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Thesis Title: Effect of Sintering on Microstructure and Mechanical Properties of Air Plasma Sprayed 7 wt.% Y_2O_3 Stabilized ZrO_2

Synopsis

Air plasma sprayed (APS) 7 wt.% Y_2O_3 stabilized ZrO_2 (7YSZ) coating is conventionally used for thermal insulations (in form of thermal barrier coating, TBC) in various hotter sections of land-based gas turbine engines and aero-engines. Due to the use of 7YSZ as TBC, the maximum temperature of gases in the turbine engines could be extended to 1300-1400 ^{0}C from 1100-1150 ^{0}C; this has led to significant increase in the thermal efficiency of the gas turbine engines. Furthermore, nowadays these coatings are also being explored to be used as heat insulator in the combustion chamber of diesel engines, which work at relatively lower temperatures (e.g., < 900 ^{0}C). Here also, the YSZ coated diesel engines (called as low heat rejection, LHR, engines) has shown improved thermal efficiency.

APS YSZ coating which is used as a thermal barrier coating (TBC) has 15-25 % of microcracks and porosity in the as-deposited condition, which is purposefully engineered to reduce the thermal conductivity and elastic modulus of the coating. However, the YSZ coatings are exposed to high temperatures during the service, which results in evolution of their microstructure, wherein the microcracks and porosity slowly start to reduce. The reduction in microcracks and porosity not only leads to an increase in the thermal conductivity of the coating, but also significantly affects (deleteriously) its mechanical properties, such as elastic modulus, hysteresis loss, etc. In practice, degradation in the mechanical properties over extended period of high temperature exposure becomes one of the main reasons of the coating failure.

Several studies have focused on understanding the effects of exposure to very high temperatures (e.g., > 1000-1100 ^{0}C) on the elastic modulus, hysteresis loss, fracture resistance, microstructure and relevant structure-property relationships. However, there are very few studies discussing the effect of low temperature (e.g., ≤ 1000 ^{0}C) exposure on the microstructure evolution and mechanical response of APS YSZ coatings and, there too, any discussion on the structure-property relationship is quite limited. In particular, a study delineating the effects of temperature across a wide range (spanning over both low and high temperatures) on microstructure of APS YSZ and, subsequently, the effects of microstructural evolution on elastic modulus, creep and fracture resistance against long cracks at room temperature is not available in the literature. Accordingly, this study discusses the effects of sintering in the temperature range of 800-1300 ^{0}C on microstructure, elastic modulus, hysteresis loss per cycle, room temperature creep and fracture resistance of free-standing APS 7YSZ coating.

Two types of cantilever samples, one with notch near the fixed end and another without any notch (i.e., unnotched), were fabricated using freestanding heat treated 7YSZ coating (see **fig. 1a and Fig. 1b**) to study the above-mentioned mechanical properties. Scanning electron microscope (SEM) was used to observe the microstructure of the cross-section of the cantilevers, and micrographs were obtained at different magnifications to study the evolution in the microstructure (including reduction in fraction of microcracks and porosity). Porosity was also measured through density measurements using Archimedes principle. It was observed that there was no measurable change in density up to a heat treatment at 1100 ^{0}C. This domain of heat treatment is mostly related to elimination of finer intra-splat microcracks and smaller pores, and possibly improving the splats bonding. On the other hand, if the heat treatment was performed above 1100 ^{0}C, then there was continuous change in the density, due to elimination of larger inter-splat microcracks and pores. It is imperative that these two domains of microstructural changes would affect the mechanical properties of the coating differently, as described next.

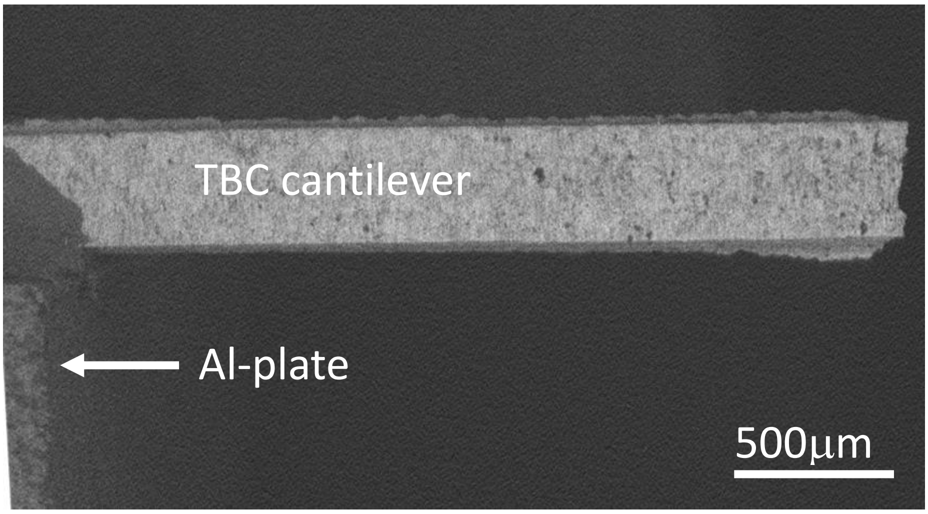

Fig. 1a: SEM micrograph showing side view of the TBC cantilever fixed on an Al-plate

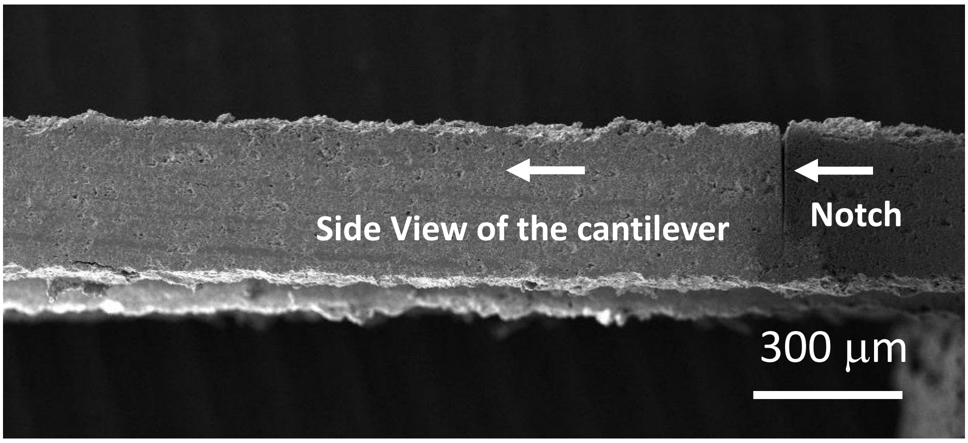

Figure 1b: SEM micrograph showing the side view of the notched TBC cantilever fixed on Al-plate

To ascertain the effect of heat treatment on modulus of the freestanding coating, unnotched cantilevers (see **Fig. 1a**) were loaded using a nanoindentation system using the sphero-conical tip of radius 300 μm. The blunt tip indenter was used to reduce the contact pressure, so that indentation induced damage during loading can be avoided. Consistent with the variation in the microstructural features, the bending modulus of the 7YSZ coating heat treated at a temperature in between 800 and 1300 ^{0}C also showed the two-domain behaviour (see **Fig. 2**). Here, the coatings heat treated at low temperatures ($\leq$ 1100 ^{0}C) showed a significant change in the bending modulus, without a corresponding change in the density of the coating. On the other hand, coatings heat treated at higher temperatures showed gradual increase in the bending modulus with a corresponding continuous increase in the density. An analytical model has been proposed for correlating the change in the microcrack density with change in the elastic modulus for low temperature sintering, where finer/sharper microcracks evolve (or heal). Furthermore, the coating microstructure were imported into ABAQUS, a commercial finite element analysis (FEM) software package, using object oriented finite elements (OOF2), an open source software, to study the evolution of the bending modulus with microstructure. The simulated results were observed to be in reasonable agreement with the experimental results.

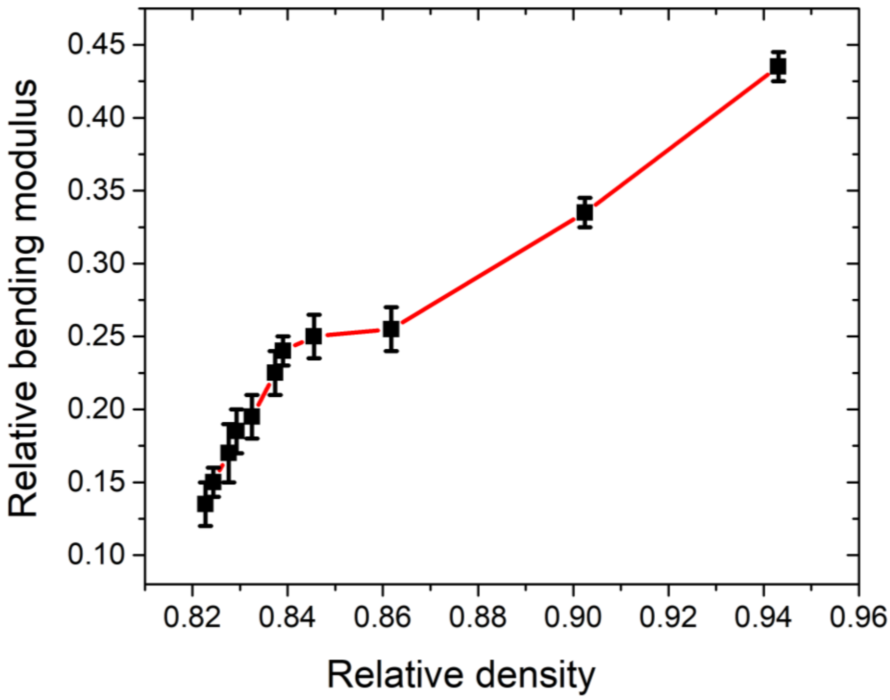

Figure 2: Variation of the relative bending modulus as function of the relative density of APS 7YSZ freestanding coating. Here, relative density was calculated by dividing the actual density by the theoretical density (i.e., when YSZ is fully dense) and the normalized bending modulus was calculated by dividing the measured bending modulus with the bending modulus of fully dense 7YSZ.

The effect of heat treatment on the hysteresis-loss and time dependent deformation behaviour (creep and stress relaxation) of the coating at the room temperature was also evaluated in bending using unnotched cantilever samples. Here, the cantilever was loaded till 100 mN and completely unloaded, and then the change in area under the curve (i.e., hysteresis-loss) was analysed. Here also, a two-domain behaviour with density (i.e., heat treatment) was observed (see **Fig. 3**). Initially, there was a significant drop in the amount of the hysteresis-loss without a significant increase in the density. This domain is related to the elimination of fine microcracks and, possibly, improvement of the inter-splat bonding. On the other hand, the second domain here, where the hysteresis-loss gradually decreased with the density, can be attributed to significant change in the density, which occurs due to elimination and reduction of larger pores and microcracks.

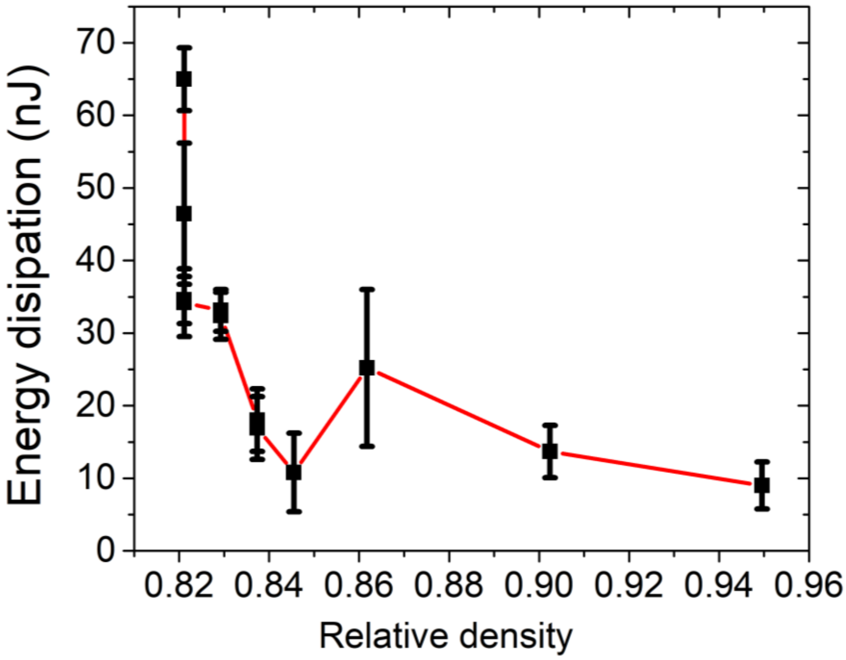

Fig. 3: Variation of the hysteresis-loss per cycle of the cantilever as function of the normalized density of 7YSZ coating.

In this study, it was observed that if the load was held constant at the any load during loading (e.g., at maximum load), the displacement of the loading point would monotonically increase with time. Correspondingly, when the displacement was held constant, then there was continuous decrease in the load. These occurred at room temperature. In order to study the room temperature creep in detail, unnotched cantilevers were loaded up to 200 mN and then the load was held constant for 200 s. The displacement growth with time was recorded and analysed. It was observed that a power law function, $\delta = At^{a}$, where δ is the displacement, and A, t and a are pre-exponent constant, time and time exponent constant, respectively, fitted the data the best; this power law is also known as Andrade creep law. The variation of A and a was analysed and compared with change in the density, and it was observed that while variation of A showed the classic two-domain of behaviour, a did not vary with change in density (see **Fig. 4a** and **Fig. 4b**). Reverse creep during unloading was also observed, which has been discussed in detail.

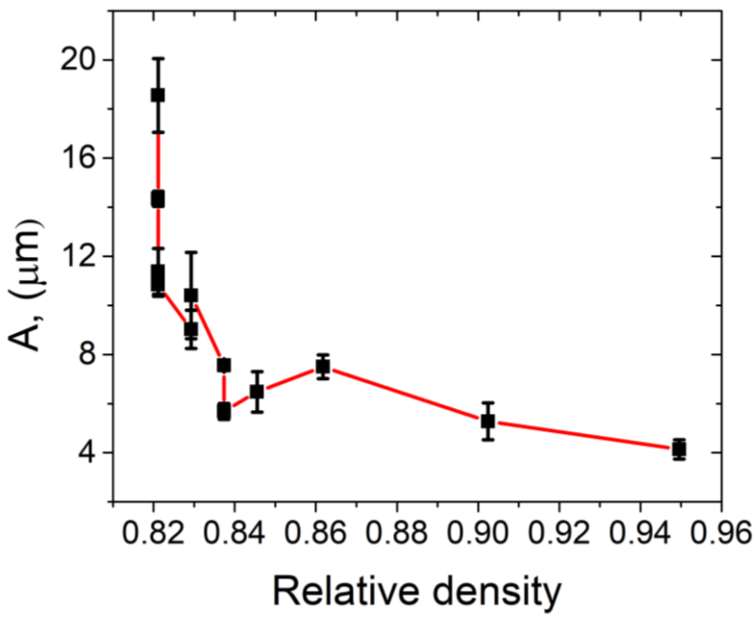

Figure 4a: Variation of pre-exponent constant “A” of power law function with normalized density of 7YSZ coating

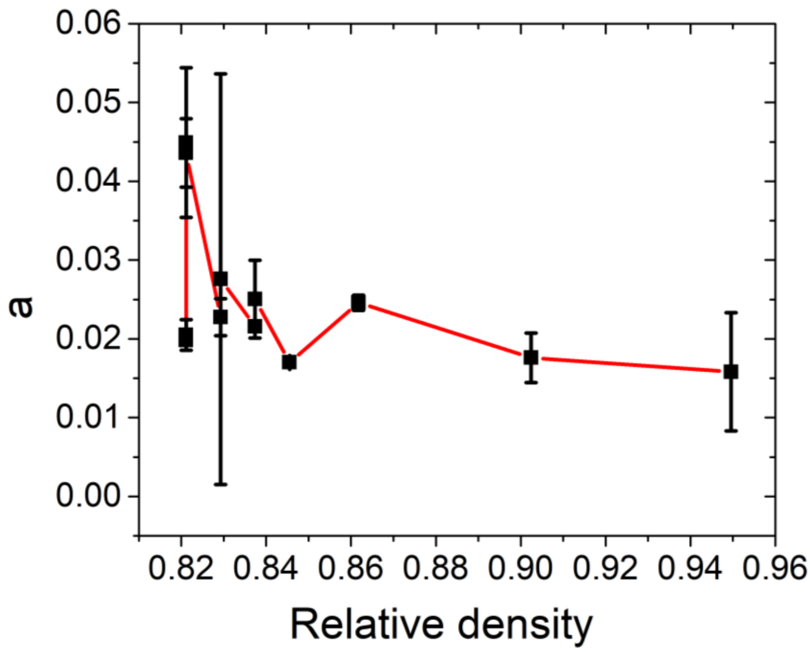

Figure 4b: Variation of exponent constant “a” of power law function with normalized density of 7YSZ coating.

Finally, the effect of heat treatment and hence sintering on the fracture resistance of the coating as well as the crack propagation behaviour was also studied. Here, the notched cantilever samples (see **Fig. 1b**) were tested in bending at room temperature. Furthermore, the samples were loaded under displacement control mode using a sphero-conical indenter with a tip radius of 300 μm tip using a nanoindenter. The cantilevers were loaded at relatively slower rate (of 4 μm/s) to avoid the catastrophic fracture of the sample. It was observed that the average fracture resistance corresponding to a crack extension of 150-200 μm increased linearly with the density (see **Fig. 5**). Furthermore, crack tortuosity was quantified to understand the effect of heat treatment on crack propagation and it was observed that the crack tortuosity decreased with the density; this explains the reduction in microcracks and porosity with density (or heat treatment) which leads crack tortuosity.

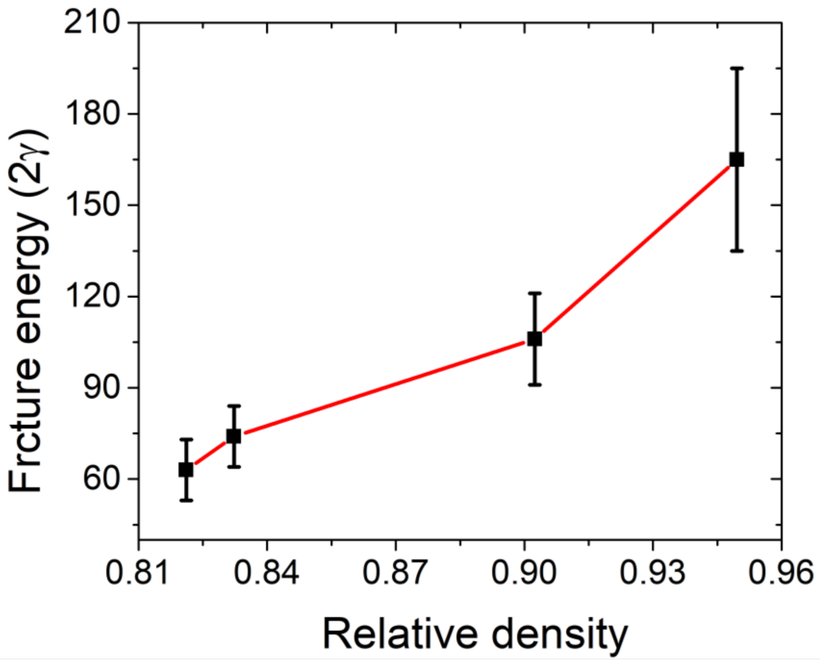

Fig. 5: Variation of the fracture resistance with the relative density of 7YSZ coating.

Overall, this thesis highlights the effect of heat treatment under wide range of temperatures on the microstructure and mechanical response of APS 7YSZ freestanding coatings. The results are not only directly relevant for the diesel engines and some sections of the gas turbine engines, but also for entirety of the gas turbine engines during the cooling cycle.