CORROSION SCIENCE AND TECHNOLOGY, Vol.2, No.3(2003), pp.155~160

High Temperature Oxidation Behavior of Plasma Sprayed ZrO_2 Having Functionally Gradient Thermal Barrier Coating

Cha-Hwan Park, Won-Jae Lee*, Kyung-Mox Cho*, and Ik-Min Park*

Defense Quality Assurance Agency, Changwon 641-600, Korea
**Department of Metallurgical Engineering*
Pusan National University, Pusan 609-735, Korea

Plasma spraying technique was used to fabricate functionally graded coating (FGC) of NiCrAlY/YSZ 8wt%Y_2O_3-ZrO_2) on a Co-base superalloy (HAYNES 188) substrate. Six layers were coated on the substrate for building up compositionally graded architecture. Conventional thermal barrier coating (TBC) of NiCrAlY/SZ with sharp interface was also fabricated. As-coated FGC and TBC samples were exposed at the temperature of 1100°C for 10, 50, 100 hours in air. Microstructural change of thermally exposed samples was examined. Pores and microcracks were formed in YSZ layer due to evolution of thermal internal stress at high temperature. The amount of pores and microcracks in YSZ layer were increased with increasing exposure time at high temperature. High temperature oxidation of coatings occurred mainly at the NiCrAlY/YSZ interface. In comparison with the case of TBC, the increased area of the NiCrAlY/YSZ interface in FGC is likely to attribute to forming the higher amount of oxides.

Keywords : *plasma spraying, functionally graded coating, thermal barrier coating, nicraly/ysz, high temperature oxidation behavior*

1. Introduction

Great interests focuses on thermal barrial coatings (TBCs) due to high quality thermal efficiency and durability of aircraft gas turbine engine.[1] TBC structures consist of partially stabilized ZrO_2 layers and metallic bond layers (MCrAlY) on the superalloy substrates. The problem is that the qualities of TBCs are degraded due to thermal expansion mismatch (ceramic/metal), temperature gradient (heating/solidification), oxide formation, plastic deformation (metallic bond layer), phase transformation(ceramic) and sintering shrinkage(ceramic).[2] In order to solve the problem, building up Functionally gradient coatings(FGCs)[3] within TBC layers have been suggested for relieving thermal mismatch between metal and ceramic interface and improving thermo-mechanical life cycles of TBCs.[4] However, the oxidation of graded layer at high temperature was accelerated, using FGCs. In this paper, in order to understand the behavior of high temperature oxidation of FGC layers having compositionally graded ones, microstructural investigation of samples exposed at high temperature was carried out.

2. Experimental procedure

Co-base superalloys (HAYNES 188) was used as substrates. The composition of HAYNES 188 was shown in Table 1. The spraying powders were consist of 8wt% partially yttria stabilized ZrO_2 (YSZ) and Ni-22Cr-10Al-1Y alloy as listed in Table 2.

The pre-mixtures of the two powders, having various volume ratios were prepared for fabricating the upper YSZ layers and step-grade layers or bond layers on HAYNES

Table 1. Chemical composition of HAYNES 188.

C	Si	Cr	Ni	Co	W	La
0.08	0.20	25.5	22	37.1	15	0.08

Table 2. Characteristics of powders used for plasma coating

Kind	Composition (wt%)	Size (μm)	Melting Point(K)	Coefficient of Thermal Expansion
Bond Powder	67Ni-22Cr-10Al-1Y	45-125	1623	13.7×10^{-6}/K
Ceramic Powder	8Y_2O_3-92ZrO_2	10-106	2988	$7\sim10\times10^{-6}$/K

Table 3. Composition and thickness design of NiCrAlY/YSZ coating systems (units : mm)

Specimen No.	Composition (vol.%)								Thickness (mm)	Remark
	100N	80N+Z	60N+Z	40N+Z	30N+Z	20N+Z	10N+Z	100Z		
T	0.	-	-	-	-	-	-	0.25	0.4	TBC
F1	0.15	0.1	0.1	0.1	-	0.1	-	0.25	0.8	Symmetry
F2	0.05	0.05	0.05	0.05	-	0.05	-	0.15	0.4	Symmetry
F3	0.05	-	-	0.05	0.05	0.05	0.05	0.15	0.4	Ceramic Rich

Note : N:NiCrAlY, Z:YSZ

188 substrates as listed in Table 3. The first sample is double layer consisting of NiCrAlY bond layers and YSZ ceramic layers. Also, the other samples include three types of functionally graded layers. F1 and F2 samples are symmetry-graded structure with difference thickness. F3 is ceramic rich four graded layer. The fabrication of TBC and the graded layers on the HAYNES 188 substrates were carried out under the Ar gas atmosphere, using an automatic 9MB single plasma gun.

As-coated TBC and FGC samples(F1, F2, F3) were exposed at temperature of 1100℃ for 10, 50, 100 hours in air and examined the change in microstructure, oxidation behavior, phase transformation. Microstructural investigation of YSZ layers, the bond layers and the graded layers were carried out using optical microscopy(OM), scanning electron microscopy(SEM), energy dispersive spectrometer(EDS) and X-ray diffraction(XRD). Also the variation of weight gain on samples with increasing exposure time was measured.

3. Results and discussion

3.1 Microstructural change in TBC and FGCs layers exposed to high temperature

Fig. 1 shows the cross-sectional optical micrographs of TBC and FGCs layers exposed at 1100℃ for 10, 50, 100 hours in air. The degree of porosity of ceramic layer in TBC layers increased with increasing exposure time to high temperature. However, the oxidation did not significantly occurred between substrate and bond layers after 100 hrs at 1100℃. The degree of porosity within ceramic layers in FGCs samples increased with increasing exposure time, also, oxidation occurred in the graded layer as well as the interface of NiCrAlY and YSZ. Especially vertical cracks within YSZ ceramic layer in the case of ceramic rich FGC samples were observed after 50hrs and oxidation occured in substrate. This indicates that thermal degradation of FGC samples is more severe than that in the case of TBC sample at high temperature.

Fig. 2 shows SEM micrographs of thermally exposed samples having surface crack formation with variation of oxidation time. With increasing exposure time to high temperature, the amount of crack increased. It is considered that in all samples, crack generation is likely to occurs due to the change of internal stress at the coated layer, shrinkage of ceramic, pore formation, phase transformation and stress generation during thermal exposure.[6)-9)]

Fig. 3 shows the amount of porosity within thermally exposed TBC and FGC samples at 1100℃ with variation of oxidation time. In both cases of TBC and FGC samples, the amount of porosity in the ceramic layers increased with increasing exposure time. Especially, the amount of porosity in FGC samples was much larger than that in the case of TBC samples during thermal exposure. It is thought that, after high temperature exposure, the porosity of YSZ layer increases proportional to the amount of YSZ as sprayed.

Fig. 4 shows change in X-ray diffraction patterns with variation of oxidation time. Non-equilibrium tetragonal(T) peaks from YSZ were mainly observed without monoclinic(M) peaks. It means that phase transformations did not occurred during high temperature oxidation. It is reported that YSZ in the spray coated layer exists metastable non-transformable tetragonal(T′) phase and non-transformable cubic(F′) phase formed during supersolidification.[10),11)] However, phases of YSZ transformed into monoclinic (M) and cubic (F) phases due to diffusion of Y_2O_3 over T-M transient temperature. Equilibrium phase, T transformed into phase, M during cooling. The increase in the amount of YSZ (3~5% volume) occurred due to T-M transition. This may give rise to form microcracks.[12)] Therefore, we can infer that crack generation did not occur by the volume expansion accompanied with phase transformation at 1100℃.

3.2 High temperature oxidation of TBC and FGCs

Fig. 5 shows the weight change in TBC and FGC samples with variation of oxidation time. The increase in weight gain of the coated layers occurred during high

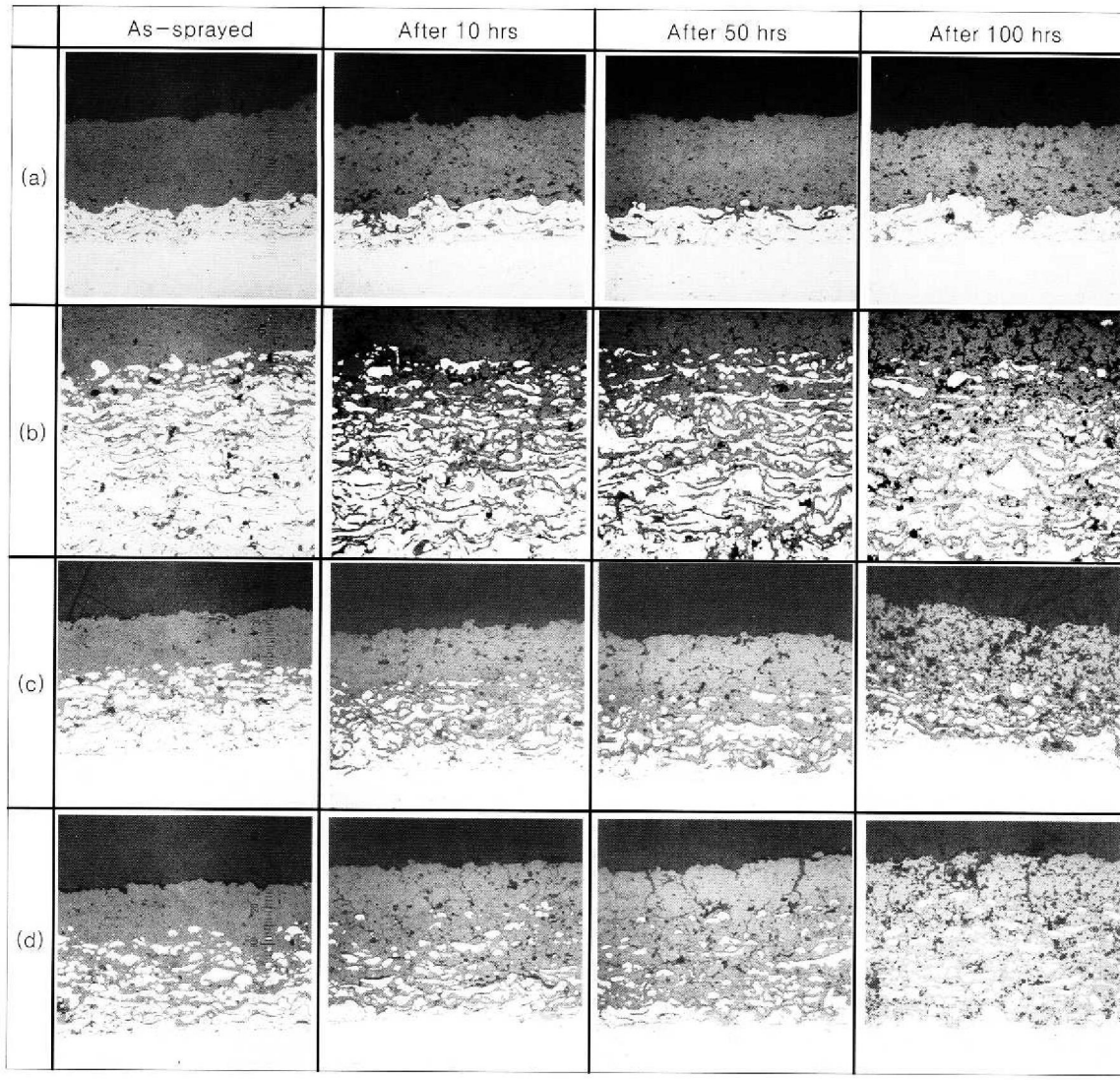
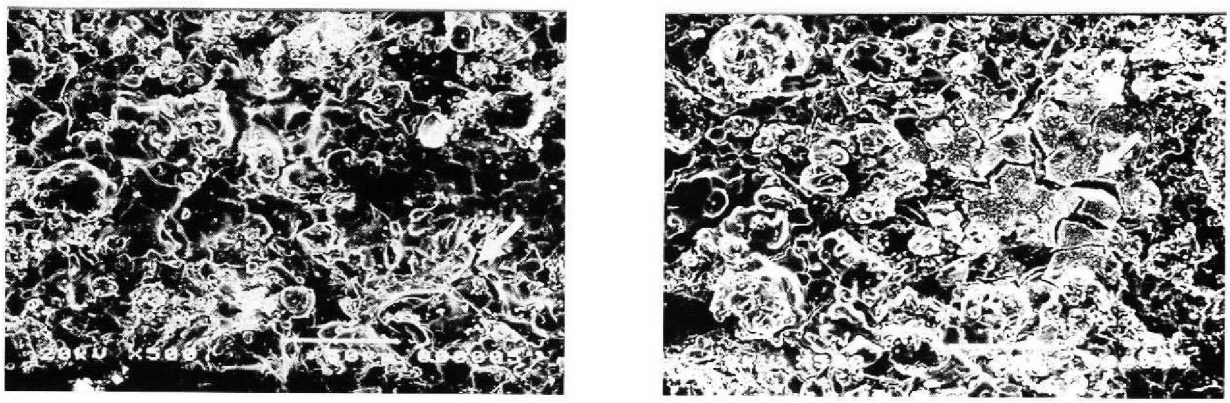


Fig. 1. Microstructural change in four ZrO_2 coating layers having four different types of grading with variation of oxidation time. (a) TBC(T) (b) symmetry four-graded layer (F1) (c) symmetry four-graded layer(F2) (d) ceramic rich four-graded layer(F3)



(a) (b)

Fig. 2. SEM micrographs showing surface crack formation with variation of oxidation time. (a) as-sprayed (b) after 100 hrs

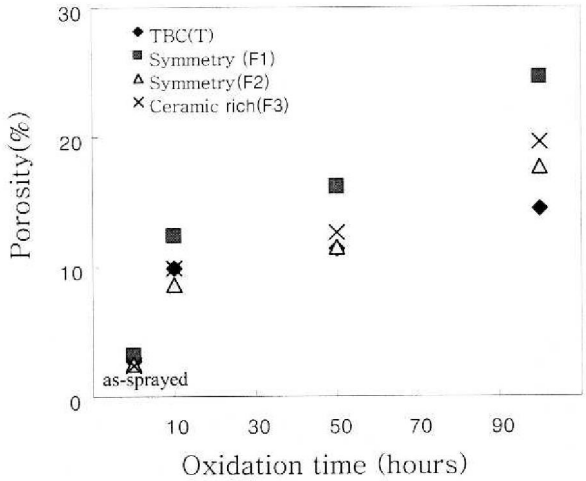


Fig. 3. Change in porosity in TBC and FGC samples (T, F1, F2, F3) with variation of oxidation time.

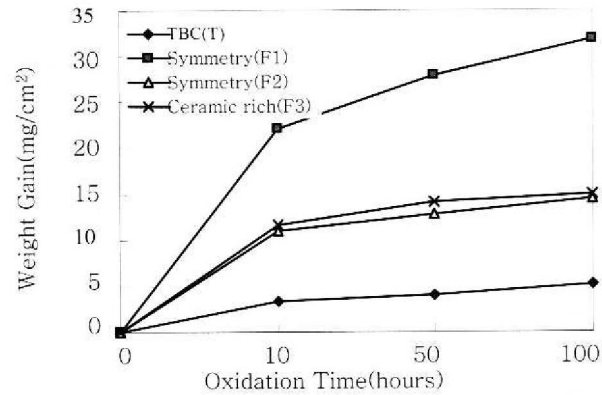


Fig. 5. Weight change of ZrO_2 coating layers having four different types of grading with variation of oxidation time.

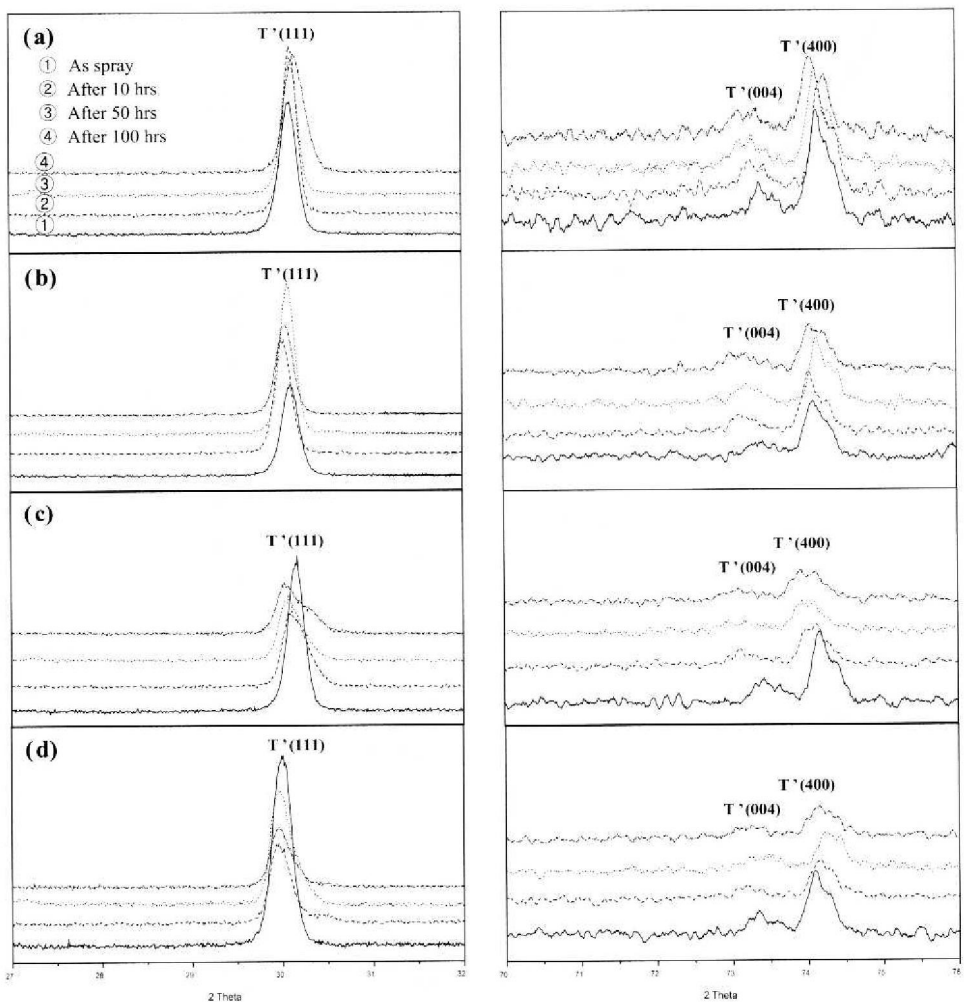


Fig. 4. The change in X-ray diffraction patterns of ZrO_2 coating layers having four different types of grading with variation of oxidation time. (a)TBC(T) (b) symmetry four-graded layer (F1) (c) symmetry four-graded layer(F2) (d) ceramic rich four-graded layer(F3)

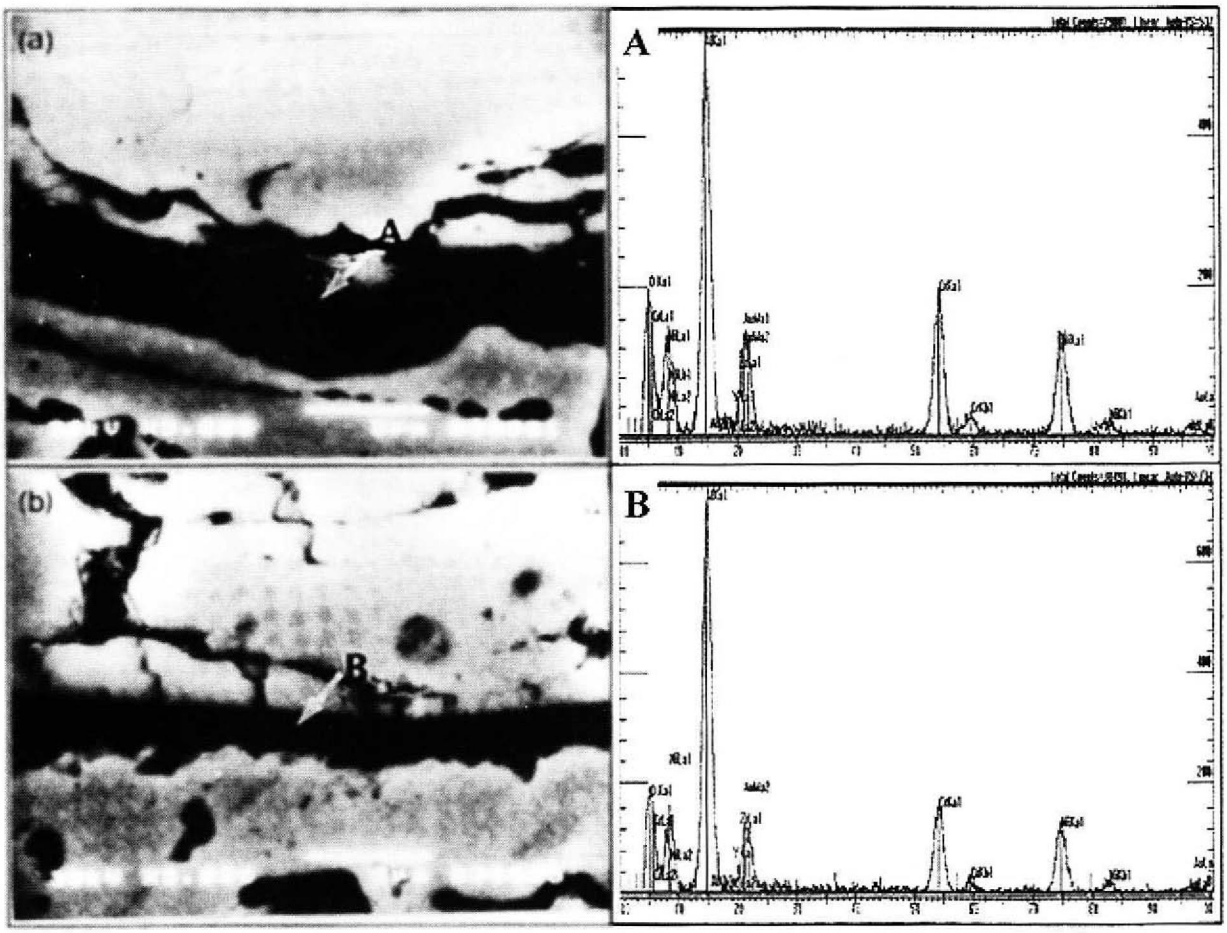


Fig. 6. SEM micrographs and EDS analysis of ZrO_2 coating layers having four different types of grading with variation of oxidation time. (a) TBC(T), after 100 hours (b) FGC(F2), after 50 hours

temperature oxidation. High temperature oxidation was observed at the interface of NiCrAlY/YSZ, where pores or microcracks formed as a result of reaction between NiCrAlY and oxygen. Oxides in TBC

samples was formed between NiCrAlY and YSZ layers, however in the case of FGCs, additional oxidation was observed at the interfaces of step-graded NiCrAlY/YSZ layers. In both cases of the TBC and FGC samples, the amount of oxidation increased rapidly at an early stage of oxidation time, following gradually slow oxidation rate. It is considered that oxides formed at an early stage of oxidation attribute to decrease further oxidation of the layer.

The amount of oxide formed at oxidation process increased in an order of TBC and FGC samples, since the interfacial area between NiCrAlY/YSZ in FGC samples is larger than that in the case of TBC

Fig. 6 shows SEM micrographs and EDS analysis near the interface of NiCrAlY/YSZ layers. Oxide consists of Al oxide formed rapidly at early thermal exposure time. On the further thermal oxidation, Ni and Cr oxides were gradually formed, increasing the thickness of oxide layers. In comparison with TBC samples, Ni and Cr oxides were formed rapidly in FGC samples

Fig. 7 shows XRD patterns of TBC and FGC samples exposed thermally at 1100℃ in air. The oxides of α -Al_2O_3, NiO, $NiCr_2O_4$, Cr_2O_3 were observed. In combination with SEM and EDS results, we can infer such oxides were mainly formed at the interface of NiCrAlY/YSZ layers. It is known that strong oxygen affinity attributes to NiCrAlY oxidation, forming Al_2O_3 from the reaction between Al and oxygen at an early stage of oxidation.[8]

It is reported that in the case that during thermal expose, Al consumption in NiCrAlY is below 10%, NiO, Cr_2O_3, $NiCr_2O_4$, $NiAl_2O_4$ and $Ni(Al,Cr)O_4$ spinels were formed

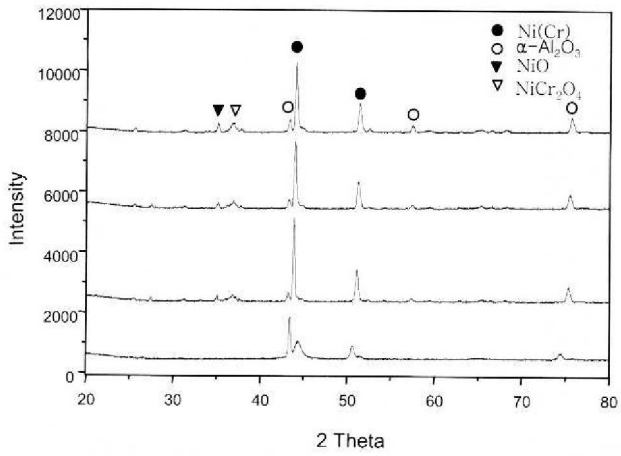


Fig. 7. The change of X-ray diffraction patterns of NiCrAlY bond layers with variation of oxidation time.

in the interface between YSZ/ NiCrAlY layers.[8] Also, it is reported that the formation of spinel structures induce the fracture within the coating layer, since they grow towards coating direction and the increase in volume by rapid growth rate occurs.[13] These reports are coincident with crack-like fractures observed in coating during thermal exposure.

Oxidation of FGC samples, F2 and F3 was observed at the interface between substrate and NiCrAlY exposed thermally for 100 hours in air. Such oxidation of NiCrAlY layers expands substrate, increasing porosities and cracks.

4. Conclusion

YSZ-NiCrAlY double and graded coating layers are successfully fabricated on Co-base superalloy substrates by plasma spray coatings. As-coated FGC samples with six layers and TBC layers were exposed at the temperature of 1100℃ for 10, 50, 100 hours. Also, change in microstructure, oxidation behavior and phase transformation were investigated, using OM, SEM and XRD. Pores and microcracks were formed in YSZ due to thermal internal stress development and shrinkage. The amount of pores and microcracks in YSZ increased with increasing exposure time at high temperature. High temperature oxidation occurred mainly at the NiCrAlY/YSZ interface. In comparison with TBC samples, the increased area of the interface in FGC samples is attributed to the increase in oxide formation.

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