Properties and Performance
of High Purity Thermal Barrier Coatings

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Abstract

It was found that the content of impurity oxides in 7YSZ, such as SiO_2 and Al_2O_3, has a significant effect on coating sintering resistance and phase stability of 7YSZ thermal barrier coatings (TBCs). The reduction of impurity content will significantly improve sintering resistance and phase stability of 7YSZ TBCs and thus allow the 7YSZ TBCs to be used at higher temperatures.

Introduction

Thermal barrier coatings (TBCs) are used to protect the metallic components in hot sections of gas turbines and aero engines against high temperature gases [1-6]. The application of TBCs allows an increase of ~100-150ºC in turbine or engine operation temperature [7]. The increase of operation temperature is directly related to the efficiency improvement of turbines and engines. Therefore, there is a continuing need to increase the operation temperature of turbines and engines, which will expose TBCs to higher temperatures.

Currently, ~7-8 wt.% Y_2O_3-ZrO_2 (7YSZ) is the material of choice due to its low thermal conductivity and high thermal expansion coefficient. However, when 7YSZ TBCs were exposed to temperatures higher than 1200 C, sintering and phase transformation of 7YSZ become significant and thus result in the degradation or even spallation of TBCs [7].

In the past decade, extensive research on advanced TBCs has resulted in the discovery of dozens of new TBC material that has either lower thermal conductivity or improved phase stability or both, as reviewed in reference [8]. Among them, the multi-doped zirconia [9] and Gadolinium zirconate ($Gd_2Zr_2O_7$) [10] have a thermal conductivity of less than half that of 7YSZ. In addition, these coatings exhibited significantly enhanced sintering resistance.

Another factor found to affect the sintering of TBCs is the content of impurity oxides in the coating, such as SiO_2 and Al_2O_3. Higher concentration of impurity oxides results in more rapid sintering of TBCs [11]. However, the effect of purity on TBC properties is not fully investigated and understood. In this paper, mechanical and thermal properties of a high purity 7YSZ TBC were evaluated and compared to those of TBCs of lower purities. In addition, the concept and potential of high purity new composition TBCs are discussed.

Table 1: Plasma spraying conditions.

N_2, l/min	H_2, l/min	CGF, N_2, l/min	I, A	P, kW	Feed rate, g/min	SD, mm
35.4	8.0	5.2	500	39.3	46	114

N_2 - primary plasma gas, H_2 – secondary plasma gas, CGF – carrier gas (N_2) flow, I – current, P – input power calculated using voltage measured at the power supply, SD – standoff distance.

Experimental

Three sets of TBCs were produced from three 7YSZ powders of different purity using identical processing conditions, as listed in Table 1. Except for thermal cycling test samples, all coatings were deposited on mild steel substrates precoated with ~50 μm aluminum so as to ease debonding of the top coat from the substrate with hydrochloric acid. As listed in Table 2, coating ZY-1 has a high concentration of SiO_2, coating ZY-2 has a high concentration of Al_2O_3, while coating ZY-3 has an extremely low concentration of all impurity oxides. After the microstructure of the coatings was found to be similar using standard metallographic procedures, freestanding coatings were obtained by removing the aluminum-coated substrate with the aid of hydrochloric acid. Dilatometry measurement (DIL 402C dilatometer, Netzsch, Selb, Germany) on these freestanding coatings was performed at 1400 C for 20 hours.

The evolution of zirconia phase structure after heat treatment at 1400 C was evaluated using X-ray diffraction. Meanwhile, the change of thermal conductivity after thermal exposure was determined using a Transient Plane Source (TPS) technique (Hot Disk TPS 2500, Uppsala, Sweden). Details of TPS technique can be found in reference [12]. The elastic modulus of as-sprayed and heat treated coatings were measured using a purpose-built four-point bending rig. Details of the test rig can be found in reference [13].

The TBCs deposited on a bond coated (air plasma sprayed CoNiCrAlY) Ni-base superalloy substrate (Hastalloy X) were thermally cycled in air using a CM^{TM} rapid temperature furnace (CM Inc. Bloomfield, N.J.). The thermal cycle consisted of a 10 min heat-up from room temperature to 1121°C (2050°F), a 40 min hold at 1121°C (2050°F) and a 10 minute forced air quench. A sample was considered to have failed when the TBC failure area reached 50% of the total area.

Table 2: Chemistry of the coatings of various purity levels.

Sample ID	ZrO$_2$	Y$_2$O$_3$	Al$_2$O$_3$	SiO$_2$	Th	U
ZY-1	Rem.	7.78	0.09	0.18	0.01	0.018
ZY-2	Rem.	7.79	0.2	0.09	0.012	0.016
ZY-3	Rem.	7.57	<0.02	<0.02	<0.002	<0.002
ZY-4	Rem.	7.41	0.07	0.02	<0.002	<0.002

Results

Sintering Shrinkage
Slab samples with a dimension of 1mm × 2mm × 2mm were cut from the freestanding coating and loaded into a heating tube with the through-thickness direction aligned with the transducer, i.e., the shrinkage in the direction normal to the coating/substrate interface is measured. After the sample was heated to 1400 C, the change of length with time is monitored and recorded. As shown in Fig. 1, the linear shrinkage of coating ZY-1 (high SiO$_2$ content) is 1.6% after 20 hours at 1400ºC and that for ZY-2 (high Al$_2$O$_3$ content) is 1.4%, while that for the high purity coating ZY-3 is less than 0.4%, which represents a reduction of shrinkage by more than 80% when compared to that of ZY-3 when compared to that of ZY-1 and ZY-2.
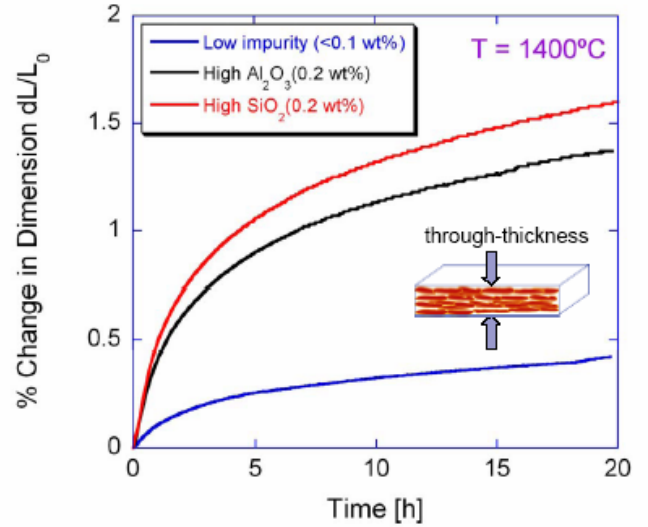

Figure 1: Linear shrinkage at 1400 C indicating less shrinkage for high purity coating.
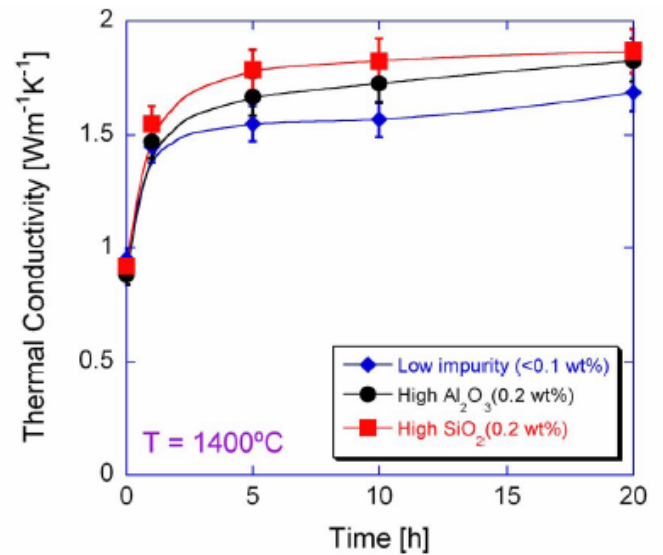

Figure 2: Change of thermal conductivity with time at 1400 C.

Thermal Conductivity
Before heat treatment, the thermal conductivity of all three coatings were found to be ~0.9 W/m.K, which is consistent to the published results measured using laser flash technique [10]. After 1 hour heat treatment at 1400 C (Fig. 2), the thermal conductivity of all three samples increased by more than 50%. The rapid increase in thermal conductivity can be attributed to the fast sintering of cracks and porosities with a nominal diameter of less than 100 nm [13]. Fig. 2 shows the increase of thermal conductivity relative to the thermal conductivity of as-sprayed samples. It can be seen that the thermal conductivity increased by 50%, 55% and 47% after the first 1 hour heat treatment for ZY-1, ZY-2 and ZY-3,

respectively. After 20 hours, the relative increase of thermal conductivity is 111%, 117% and 80%, respectively. The reduction of thermal conductivity increase for the high purity TBC (ZY-3) is believed to be related to its slower sintering rate, as shown in Fig. 1.
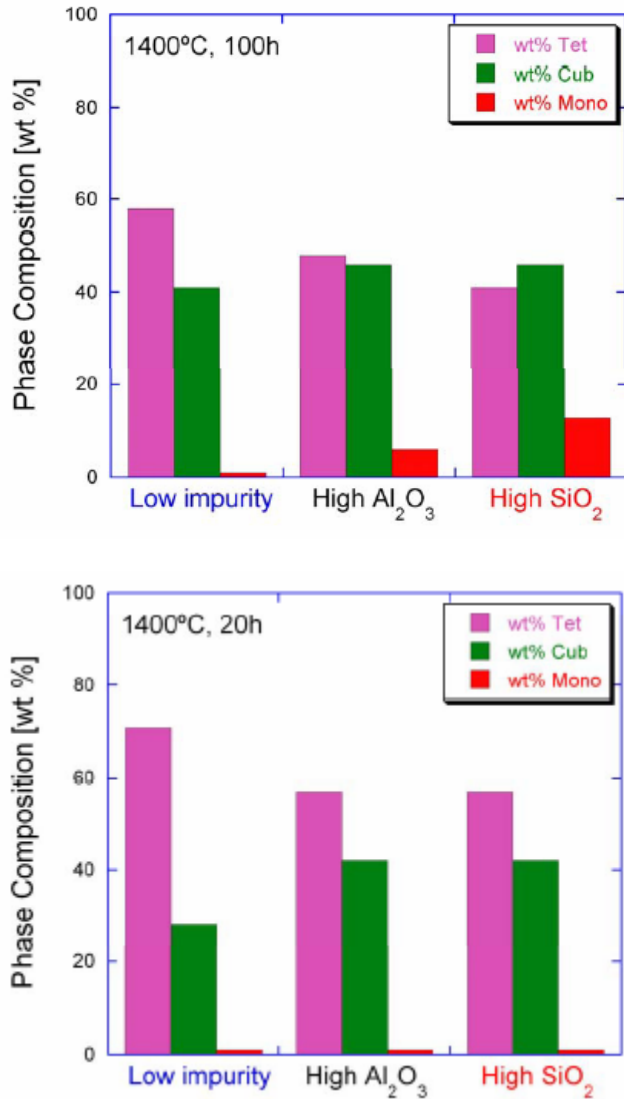

Figure 3: Evolution of coating phase structure after (a) 20 hours and (b) 100 hours heat treatment at 1400 ℃.

Phase Stability

Prior to heat treatment, only the non-transformable tetragonal phase (t') was detected in all three coatings. After 20 hours at 1400 C (Fig. 3a), less than 1% of monoclinic phase Zirconia was detected for all three coatings. However, significant amount of cubic phase zirconia was identified in these coatings and the volume percentage of cubic phase was estimated using the intensity of (111) peaks as 42%, 45% and 27% for coating ZY-1, ZY-2 and ZY-3, respectively. With the

increase of thermal exposure time (Fig. 3b), more t' phase zirconia is transformed to cubic and then to monoclinic phase due to the partitioning of yttria at high temperatures. Relative to coating ZY-1 (high SiO_2 content) and ZY-2 (high Al_2O_3 content), it can be seen (Fig. 3) that after 100 hours at 1400°C the high purity coating (ZY-3) retained more tetragonal phase (56%) and formed less than 1% of monoclinic phase, while the monoclinic phase content for ZY-1 and ZY-2 is 16% and 7%, respectively.
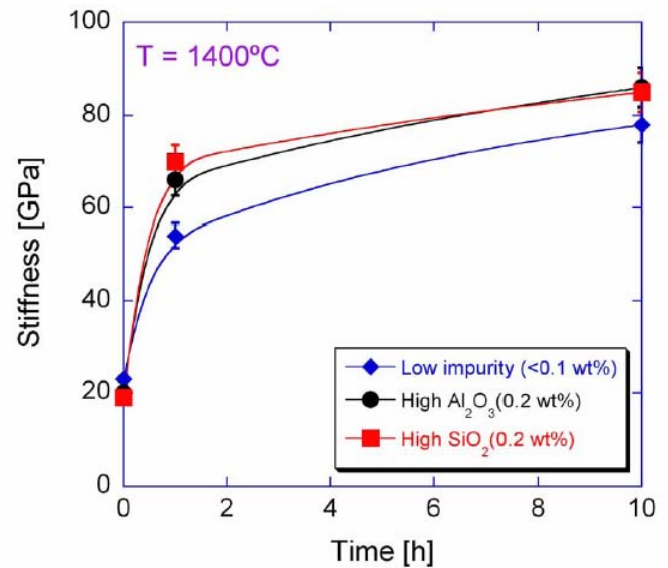

Figure 4: Evolution of elastic modulus.

Elastic Modulus

All three coatings have an elastic modulus of about 20 GPa at the as-sprayed state and the trend of its evolution during thermal exposure is very similar (Fig. 4), i.e., rapid increase in the first hour and continuing increase at a slower rate until 10 hours. Further increase of elastic modulus is expected when the coatings are subject to longer thermal exposure. However, the magnitude of elastic modulus increase for the three different coatings is different. After 10 hours at 1400 C, the elastic modulus of high purity coating (ZY-3) increased from 21 GPa to 75 GPa, while that of lower purity coatings (ZY-1 and ZY-2) developed from less than 20 GPa to about 85 GPa.

Thermal Cyclic Life

Initial comparison was performed between the high purity coating (ZY-3) and coating (ZY-4) which has a purity higher than ZY-1 and ZY-2 but lower than ZY-3 (Table 2). As shown in Fig. 5, the first failure of ZY-3 coating occurred at 570 cycles and last sample failed at 730 cycles, while the ZY-4 samples failed between 510 to 550 cycles. In other words, the thermal cyclic life of ZY-3 is equal or better than that of ZY-4 samples (Fig. 5).
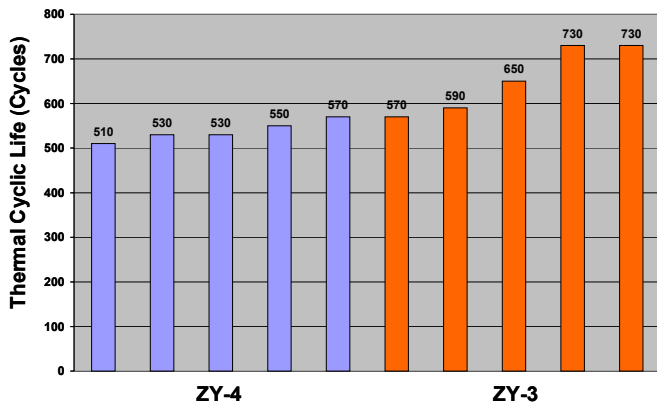
Figure 5: Thermal cyclic life of ZY-3 and ZY-4.

Discussion

High concentration of impurity oxides, especially SiO_2 and Al_2O_3, promotes the sintering of 7YSZ coating has been reported previously [11] and verified in this work. It is believed that this effect is attributed to several factors. Firstly, impurity oxides were observed to segregate on the fracture surface of 7YSZ TBCs exposed to high temperatures [14]. Some of these oxides were found to form amorphous phases with low glass transition temperatures or phases with lower melting point than 7YSZ [15]. These undesirable phases will promote surface diffusion and thus accelerate TBC sintering. Secondly, the impurity elements, when form a solid solution with zirconia, will create more lattice defects and lower melting temperature of zirconia. As a result, the diffusion coefficient zirconium and yttrium ions will increase due to the reduction of bonding forces.

Sintering of TBCs leads to the removal of porosities and healing of cracks. Porosity and cracks, especially fine pores and cracks normal to the heat transport direction, are an effective barrier to heat transfer. In addition, these defects provide the needed strain tolerance so as to accommodate the thermal mismatch strain generated in application. Accordingly, the coating with a faster sintering rate due to higher concentration of impurity oxides experience more significant increase in thermal conductivity and elastic modulus. The increase of thermal conductivity makes TBCs less effective and the stiffening may reduce the coating durability.

The improved durability of coating ZY-3 relative to ZY-4 can be attributed to the reduced sintering of the high purity coating. Less sintering results in a lower degree of coating stiffening after thermal exposure, and a lower level of residual stress due to sintering shrinkage. This, in turn, lowers the strain energy stored in the coating and thus diminishes the driving force for coating spallation. Furthermore, when thermal gradient across coating thickness exists as in real application, less increase in thermal conductivity due to a slower sintering rate will lower the temperature of bond coat and thus slow down its oxidation and thermally grown oxide (TGO) growth rate. Since bond coat oxidation is a major factor for TBC failure [16], the effect of purity on coating durability is expected to be more significant in a condition with thermal gradient than what is observed in an isothermal cycling test (Fig. 5).

As mentioned earlier in this section, high purity slows down sintering by limiting the formation of undesirable phases and solid solution of impurity elements in zirconia. Extensive efforts have also been focused on reducing the mobility of dopants to improve sintering resistance and to lower thermal conductivity of TBCs [9, 10]. Since these two mechanisms are different and complimentary, it is believed that the combination of high purity and advanced composition will result in a coating that has a sintering resistance better than that of high purity TBCs and advanced TBCs.

Summary and Conclusion

Mechanical and thermal properties of a high purity 7YSZ TBC were evaluated and compared to TBCs of lower purities. It was found that the reduction of impurity oxides in 7YSZ coatings, such as SiO_2 and Al_2O_3, significantly enhance the sintering resistance and phase stability of 7YSZ coatings. Due to the improved sintering resistance, less increase of thermal conductivity after thermal exposure and improved durability were observed for the high purity coating. Furthermore, it is proposed that the combination of high purity and advanced TBC chemistries will lead to further improvement in coating properties.

Acknowledgements

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