Al피복 Ni기 초합금의 내산화성에 미치는 증착 Yttrium의 영향

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Effect of Yttrium Deposition on the Oxidation Resistance of Al-Pack Coated Ni-Based Superalloys

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With the aim of formation of thin and solid diffusion layers adherent to superalloys and suppression of void formation, composite aluminide coatings by combination of aluminide pack cementation with yttrium PVD coatings were investigated on ODS superalloys which contain 0.5 to 4.0 mass % Al. The subsequent oxidation of aluminide coated alloys was carried out for 72ks at 1373K in atmospheric pressure of oxygen. The thickness of diffusion zone and the density of precipitates increased in the combination of aluminizing with yttrium coatings.

Yttrium coatings are effective in suppressing void formation in the subsequent oxidation not only in the subsurface of the diffusion zone but also in the inside of ODS alloys irrespective of formation of large voids and effective in an increase in their density in the oxidation of aluminide coatings.

1. Introduction

Oxidation and hot corrosion resistance are required for materials used in combustion-type energy conversion systems such as gas turbine operating in aggressive environment at high temperature.

Al pack cementation is one of the most widely used aluminide coating process. Aluminide coating has been used on superalloys in terms of its intrinsic advantages of simplicity of operation, the low cost and the fact that it is not a "line of sight"

process irrespective of a tendency to be replaced with overlay coatings.[1]

The stability of the coating layers and these adhesion to the materials are required for aluminide coatings for the protection of superalloys. Particularly, it is difficult to coat on the oxide dispersion strengthened(ODS) superalloys because interior mechanical properties of coatings increase susceptibility to thermal mechanical fatigue cracking.[2] Void formation is occurred by aluminide coating on superalloys and subsequent exposure to oxygen at high temperature.[3] Generally, addition of rare

earth metals to the materials of coating and substrates results in the significant adhesion of aluminide pack cementation. Yttrium PVD(physical vapourized deposition) coatings with the object of formation of thin and solid diffusion layers adherent to the materials and suppression of void formation after exposure to oxygen at high temperature were investigated in this research.

2. Experimental

The chemical compositions of superalloys used in this experiment are given in Table 1. Three MA alloys which contain 0.6, 2.5 and 4.2 mass % Al were made by the mechanical alloying process and extrusion ratio of these alloys is 13.9. Yttrium is added as oxides in these alloys. AF115 was made by the hot-isostatically pressing process at 1500K for 10Ks in the pressure of 10MPa Ar.

The specimens used in aluminide coating and oxidation were cut into 15mm×10mm×1.5mm, polished with 600 grid SiC papers and cleaned in acetone. Particularly, polishing surfaces of the samples were cut to parallel to the direction of the extrusion.

Yttrium was coated on the coupons of alloys in the ion coater of which the oxygen pressure is 5Pa in 1000V×7mA. The thickness of the coating layer of yttrium was 5 to 10nm and controlled with change in the ion current and time. Aluminide pack coatings were applied in a pack with a mixture of pack reagents which is composed of aluminum powder(99.5%, particle size 74μm), ammonium chloride and alumina powder(74μm). Coupons of alloys and of pack reagents in nickel crucibles were sealed with alumina cement and hold in an atmosphere of argon.

The high activity pack coatings were applied at 1023K for 2hr in a pack with a large source of 20 mass % Al, an activator of 2 mass % ammonium chloride and a inert filler of 78 mass % of alumina followed by the diffusion treatment for 4hr.

In the low activity pack coatings, a mixture of 1 to 5 mass % aluminum, 1 mass % ammonium chloride and 98 to 94 mass % of alumina was used at 1023K for 1 to 2hr.

The aluminide coatings were subsequently oxidized in an atmosphere of 101.3kPa oxygen at 1373 K and mass gain was continuously recorded by an automatic balance. The morphology of coating layers and substrates was investigated by EPMA, SEM and X-ray diffraction analysis.

3. Results

3.1 Morphology of diffusion layers in aluminide and yttrium aluminide coatings on superalloys

Table 1. The chemical composition of alloys

Alloys	Composition(mass %)														
	Ni	Cr	Al	Co	Mn	Mo	W	Nb	Ta	Zr	Ti	Hf	B	Y	C
MA6000**	70.59	14.03	4.12	—	0.22	1.92	3.72	—	2.04	0.16	2.3	—	0.011	0.78	0.11
AF115*	54.87	10.6	3.8	15.2	—	2.82	6.09	1.72	—	0.07	4.03	0.74	0.02	—	0.04
MA-X**	72.34	16.26	2.49	—	—	1.94	3.87	—	1.99	—	0.53	—	—	0.64	0.065
MA754**	77.72	18.8	0.58	—	—	0.33	0.64	—	0.34	—	0.61	—	—	0.52	0.061

* HIP(1500K, 100MPa, 10ks)
** MA(1323K, extrusion ratio 13.9)

Photo. 1 shows the microstructures of aluminide coatings on superalloys of AF115 and MA6000 in high activity((a) and (b)) and low activity((c) and (d)) processes. The diffusion layers formed on the materials are composed of the structures of the Al-rich outer part and the Ni-rich inner part in high activity coatings. Table 2 shows the chemi-

cal composition of the matrix and the precipitates in the diffusion layers measured by EPMA technique.

The outer layers in aluminide coatings on superalloys comprise the Al-rich phase, the β phase and the precipitates which contain high Al and low Cr, W content. The content of Cr in the outer layers
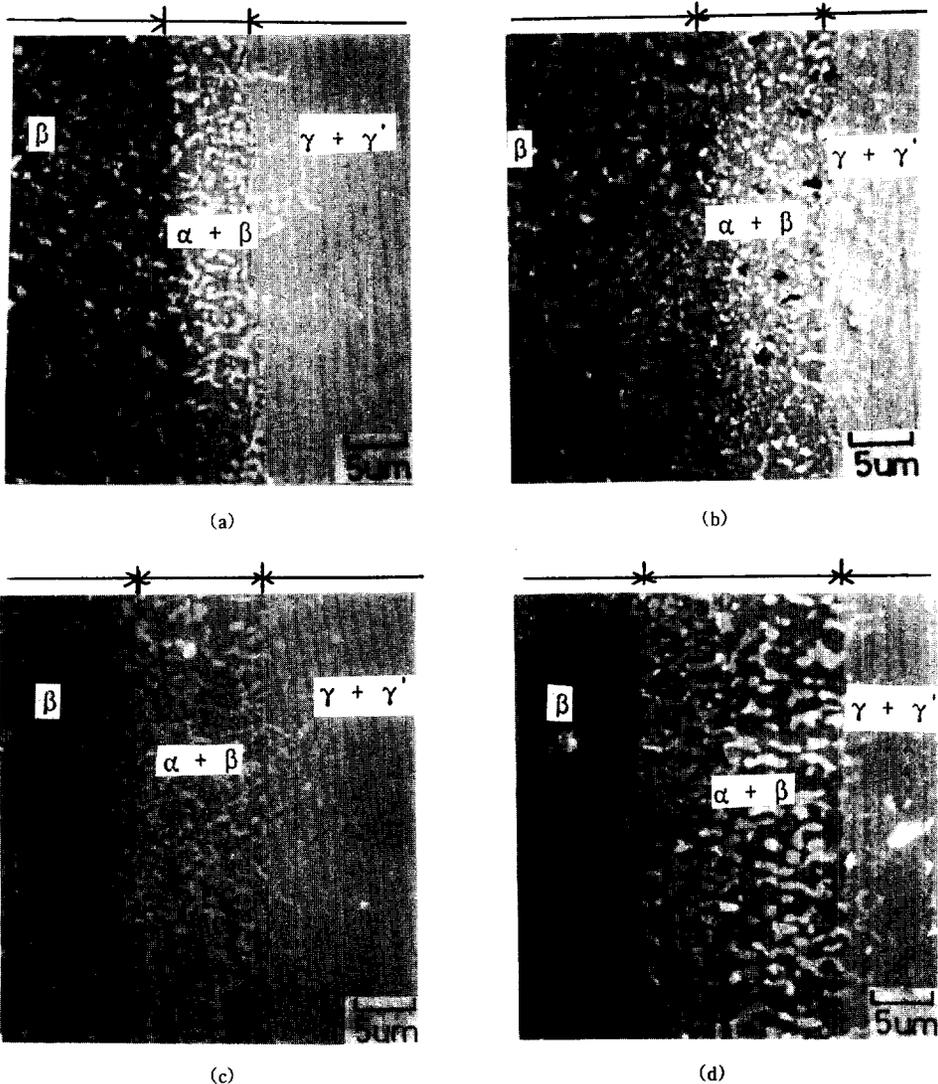
Photo. 1. Microstructures of aluminide coatings on AF115 and MA6000. High activity : (a) AF115, (b) MA6000, Low activity : (c) AF115, (d) MA6000.

Table 2. The chemical composition of aluminized coating zone on AF115 and MA6000

			High activity							Low activity						
			Composition (at %)													
			Ni	Al	Cr	Co	W	Ni/Al	(Cr, Mo)/(Ni, Co)	Ni	Al	Cr	Co	W	Ni/Al	(Cr, Mo)/(Ni, Co)
AF115	I	M	30.0	60.9	2.0	7.1	—	0.5		29.1	59.5	3.2	7.3	—	0.5	
		P	5.4	73.0	3.0	1.1	2.5		0.5	5.2	42.7	37.0	2.0	6.2		3
	II	M	40.5	32.3	5.6	9.5	1.1	1.3		42.8	31.3	5.8	10.4	—	1.4	
		P	18.8	3.8	30.0	18.0	11.8		1.0	18.8	3.3	36.8	17.5	10.4		1.6
MA600	I	M	38.8	56.8	3.3	—	—	0.7		42.8	53.1	3.2	—	—	0.8	
		P								21.4	50.0	12.5	—	8.9		0.6
	II	M	49.7	34.3	3.3	—	0.3	1.4		44.9	29.0	17.3	—	1.7	1.5	
		P	17.2	2.8	37.1	—	6.3		2	19.8	11.2	31.5	—	11.7		0.6

M : Matrix   I : The outer coating layer(Al rich)

P : Precipitate   II : The inner coating layer(Cr rich)

and the precipitates is less than 5 at %.

And then, the inner layers comprise the β phase and the γ phase which includes the precipitates of α phase. The precipitates in the inner zone adjacent to the substrate have a low content of Al and a high content of Ni, Cr, Mo and W. The compositions of the precipitates in the exterior diffusion layer were not determined due to the small size of the precipitates. The microstructures of the coatings in the low activity process are similar to those of the high activity process.

The low activity process were mainly applied in this experiments because the thickness of coating layers because it was more than 100μm and some voids formed in the coatings on the superalloy(MA6000) in the high activity process(Photo. 1(b)).
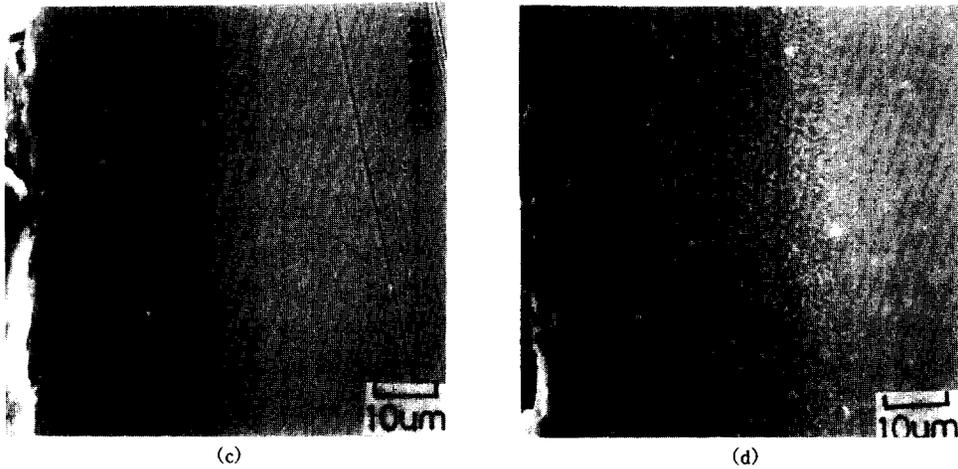
Photo. 2 shows the microstructures of coatings layers obtained by low activity process on the superalloys. Some voids are visible in the coatings.
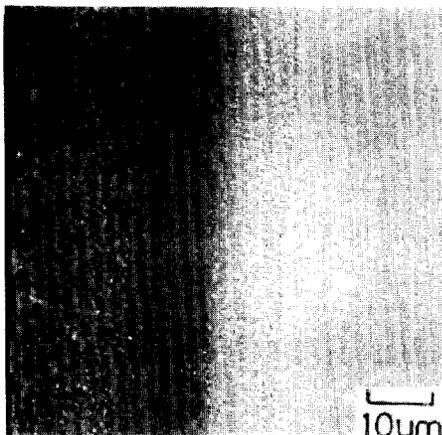
(a)
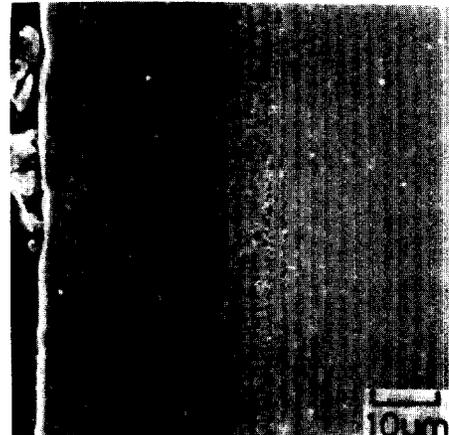
(b)

Phogo. 2. Microstructures of aluminide coatings on ODS superalloys and AF115 with varying aluminum contents. (a) MA6000, (b) MA-X, (c) MA754, (d) AF115.
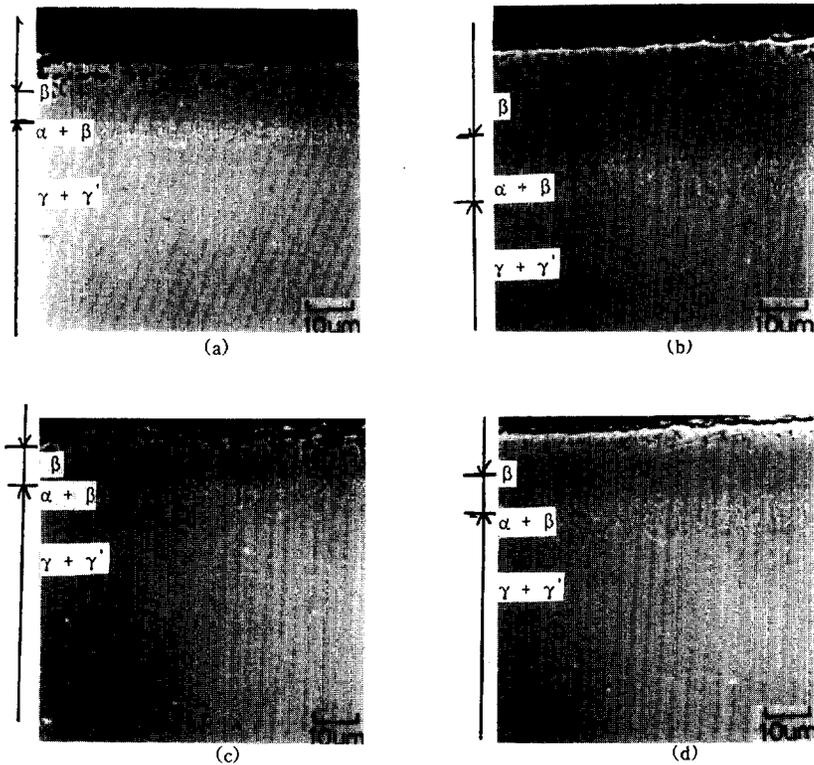

Photo. 3. Microstructures of aluminide and Y-aluminide coatings on MA6000 and AF115. (a) Al coated on MA6000, (b) Al coated on AF115, (c) Y-Al coated on MA6000, (d) Y-Al coated on AF115.

The density and size of voids formed in the interfaces between coatings layers and substrates increased with the decrease of Al content of in superalloys.

Photo. 3 shows the microstructures of yttrium-aluminide coatings on MA6000 and AF115 superalloys. The thickness of coating layers and the size of precipitates in yttrium-aluminide coating layers on the superalloys were bigger than those of aluminide coating layers.
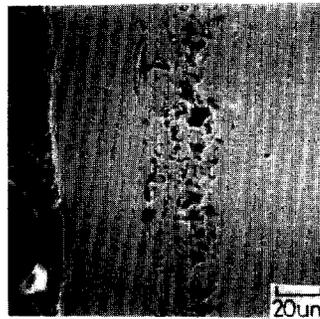
3.2 Morphology of coating layers after oxidation

Photo. 4 shows the microstructures of aluminide coatings on superalloys exposed in atmospheric pressures of oxygen at 1373K for 360ks. The amounts and size of voids in the coating layers and substrates of MA superalloys made by mechanical alloying process increase with the decrease of Al content in the superalloys. On the other hand, the voids observed in the AF115 superalloy which was made by the HIP process were small and negligible.
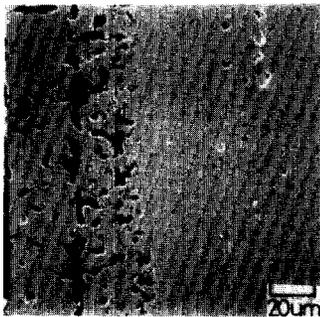
The voids were concentrated in the Al coating zone, especially along the boundaries of unidirectionally grown grains, of the MA754 superalloys of which Al content is about 0.6%. Voids are visible in the coating-substrate interface of the 2.5% Al superalloys(MA-X) and in the substrate of the 4.5 % Al superalloys(MA6000).
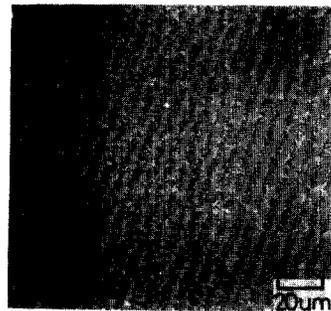

(a)

(b)

(c)

(d)

Photo. 4. Microstructures of aluminide coatings on superalloys after oxidation in 101.3kPa O_2 at 1373K for 360ks. (a) MA6000, (b) MA-X, (c) MA754, (d) AF115.
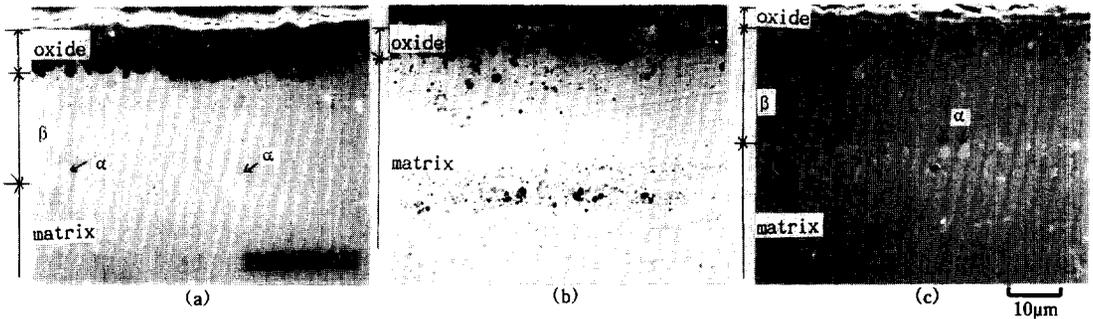
Photo. 5. Microstructures of Y-aluminide coatings on superalloys after oxidation in 101.3kPa O₂ at 1373K for 360ks. (a) MA6000, (b) MA754, (c) AF115.

Photo. 5 shows the microstructures of the substrates and coating layers in yttrium-aluminide coatings in the MA754, MA6000 and AF115 superalloys exposed in an atmospheric pressure of oxygen at 1373K for 360ks. Voids were not observed in yttrium treated superalloys. The inner layers comprise the β phase, the γ phase and precipitates included the high Cr, W and Mo content in the interface between the β and substrate. The zone of the β phase and the γ phase characterized by the existence of precipitates and disappearance of some voids in the yttrium treated superalloys. Table 3 and 4 shows the chemical composition of ytt-

rium-aluminide coating layers on superalloys exposed to the atmospheric pressure of oxygen at 1373K for 360ks measured by EPMA technique.

Weight changes due to oxidation of these superalloys were extremely small and negligible.

Photo. 6 shows the microstructures of various coating layers on MA754 superalloy exposed to an atmospheric pressure of oxygen at 1373K for 360 ks. In the uncoated MA754 superalloy(a), voids are concentrated in the grain boundaries and are parallel to the surface of the sample. In the case of aluminide coated MA754 superalloy(b), large voids are formed in the Al coating layers and mat-

Table 3. Chemical composition of yttrium-aluminide coating layers on superalloys(MA6000) exposed to the atmospheric pressure of oxygen at 1373K for 360ks

Phase		Composition(at %)								
		Ni	Al	Cr	Ti	Co	W	Nb	Mo	O
Oxide	①	1.33	43.24	0.51	1.76	—	—	0.84	0.16	40.68
β	②	50.77	32.02	5.66	1.32	9.87	0.35	—	—	—
Matrix	③	58.53	16.84	4.65	3.84	12.45	1.39	2.06	0.24	—
α	④	9.28	0.68	32.46	3.37	3.34	21.0	10.72	19.17	—

· —①
· —②
· —③   ④
· Matrix

Table 4. Chemical composition of yttrium-aluminide coating layers on superalloys(AF115) exposed to the atmospheric pressure of oxygen at 1373K for 360ks

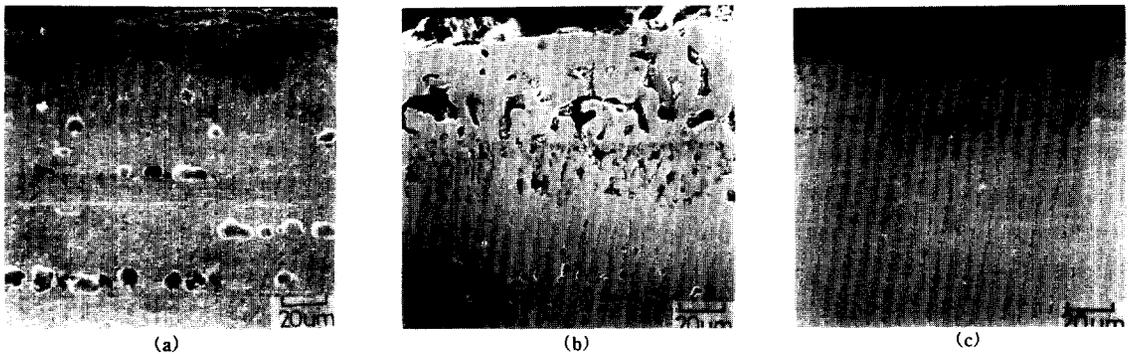| Phase		Composition(at %)								
		Ni	Al	Cr	Ti	Co	W	Nb	Mo	O
Oxide	①	1.33	43.24	0.51	1.76	—	—	0.84	0.16	40.68
β	②	50.77	32.02	5.66	1.32	9.87	0.35	—	—	—
Matrix	③	58.53	16.84	4.65	3.84	12.45	1.39	2.06	0.24	—
α	④	9.28	0.68	32.46	3.37	3.34	21.0	10.72	19.17	—

· — ①
· — ②
· — ③　　④
· Matrix

Photo. 6. Microstructures of MA754 after oxidation in 101.3kPa O₂ at 1373K for 360ks. (a) MA754, (b) Al coated MA754, (c) Y+Al coated MA754.

rix. But in the case of yttrium-aluminide coated MA754 superalloy(c), void formation was negligible and weight changes due to oxidation were extremely small. However, high density of fine and black precipitates are observed.

4. Discussion

Generally, it is known that, when ODS superalloys are oxidized at high temperature or coated by Al-pack treatment, PVD and Plasma, voids are formed in the oxidized layers, the coating layers and the substrate beneath the coating layers.[3,7 · 13]

Thus, void formation has an effect on (a) Al content of a substrate, (b) dispersion of Y_2O_3, (c) size and amount of precipitates, (d) content of precipitate-forming elements, (e) grain size of a substrate and (f) appearance of Cr-exhausted zone caused by an outward diffusion of Cr.

Fig. 1 shows the cross-sectional morphology of aluminide coated MA6000, MA754 and AF115 schematically. In the aluminide coated ODS(MA 6000, MA754) superalloys, voids are formed in the Al coating layers but in HIP(AF115) superalloy, voids are not formed.

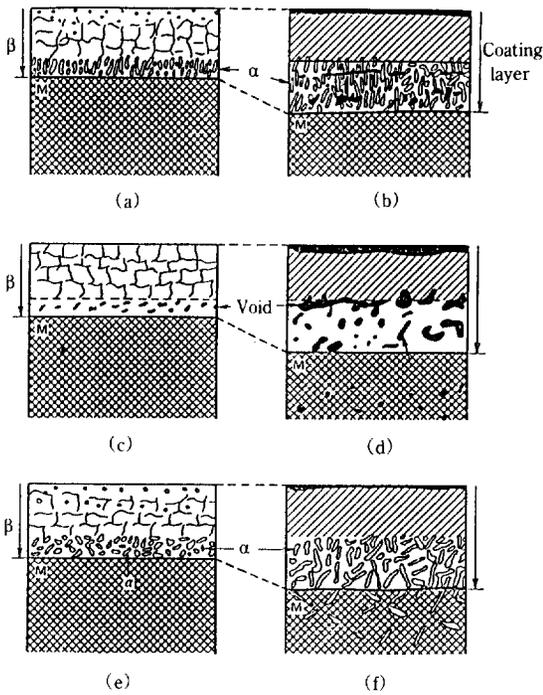Void formation in superalloys has been attribu-

Fig. 1. The schematic reprensentation of the microstructures of aluminide coatings on superalloys. (a) Al-MA6000, (b) Oxidized Al-MA6000, (c) Al-MA754, (d) Oxidized Al-MA754, (e) Al-AF 115, (f) Oxidized Al-AF115.

ted to Kirkendall porosity which results from the movement of vacancies and also affected by the composition of the superalloys, particularly Al content, existence of rare earth metals, the grain size of materials and morphology of the precipitates.

In the oxidation of aluminide coated ODS superalloys of various Al content which was prepared by mechanical alloying, some voids appear in the coating layer and the substrate as shown in Photo. 4.

Fig. 2 shows the concentration profiles of aluminide coating layers on MA754 as-coated and subsequently exposed to oxygen at 1373K for 360Ks. The parts of high Cr content in Fig. 2(a) shows the precipitates of Cr-rich phases in the distance
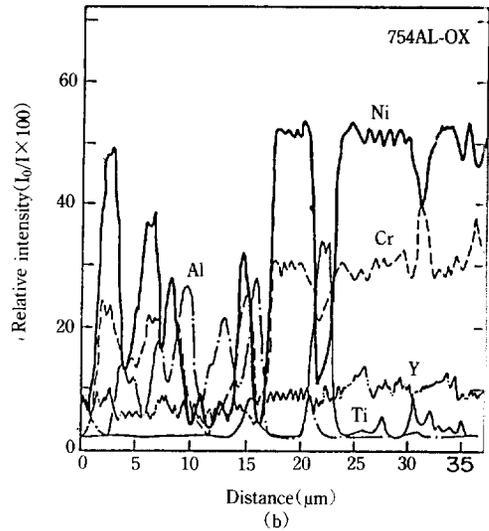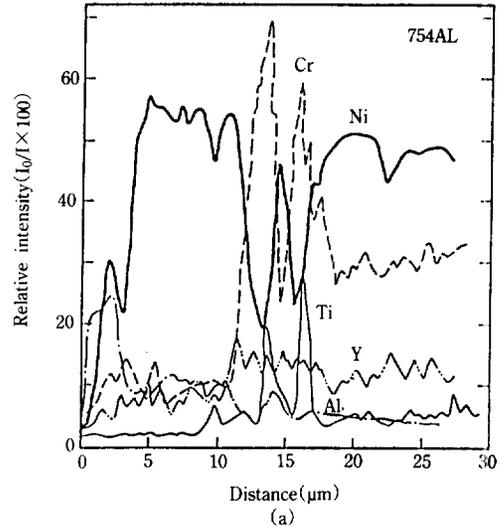

Fig. 2. The concentration profiles of pack aluminized MA 754. (a) as coated, (b) oxidized for 72ks at 1373K.

of 10 to 15μm from the surface of the coating layer.

After oxidation of aluminide MA754, Cr content in the coating-substrate interface and Ni content in subsurface of the coating layer decrease as shown in Fig. 2(b). The layer under 10μm from the surface shows the low Cr and Al content except

the part adjacent to the surface. It is believed that in subsequent oxidation of the aluminide coating on the MA754, Ni and Cr outward diffusion from the β layer, Cr volatilization from the surface of the coating layer and the Al inward diffusion result in void formation in the diffusion layer in Photo. 4(c) and some voids along the boundaries of long grains in the substrate are mainly attributed to the outward diffusion of Ni and Cr. The Al content fell slowly from that of the δ phase to a higher level than a value representing the concentration of MA754 at a position of the high yttrium content. MA6000 characterizes by appearance of voids along the grain boundaries attributed to the outward diffusion of Cr and Ni and little evidence of voids in the diffusion layers. On the contrary, void formation is suppressed in the AF115 which contains 9 at % Al. The AF115 has both the fine grain size of materials and the fine precipitates which contains 20 at % W, 20 at % Mo and 10 at % Nb. The fine grains and precipitates in the layer are also considered to act as a sink of vacancies.

Seybolt exhibited that the experiment of oxidation of chromium containing Y_2O_3 may constitute an increasingly effective blocking layer to continued chromium ion diffusion through the growing Cr_2O_3 layer.[6] The plasma-sprayed duplex coating Y_2O_3 on superalloys shows very little evidence of Kirkendall voids along the bond interface after cyclic oxidation.[7] This is attributed to the cermet base coating which acts as a diffusion inhibitor and the shallower concentration gradients.

Fig. 3(a) shows the concentration profiles of the yttrium-aluminide coating and the subsequent oxidation of MA754(Fig. 3(b)). The content of aluminum in the coating layer is higher than that in as-aluminide coating layer. The thickness of the coating layer increases compared with that of the
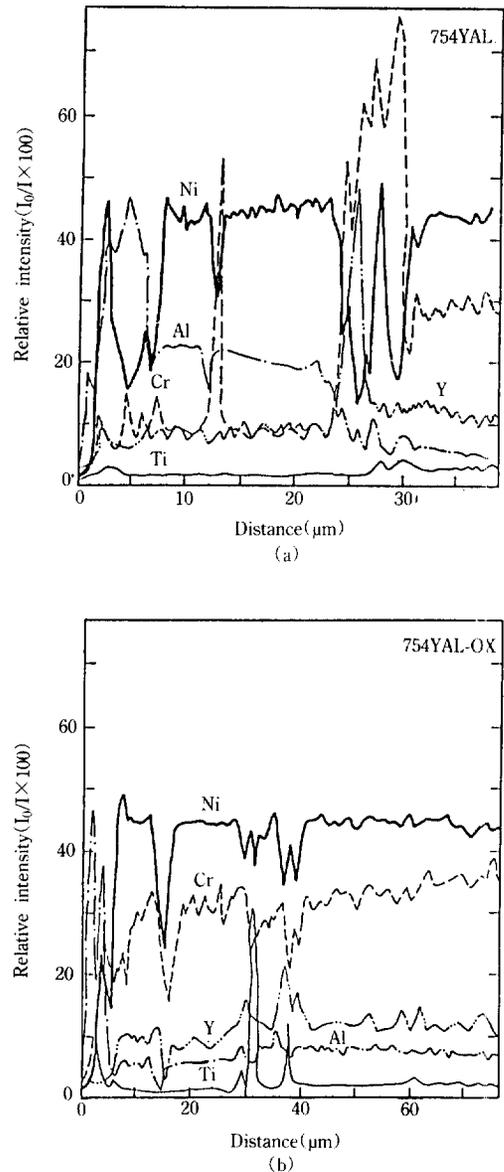

Fig. 3. The concentration profiles of pack aluminized and Y-coated MA 754. (a) as coated, (b) oxidized for 72ks at 1373K.

aluminide coatings as shown in Phogo. 3.

Yttrium is concentrated at the interface between the diffusion layer and the substrate. Yttrium seems to be coated on the material as yttrium oxide

since yttrium was sputtered in the low pressure of oxygen, about 20 Pa Po_2.

The distribution of a high Al content is considered to result from retardation of the rate of the inward diffusion of Al by the barrier attributed to yttrium. The concentration profile of Cr in the coating layer-substrate interface shows the precipitates similar to that in as-aluminide coating.

Although Cr and Ni diffuse outward and Al inward in the subsequent oxidation of yttrium-aluminide coating layer, void formation is suppressed because yttrium presents the sites as a sink of vacancies. The yttrium sputtering-aluminide coating process has also a beneficient effect of suppressing the void formation for MA6000 and MA754 acts as a diffusion inhibitor.

Thus, it is more useful process for suppressing the void formation of superalloys to coat the yttrium prior to aluminide coatings, to increase the Al content of substrates, and to reduce the grain size and to form the appropriate precipitates in the materials.

5. Conclusions

The morphology of the diffusion layers were investigated in aluminide and the composite aluminide coatings by combination of aluminide pack cementation with yttrium PVD coatings and the subsequent exposure to the atmospheric pressure of oxygen at 1473K for 360ks.

The principal observations were as follows :

1. In the high activity of aluminide treatment, voids were formed in the subsurface of the diffusion zone of ODS superalloys and were not formed in the alloy which contains mainly chromium, molybdenum and tungsten without dispersion oxides.

2. In the low activity, voids decreased as the content of aluminum in the alloy increases and the diffusion zone consisted of the β phase and a high density of chromium-rich precipitates which contain tungsten and molybdenum.

3. The thickness of diffusion zone and the size of precipitates increased in the combination of aluminide with yttrium coatings.

4. Yttrium coatings are more effective in suppressing void formation in the subsequent oxidation not only in the subsurface of the diffusion zone but also in the inside of ODS alloys irrespective of an increase in large voids and these amounts in the subsequent oxidation of aluminide coatings.

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