



Thermal durability and fracture behavior of layered Yb-Gd-Y-based thermal barrier coatings in thermal cyclic exposure



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ABSTRACT

The effects of structural design on the thermal durability and fracture behavior of Yb-Gd-Y-based thermal barrier coatings (TBCs) were investigated through thermal cyclic exposure tests, such as furnace cyclic thermal fatigue (FCTF) and jet engine thermal shock (JETS) tests. The effects of composition in the bond coat and feedstock purity for the buffer layer on its lifetime performance were also examined. To overcome the drawbacks of Yb-Gd-Y-based material with inferior thermal durability due to poor mechanical properties and low coefficient of thermal expansion, a buffer layer was introduced in the Yb-Gd-Y-based TBC systems. In FCTF tests, the TBCs with the buffer layer showed a longer lifetime performance than those without the buffer layer, showing the longest thermal durability in the TBC with the Co-Ni-based bond coat and the buffer layer of regular purity. In JETS tests, the TBC with the Ni-based bond coat and the buffer layer of high purity showed a sound condition after 2000 cycles, showing better thermal durability for TBC with the Co-Ni-based bond coat rather than that with the Ni-based bond coat in the single layer coating without the buffer layer. The buffer layer effectively enhanced the thermal durability in slow temperature change (in the FCTF test), while the bond-coat composition and the feedstock purity for the buffer layer were found to be important factor to improve the thermal durability of the TBC in fast temperature change (in the JETS test). Finally, these research findings allow us to control the structure, composition, and feedstock purity in TBC system for improving the thermal durability in cyclic thermal environments.

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1. Introduction

Thermal barrier coatings (TBCs) have been widely used to protect the hot-section components of turbines and combustors for aircraft and land-based gas turbines from hot gases [1,2]. The TBCs accommodate the increase in operating temperature in turbine engines, reducing the substrate temperature of hot-section components. To improve fuel efficiency with increasing turbine inlet temperature (TIT), many researchers have attempted to design a cooling system for the turbine and combustor components, and develop substrate and TBC materials [3–6]. TBCs were first introduced to the gas turbine industry in the mid-1970s, after which the most widely used ceramic top-coat material has been 7–8 wt% yttria-doped stabilized zirconia (7–8YSZ) because it provides the best performance in high-temperature applications [7]. However, a commercial TBC material, 7–8YSZ, has been limited with inferior phase stability and low sintering resistance as the TIT has increased in gas turbine engines [8,9]. Therefore, alternative TBC materials

are required with better phase stability, higher chemical inertness, lower thermal conductivity, and higher sintering resistance.

The most effective approach to meeting these needs appears to be the use of low thermal conductivity materials of RE-stabilized cubic zirconia (where RE indicates a rare-earth element) type for the outer ceramic layer [10–12]. The advanced TBCs with a low thermal conductivity have been continuously investigated with zirconate materials doped with lanthanum, gadolinium (Gd), ytterbium (Yb), etc. [13–15]. One of the promising leading candidates for advanced TBC materials is the Yb-Gd-Y-stabilized zirconia (hereinafter YGYZ). The YGYZ coating has better oxidation resistance, improved sintering resistance, higher calcium-magnesium-alumino-silicate (CMAS) resistance, excellent phase stability, and lower thermal conductivity than YSZ coating; it has thermal conductivity of $0.80\text{--}1.24\text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ for bulk YGYZ and of $2.1\text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$ for bulk 8YSZ [16–19]. The principal drawback of YGYZ coating is its low coefficient of thermal expansion (CTE), which does not match the bond coat with a relatively large CTE; CTE is $9\text{--}10 \times 10^{-6}\cdot\text{K}^{-1}$ for bulk YGYZ, $10.5\text{--}11.5 \times 10^{-6}\cdot\text{K}^{-1}$ for bulk 8YSZ, and $15.0 \times 10^{-6}\cdot\text{K}^{-1}$ at 1000 °C for Ni-based bond coat [20–22]. Therefore, the YGYZ coating can be easily delaminated because of

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the CTE mismatch between the YGYZ top coat and the bond coat. Another reason for the relatively short thermal durability of YGYZ coating is its low fracture toughness (K_{IC}) (K_{IC} is 0.95–1.25 MPa·m^{1/2} for YGYZ coating, and 1.85–2.23 MPa·m^{1/2} for 8YSZ coating) [23]. K_{IC} describes the ability of fracture resistance to maintain cracks in the material without the propagation of cracks. Therefore, K_{IC} should be improved to enhance the thermal durability of the YGYZ coating. In addition, YGYZ coating is less compatible with thermally grown oxide (TGO) layer than 8YSZ coating, resulting in premature failure of YGYZ-based TBC in working environments [24,25].

One of the solutions to improve the thermal durability of YGYZ coatings as mentioned above is the layered TBC with multifunctions through structural design [26]. Many studies reported that a double-layer TBC exhibits a higher level of durability and reliability relative to a single YSZ coating [27,28]. The buffer layer as a stress accommodating layer during thermal cycling can also be designed with a double-layer coating (DLC) to reduce stress levels and ensure thermal durability [29–31]. Therefore, the YGYZ-based layered TBC system is believed to provide a good heat-insulating performance because the top coat is made of YGYZ material with intrinsic low thermal conductivity, and the layered structure improves the thermal durability, as the buffer layer between the top and bond coats reduces the CTE mismatch. However, the failure or delamination mechanisms in the YGYZ-based layered TBCs are not fully understood.

The high-velocity oxy-fuel (HVOF) process is a very useful for forming bond coats with a dense microstructure and a high adhesive strength in TBCs and its development has been gaining attention for TBC applications [32–34]. There is a wide range of metallic alloys owing to its outstanding resistance to oxidation and corrosion [35], normally consisting of a MCrAlY bond coat, where M = nickel (Ni), cobalt (Co), or a combination of them (Co/Ni). The characteristics of Ni are high corrosion resistance and high melting point; Co can give temperature stability, corrosion, and wear resistance; Cr can improve hot corrosion resistance; Al can improve ductility, determining oxidation degree related with TGO layer; and Y can improve adherence to TGO layer. The Co–Ni-based bond coat is widely used because of their superior thermomechanical properties [36,37]. Usually, the bond coat of TBC system applied at high temperature involves Co because of the high-temperature oxidation resistance, thus enhancing the cycle life of TBCs [38]. Even though the working temperature of gas turbines increases continuously and reaches to 1600 °C, the surface temperature of components (the surface of top coat), such as blade and vane, is still within 1100 °C in actual operation circumstance, owing to the improvement of cooling system. Therefore, the thermal durability of TBCs with the bond coats with and without Co additive should be analyzed in the working condition, which has not been studied yet.

Therefore, in this study, to understand the failure mechanism in the YGYZ-based TBC, the effects of structural design and bond coat species on the thermal durability and fracture behavior of the single-layer coating (SLC) and DLC TBC systems were investigated through thermal cyclic exposure, namely the furnace cyclic thermal fatigue (FCTF) test with slow and small temperature change and the jet engine thermal shock (JETS) test with fast and large temperature change. The relationship between thermal durability and coating structure in the YGYZ-based TBC systems is discussed, with a focus on the microstructure evolution and mechanical properties before and after cyclic thermal exposure.

2. Experiment procedure

2.1. Preparation of TBC samples

A nickel-based directionally solidified superalloy (nominal composition of 65.0Ni–10.0Cr–7.5Ta–7.0W–5.0Al–4.4Co–1.0Ti–0.08C–0.01Zr–0.01B) was used as a substrate. The dimensions of the coin-shaped sample were 25 mm and 5 mm in diameter and thickness, respectively. The

substrate was sand-blasted using alumina powder with particle size of 60 mesh, and then the HVOF process using a Diamond Jet–2600 DJM (Sulzer Metco Holding AG, Switzerland) was conducted for a bond coat within 2 h. Two kinds of feedstock powder with different compositions were used to prepare the bond coat (AMDRY 9951; Sulzer Metco Holding AG, nominal composition of Co–32Ni–21Cr–8Al–0.5Y in wt% and nominal particle size distribution of 5–37 μm, hereinafter Co–Ni-based bond coat, and AMDRY; 9624, Sulzer Metco Holding AG, nominal composition of Ni–22Cr–10Al–1.0Y in wt% and nominal particle size distribution of 11–37 μm, hereinafter Ni-based bond coat). Two YSZ buffer layers were deposited on the bond coat using two feedstock powders (METCO 204C-NS with regular purity: 8.0Y₂O₃–0.7SiO₂–0.2TiO₂–0.2Al₂O₃–0.2Fe₂O₃ doped in ZrO₂ and METCO 204C-XCL with high purity: 8.0Y₂O₃–0.05SiO₂–0.05TiO₂–0.05Al₂O₃–0.05Fe₂O₃ doped in ZrO₂, Sulzer Metco Holding AG, Switzerland, nominal particle size distribution of 45–140 μm, D50 of 68–77 μm). The YGYZ top coat was coated on each bond coat or each buffer layer using a commercial feedstock powder (METCO 206A, Sulzer Metco Holding AG, Switzerland, 9.5Y₂O₃–5.6Yb₂O₃–5.2Gd₂O₃ doped in ZrO₂, nominal particle size distribution of 45–125 μm, D50 of 50–70 μm). The buffer and top-coat layers were sprayed following the air plasma spraying (APS) method using the 9 MB coating system (Sulzer Metco Holding AG, Switzerland). A schematic diagram of the structural design employed in this study is shown in Fig. 1. The thicknesses of the bond and top coats were designed as 250 ± 50 μm and 600 ± 50 μm, respectively, in the SLC TBCs. The thicknesses of the buffer layer and the top coat are designed as 100 ± 30 μm and 600 ± 50 μm, respectively, with the same bond coat thickness in the DLC TBCs. The deposition parameters for the bond and top coats are shown in Table 1.

2.2. Thermal cyclic exposure tests

Thermal cyclic exposure tests were conducted to evaluate the thermal durability of TBC samples through two kinds of test methods, FCTF and JETS tests. The FCTF test was designed to simulate actual operation circumstances of gas turbines. During actual operation, the surface temperature of TBC is increased about 1100 °C due to a film cooling even though the TIT of gas turbines reaches to 1600 °C, while the substrate is reduced to 950 °C by an internal steam cooling. Also, the FCTF test can be a suitable method to evaluate the TGO growth due to the longer thermal exposure time different from the JETS test. The JETS test was designed to evaluate thermal shock behavior with the rapid heating and cooling rates. This thermal shock is the description of specific operation conditions (i.e., engines start and shut off), when high thermal load is applied on TBCs. The flame temperature above 1400 °C and nitrogen cooling are sufficient to impose the thermal shock environment on TBCs.

The FCTF tests were performed for 1429 cycles in a specially designed furnace; one side of the sample was exposed and the other side air-cooled. The surface temperature of the sample (coating) was about 1100 °C with a temperature difference of 150 °C between the top and bottom surfaces of the sample and a dwell time of 60 min, followed by natural air cooling for 10 min at room temperature. The failure criterion was defined as 25% buckling or spallation of the top coat in the FCTF test. The JETS tests using liquefied petroleum gas and oxygen were performed for 2000 cycles at a surface temperature of 1400 °C with a dwell time of 20 s, and then the sample was cooled using nitrogen gas to about 550 °C for 20 s and the surface temperature reached 150 °C before the next heating. During the tests, the surface and backside temperatures were measured using pyrometers (infrared thermometer with the wavelength of 3.9 μm, CTlaser MT, Optris, Germany). The failure criterion in the JETS test was typically >50% spallation of the top coat or cracked at the interface between the top and bond coats. At least three samples were tested for each condition. For clear understanding of test methods, photos of each apparatus for the FCTF and JETS tests are shown in Fig. 2. In Fig. 2 (B), the heating and cooling regions marked with the dotted and solid circles, respectively.

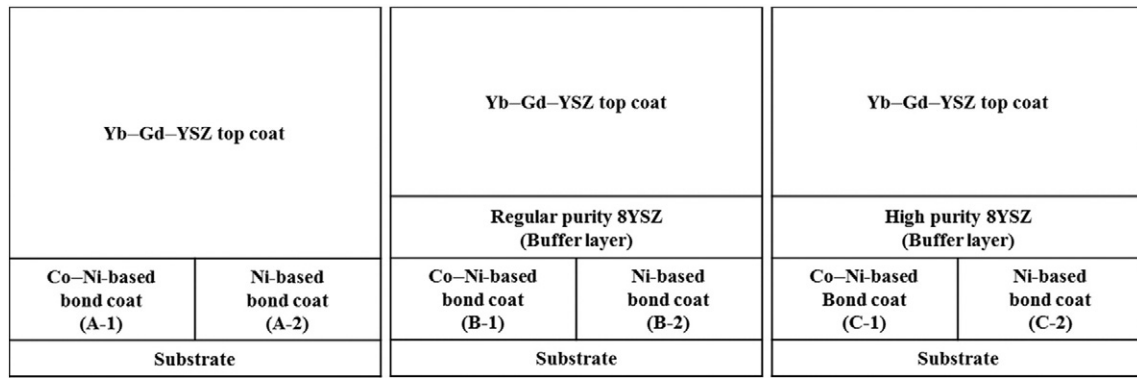


Fig. 1. Schematic diagram for structural design employed in this study.

2.3. Characterizations

The selected samples before and after thermal cyclic exposure tests were preprocessed to observe the cross-sectional microstructure. The samples were cut and cold-mounted using a liquid epoxy resin, and then polished using silicon carbide paper, and 3 and 1 μm diamond pastes, respectively. The cross-sectional microstructure of the TBC samples was observed using a scanning electron microscope (SEM; Model JSM–5610, JEOL, Japan). Elemental analysis at the interface between the buffer layer and the bond coat was conducted using energy-dispersive X-ray analysis (EDS; S2700, Hitachi, Japan). Before measuring the mechanical properties, cutting, cold-mounting, and polishing processes were performed consecutively. The 2-D porosity of the top coats was measured using Image-pro Plus software (Media cybernetics, USA). The mechanical properties were characterized by two types of indentation method, nano-indentation and micro-indentation in the in-plane direction. Localized elastic modulus (E), and hardness (H) were evaluated using a nano-indenter (Nano Instruments, MTS Systems Corp., Eden Prairie, USA) with a Berkovich tip (radius of tip < 100 nm). To minimize the deviation of the data the indentation position was changed and the test was conducted at least five times. The data were selected after indentation of up to 2000 nm depth. The data were selected after indentation up to 50 gf (0.49 N). The relatively global H values of the bond and top coats were determined using a micro-indenter (HM–114, Mitutoyo Corp., Japan) with a Vickers tip for a load of 3 N and holding for 15 s, based on ASTM C1327–03 [38]. Ten indentations were performed to determine the standard deviation of each value. The size of indentation impression was measured using SEM and all indentations were performed at room temperature.

3. Results and discussions

3.1. Microstructure of as-prepared TBCs

The cross-sectional microstructures of as-prepared TBCs are shown in Fig. 3. The top and bond coats were well deposited with thicknesses of 580–760 and 200–320 μm in the top and bond coats, respectively, even though the sample B (Fig. 3(B-2)) showed a slightly thicker top coat than others. The measured porosity of the top coat was in the

range of 10.6–12.5%, while the mean porosities for the buffer layers of the regular and high purities were 7.7 and 7.9%, respectively. The surface temperature of the coating during deposition is increased by melted feedstock particle (i.e., the thicker the coating is, the higher temperature the coating surface is). After coating process, the thermal and residual stresses are generated during deposition and cooling stages, respectively. Especially, the thicker coating shows higher temperature drop than the relatively thinner coating, inducing higher thermal and residual stresses at the interface between the top and bond coat than the thinner coating [14,39]. However, in this study, the thickness difference was minimal so that the difference of stresses can be negligible. The relationship between the thickness and the stress is based on our previous work using a linear-elasticity theory [14]. The microstructures in the bond coats of all of the TBCs prepared using the HVOF process showed a similar status with a dense microstructure, independent of feedstock powder. The buffer layers in both of the DLC TBCs could be observed as shown in Figs. 3(B) and 3(C). The buffer layer was coated with a thickness of 70–120 μm . The YGYZ top coat and the 8YSZ buffer layer showed intrinsic defects with the APS process, showing pores, unmelted particles, and splat boundaries. The TBC systems did not show any delamination or cracking at the interface between the top and bond coats or between the buffer layer and the top coat. The samples with the buffer layer showed a relatively irregular interface between the buffer layer and the top coat, while all of the samples showed a relatively smooth interface between the bond and top coats in the SLC TBCs or between the bond coat and the buffer layer in the DLC TBCs, compared with the interface between the buffer layer and the top coat, owing to the coating method [40,41]. The particle velocity in the HVOF system for the bond coat can be produced up to 700 m/s, and that in the APS system for the buffer layer is 350 m/s [32–34]. For this reason, the interface between the buffer layer and the top coat is more in irregular shape than those between the bond and top coats in the SLC TBCs, and between the buffer layer and the bond coat in the DLC TBCs. In addition, an indistinguishable interface without obvious large cracks was observed within the top coats, indicating that minimal thermal and residual stresses were imposed at the interfaces during coating processes.

The mechanical properties E and H of each layer, top coat and buffer layer, from nanoindentation are shown in Fig. 4. Even though the values correspond to localized properties, both the E and H values of the buffer

Table 1

Deposition parameters for the bond and top coats in TBCs.

Item	Gun	Feeding rate	Gun distance	Gun speed	Step distance	Carrier gas	Flow rate
Bond coat (HVOF)	DJ2600	30 \pm 3 g/min	300 \pm 3 mm	700 mm/s	4 mm	Ar	30 \pm 2 L/min
Top coat (APS)	9 MB	60 \pm 5 g/min	100 \pm 10 mm	700 mm/s	5 mm	N ₂	15 \pm 1 L/min

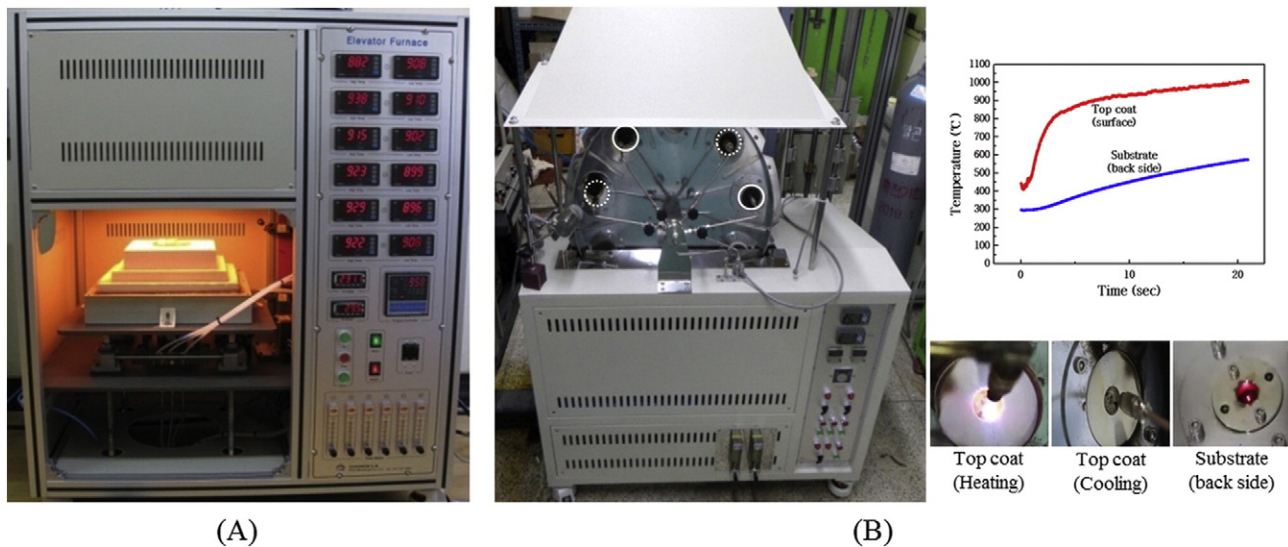


Fig. 2. Photos of each test apparatus: (A) furnace cyclic thermal fatigue (FCTF) and (B) jet engine thermal shock (JETS). The dotted and solid circles indicate the heating and cooling regions, respectively.

layer were not significantly different, being 123.0 ± 23.8 and 7.2 ± 2.7 GPa (mean \pm standard deviation) for the buffer layer of regular purity, 121.0 ± 21.7 and 7.4 ± 2.7 GPa for the buffer layer of high purity buffer layer, and 113.9 ± 23.8 and 6.7 ± 3.0 GPa for the YGYZ top coat. The H values from Vickers indentation inserted in Fig. 4 showed a lower trend than those measured by nanoindentation, being 4.4 ± 0.3 GPa for the buffer layer and 4.1 ± 0.2 GPa for the YGYZ coating. The values obtained from localized regions by nanoindentation are higher than those from relatively micro regions, because of its microstructural distinctions. Fewer defects such as pore, splat boundaries, and microcracks are included upon decreasing the indentation range. Usually, fracture or failure in a TBC system originates at the near-interface region, and the requirement of high mechanical properties is desired within this region [42]. However, the general mechanical properties are not much dependent on the starting feedstock powder in the as-prepared status, contrary to expectations, even though the mechanical properties of the 8YSZ buffer layer are slightly higher than those of the YGYZ top coat, due to the relatively dense microstructure.

3.2. Furnace cyclic thermal fatigue test

The FCTF tests were performed for all samples, and the numbers of cycle-to-failure and its status are summarized in Table 2. The cross-sectional microstructures of each TBC with different bond coats are shown in Fig. 5 after the FCTF tests. For the SLC TBCs, the top coats were completely delaminated in the ranges of 170–238 and 323–340 cycles for the Co-Ni-based and Ni-based bond coats, respectively. The lifetime of all samples with all layered structure was longer than that without the buffer layer. The relatively early failure of the SLC TBCs can be attributed to its lower fracture toughness of the YGYZ top coat, compared with the buffer layer. The DLC TBCs with the Co-Ni-based bond coat were sustained for a longer lifetime than those with the Ni-based bond coat, independent of the buffer layer species. In FCTF tests, although the SLC TBC with the Ni-base bond coat showed longer lifetime performance than that with the Co-Ni-based bond coat, the longest lifetime performance was shown in the DLC TBC with the Co-Ni-based bond coat and the buffer layer of regular purity due to the temperature

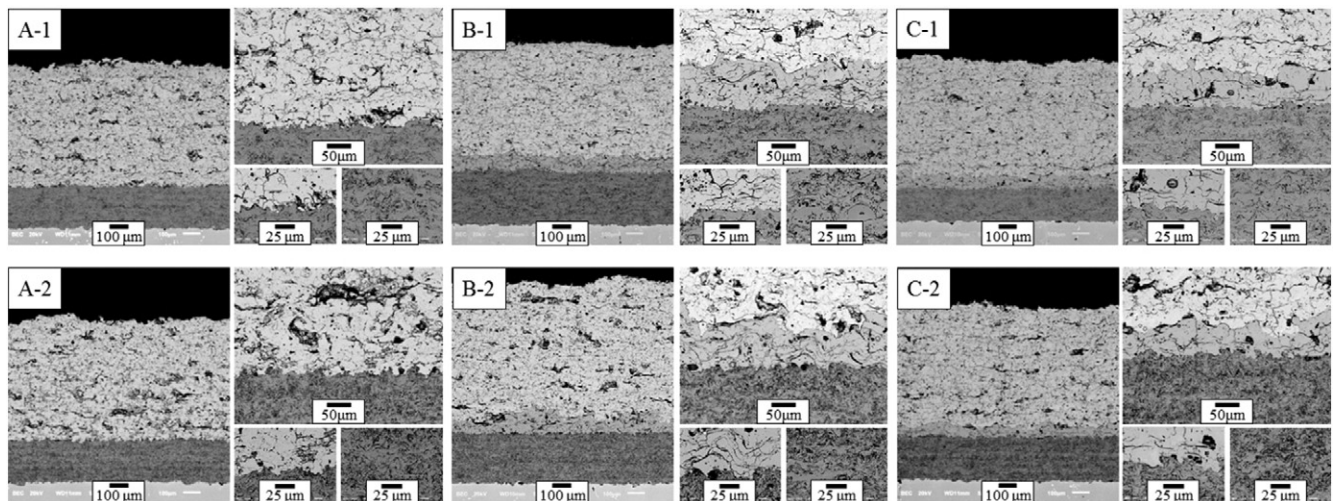


Fig. 3. Cross-sectional microstructures of as-prepared TBCs: (A) SLC TBCs, (B) DLC TBCs with the buffer layer of regular purity, and (C) DLC TBCs with the buffer layer of high purity. Each number indicates TBCs with different bond coats, Co-Ni-based bond coat and Ni-based bond coat, respectively.

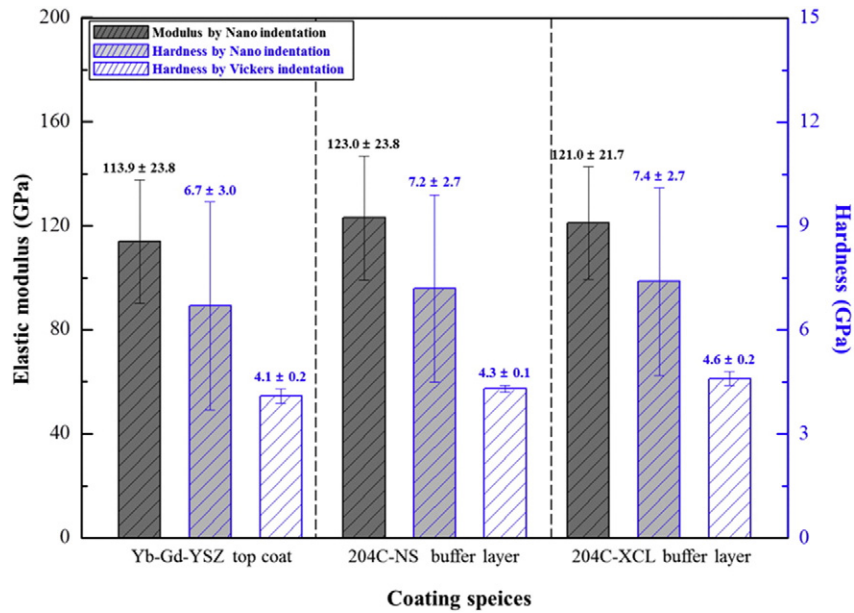


Fig. 4. Elastic modulus (E) hardness (H) values of as-prepared TBCs obtained by nano-indentation and H values obtained by Vickers indentation.

stability of composition and the relatively thick thickness, respectively [4,36,37]. The fracture originated at the interface between the top coat and the buffer layer or within the top coat near the interface, independent of the buffer layer species and the bond-coat composition. Usually fracture or delamination in TBC system happens within 100 μm from the interface of the top and bond coats [42,43]. Therefore, the mechanical properties at the near-interface should be enhanced to improve fracture resistance through crack propagation.

In high-magnification cross-sectional microstructures at the interface between the bond and top coats, and between the bond coat and the buffer layer, the top-coat layer was delaminated after FCTF tests while the YGYZ layer was left as shown in Figs. 5 and 6. Especially both of the DLC TBCs contain the buffer and YGYZ layers after FCTF tests and the remained YGYZ layer in the TBC with the buffer layer of high purity is thicker than that of regular purity, indicating that a catastrophic failure of TBC resulted from the full delamination during actual operation can be prevented by introducing the buffer layer of high purity. On the other hand, it was found that the TGO growth behavior was affected by the bond coat composition. The TGO layer in the TBCs with the Co-Ni-based bond coat formed well with a thickness of $6.3 \pm 2.5 \mu\text{m}$. The thickness of the TGO layer is strongly dependent on the exposure time and bond-coat composition, consisting of two regions; the gray color (position (1) in Fig. 6(B-1)) formed later and the black color (position (2) in Fig. 6(B-1)) formed earlier. The elemental compositions of TGO layers are given in Table 3. It can be seen that the gray region (position (2)) is composed of Ni, Co, Cr, O and Al elements, whereas the black region (position (1)) is mainly composed of Al and O elements. Even though Ni, Co, and Cr elements were detected together in position (1) of Fig. 6(B-1), it can be a negligible amount and from near the detected spot. While the TBCs with the Ni-based bond coat formed a thinner TGO thickness of $3.7 \pm 1.2 \mu\text{m}$, it showed a more serious

internal oxidation on the bond coats near the interface compared with those with the Co-Ni-based bond coat which has superior oxidation resistance. [36–38,44]. For the Ni-based bond coat (Fig. 6(B-2)), the gray region (position (2)) is composed of Ni, Cr, O, and Al elements, whereas the black region (position (1)) is mainly composed of Al and O elements. The EDS analysis indicated that Co element in the bond-coat composition can easily form the TGO layer, and the TBCs with the Co-Ni-based bond coat showed an element diffusion area (element-depletion area), near the interface between the top coat or the buffer layer and the bond coat. Although YGYZ top coat was directly deposited on the bond coat, there were no additional compositions in TGO layer resulted from chemical reaction between the YGYZ and the bond coats. Gue et. al. performed hot corrosion resistance test for the $\text{Gd}_2\text{Zr}_2\text{O}_7$ - and YSZ- based coatings, and they concluded the $\text{Gd}_2\text{Zr}_2\text{O}_7$ -based coating is more thermally and chemically stable than the YSZ-based coating [45].

The bond coat is inevitably oxidized and the TGO layer is formed at the interface between the bond and top coats with a thickness of 3.7–6.3 μm . The thickness of the TGO layer gives a difference in stress intensity factors. The thicker TGO layer results in a markedly large stress intensity factor during the intermediate and late stage of crack growth, although it is slightly lower during the initiation of crack. As a result, the fast growth rate of the TGO layer leads to the short lifetime performance of the TBC [46]. The TBC is a multilayer coating system including superalloy, intermetallic bond coat, TGO layer, and ceramic top coat. Therefore, the volume change accompanied by the thermal cycling process is different due to the different CTEs. The bond coat has a similar CTE as the substrate, so lower thermal and residual stresses are created at the interface between the bond coat and the substrate during the heating and cooling processes, respectively. The main fracture or failure source considered between the bond and top coats is the residual stress due to the mismatch of CTEs among the corresponding parameters of E ,

Table 2

Summary of the numbers of cycle-to-failure and its status after each thermal exposure test.

Sample	Bond coat	Top coat	FCTF test/status	JETS test/status
A-1	Co-Ni-based	Yb-Gd-YSZ	170–238 cycles/Delamination	510–1130 cycles/Delamination
B-1		Yb-Gd-YSZ/Regular purity 8YSZ (buffer layer)	880–1096 cycles/Delamination	360–760 cycles/Delamination
C-1		Yb-Gd-YSZ/High purity YSZ (buffer layer)	690–696 cycles/Delamination	218–530 cycles/Delamination
A-2	Ni-based	Yb-Gd-YSZ	323–340 cycles/Delamination	350–678 cycles/Delamination
B-2		Yb-Gd-YSZ/Regular purity 8YSZ (buffer layer)	400–440 cycles/Delamination	1127–1130 cycles/Delamination
C-2		Yb-Gd-YSZ/High purity 8YSZ (buffer layer)	400–443 cycles/Delamination	2000 cycles/Sound condition

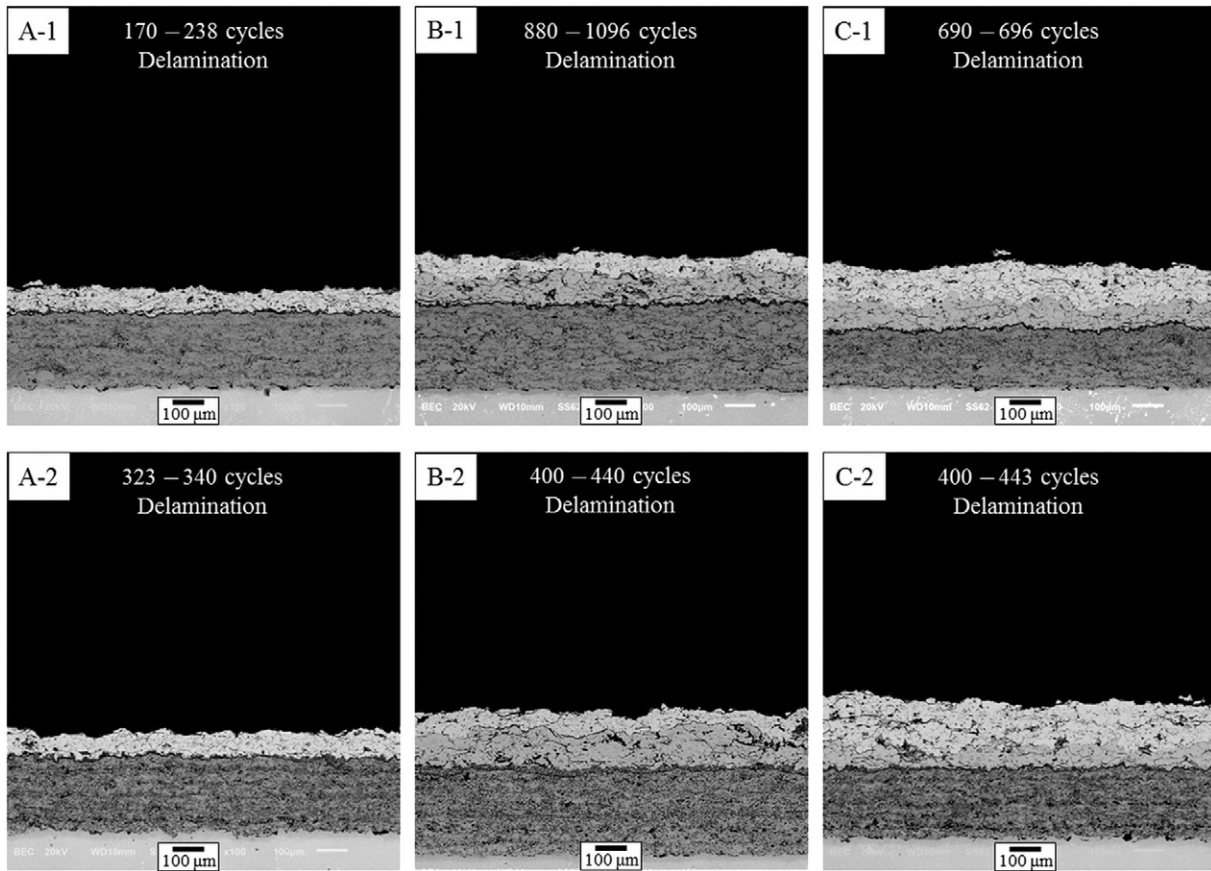


Fig. 5. Cross-sectional microstructures after FCTF tests: (A) SLC TBCs, (B) DLC TBCs with the buffer layer of regular purity, and (C) DLC TBCs with the buffer layer of high purity. Each number indicates TBCs with different bond coats, Co-Ni-based bond coat and Ni-based bond coat, respectively. The numbers of cycle-to-failure corresponding to each figure are shown inside each figure.

Poisson's ratio, and CTE, which is introduced during cooling. In addition, in the layered structure, the thermal and residual stresses generated among layers due to the CTE mismatch become the most important reasons for failure [3]. The CTE value of Ni-based bond coat is usually $\sim 15 \times 10^{-6} \cdot \text{K}^{-1}$ at 1000 °C, which is much larger than those of ceramic top coats: $9\text{--}10 \times 10^{-6} \cdot \text{K}^{-1}$ for bulk YGYZ and $10.5\text{--}11.5 \times 10^{-6} \cdot \text{K}^{-1}$ for bulk 8YSZ [26–28]. Therefore, large CTE is preferred for the ceramic top coat to enhance the thermal durability.

3.3. Jet engine thermal shock test

The heating temperature (1400 °C), liquid nitrogen cooling, and cycling frequency used in the JETS test follow the industrial standards of a leading thermal spray company. Even though the cycling frequency of the JETS test is significantly higher compared with that of the FCTF test, the JETS test was designed to observe the thermal shock behavior of TBC system through exposure of direct flame with the temperature

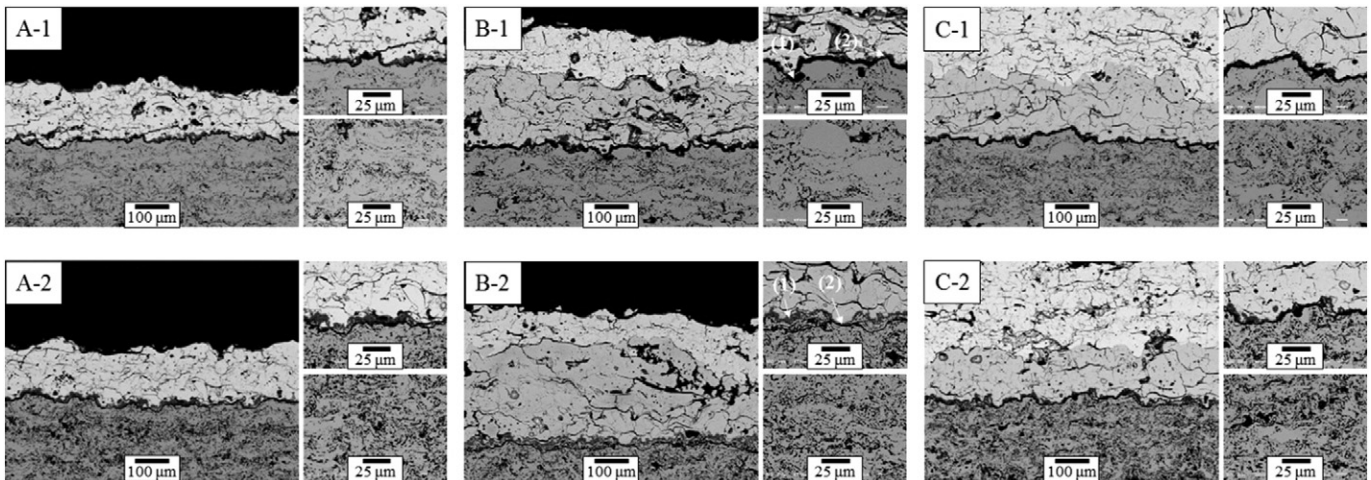


Fig. 6. High magnified cross-sectional microstructures after FCTF tests: (A) SLC TBCs, (B) DLC TBCs with the buffer layer of regular purity, and (C) DLC TBCs with the buffer layer of high purity. Each number indicates TBCs with different bond coats, Co-Ni-based bond coat and Ni-based bond coat, respectively.

Table 3

EDS analysis for TGO layers developed after FCTF tests (at.%).

Sample & position	Gun	Feeding rate	Gun distance	Gun speed	Step distance	Carrier gas
B-1 (position 1)	1.03	1.90	1.72	37.72	57.63	100%
B-1 (position 2)	12.09	8.55	3.09	18.02	58.25	100%
B-2 (position 1)	2.23		4.13	35.26	58.38	100%
B-2 (position 2)	14.52		11.27	14.78	59.43	100%

above 1400 °C. When we measured the surface temperature by a pyrometer, the surface temperature was increased to about 1000 °C during heating even the exposure time was just 20 s. At that time the bottom temperature of substrate was in the range of 560–610 °C, depending on the bond coat species and structure design. The coating was cooled using nitrogen gas to about 550 °C (the surface temperature of coating) and 350 °C (the bottom temperature of substrate) for 20 s. Therefore, although the exposure time is short, the increase rate of surface temperature was sufficiently rapid and the temperature difference was enough to evaluate the thermal shock behavior.

The numbers of cycle-to-failure and its status in JETS tests are summarized in Table 2. The surface micrographs of TBCs after JETS tests are shown in Fig. 7. As shown in Fig. 7(C-2), the DLC TBC with the buffer layer of high purity and the Ni-based bond coat did not show any fracture evidence after JETS tests for 2000 cycles—the broken part in the edge was due to the sample holder. In Figs. 7(A-1) and 7(A-2), the delamination (or fracture) area of SLC TBCs was >50% within the top coat near the interface of the top and bond coats. In the DLC TBCs, damage morphology was very similar to that in the SLC TBCs. Cracking started from the center, then extended to the edge and led to coating fracture. The failure in the DLC TBCs occurred within the top coat or at the interface of the top coat and the buffer layer, showing a delamination area of >50%.

The cross-sectional microstructures of TBCs after JETS tests are shown in Figs. 8 and 9. For the SLC TBCs, the TBCs were delaminated within the top coat near the interface of the top and bond coats in the range of 510–1130 cycles for the Co-Ni based bond coat and in the range of 350–678 cycles for the Ni-based bond coat. Lower CTE of the top coat, the YGYZ layer, may lead to higher stress generation at the

interface between the top and bond coats during the JETS test, which is a disadvantage with respect to the YSZ based TBC. The lifetime of the SLC TBC with the Co-Ni-based bond coat was far longer than that with the Ni-based bond coat. For the SLC TBC system, the thermal durability can be effectively improved by controlling the bond-coat composition. The DLC TBCs with the Co-Ni-based bond coat was delaminated at the interface between the top coat and the buffer layer or within the top coat near the interface in the range of 360–760 cycles for the buffer layer of regular purity (Fig. 8(B-1)) and 218–530 cycles for the buffer layer of high purity (Fig. 8(C-1)). The DLC TBC with the buffer layer of regular purity and the Ni-based bond coat was delaminated at the interface between the top coat and the buffer layer coat in the range of 1127–1130 cycles (Fig. 8(B-2)). The DLC TBC with the buffer layer of high purity and the Ni-based bond coat showed a sound condition without cracking or delamination, whereas a long vertical crack was found throughout the entire top coat and transverse cracks at the interface between the top coat and the buffer layer.

After JETS tests, the buffer layer of regular purity was fully delaminated at the interface between top coat and buffer layer, while a thin YGYZ layer was remained in the TBC with the buffer layer of high purity (Fig. 9(C-1)). On the other hand, any TGO scale and growth observed as shown in Fig. 9, even compared with the as-coated microstructures in Fig. 3. This is the result of the thermal barrier's characteristics of low thermal conductivity, thick coating thickness (over 600 μm), and relatively short thermal exposure time (700 min) compared with FCTF test results. When the results after JETS tests were compared with those of FCTF tests, the growth of TGO was significantly observed with global oxidation in the bond coat after FCTF tests, while the TGO growth was not observed after JETS tests due to the difference of

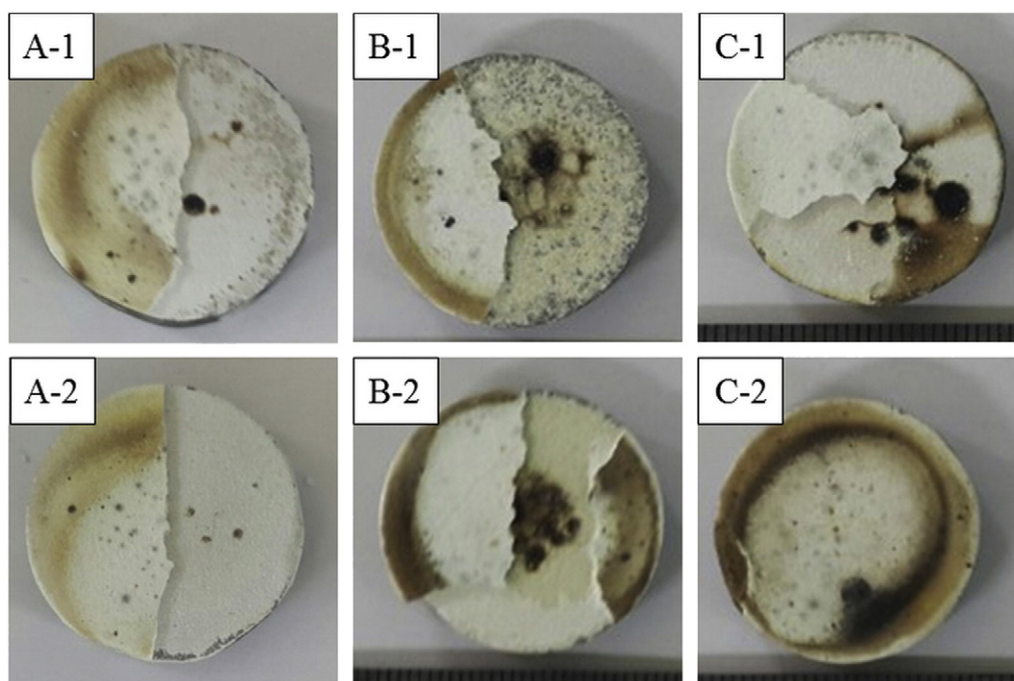


Fig. 7. Surface micrographs of TBCs after JETS tests: (A) SLC TBCs, (B) DLC TBCs with the buffer layer of regular purity, and (C) DLC TBCs with the buffer layer of high purity. Each number indicates TBCs with different bond coats, Co-Ni-based bond coat and Ni-based bond coat, respectively.

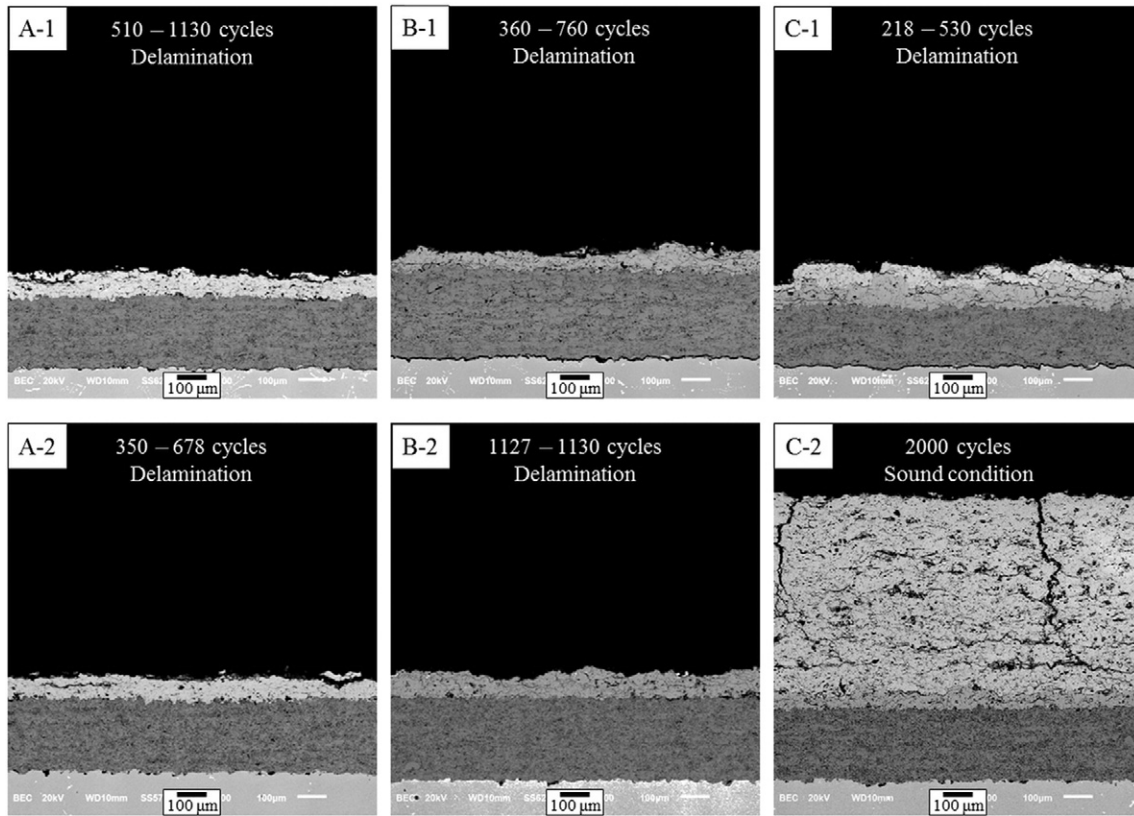


Fig. 8. Cross-sectional microstructures after JETS tests: (A) SLC TBCs, (B) DLC TBCs with the buffer layer of regular purity, and (C) DLC TBCs with the buffer layer of high purity. Each number indicates TBCs with different bond coats, Co-Ni-based bond coat and Ni-based bond coat, respectively. The numbers of cycle-to-failure corresponding to each figure are shown inside each figure.

whole thermal exposure time. Although the thermal durability was not significantly improved by introducing the buffer layer of high purity feedstock in FCTF tests, the thermal shock resistance was enhanced in the rapid heating and cooling processes like the moment of turning on and off in actual gas turbine systems.

In JETS tests, once the surface of top-coat layer is exposed by direct flame, the surface temperature reaches to about 1000 °C with volume expansion, and nitrogen cooling with the vertical direction causes rapid quenching with shrinkage. Therefore, a thermal gradient from the surface to the interface can be created within the sample as the surface of the sample is exposed to the high-temperature flame—relatively

high and low temperatures on the surface and at the interface, respectively. After the short heating process, partial densification occurred on the surface of the top coat. The fast cooling process causes a compressive stress on the surface of the sample, which induces intra-lamellar cracks due to the stiffness and lack of compliance. In further JETS tests, the intra-lamellar cracks formed at the initial stage will be coalesced by the in-plane tensile stress during the heating process and turned into an initial vertical crack. The initially formed vertical cracks can be propagated perpendicular to the interface due to the contraction of other parts by the in-plane compressive stress in the relatively rapid cooling process, generating visible vertical cracks with the interval of

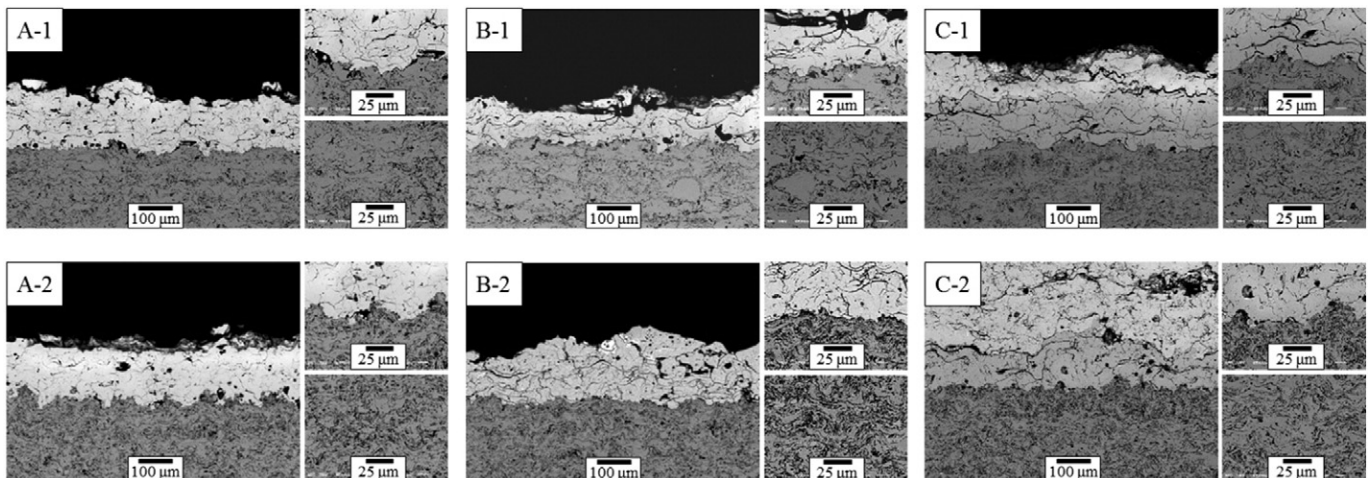


Fig. 9. High magnified cross-sectional microstructures after JETS tests: (A) SLC TBCs, (B) DLC TBCs with the buffer layer of regular purity, and (C) DLC TBCs with the buffer layer of high purity. Each number indicates TBCs with different bond coats, Co-Ni-based bond coat and Ni-based bond coat, respectively.

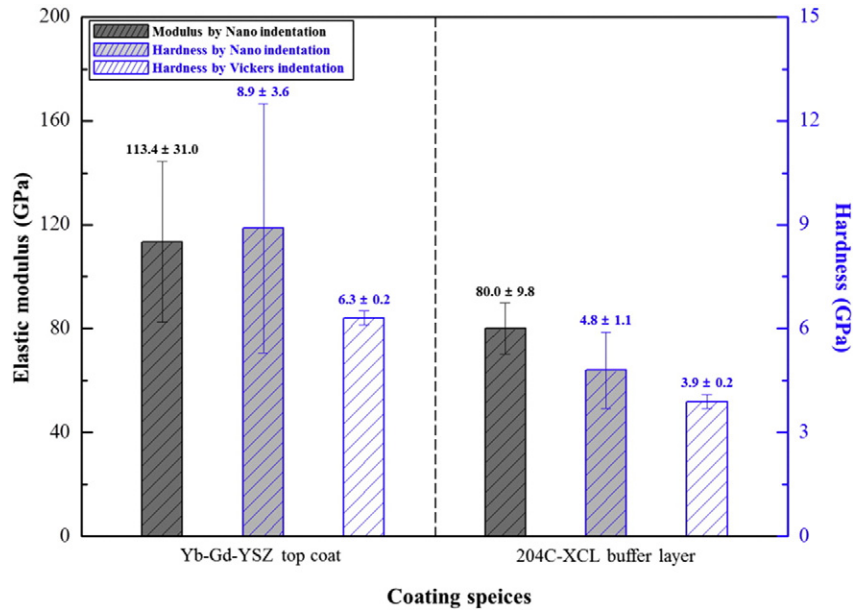


Fig. 10. Elastic modulus (E) and hardness (H) values measured by nano-indentation, and H values obtained by Vickers indentation for TBCs survived after JETS tests.

about 0.5 mm in this study, indicating that the thickness of vertical cracks is getting larger near the surface of top coat. The tensile stress out-of-plane during the cooling process due to the CTE mismatch between the top and bond coats can promote the propagation of parallel cracks created or existing at the interface or near the interface [47]. The vertical cracked TBC system can enhance the thermal durability with improved strain compliance during operations [48].

The E and H values for the TBC that survived after JETS tests are shown in Fig. 10. The H values were more sensitive to the JETS test than the E values, showing a similar E value of 113.4 ± 31.0 GPa and a slightly higher H value of 8.9 ± 3.6 GPa compared with those of as-prepared status which E and H values are 113.9 ± 23.8 GPa and 6.7 ± 3.0 GPa. The similar modulus values in the YGYZ top coat are likely due to localized nanoindentation measurements, which only regions away from vertical cracks were selected. The hardness values are increased in both measurements after JETS tests, meaning the stress reduction. However, the E and H values for the buffer layer were lower than those of as-prepared status which E and H values are 120.0 ± 21.7 GPa and 7.4 ± 2.7 GPa, being 80.0 ± 9.8 GPa and 4.8 ± 1.1 GPa, respectively. The lower values are due to the stress increase and the newly developed microcracks, such as intralamellar cracks and/or interlamellar cracks, during the rapid heating and cooling processes. After JETS tests, the H values from Vickers indentation showed lower values compared with those from nanoindentation, showing 3.9 ± 0.2 GPa for the buffer layer and 6.3 ± 0.2 GPa for the YGYZ coating. The higher H value of the YGYZ coating after JETS tests implies the stress reduction, and the lower H value of the buffer layer confirms the stress increase and the newly formed internal defects, as mentioned above.

4. Conclusions

New architectures of TBC were designed and prepared using the low thermal conductivity material, YGYZ, and the buffer layers of 8YSZ. The influences of the structural design, composition in the bond coat, and feedstock purity of the buffer layer on the thermal durability of the YGYZ-based TBC system with the top coat prepared by the APS method and the bond coat prepared by the HVOF method were investigated through the FCTF and JETS tests. The SLC and DLC TBCs showed a sound condition in the as-prepared status. The relatively early failure of the SLC TBCs in FCTF tests can be attributed to its lower fracture toughness of the YGYZ top coat, compared with the buffer layer

(8YSZ). After FCTF tests, the DLC TBC with the buffer layer of regular purity and the Co-Ni-based bond coat showed a better thermal durability. However, all of the TBC samples were delaminated at the interface between the YGYZ top coat and the bond coat or within the YGYZ top coat near the interface. The DLC TBC with the buffer layer of high purity and the Ni-based bond coat was in a sound condition after 2000 cycles in JETS tests, whereas the other TBCs were delaminated before 1130 cycles. Structural design by introducing a buffer layer enhanced thermal durability in the slow cooling environment similar to the FCTF test. In the fast cooling environment similar to the JETS test, the fracture behavior would be changed from fully delamination near the interface to partial delamination within the YGYZ top coat by introducing the buffer layer of high purity and controlling the bond-coat composition.

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