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Hot corrosion behaviour of rare-earth magnesium hexaaluminate based thermal barrier coatings under molten sulphate-vanadate salts

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ABSTRACT

Hot corrosion behaviour of rare earth magnesium hexaaluminate (REMHA) based thermal barrier coatings (TBCs) such as i) lanthanum magnesium hexaaluminate (LMHA), ii) neodymium doped LMHA (LNMHA) and iii) LNMHA-yttrium aluminium garnet composite were investigated and compared with standard yttria stabilized zirconia (YSZ). The hot corrosion was carried out at 1050 °C for 100 h under molten sulphate-vanadate salts. REMHA shows superior hot corrosion resistance than YSZ. The hot corrosion reaction zone and the morphology of corrosion product are highly influenced by the rare earths in the coating. LNMHA has the best hot corrosion resistance and can meet the requirement of advanced TBC.

1. Introduction

In order to protect hot section of gas turbine components and increase efficiency, thermal barrier coatings (TBC) are exclusively used. The TBC generally consists of metallic (MCrAlY; M = Ni, Co) bond coat and ceramic top coat (YSZ) [1–3]. The most commonly used YSZ provides superior performance up to 1200 °C but fall short beyond this temperature. It undergoes phase changes, excessive sintering, and poor hot corrosion resistance in sulphate-vanadate salts [4–6]. The metastable tetragonal phase of zirconia (t') transforms into equilibrium tetragonal (t) and cubic (c) phase during thermal cycling. The equilibrium tetragonal phase transform to monoclinic phase (m) which is associated with 3–5% volume increase. This phase transformation causes premature failure of the YSZ coatings [6]. In the case of hot corrosion, yttria is leached out from t'-ZrO_2 and it destabilizes the zirconia to monoclinic phase, which also leads to similar failure [5,7].

The demand of increased turbine inlet temperature and improved TBC performance has motivated several researchers to find out alternate ceramic materials for top coat. Rare earth zirconates ($Re_2Zr_2O_7$; Re = La, Gd, Nd etc. or combinations thereof) and rare earth hexaaluminates ($ReMgAl_{11}O_{19}$; Re = La, Gd, Nd etc. or combinations thereof) emerge as new TBC materials and studied extensively in last decade [8–11]. Out of them, the lanthanum magnesium hexaaluminate (LMHA, $LaMgAl_{11}O_{19}$) is found to be one of the most promising material for advanced TBC [6]. It has low thermal conductivity, high thermal expansion coefficient, excellent high temperature stability, high resistance to sintering, low oxygen transparency etc. [12,13].

TBC used for land based and marine gas turbines are generally operated using low quality fuel and also face corrosive environments. The impurities of low quality fuel are mainly sodium vanadium and sulphur, which can form Na_2SO_4 and V_2O_5 at operating temperature and get deposited on the surface of turbine blades [14,15]. The molten salts react with Y_2O_3 and La_2O_3 of YSZ and $La_2Zr_2O_7$ respectively. This reaction leaches out the rare earth part and forms transformable tetragonal zirconia phase [7,14,16]. The hot corrosion resistance of graded coating of YSZ/$LaMgAl_{11}O_{19}$ is also reported in literature and found improved performance [16]. The hot corrosion behaviour of plasma sprayed LMHA, neodymium doped LMHA (LNMHA, $La_{0.5}Nd_{0.5}Al_{11}O_{19}$) and LNMHA-yttrium aluminium garnet composite (YAG, $Y_3Al_5O_{12}$) coatings are very limited.

Therefore, the main objective of this present work is to investigate the hot corrosion behaviour of LMHA, LNMHA and LNMHA-YAG coatings under molten sulphate-vanadate salts at 1050 °C for 100 h. Standard 7 wt% YSZ coating is also tested in similar conditions to compare the hot corrosion behaviour.

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2. Experimental procedure

2.1. Materials synthesis

Lanthanum magnesium hexaaluminate (LMHA, $LaMgAl_{11}O_{19}$), neodymium doped LMHA (LNMHA, $La_{0.5}Nd_{0.5}MgAl_{11}O_{19}$) and LNMHA-YAG ($\{0.7La_{0.5}Nd_{0.5}MgAl_{11}O_{19}–0.3Y_3Al_5O_{12}$) composite powders were synthesized by advanced sol gel processing [17,18]. The boehmite (99.9%), lanthanum nitrate (99.99%), neodymium nitrate (99.99%), yttrium nitrate (99.99%) and magnesium nitrate (99.9%) were used as precursors. Boehmite hydrosol (8 wt%) was prepared by dispersing it in hot water and peptized by adding dilute nitric acid (4 M) [17,19]. Desired amount of these metal salts are added to the boehmite sol as their water solution. The hydrosol was homogenized by continuous stirring and spread over a stainless steel stray where sol gets converted into gel. The gel was dried initially at 80 °C and then at 200 °C. The dry gel was crushed into powder and screened using ASTM sieves. Graded powders were calcination at 1600 °C for 2 h and the powder of 20 to 65 μm were used for plasma spray coatings.

2.2. TBC development

Disc shape nickel based super alloy (Inconel 718) of Φ 30 mm and 3.8 mm thickness was used as substrate. The substrate was grit basted and cleaned thoroughly prior to the TBC formation, which generally improves the bond strength. The surface roughness of the grit blasted substrate is ~6.64 μm. Thermal barrier coatings were prepared by atmospheric plasma spraying using the Advanced Materials Technology plasma spray units with a F4-MB gun. The Ar and H_2 were used as a primary and secondary plasma gases, respectively. A 150 ± 30 μm thick bond coat of NiCrAlY was applied first followed by a 320 ± 30 μm thick ceramic top coat. The reference for atmospheric plasma spraying parameters was taken from the literature [20,21], which is optimized further by several trial and errors. The plasma spraying conditions for the bond coat and top coat are given in Table 1.

2.3. Hot corrosion test

The coated disc cut into four pieces using water jet cutter, ultrasonically cleaned and dried. A corrosive salt mixture of 55 wt% V_2O_5 and 45 wt% Na_2SO_4 powder was spread uniformly over the coating surface. Premixed and ground salt powder was used for the test. The salt concentration was 25 mg/cm^2 and a gap of 2 mm left from the edges. An electric furnace was used to heat the specimen isothermally at 1050 °C up to 100 h in air. The heating rare was maintained at 5 °C/min and the specimens were cooled down to room temperature inside the furnace after the test.

2.4. Characterizations

XRD pattern of as prayed coatings and coatings after hot corrosion were obtained by X-ray diffractometer (XRD) (Bruker AXS, D8 Advance, Germany) using Ni filtered CuK_α radiation ($\lambda = 0.15405$ nm). The samples were scanned continuously from 10° to 80° (2θ) with a step size of 0.02° (2θ) and a scan rate of 3°/min.

Surface morphology and cross section of these specimens were studied using scanning electron microscope (JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDS). The specimens were mounted in phenolic powder and polished in order to investigate the cross section.

3. Results and discussion

3.1. Characterization of coatings

X-ray diffraction patterns of as coated YSZ, LMHA, LNMHA and LNMHA-YAG composite are shown in Fig. 1. The YSZ coating is well crystalline and the primary peaks belong to tetragonal phase. A trace amount of monoclinic phase is also noticed. On the other hand, other three TBCs are amorphous in nature and expected to be crystallized during heat treatment beyond 800 °C. The similar crystallization phenomena for LMHA coating during heat treatment are reported elsewhere [11,22]. The surface morphology of as coated TBCs is shown in Fig. 2. It is observed that all the TBCs have a significant amount of porosity but there are no visible cracks. The un-melted particles are also present along with solidified splats. The YSZ coating seems to have more un-melted particle than others. The cross sectional view of these four TBCs is shown in Fig. 3. The porous and lamellar structure is observed for all the four TBCs, which generally consider as a signature of APS process. The amount of porosity is found to be higher for YSZ coatings than others and this could be due to the presence of more un-melted particles.

3.2. Phase analysis

X-ray diffraction patterns of TBCs after hot corrosion are shown in Fig. 4. The XRD results of YSZ coating (Fig. 4a) reveal that the hot corrosion products are primarily YVO_4 and monoclinic zirconia (m-ZrO_2). These phases are present along with the parent metastable tetragonal phase (t'-ZrO_2). The intensities of these phases increase with the dwelling time. The monoclinic phase content in the hot corroded specimens is determined using Eq. (1) [7] and summarized in Table 2.

$$\%m\text{–}ZrO_2 = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(111)} \times 100 \quad (1)$$

where, I is the diffraction peak intensity of the respective planes.

The formation of YVO_4 is almost completed within 10 h duration whereas the conversion of m-ZrO_2 phase is around 63%. The m-ZrO_2 phase is increased by another 6% after 50 h of hot corrosion and no further increase occurs even after 100 h of dwelling time. The formation of m-ZrO_2 phase can be taken as an indication of the progress of hot corrosion process [23,24].

The main corrosion product of LMHA system is $LaVO_4$ (Fig. 4b). A trace amount of α-Al_2O_3 is also appeared in the pattern along with the parent $LaMgAl_{11}O_{19}$ phase. In case of LNMHA coating (Fig. 4c), additional $NdVO_4$ phase is present in the XRD pattern. Most of the peaks of $LaVO_4$ and $NdVO_4$ are coincided which made little ambiguity for identifying. In case of LNMHA-YAG composites, the YVO_4 phase is observed in addition to the other phases (Fig. 4d). The intensities of these phases increase with increase in hot corrosion time, which indicates the gradual degradation of hexaaluminate coatings.

Table 1
Plasma spraying conditions for TBC formation.

Type of coating	Spray distance (mm)	Voltage (V)	Current (A)	Plasma gas, Ar/H_2 (NLPM)	Carrier gas, Ar (NLPM)	Powder feed rate (g/min)	Coating thickness, (μm)	Substrate temperature (°C)
Bond coat	150	78	550	44/9.5	3.2	30	150 ± 30	250
Top coat	120	80	600	35/12	3.4	30	320 ± 30	250

Note: Anode-nozzle internal diameter is 6 mm; particle injector internal diameter and position are 1.8 mm and 90° respectively.