Evaluation of degradation of high temperature materials including coatings in a reducing environment

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Introduction

A diagram of a gas turbine engine
https://car.motor-fan.jp/tech/10014243

Higher performance and efficiency of gas turbines

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Thermal Barrier Coating (TBC)

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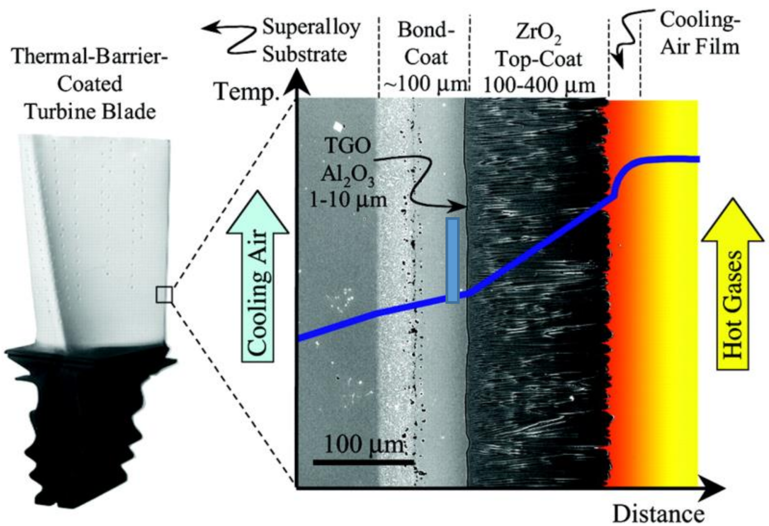
Protect hot-section components from oxidation and corrosion under high temperature



Photograph of a turbine blade with thermal barrier coating (TBC)

① **Top coat**: Y_2O_3 stabilized ZrO_2 (YSZ)
・Role: Thermal barrier

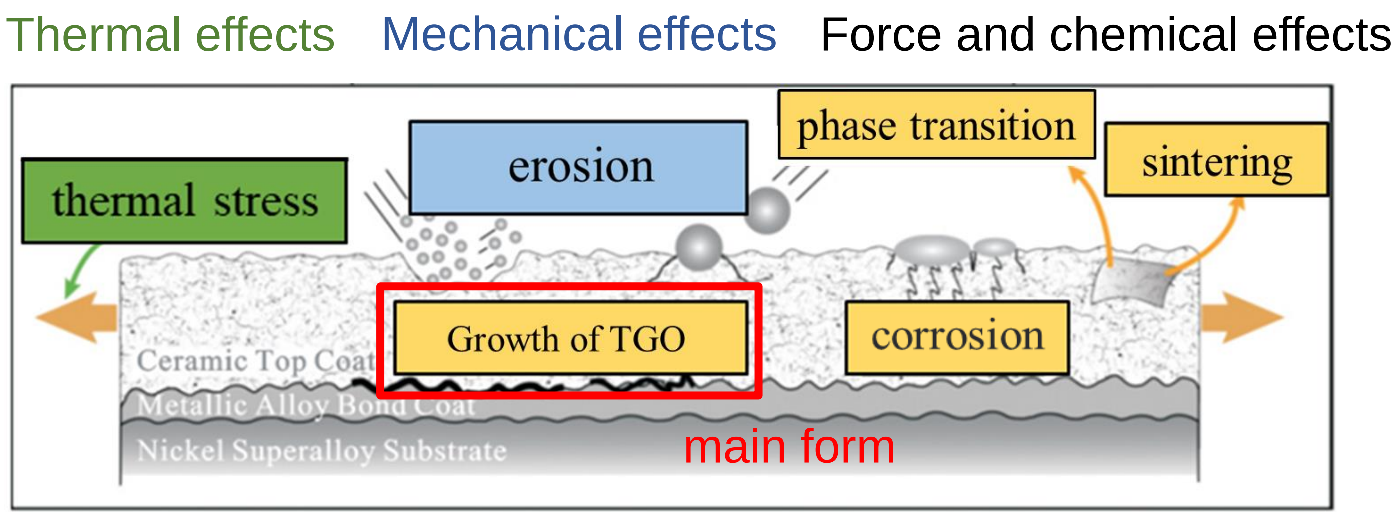
② **Bond coat**: MCrAlY (M means Ni and/or Co)
・Role: Improvement of bonding strength and inhibition of oxidation and hot corrosion

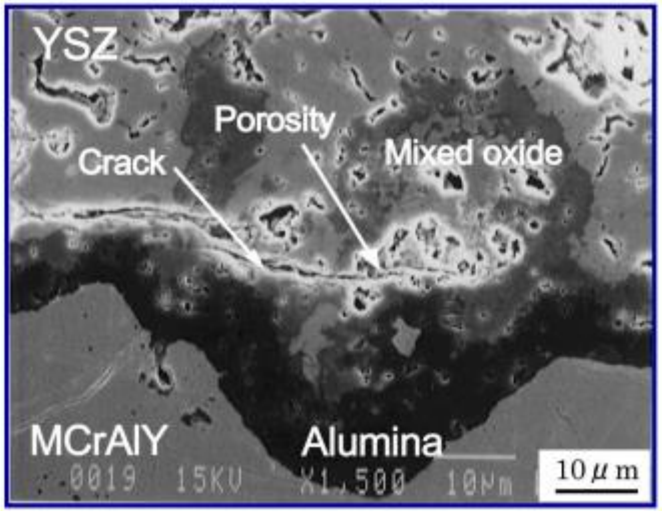
③ **Substrate**: Ni-based superalloy

④ **Thermally grown oxide** (TGO): formed with prolonged oxidation at high temperature between top coat and bond coat

Padture, Nitin P., Maurice Gell, and Eric H. Jordan. Science 296.5566 (2002): 280-284.

Traditional failure mechanisms





Cross-sectional SEM image of TBC aged for 3000 hours at 1000°C

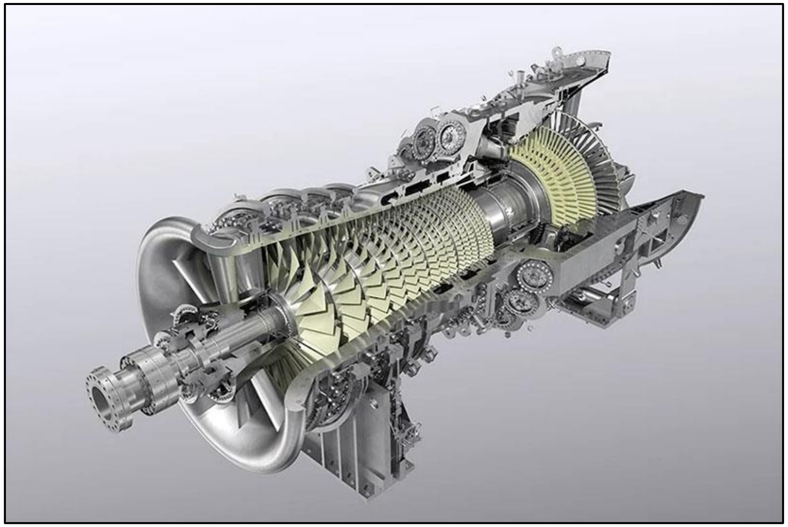
Two characteristic morphology of TGO: dense Al_2O_3 and porous mixed oxide layer

The growth of TGO will cause interfacial delamination and accelerate the spallation

K.Ogawa, T.Shoji, H.Aoki, N.Fujita, T.Torigoe. JSME int. J, 44A, 4(2001), 507-513

Wang Tiejun. Chinese Journal of Solid Mechanics, 2016, 37(6):41

Research status



https://newswitch.jp/p/36219

To achieve the carbon neutrality goal by 2050, using hydrogen fuel instead of fossil fuel in gas turbines can significantly reduce carbon dioxide emissions.

Fossil fuel gas turbines → Hydrogen・Ammonia gas turbines

High temperature oxidation

Will hydrogen and ammonia gas turbines eliminate degradation due to high temperature oxidation compared to conventional ones?

Oxidation?
Or Nitriding?
Reducing reaction?

ETN Global, Hydrogen Gas Turbines – The Path Towards a Zero-Carbon Gas Turbine Stefan, et al. International Materials Reviews 67.5 (2022): 461-486.

Research purpose

In ammonia gas turbines, two types of degradation are possible: nitriding and reduction. In this study, as a first step, we investigated the reduction reaction in a hydrogen environment.

New challenge: If the hydrogen fuel is not completely combusted, the oxidizing environment will be replaced by a reducing environment.

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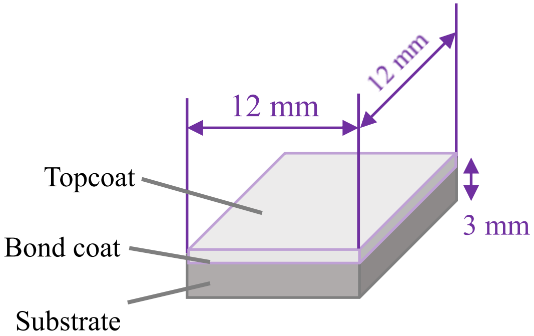
Further discussion is needed on how hydrogen affects the new degradation mechanism of the thermal barrier coating systems.

In particular, it is not known what kind of material degradation occurs in TBCs, which use oxide ceramics, in a reducing environment. In this study, material degradation in a hydrogen environment was first evaluated.

Experimental

Substrate: Inconel 738LC
Bond Coat: CoNiCrAlY
Topcoat: 8YSZ

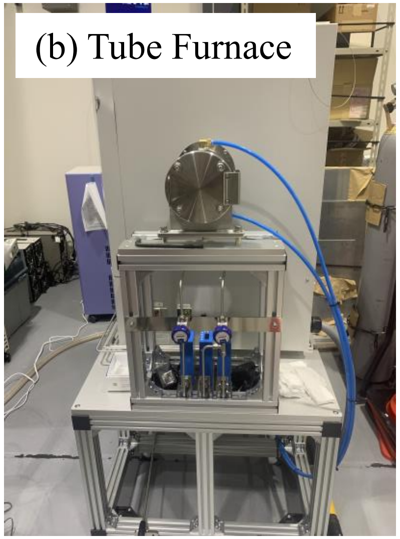


Bond Coat	Co	Ni	Cr	Al	Y
CoNiCrAlY	Bal.	32	22	8	0.5

Bond Coat Spray Method	Thickness
High Pressure Cold Spray	100 μm

Topcoat Material	Spray Method	Thickness
8 wt.% Yttria Stabilized Zirconia	Atmospheric Plasma Spray	300 μm


(a) Muffle Furnace


(b) Tube Furnace

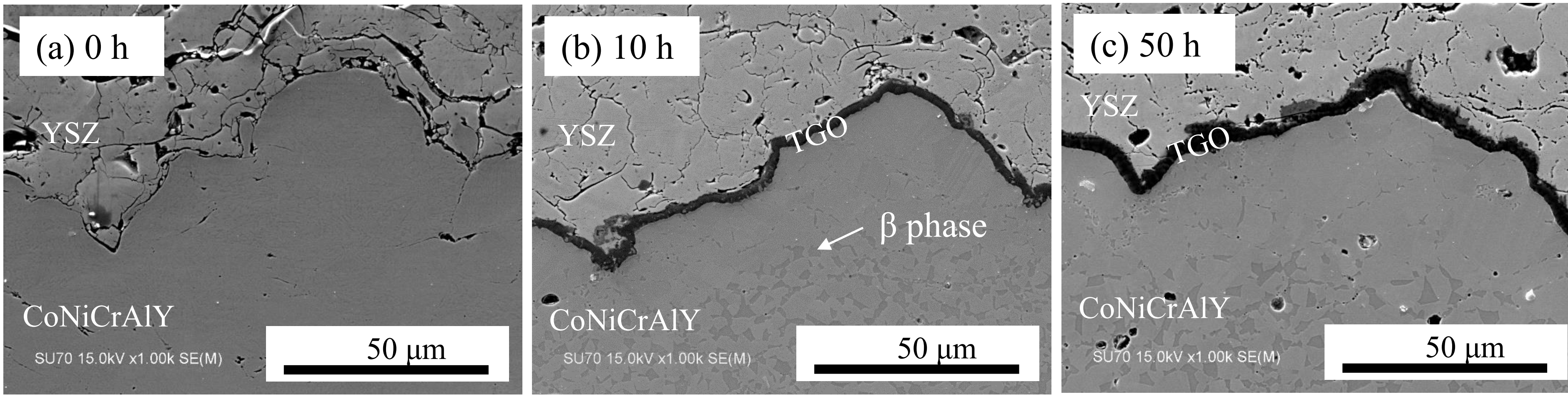
Heat treatment conditions:
Temperature: 1100°C
Time: 0 h, 10 h, 50 h, 100 h, and 500 h

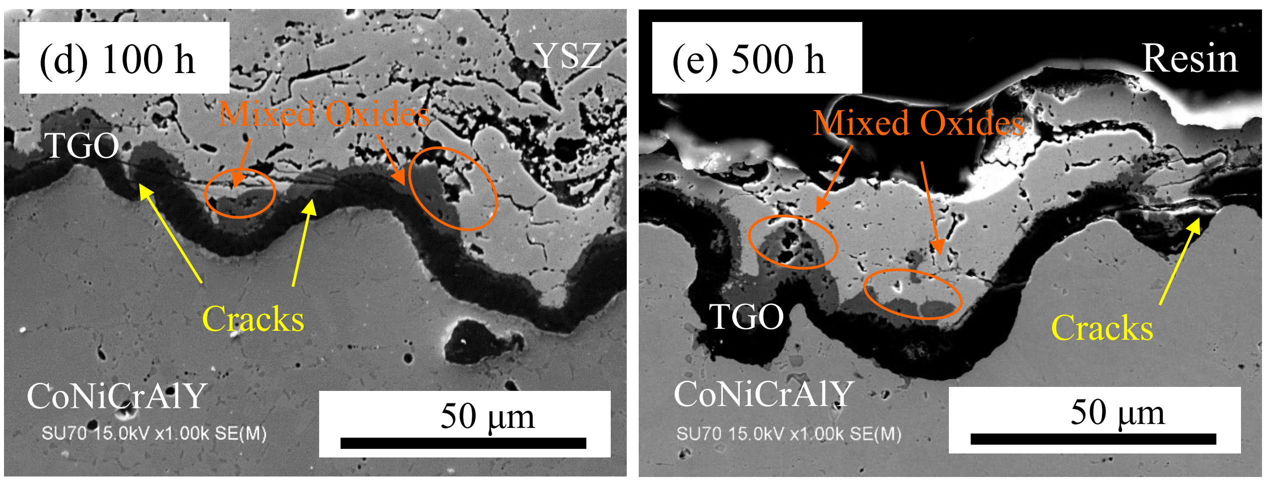
Gas Type: (a) Air
(b) 5% H_2 + 95% pure Ar gas

Interface degradation behavior at the interface between TC and BC

Microstructural changes of TBCs samples after heat treatment at 1100°C in air

SEM Results





Topcoat separation occurred after heat treatment at 1100°C for 500 h in air.

Microstructural changes of TBCs samples after heat treatment at 1100 ℃ in 5% H2 gas

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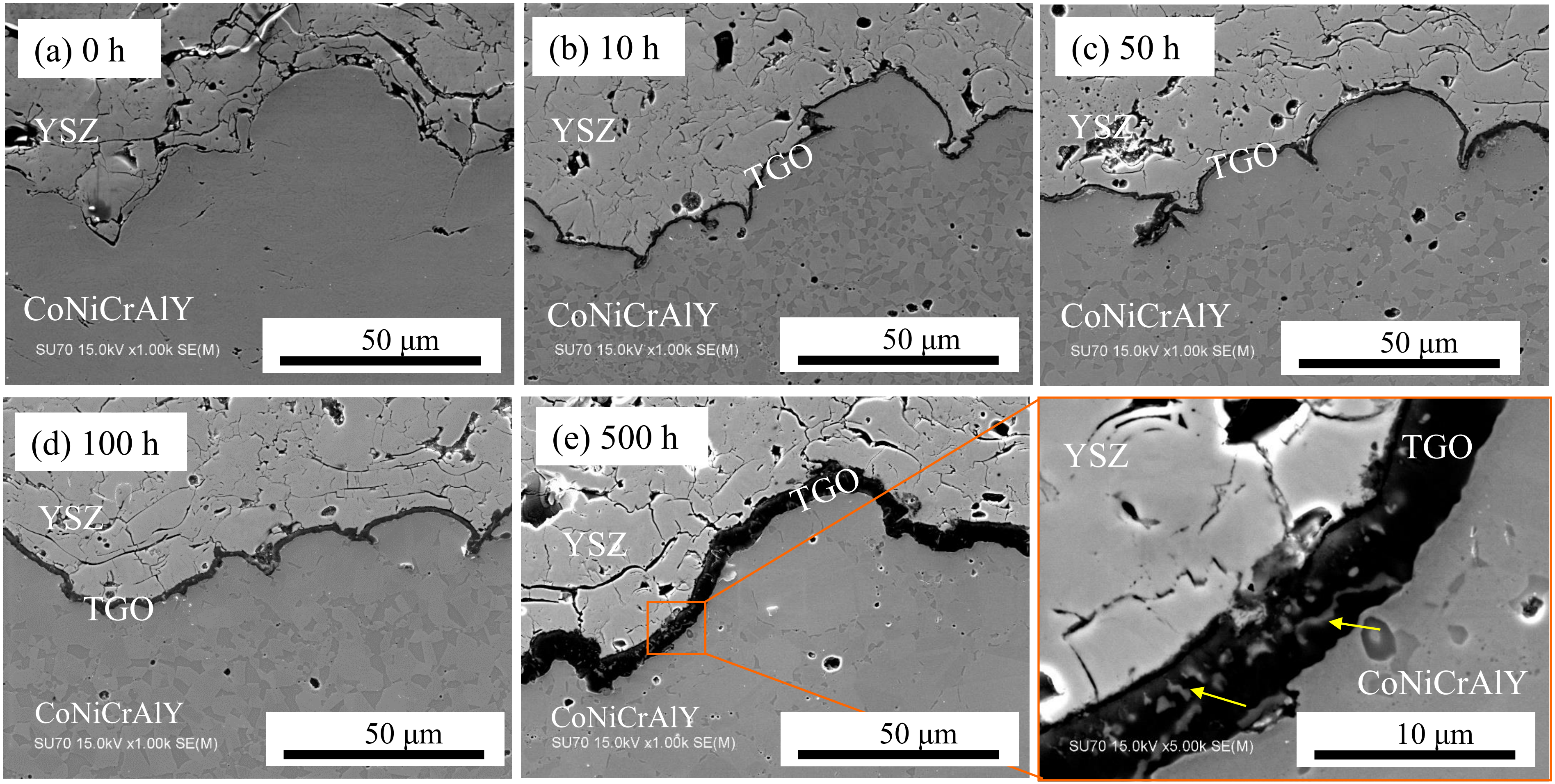
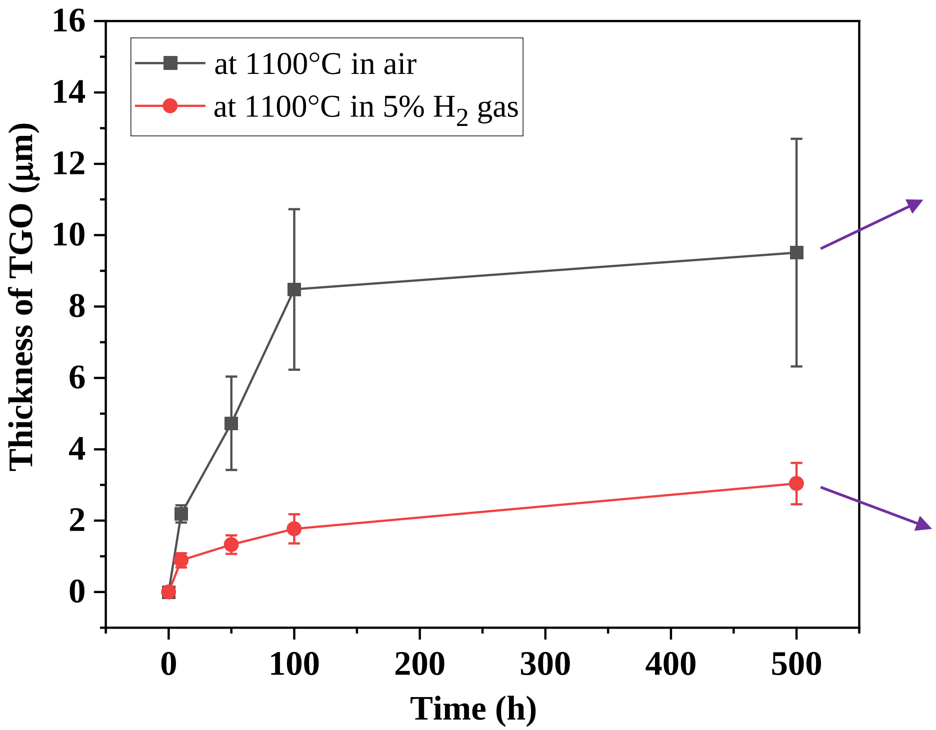
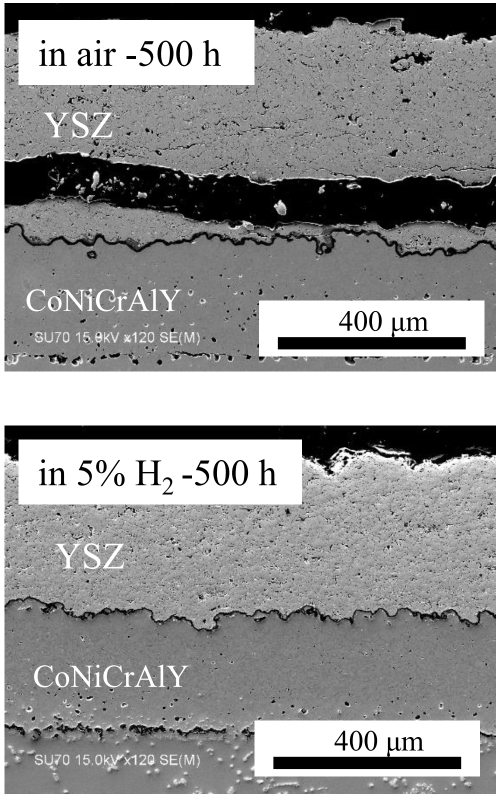
SEM Results



No separation occurred at TC-TGO interface after heat treatment at 1100 °C in 5% H_2 for 500 h.

TGO thickness with time variation

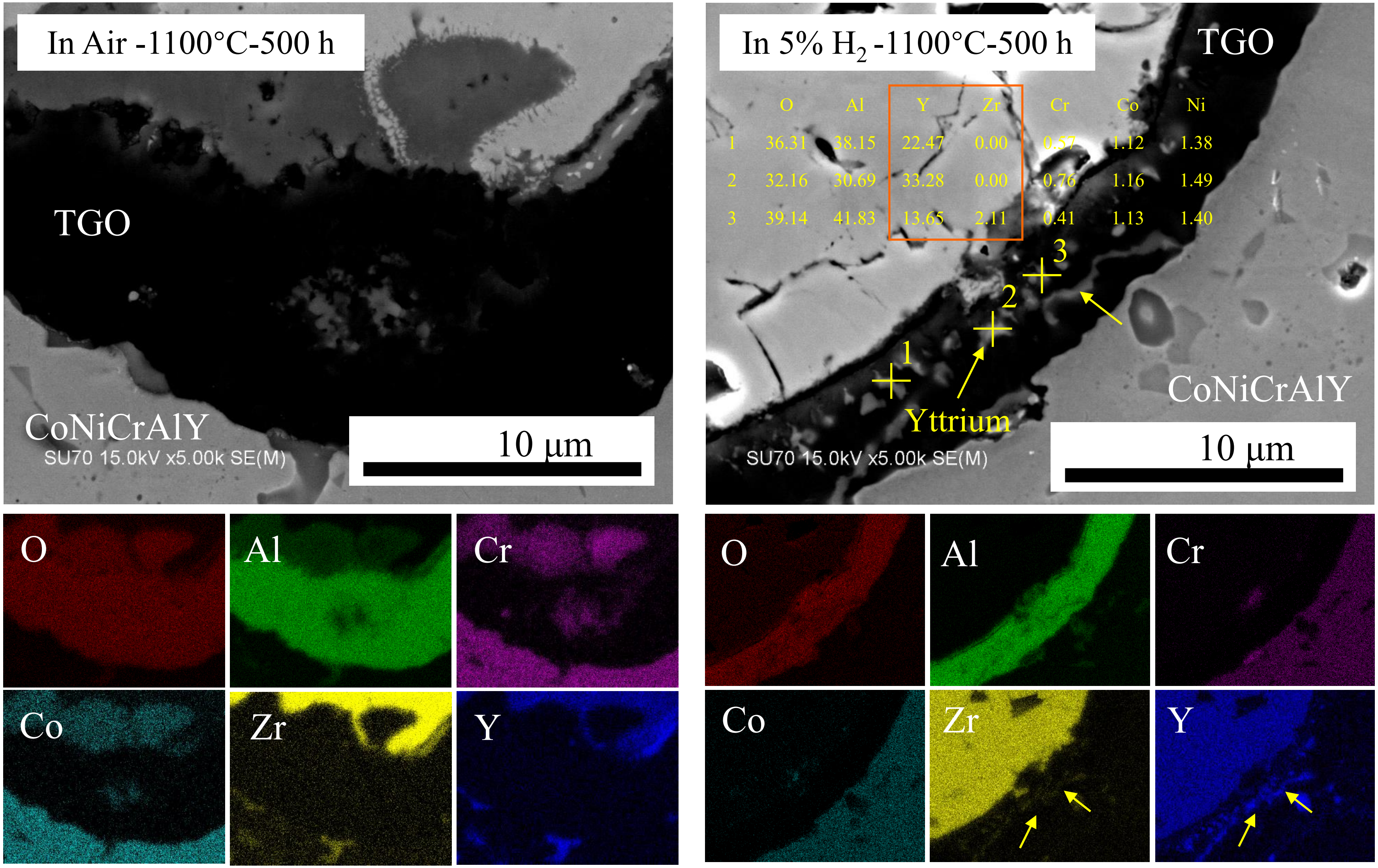




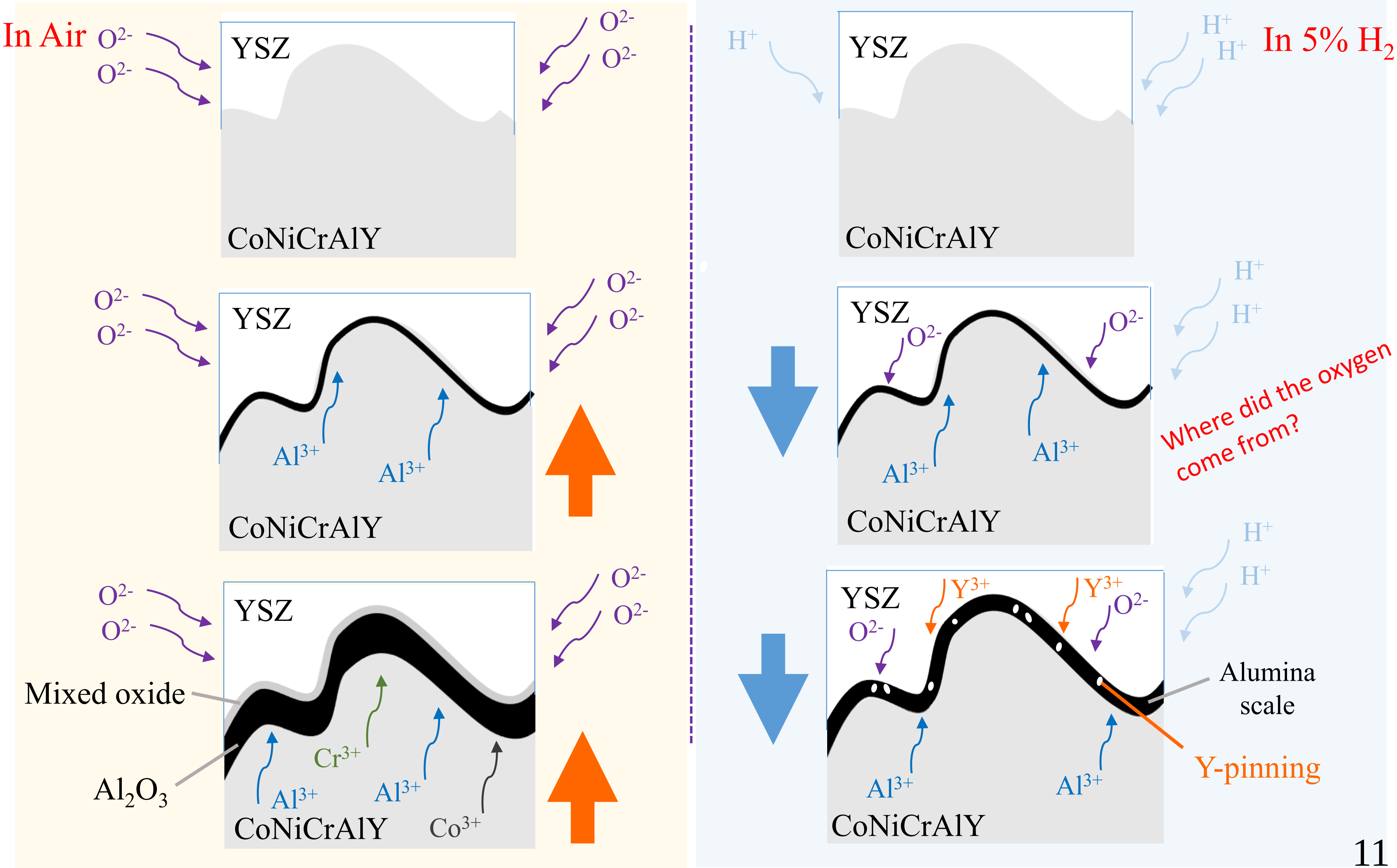
	In Air	In 5% H_2
1100°C-10 h	2.19±0.24 μm	0.89±0.20 μm
1100°C-50 h	4.73±1.31 μm	1.33±0.26 μm
1100°C-100 h	8.48±2.25 μm	1.77±0.41 μm
1100°C-500 h	9.51±3.19 μm	3.04±0.58 μm

TBC systems exposed in air and 5% H_2 gas enabled the formation of oxide scales at different growth rates.

Elements composition of the oxide scales



Schematic illustration of TGO formation



Phase transition of topcoat surface

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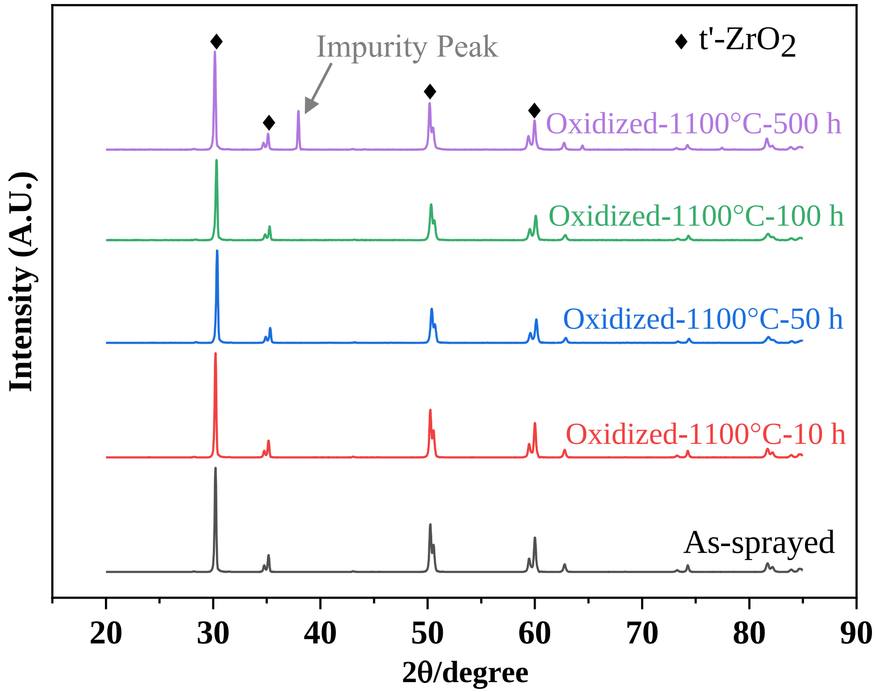
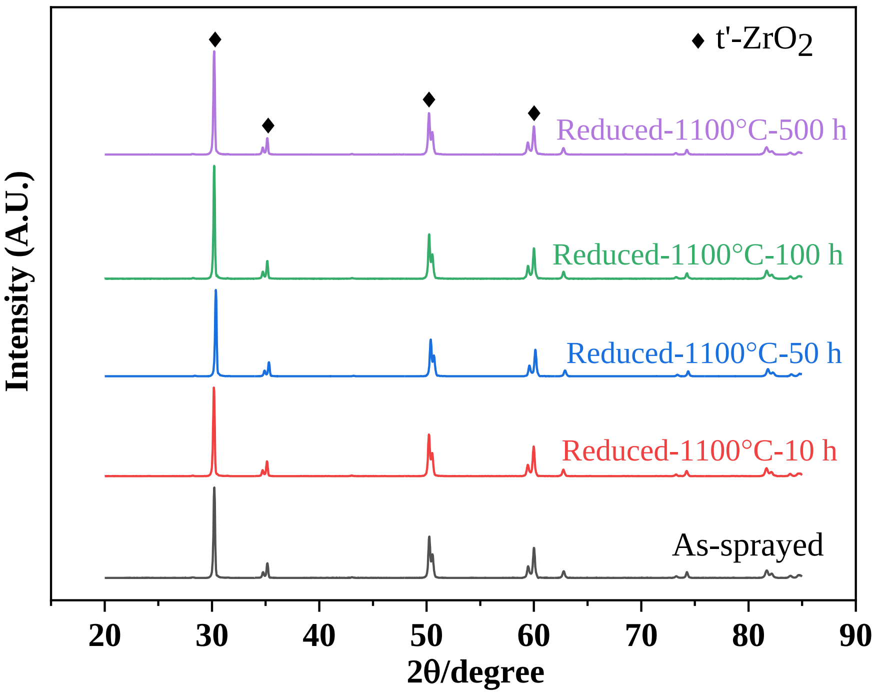
In Air Oxidizing environment



In 5% H_2 Reducing environment

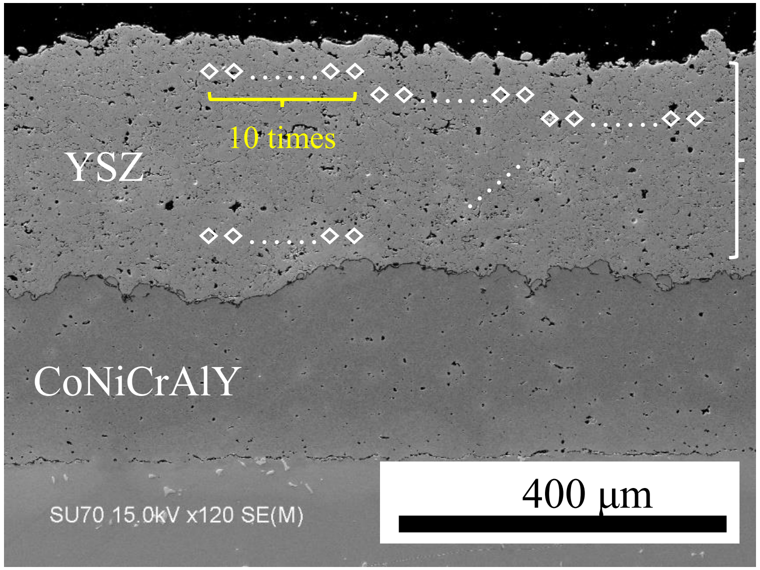


XRD results show that after heat treatment at 1100°C for 0~500 h, the topcoat surface of TBCs samples consist of t′-ZrO_2, which means there is no any phase transformation of the topcoat surface under **both** environments.

Micro-Vickers Indentation Test

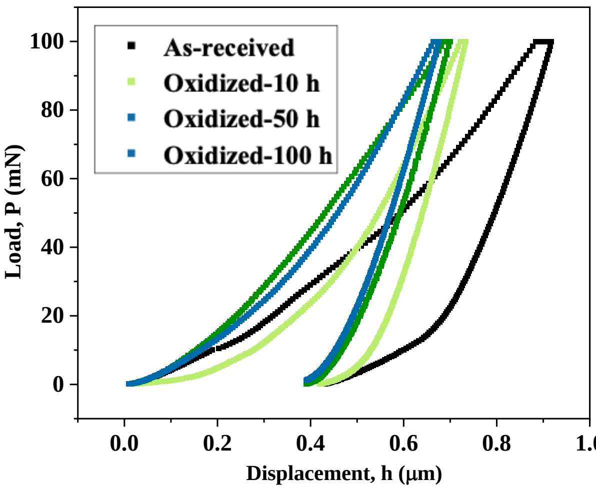
The microhardness testing system
FISCHERSCOPE HM 2000

Micro-Vickers indentation test conditions:
Load: 100 mN/15 s

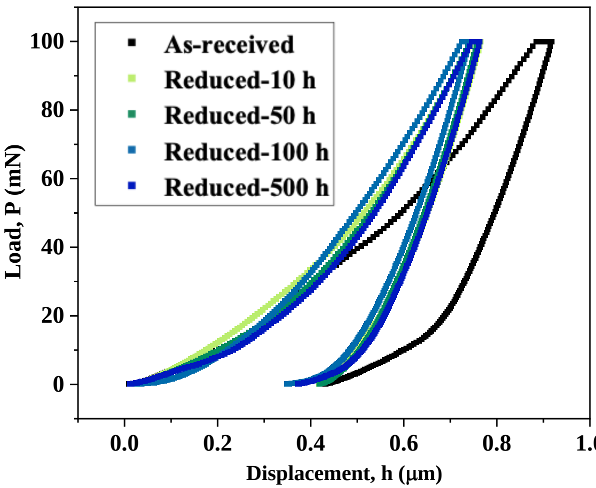


Schematic diagram of mechanical properties measurement.

In Air



In 5% H_2



Typical load-displacement curves of the cross-section of the YSZ topcoat.

Hardness and Young's Modulus

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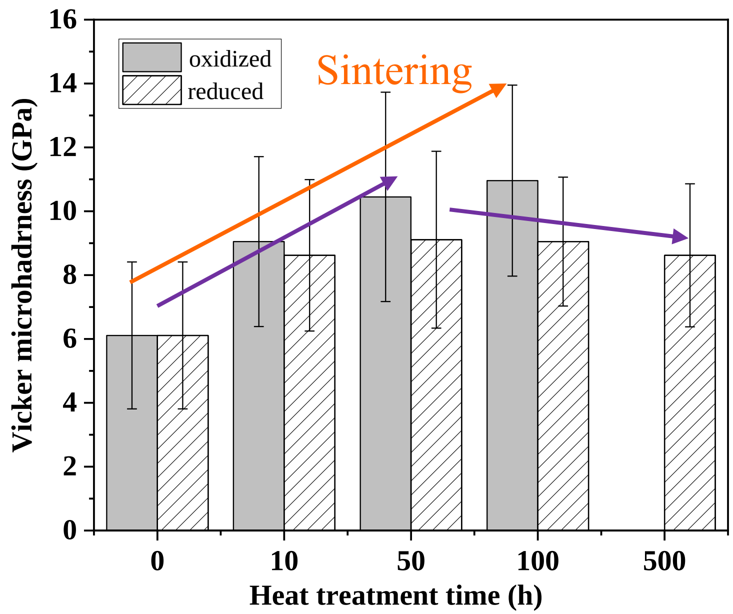
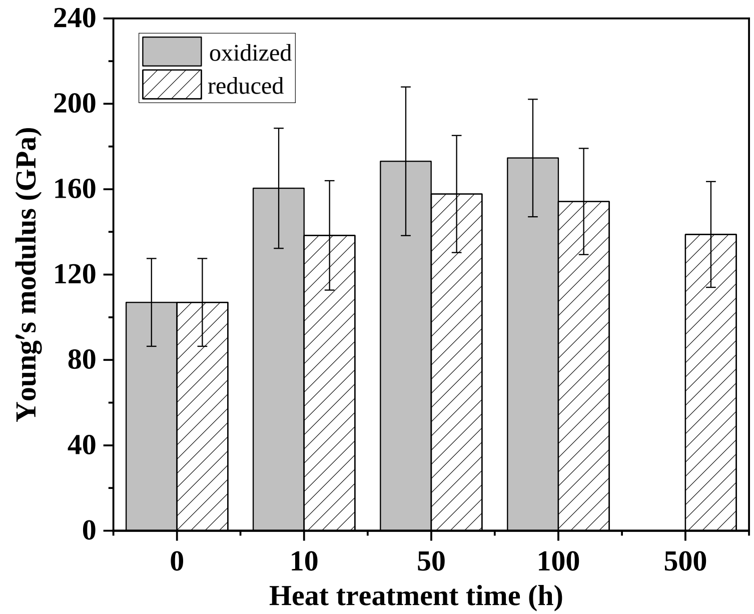




Hardness (GPa)	Oxidized	Reduced
As-received	6.11±2.30	6.11±2.30
10 h	9.05±2.66	8.62±2.37
50 h	10.45+3.28	9.11+2.77
100 h	10.96±2.99	9.05±2.02
500 h	-	8.62±2.24

decrease

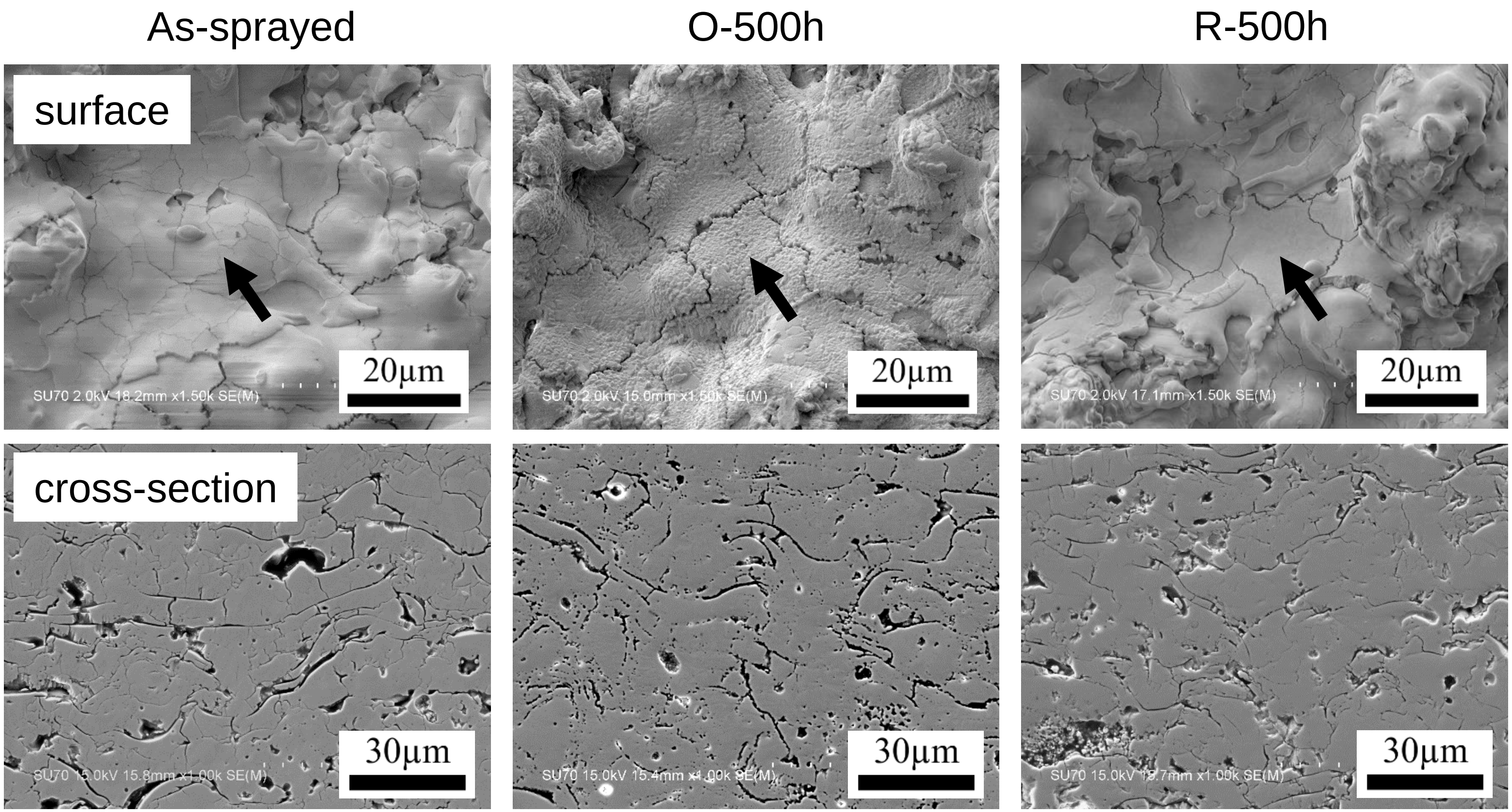
(peeled off)

Young's modulus (GPa)	Oxidized	Reduced
As-received	106.96±20.59	106.96±20.59
10 h	160.43+28.12	138.35+25.64
50 h	173.09+34.82	157.74+27.43
100 h	174.61+27.53	154.24±24.88
500 h	-	138.82±24.78

(peeled off)

The TBCs lifetime is extended in 5% H_2 gas, which might be attributed to the slower growth rate of the alumina scale.

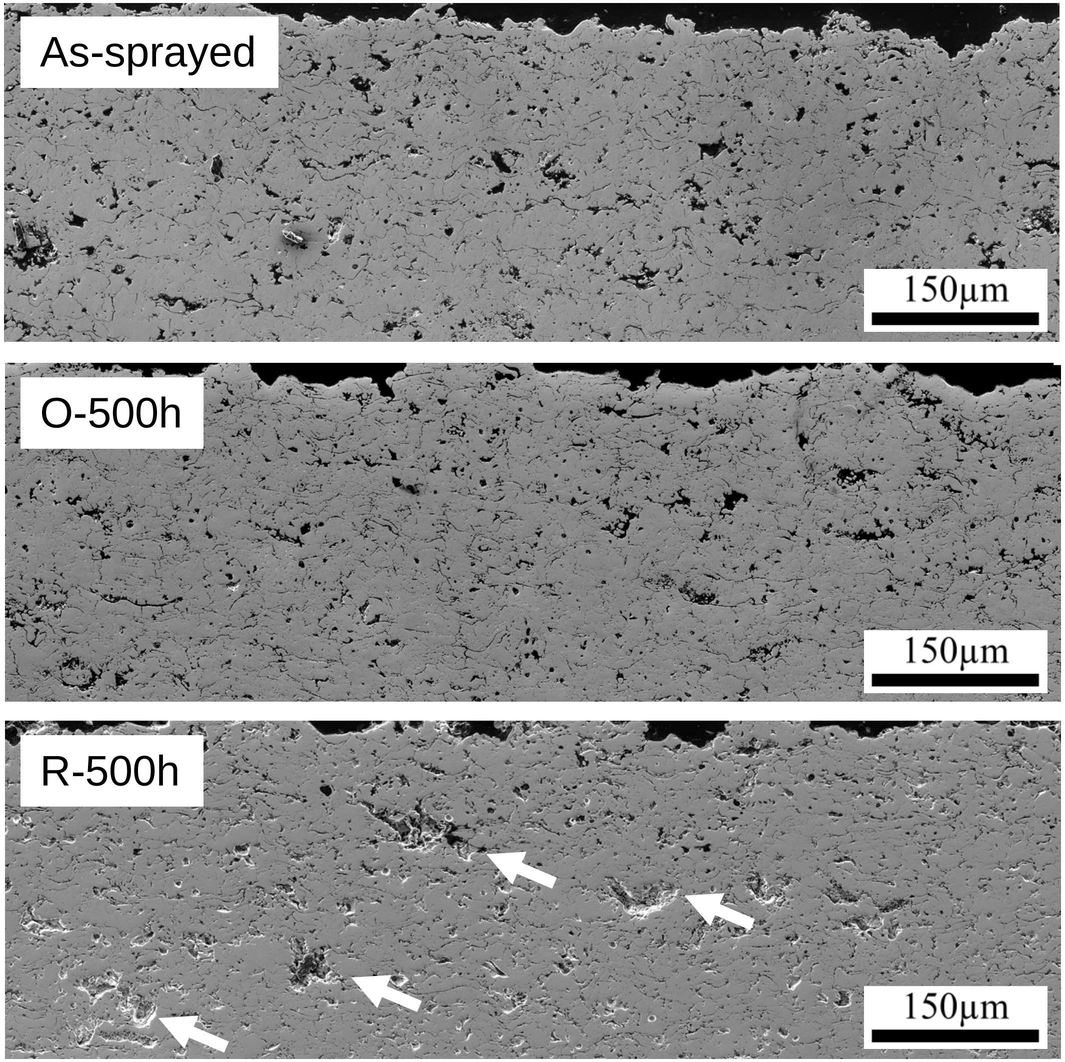
Sintering behavior of top coat



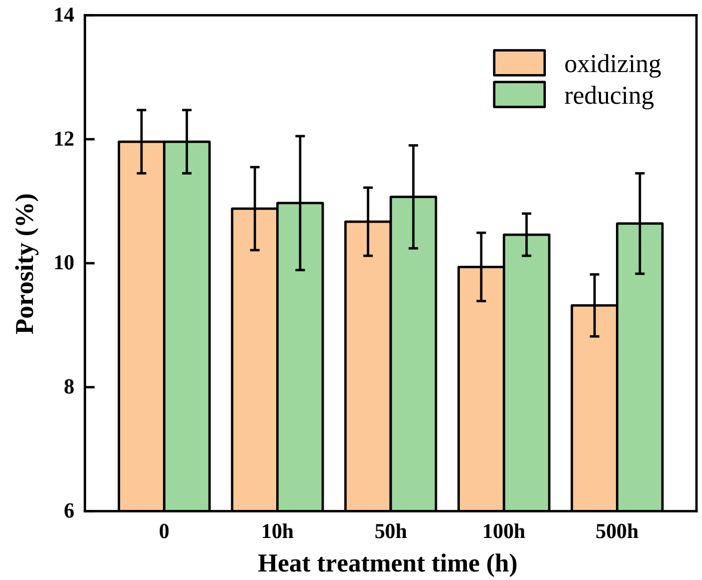
1. healing of micro-cracks and micro-pores due to sintering effects
2. sintering under reducing environments shows a lower degree compared to oxidizing environments

* The reduced sintering rate may be due to the reaction of hydrogen with the pre-existing oxygen in the holes created by the APS spraying process, and the formation of local water vapor at high temperatures may further prevent the healing of the cracks. It may be accurately proven in the future pure Ar atmosphere experiment.

Sintering behavior of top coat



Cross-section morphology of top coat in a large range



larger-sized voids are observed
➡ The statistical results of porosity show no significant decrease.

Sintering characteristics:

Micro-cracks heal and original large size holes become larger

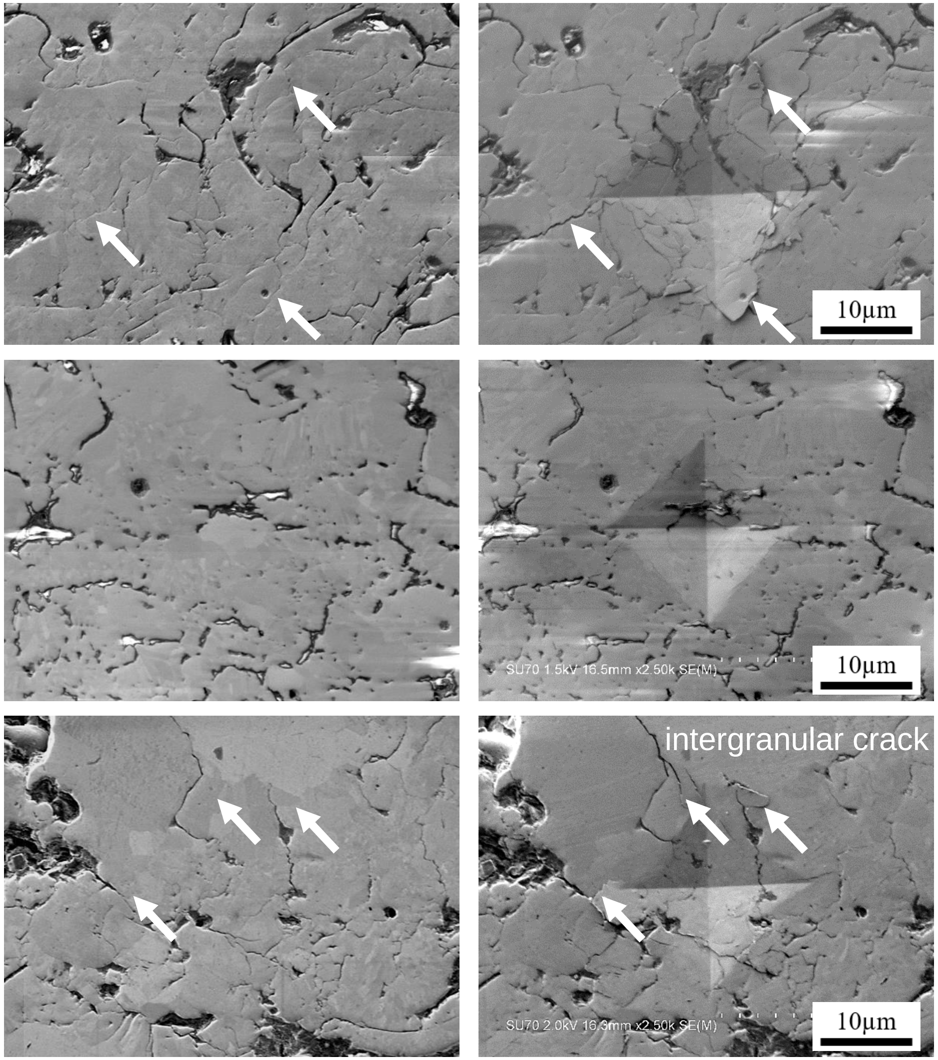
Crack propagation by indentation test

Top coat Load : 2N / 15s

as-sprayed

O-500h

R-500h



the same area before and after the indentation test

as-sprayed: Cracks generate and propagate at the location of pre-existing microcracks.

O-500h: no obvious cracks are caused by the indentation test

R-500h:

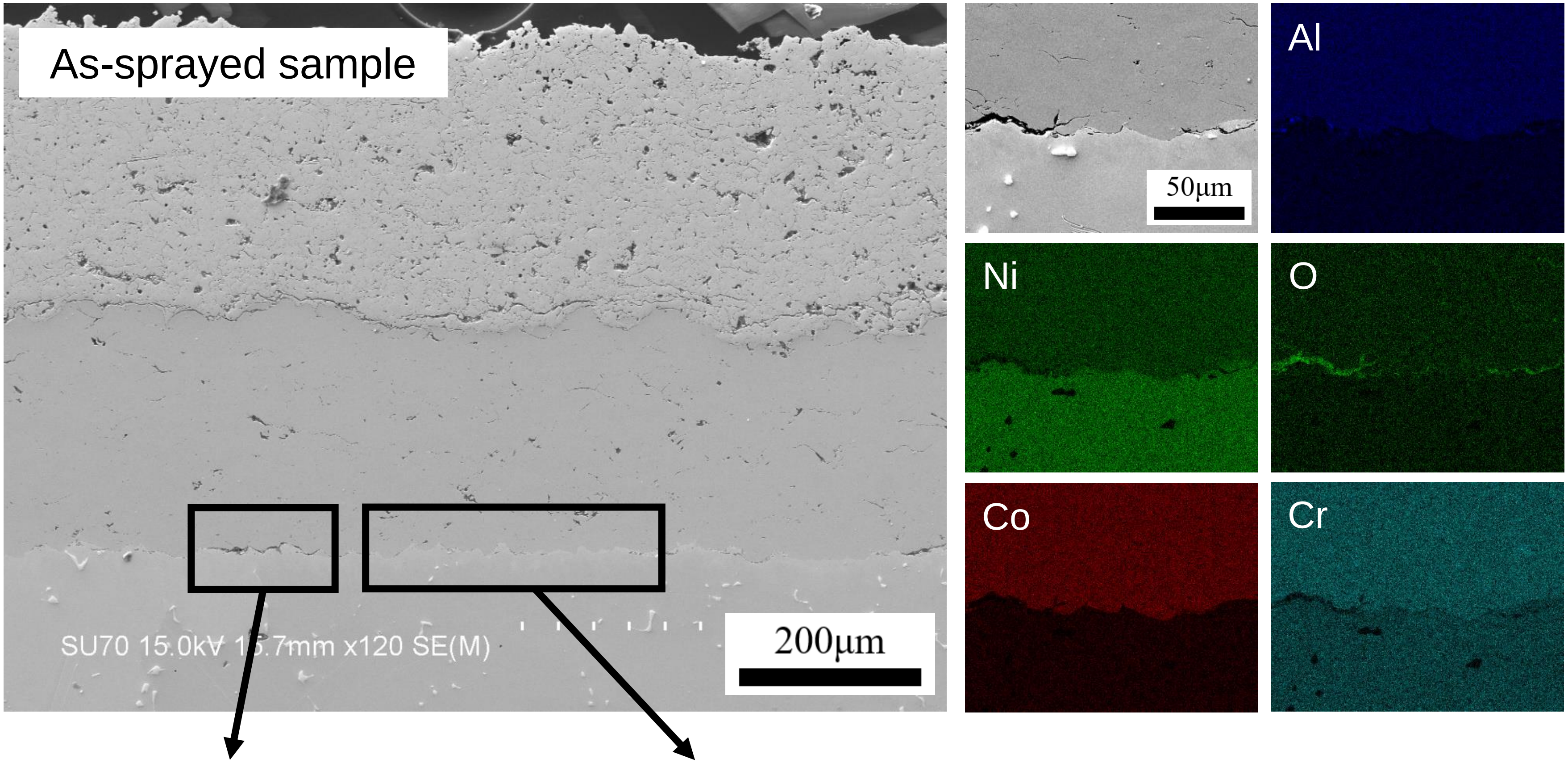
① Cracks occur at the pre-existing microcracks area.

② Cracks show obvious intergranular propagation.

➞ intergranular embrittlement

Interface degradation behavior at the interface between substrate and BC

Initial BC/substrate interface

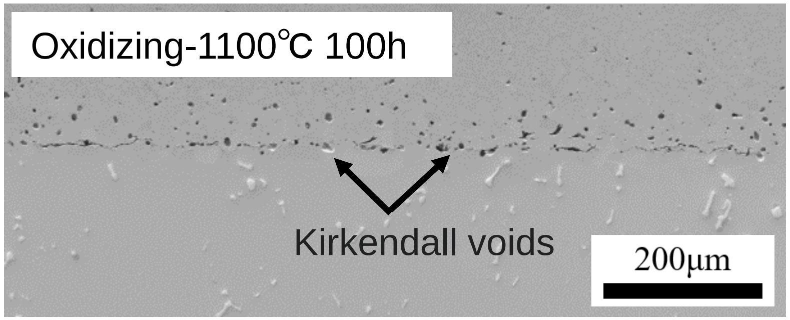


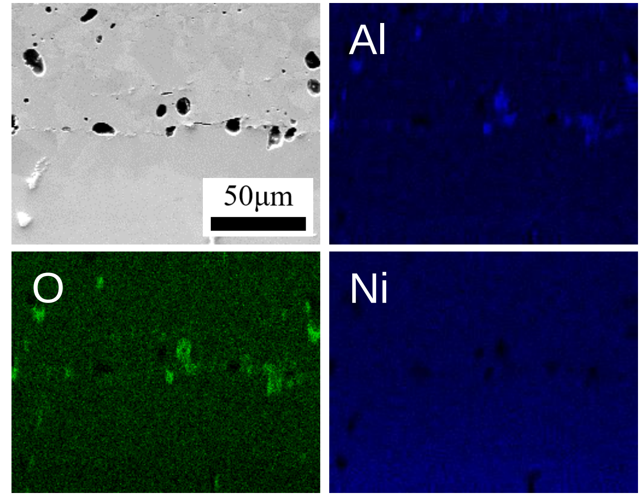
initial oxide film of powders

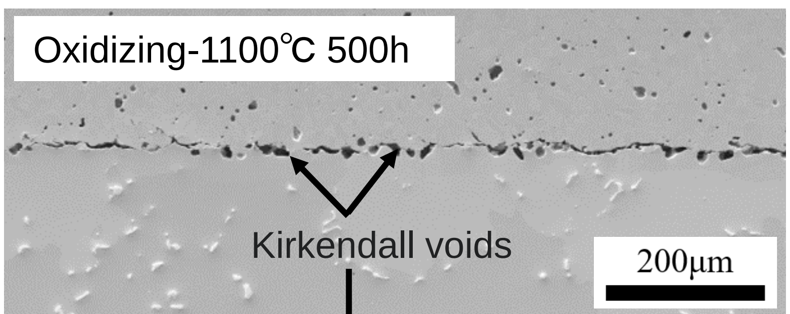
dense bonding

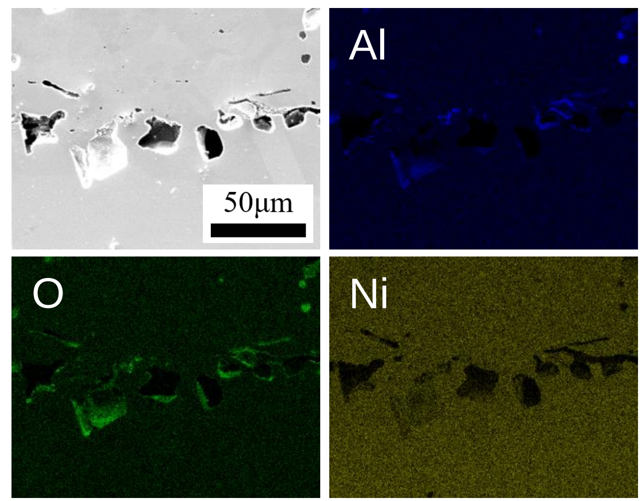
no delamination and pores between coating and substrate

BC/substrate interface



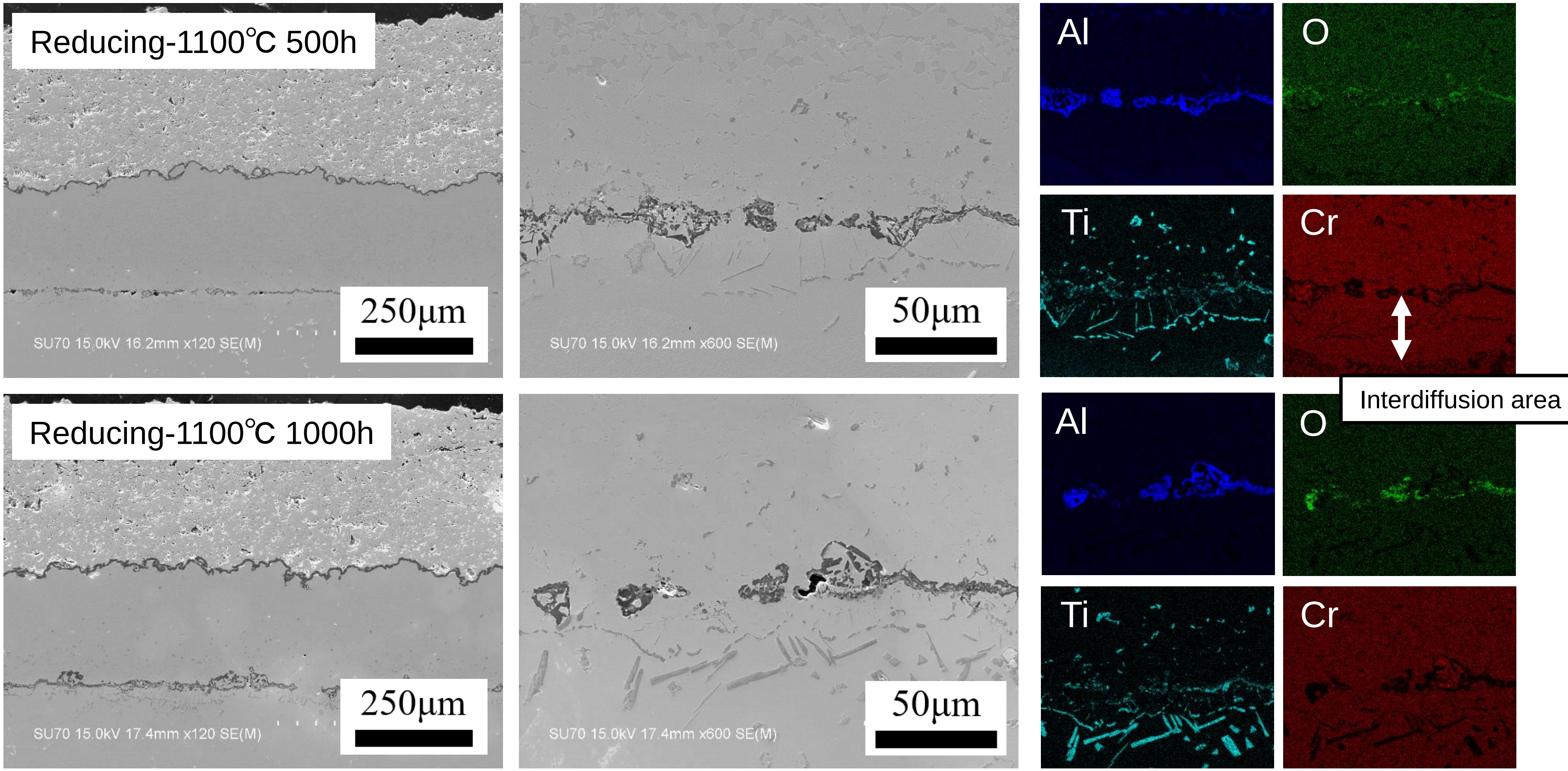






unequal element diffusion
between substrate and coating

BC/substrate interface



Interdiffusion area

Although metallurgical bonding is enhanced, the segregation of elements at the interface will lead to a decrease in bond strength between bond coat and substrate during isothermal exposure, proving a new failure position in the reducing environment.

Conclusions

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1. TBC systems exposed in air and 5% H_2 gas enabled the formation of oxide scales at different growth rates. The TBCs lifetime is extended in 5% H_2 gas, which might be attributed to the slower growth rate of the alumina scale.
2. After heat treatment in 5% H_2, TGO mainly composed of Al and O, with a large amounts of Yttrium.
3. The presently available results indicate that H_2 might promote the diffusion of oxygen in YSZ topcoat to the BC-TC interface, which reduces the stability of YSZ. The decrease in mechanical properties of the cross-section of YSZ after heat treatment in H_2 is a strong evidence.
4. The presence of a large amount of hydrogen will destroy the homogeneity of the alumina layer, and the ability of Al_2O_3 to prevent the diffusion of elements is decreased.
5. The bond strength between the coating and substrate tends to be decreased under the reducing environment. This conclusion will be further investigated in the future.

Thank you for your kind attention!