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Molten salt attack on t' yttria-stabilised zirconia by dissolution and precipitation

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Abstract

Degradation due to molten salt attack is one of the failure mechanisms of thermal barrier coatings. Thermochemical attack of the salt mixture Na_2SO_4–30 mol% $NaVO_3$ on ZrO_2–8 mol% $YO_{1.5}$ (8YSZ) at 950 °C was studied by two types of experiments. Sintered compacts were exposed to 25 mg cm^{-2} salt dosage for up to 96 h. In the other set of experiments, 10–35 wt.% 8YSZ powder was mixed with the salts to study the dissolution of 8YSZ in the molten salt. The role of volatile losses was also examined. The results show that more than 25 wt.% 8YSZ dissolves in the sulphate-vanadate melt at 950 °C, followed by slow reactions to form YVO_4 and $NaYV_2O_7$ at 950 °C. The unreacted Y_2O_3 and monoclinic ZrO_2 precipitate out separately during rapid cooling (∼300 °C/min). Slow cooling at ∼3 °C/min leads to the formation of ZrOS apart from ZrO_2 and Y_2O_3.

Keywords: Y_2O_3; ZrO_2; Thermal barrier coating; Corrosion; Engine components

1. Introduction

Thermal barrier coatings (TBCs) used for insulating the high temperature superalloy components in gas turbine engines are currently made of yttria stabilised zirconia (YSZ) with ∼7 wt.% of $YO_{1.5}$.[1,2] Upon deposition, the non-transformable tetragonal (t') phase constitutes the TBC.[3] This phase is inherently metastable and can be rendered transformable to the monoclinic (m) zirconia phase if depleted in yttria. Yttria depletion may be due to the transformation to a mixture of yttria-lean tetragonal (t) and yttria-rich cubic (c) phases during prolonged thermal exposure.[3] However, the t' phase can also be degraded by molten salt deposits to form m-zirconia and other products. For instance, gas turbines for power generation and marine applications are often operated with fuels contaminated with sulphur and vanadium. Moreover, saline water may be ingested into the gas turbine. Under such circumstances, molten salt deposits may condense on the TBCs.[1] The salt deposits mainly consist of Na_2SO_4 and $NaVO_3$.[4,5] These low melting salt deposits destabilise the t' YSZ through thermochemical attack in the temperature range of ∼700 to 1000 °C. The products of destabilisation consist of m-ZrO_2 and yttrium compounds, typically YVO_4. Such destabilisation is undesirable as the formation of m is considered detrimental to the durability of the TBC.[1–3] It must also be noted that the thermal conductivity of m-ZrO_2 is about twice that of the TBC composition.[1]

The typical composition of molten salt deposits is Na_2SO_4–30 mol% $NaVO_3$ above 900 °C.[4] Some of the studies have used pure V_2O_5 to investigate the basic aspects of the molten salt attack.[6–8] Among the many possible reactions, the following two provide an insight into the relevant factors[1]:

$$Y_2O_3\,(\text{in } t' \text{ zirconia}) + V_2O_5\,(\text{in melt}) \rightarrow 2YVO_4 \qquad (1)$$

$$Y_2O_3\,(\text{in } t' \text{ zirconia}) + 3SO_3\,(\text{in melt}) \rightarrow Y_2(SO_4)_3 \qquad (2)$$

Very high SO_3 partial pressure is necessary for significant rate of the reaction in Eq. (2). Therefore, reaction in Eq. (1) is considered more important. Also, products other than YVO_4 may form, though they are not considered as important in the literature.

While it is clear that the consumption of yttria leads to the appearance of m-ZrO_2, the exact mechanism has not been understood so far. Several mechanisms have been proposed for the degradation of the TBCs due to the molten salts. They are as follows: leaching of yttria from the zirconia matrix and reac-

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ting with the salts,[5,9] dissolution of the ceramic in the molten salt,[6,7,10] and Lewis acid-base theory.[10,11] It is reported that the salts infiltrate the porous coating and degrade it by reacting with the YSZ,[7] as well as cause physical damage due to solidification of the liquid salts in the pores. Consequently, spallation of TBC occurs.[9,12,13] It is also reported that the infiltration of molten salts depends on the relative density of the coating, as the more dense coatings degrade slower than the low density (porous) coatings.[12]

The molten salt constitution and its reactions with YSZ are expected to depend on temperature. Therefore, the corrosion products may also vary with temperature. The mechanism of these reactions has been often described as leaching.[5,14] However, the diffusion of Y^{3+} in YSZ is too slow for its extraction without the dissolution of YSZ in the molten salts. Moreover, *m*-ZrO_2 has been reported to form directly during vanadate attack on cubic YSZ, instead of going through tetragonal phase in few cases.[8] This indicates that there is no gradual depletion of yttria, at least during the interaction of a coating with the molten salt. Also, it has been reported that the YSZ in contact with the molten salt dissolves in it, followed by precipitation of YVO_4 and *m*-ZrO_2. However, the steps involved in the process are not clearly identified. The present work aims at understanding the details of S/V attack on yttria stabilised zirconia using a mixture of Na_2SO_4 with 30 mol% $NaVO_3$ as the corrodent.

2. Experimental details

2.1. Synthesis

Stabilised zirconia with 8 mol% $YO_{1.5}$ (8YSZ) was synthesised using the reverse co-precipitation technique reported earlier.[15,16] Zirconyl nitrate, $ZrO(NO_3)_2{\cdot}xH_2O$, and yttrium nitrate, $Y(NO_3)_3{\cdot}xH_2O$, were dissolved in de-ionised water to obtain a 0.3 M solution. This solution was added drop by drop into an NH_4OH solution with pH maintained at 9 under continuous stirring. Additionally, in order to avoid agglomeration of the precipitates PEG was added to the NH_4OH solution before commencing the precipitation process. The white gelatinous precipitate was filtered and washed with alcohol. The precipitate was dried at 150 °C and ground in an agate mortar and pestle. The ground powder was calcined at 700 °C for 2 h. The calcined powder was ground again in the mortar and pestle.

The ground powder was used for preparing sintered 8YSZ compacts. Green compacts of 10 mm diameter and 2 mm height were made using a compaction pressure of 850 MPa. These green compacts were sintered at 1250 °C for 2 h after heating at 10 °C/min in a muffle furnace with $MoSi_2$ heating elements (OKAY 70F 4). The top surfaces of the sintered compacts were polished. The relative density was measured using Archimedes' principle.

2.2. Molten salt attack experiments

The sintered and polished 8YSZ compacts were exposed to the salt mixture of composition Na_2SO_4–30 mol% $NaVO_3$. The salt mixture was prepared by grinding a mixture of this composition using a mortar and a pestle. The dosage of the salt mixture on the surface of the 8YSZ compacts was 25 mg/cm^2. The compacts with the pile-up of the salt mixture with this dosage were heated in a tube furnace to 950 °C and exposed to molten salts for 24, 48 and 96 h, followed by furnace cooling. The salt dosage was *not* repeated at any interval, to simulate the condition that the molten salt may condense only once at any given place in the gas turbine.

2.3. Evaporation and solubility studies

A part of the loose, calcined powder was heat treated at 1250 °C for 2 h to mimic the thermal exposure experienced by the sintered compacts during sintering. This heat treated powder was mixed with the salt mixture of Na_2SO_4–30 mol% $NaVO_3$ to study the dissolution behaviour of 8YSZ in the molten salt mixture, as well as the evaporative losses in the mixture at 950 °C. The ground mixture was exposed to 950 °C for time in the range of 2–24 h for solubility studies. The molten mixture was checked regularly for the reaction products formed by removing a part of the melt periodically to perform XRD on the powder. One set of such samples was air cooled while another was furnace cooled to identify the effect of cooling rate on the phases formed. The weight changes in the 8YSZ/salt mixtures were monitored for 48 h at 950 °C.

2.4. Characterisation

The as-synthesised powders, sintered compacts, as well as the compacts exposed to the molten salts were subjected to X-ray diffraction (XRD) studies to identify the phases formed. Data were collected using a Bruker Discover D8 diffractometer with Cu-Kα radiation (1.5405 Å), step size of 0.02°, time per step of 2 s and diffraction angle (2θ) range from 10 to 90° at room temperature.

Scanning electron microscopy (SEM, FEI Quanta 200) including energy dispersive spectroscopy (EDS, EDAX) was carried out on the specimens exposed to molten salts to know the morphology as well the phases formed after the reaction of the stabilised zirconia with molten salt. Both, the top surfaces and cross-sections were studied. Specimens were sectioned and mounted in a cold-setting resin such that the phases formed due to corrosion were immobilised for SEM studies.

3. Results

The XRD patterns in Fig. 1 show the phase constitution of the as-sintered 8YSZ and that of the loose powder subjected to the same thermal exposure as sintering. Both the materials consisted of single-phase tetragonal zirconia (JCPDS file 48-0224) described as the t' phase based on comparison with literature reports.[15–17] Based on XRD analysis,