evaporator. The temperature was controlled by a Pt–Rh thermocouple near to the sample holder. In the test section the test specimens are placed into a Al_2O_3/mullite CMC specimen holder and exposed to the free gas flow. In summary the test conditions are:

Temperature	1450 °C
Gas flow velocity	100 m/s
Total pressure	1 atm
Water vapor partial pressure	0.28 atm
Fuel	Natural gas
Equivalence ratio fuel/air	$\Phi = 0.7$ (fuel lean)
Composition of the combustion gas	$0.61N_2$, $0.28H_2O$, $0.06O_2$, $0.05CO_2$ (in partial pressure of each species)
Testing times	200. . .450 h

The recession of the specimens was obtained by measuring the weight difference before and after the corrosion test. It is expressed by weight change ΔW (mg/cm^2) relating to the area of the test specimen exposed to the gas flow. From the weight change ΔW with time the weight loss rate K_w (mg/cm^2 h) was determined. For linear corrosion kinetics the weight loss rate K_w can be calculated with a linear fit. The tests were conducted for 200–450 h at 1450 °C. The weight loss rate was calculated after reaching equilibrium conditions (after 30–50 h). Information about microstructure alterations and corrosion attack was obtained by observations of the sample surfaces and polished cross-sections in the SEM.

3. Results and discussions

A summary of the corrosion test results is given in Table 1. Fig. 1 demonstrates the corrosion behavior as weight loss as a function of time for the investigated materials. A linear corrosion kinetics was found for Al_2O_3 and sapphire. This indicates a surface reaction controlled corrosion mechanism. For short corrosion time (<200 h) parabolic corrosion kinetics were found for the MGC materials. For longer corrosion times (>200 h) a switch to linear corrosion kinetics was observed. To show the differences in the corrosion surface layer with increasing corrosion time, two sets of MGC materials were investigated and corroded to 215 and 455 h.

Table 1

Summary of corrosion test results of oxide ceramic materials investigated at $T = 1450\,°C$, $v = 100\,m/s$, $p_{H_2O} = 0.28$ atm and $P = 1$ atm

Material	Time (h)	Δm_t (mg)	K_w (mg/cm^2 h)	R^2 fit K_w
α-Al_2O_3	294.7	31.4	3.25×10^{-2}	0.9995
Sapphire	294.7	30.1	3.14×10^{-2}	0.9999
Al_2O_3/YAG MGC	215	18.0	Parabolic kinetic	–
Al_2O_3/YAG MGC	455.5	29.0	1.69×10^{-2} [a]	0.9995
Al_2O_3/GAP MGC	215	16.3	Parabolic kinetic	–
Al_2O_3/GAP MGC	455.5	25.4	1.31×10^{-2} [b]	0.9996

[a] Linear fit in the time range: 215.1–455.5 h.

[b] Linear fit in the time range: 340.2–455.5 h.

3.1. Corrosion of alumina in comparison to sapphire

The weight loss rate of alumina was comparable to single crystalline sapphire. The main corrosion reaction was the formation of Al-hydroxides like $Al(OH)_3$ with water vapor from the combustion gas.[8–10] Fig. 2a shows the corroded surface of the polycrystalline alumina after corrosion for 295 h. The grain boundaries can be seen clearly, similar to thermal etching techniques. Fig. 2b shows that especially the alumina grains were attacked by the water vapor. The same traces of corrosion were observed on the corroded sapphire surface (Fig. 2c). Similar corrosion traces were reported for the water vapor corrosion of sapphire for low[10,16] and high gas flow velocities.[14] Based on these observations and the same rate of weight loss for alumina and sapphire, it can be concluded that the pure grain boundary in the polycrystalline alumina does not have any significant influence on the corrosion process.

3.2. Corrosion of Al_2O_3/YAG and Al_2O_3/GAP MGC

Figs. 3a and 4a show the microstructure of the two MGC materials, Al_2O_3/YAG and Al_2O_3/GAP. In comparison to Al_2O_3/YAG the lamellar size for Al_2O_3/GAP was smaller.[14] During the corrosion exposure water vapor led to the favored degradation of the alumina phase. As reported prior[8,17] aluminates like YAG, YAM and YAP showed a superior corrosion resistance in comparison to alumina, and more than one order in magnitude lower corrosion rates. Therefore, the first sample set of the investigated MGC materials showed the formation of a porous YAG (for the Al_2O_3/YAG MGC Fig. 3b–d) or GAP (for the Al_2O_3/GAP MGC Fig. 4b–d) surface layer with increasing corrosion time. For short corrosion times (<200 h) this porous YAG or GAP layer led to parabolic corrosion kinetics with a small corrosion protection. Another set of MGC samples showed a switch to linear corrosion kinetics (Fig. 1) for long corrosion

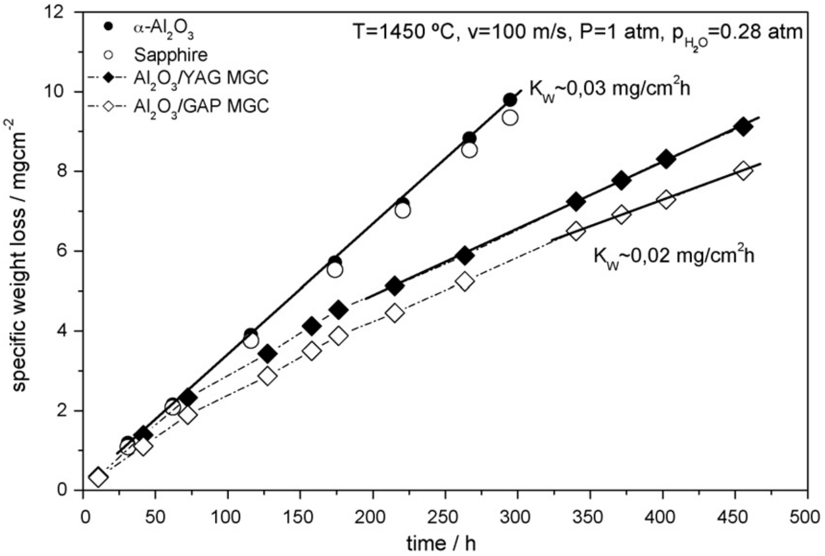

Fig. 1. Corrosion kinetics of alumina, sapphire, Al_2O_3/YAG MGC and Al_2O_3/GAP MGC at 1450 °C.

times (>200 h). This was the consequence of the degradation of the porous YAG or GAP surface layer with increasing time due to cracking and spalling (Fig. 3d and Fig. 4d). After long time corrosion exposure, a dynamic equilibrium between the formation of the porous passivation layer and the spalling of it was reached. The observed preferred corrosion degradation of the alumina phase in the MGC materials is in agreement with water vapor corrosion studies of these materials done by low gas flow velocities [12,13] or by high gas flow velocities and short corrosion times.[3,14] In both cases an increase in the surface roughness was reported due to selective corrosion and degradation of the alumina phase.

For the water vapor corrosion of aluminates in the Al_2O_3–Y_2O_3 (YAG, YAP and YAM) it was reported that the water vapor led to the formation of Al-hydroxides and so to a phase change into aluminum poor phases, or at the end to Y_2O_3

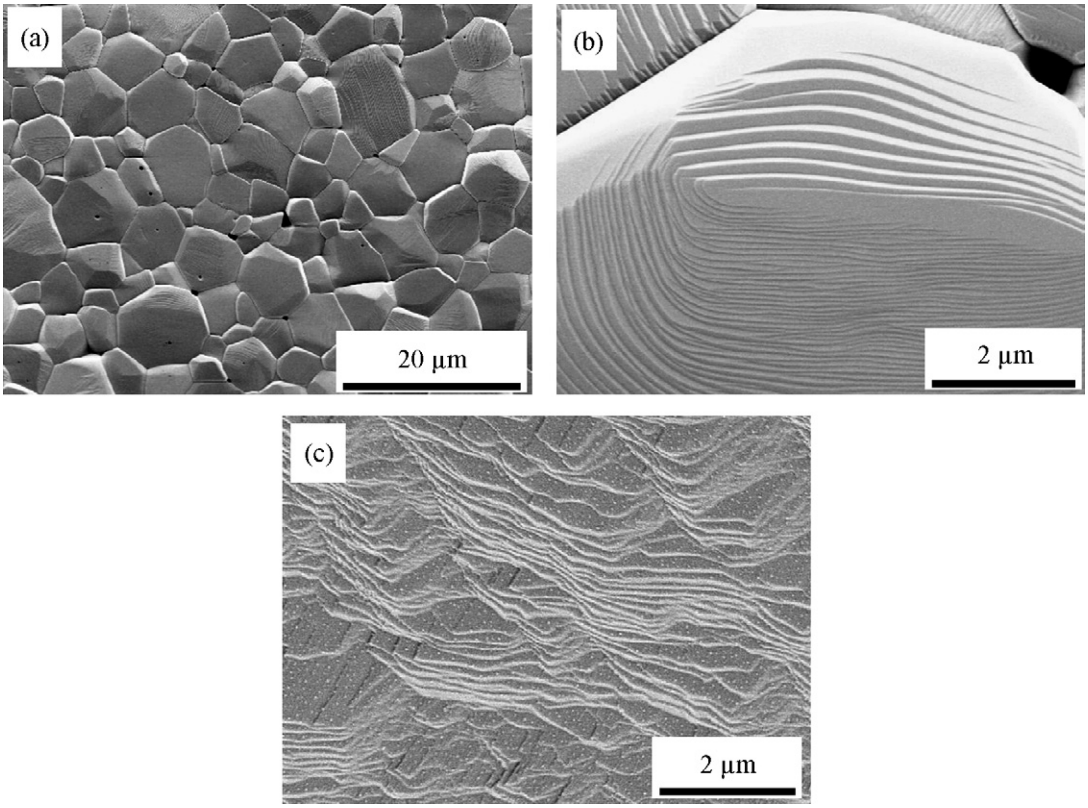

Fig. 2. Corroded surface of alumina (a and b) and sapphire (c) after corrosion at 1450 °C for 295 h.

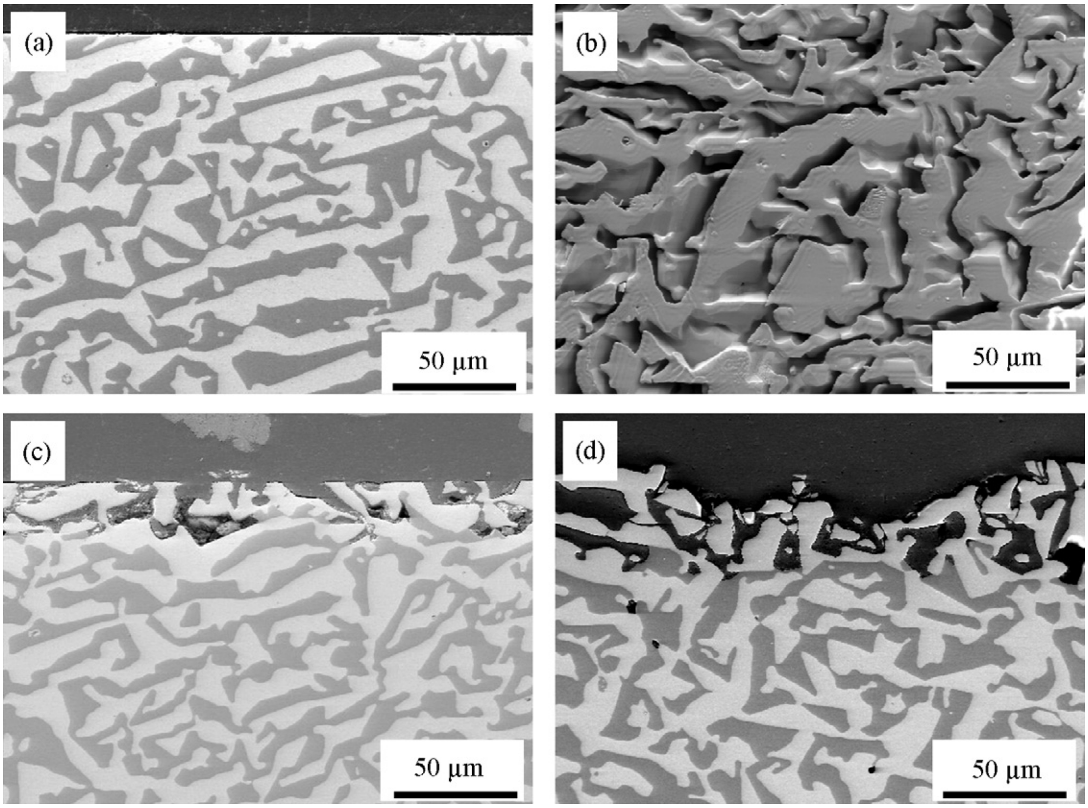

Fig. 3. (a) Cross-section of Al_2O_3/YAG MGC after fabrication. Surface (b) and cross-section (c) after corrosion at 1450 °C for 215 h and (d) 455 h.

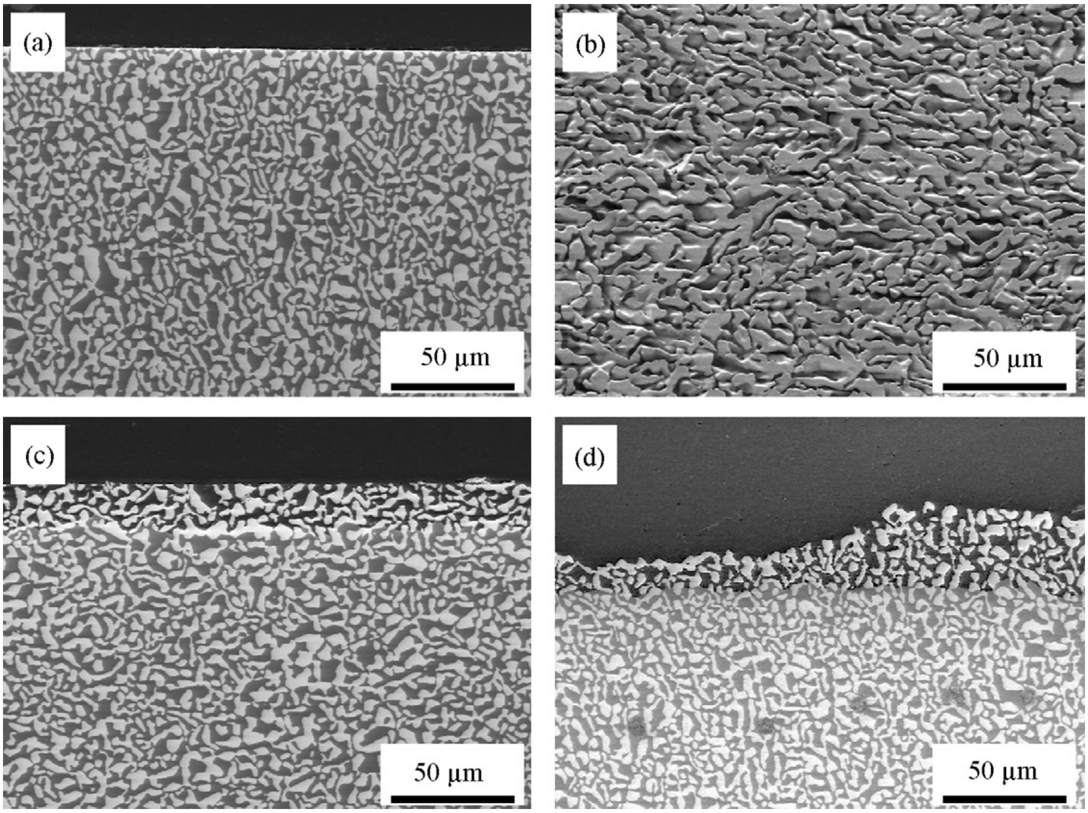

Fig. 4. (a) Cross-section of Al_2O_3/GAP MGC after fabrication. Surface (b) and cross-section (c) after corrosion at 1450 °C for 215 h and (d) 455 h.

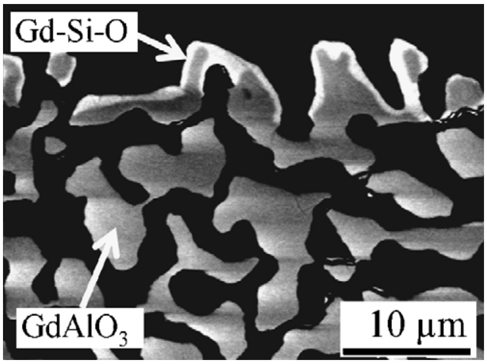

Fig. 5. Formation of a Gd-silicate on top of the Al_2O_3/GAP MGC during corrosion exposure at 1450 °C for 455 h.

on the corroded surface.[8,17] As a consequence of the corrosion degradation of the SiC lining in the combustor of the corrosion test rig, a small partial pressure of Si-hydroxides existed in the combustion gas. An estimation by means of an assumed corrosion rate of the SiC lining and of the known flow conditions led to a Si-hydroxide partial pressure around 10^{-8} atm by 1 atm total pressure of the system. This small partial pressure of Si-hydroxides is sufficient enough to react with the corroded surface of the aluminates, in general with the rare earth oxides to form a silicate. In the case of the Y_2O_3–Al_2O_3 aluminates a small Y_2SiO_5 layer was found on the corroded surface of YAG, YAP and YAM.[8,17] Similar corrosion traces were found on the corroded surface of the MGC materials. Fig. 5 shows the porous GAP corrosion layer of the Al_2O_3/GAP material. On the surface of this corrosion layer a new phase was formed. With energy disperse X-ray analyses a Gd–Si–O phase was detected, indicating the formation of a Gd_2SiO_5 phase.

Nevertheless, these secondary corrosion reactions of the porous YAG or GAP surface layer with the formation of small amounts of silicates have no dominant influence of the overall corrosion behavior of the MGC material. For long corrosion times the mechanical stability of the formed corrosion layer is critical. Due to the fact that a spalling of these layers was observed and that the corrosion rate for long time exposure is only negligible smaller in comparison to alumina, it can be concluded that MGC materials with alumina as a phase constituent show insufficient long time corrosion stability in gas turbine environments. One possibility to protect such materials is to coat them with an environmental barrier coating (EBC). As it was shown[17], dense YAG EBCs have the potential for corrosion protection of materials with alumina. Particularly the similar thermal expansion coefficient between YAG and the Al_2O_3/YAG or Al_2O_3/GAP substrate will lead to a promising mechanical stability.

4. Conclusions

The water vapor hot gas corrosion behavior of polycrystalline Al_2O_3, sapphire and of two melt grown composites (Al_2O_3/YAG MGC and Al_2O_3/GAP MGC) were investigated. For alumina in comparison to sapphire similar corrosion traces were found on the corroded surface. Furthermore, the same corrosion rates for alumina and sapphire showed that single crystalline materials like sapphire have a better high temperature mechanical potential (e.g., creep resistance[15]), but the water vapor corrosion will be a serious problem in material systems with Al_2O_3 as a phase constituent. Consequently, the MGC materials investigated showed the preferred corrosion attack of the alumina phase. For long corrosion times, the formation of a porous YAG or GAP surface layer was observed. In principle, the corrosion degradation was comparable to polycrystalline Al_2O_3/YAG composites.[17] Insufficient mechanical stability of the porous corrosion layer led to linear corrosion kinetics with a corrosion rate in the dimensions of pure alumina. For the long time exposure of MGC materials in gas turbines the use of environmental barrier coatings like dense YAG is proposed.

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