

PHASE TRANSFORMATION OF Al-Ti COATINGS ON Co-BASE SUPERALLOY DZ40M DURING HIGH TEMPERATURE OXIDATION^①

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ABSTRACT Both the formation of simple aluminide and Ti-modified aluminide coating on Co-base superalloy DZ40M and the phase transformation in high temperature oxidation have been studied. The results indicate that the deposition coatings consist of an outer layer of CoAl phase and an internal layer of Cr, W, Ti-rich carbide zone. The transformation of the phase for all these coatings has occurred as follows: $\text{CoAl} \rightarrow \text{CoAl (majority)} + \alpha\text{-Co} \rightarrow \alpha\text{-Co (majority)} + \text{CoAl} \rightarrow \alpha\text{-Co}$ at a high temperature of 900~1100 °C. The appearance of $\alpha\text{-Co}$ marks the beginning of degradation which is over when all of CoAl changes into $\alpha\text{-Co}$. The addition of Ti into reagent during deposition can lower the Al-activity, reduce the Al content and thickness of coatings relevantly, and speed up the degradation of coatings.

Key words Co-base superalloy coating phase transformation

1 INTRODUCTION

There is a serious problem of high temperature oxidation on turbine components, hence, various coatings with aluminide are manufactured for protecting them^[1, 2]. The relatively simple and economical production techniques for developing coatings are mainly the pack cementation, slurry coating and vapor deposition^[1, 3]. The previous two methods have a longer history, and the coatings produced by them are mostly studied. As to the coatings produced by the low pressure vapor deposition, the work on Ni-base superalloy has also been taken in the relative aspect^[4], but the report about the corresponding work on Co-base superalloy, especially with the Al-Ti co-deposition, has not been found yet. In this paper, the technology of low pressure vapor deposition is adopted to make simple aluminide and Ti-modified aluminide coatings on a new Co-base superalloy DZ40M^[5, 6], and the growth mechanism of the coatings and phase transformation during high temperature oxidation are

investigated.

2 EXPERIMENTAL METHOD

The directionally solidified Co-base superalloy DZ40M was used, and it was processed to thin pieces with the overall dimensions of $d 14.5 \text{ mm} \times 3.3 \text{ mm}$. The nominal composition (mass ratio, %) of the alloy is: Ni-11, Cr-25, W-7.5, Mo-0.2, Ti-0.15, Ta-0.25, Al-0.8, Zr-0.15, C-0.45, B-0.01, Co-bal. The technology for producing the coatings is low pressure vapor deposition^[4], the compounds of FeAl_2 and TiAl with granularity about 250 μm were employed as aluminizing reagent, NH_4Cl as activating agent, and the composition proportions of the coating reagent as well as the processing parameters are all shown in Table 1.

The coatings made by techniques I, II and III are known as Coating-I, -II and -III successively hereafter.

Three kinds of coating samples were all oxidized isothermally at 900, 1000 and 1100 °C re-

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spectively in air. Samples were taken out after 200 and 2 000 h respectively for 900 and 1 000 °C, but 60 and 200 h for 1 100 °C. The coating composition and high temperature phase transformation were studied with XRD, EPMA and optical micrograph. In addition, the coating structure was displayed by electrolytic etching (electrolyte 120 mL H₂O+ 210 mL H₃PO₄+ 170 mL H₂SO₄, voltage 3 V).

Table 1 Technology for developing coatings

Technique number	TiAl : FeAl ₂ : NH ₄ Cl (mass ratio)	Temperature / °C	Time / h	Gas pressure / MPa
I	0: 100: 2	1 080	4	0~ 0.012
II	20: 80: 2	1 080	4	0~ 0.010
III	50: 50: 2	1 080	4	0~ 0.014

3 EXPERIMENTAL RESULTS

3.1 Original coating structure

Three coatings have almost the same structure, with the wider grey outer layer of CoAl phase, and the narrower white internal layer of Cr, W, Ti-rich carbide which is primarily Cr₂₃C₆ in continuous flake and strip shapes. Fig. 1 shows the micrograph of the aluminide coating made by technique I.

All main element concentration distributions along the coating depth are similar for three

coatings, as displayed in Fig. 2. The outer layer was confirmed to be CoAl by XRD and EPMA (see Fig. 3a). Al contents in the outer layer of Coating- I, - II and - III are 50%, 48% and 45% (mole fraction) respectively, and the corresponding thickness 28, 23 and 20 μm. While in the internal layer, there are abundant Cr, W, Ti and high-content C, which is the evidence of Cr₂₃C₆ examined by XRD (Fig. 3b). Although Ti contents in the three coatings are all low, they still correspond to their original compositions of reagents (Fig. 2b).

3.2 Phase transformation of coatings during oxidation

Fig. 4 shows the phase transformation of each coating during oxidation at 900, 1 000 and 1 100 °C respectively. It was known by XRD and EPMA that the three coatings oxidized at 900 °C for 2 000 h both α-Al₂O₃ and θ-Al₂O₃ on their surface, but still contain single phase CoAl basically in outer layer and and Cr, W and Ti-rich phases with abundance of M₂₃C₆ in interface layer. In comparison with the coatings before oxidation, there is no obvious variation for the coating structure.

After oxidation at 1 000 °C for 2 000 h, α-Co precipitates and grows from CoAl phase, and the external layer changes from original single phase CoAl to three layers of A, B and C (see

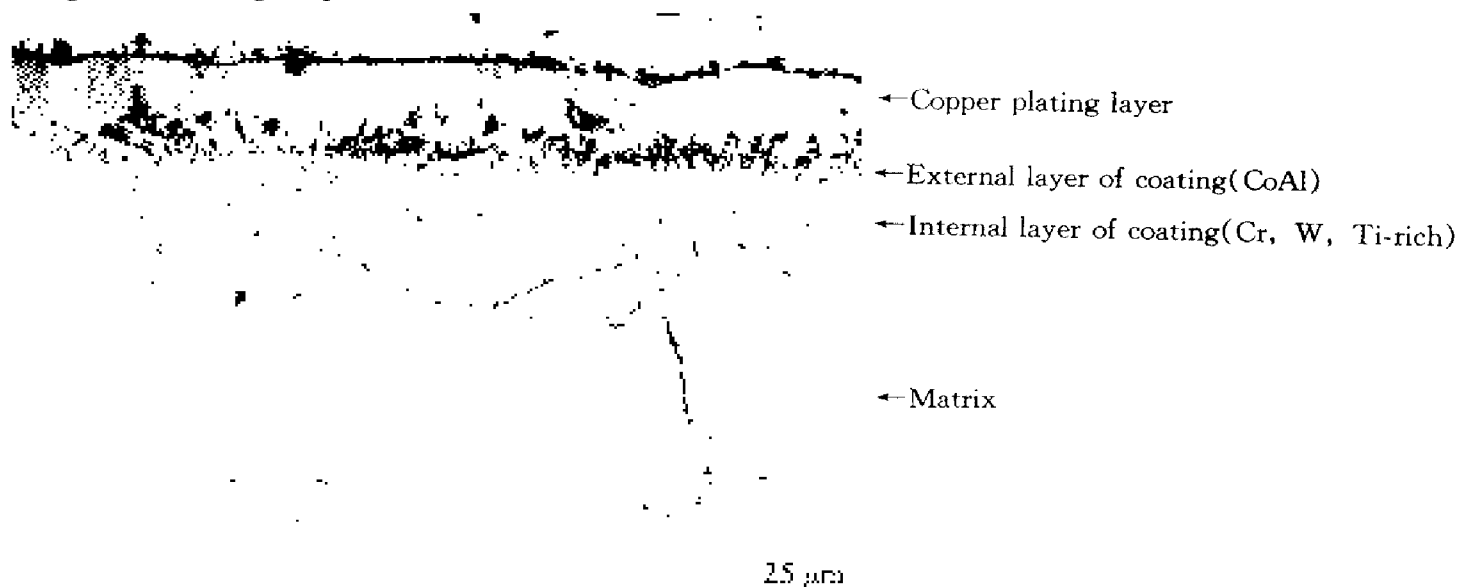


Fig. 1 Optical micrograph of coating-I

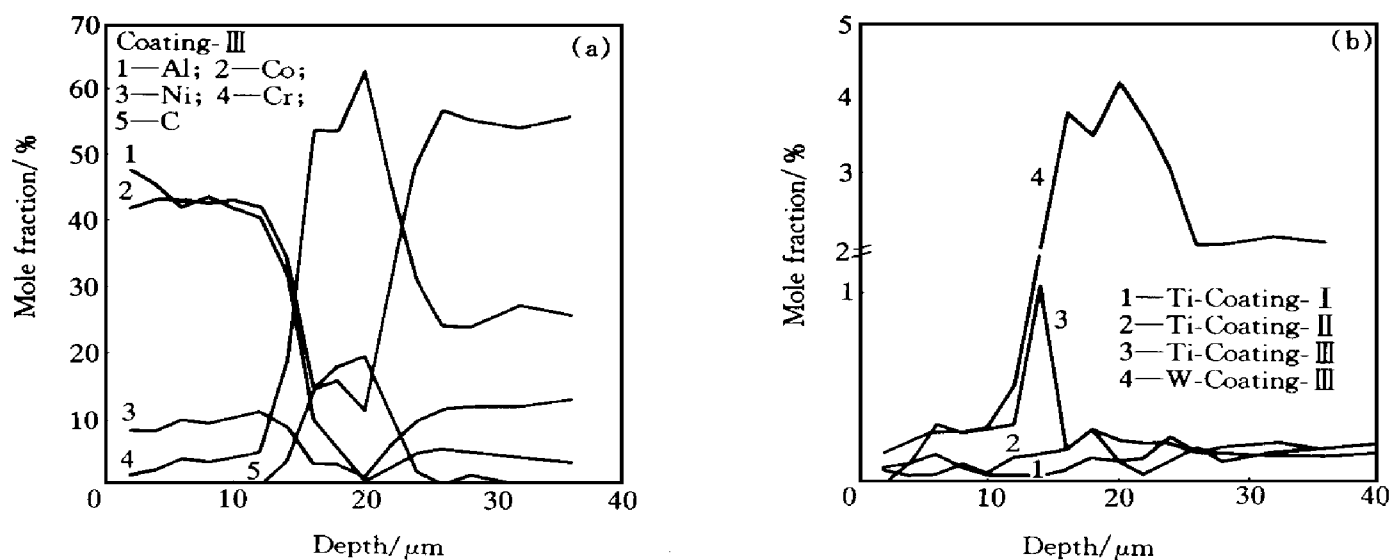


Fig. 2 Distributions of elements in coatings

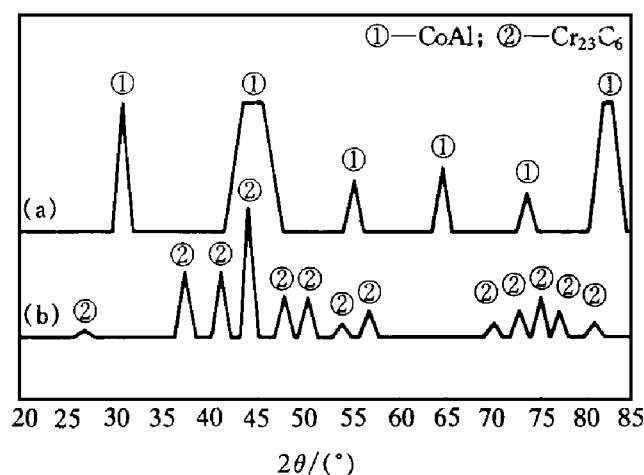


Fig. 3 X-ray diffraction patterns of coatings
(a) —Surface of coatings; (b) —Carbide zone of coatings

Figs. 4a₂, b₂ and c₂). Among them, *A* and *C* represent single phase α -Co, while *B* represents dual-phase zone for CoAl and α -Co. Amount of α -Co precipitating from CoAl increases in the sequence of Coating-I, -II and -III. The mean compositions are listed in Table 2, which are roughly the same. In comparison with the alloy matrix, α -Co precipitating from the coating belongs to α -solid solution of “low W and high Al”, in which W decreases to 1.7% (mole fraction) and Al increases to 5% ~ 7% (mole fraction). In contrast to the coatings before oxidation (Fig. 2), the content in CoAl phase rises greatly for Ni, slightly for W, Cr and Ti, but reduces remarkably for Al, so CoAl becomes a

Ni-rich and Al-poor phase. The contents of Cr and C are very high in carbide layer, and which is proved to be Cr_{23}C_6 by XRD again.

After the samples were oxidized at 1100 °C for 200h (Figs. 4a₃, b₃ and c₃), the phase transformation speeds up. Only Coating-I remains partial CoAl, and both Coating-II and -III transform their CoAl into α -Co thoroughly.

4 DISCUSSION

4.1 Formation of coatings

In the environment of low pressure vapor, activated Al atoms deposit on the alloy surface to form CoAl film. At a high temperature of 1080 °C, the outward diffusion of Co through the grown CoAl film is faster than the inward one of deposited Al through CoAl, the unceasing reaction of those two elements Co and Al causes the Al-rich CoAl layer on the surface, and the coating grows thicker continuously. This technology produces the coating of “high-temperature low-activity outward-diffusion type”, in which the mark of the original carbides in matrix is not found. With the CoAl layer thickening, Co at the original surface of alloy is depleted gradually, and some other elements such as Cr, W and C enrich relatively at this position, where C in the matrix also diffuses partly. As Cr and W have large affinity with C, the inner layer of carbide forms predominate Cr_{23}C_6 .

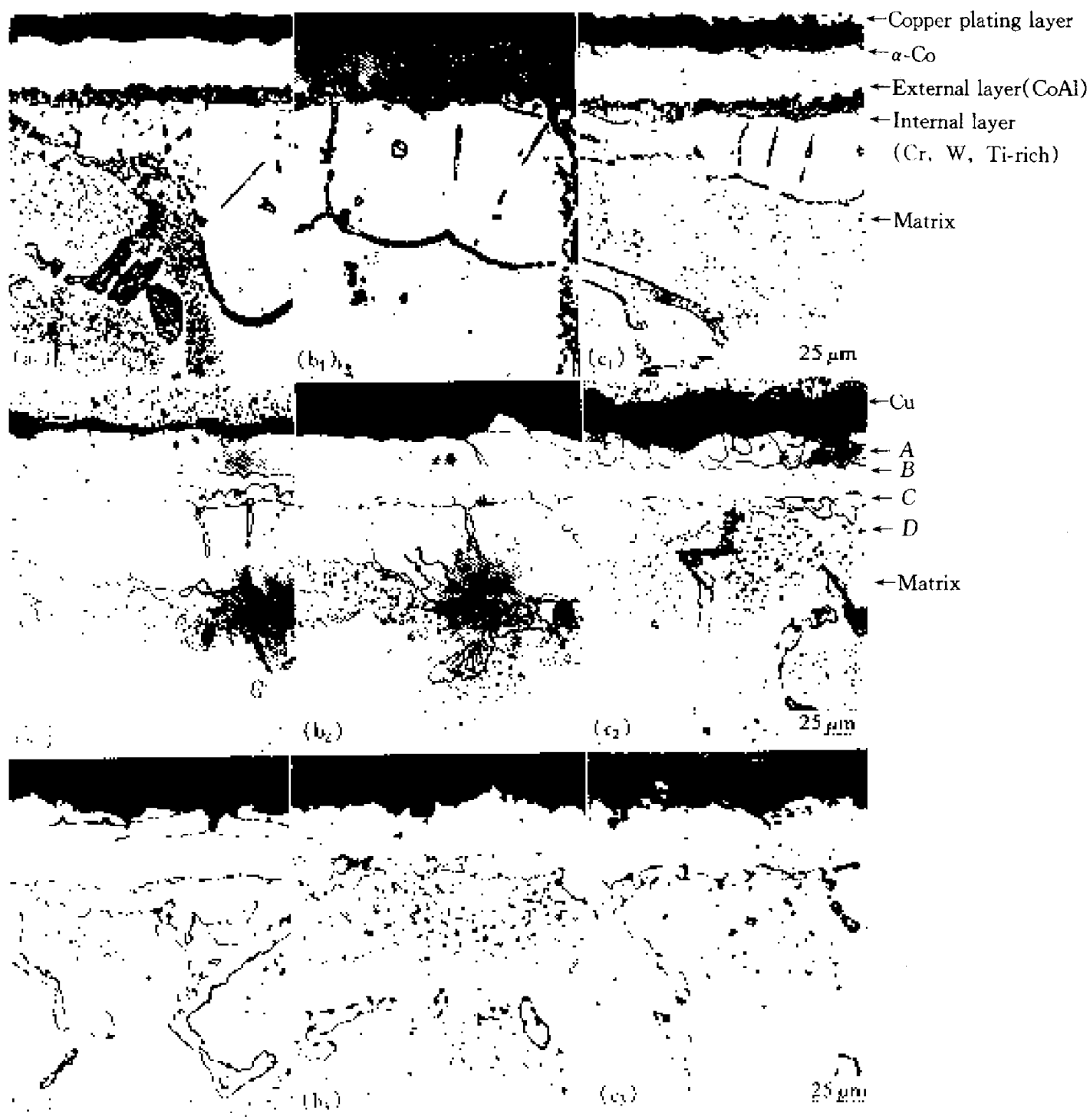


Fig. 4 Optical micrographs of coatings in air at 900, 1000 and 1100 °C

a₁, b₁, c₁: Coating I, II, III respectively for 2000 h at 900 °C

a₂, b₂, c₂: Coating I, II, III respectively for 2000 h at 1000 °C

a₃, b₃, c₃: Coating I, II, III respectively for 200 h at 1100 °C

Although Fe, Ti and Al are all contained in the coating reagent, their gas chlorides have free energy of formation getting more negative successively and being discrepant greatly, moreover, the content and activity of Al are the high-

est in reagent, so the main gas composition for deposition is a halide of Al, Ti and little Fe. Thus, the metal deposition reactions of gas metal halides on alloy surface are mainly deposition of Al and a little Ti.

Table 2 Contents of elements in coatings oxidized in air at 1 000 °C for 2 000 h from Figs. 4 a₂, b₂, c₂(mole fraction, %)

Position	Phase	C	Ni	W	Cr	Ti	Al	Co
A	α -Co	0.00	12.30	1.65	19.92	0.23	7.73	58.10
B	CoAl	0.18	21.80	0.47	6.00	0.30	33.78	37.45
C	α -Co	0.02	12.20	1.77	20.93	0.17	7.5	57.43
D	Cr ₂₃ C ₆	19.13	1.38	4.20	64.83	0.10	0.27	10.43
E	Matrix adjacent to D layer	0.00	11.45	1.97	22.98	0.17	5.52	57.95
Alloy	Nominal composition	0.45	11.00	7.50	25.00	0.15	0.80	bal.

The thickness and Al content of the coatings all reduce with increasing TiAl content in the reagent, and the Ti content in coatings rises little. That is caused directly by the decrease of Fe-Al alloy powder and lowering Al activity for the addition of TiAl powder. At present, though there are not enough data clarifying that the above result associates with a little Ti permeation, the possibility can not be eliminated that some restraint may be engendered by permeated Ti both for the formation of CoAl and the cementation of Al.

4.2 Degradation of coatings

Oxidized at 900 °C, the protective scale of Al₂O₃ can grow on the surface of CoAl layer both by the diffusions of O toward coatings and Al outward from the coating. Meanwhile, at this temperature, the amount of Al diffusing into matrix is just a little. Hence, the CoAl coatings still remain Al content enough to form stable Al₂O₃ on the surface, thus keeping the outer layer of single phase CoAl basically; only after oxidation for 2 000 h a little α -Co precipitate appears (Fig. 4c₁).

Raising the oxidation temperature to 1 000 °C, the diffusion velocities both of O inward and Al outward through the oxide scale get much higher than that at 900 °C, and growth stress and thermal stress increase in alumina scale, so the oxide layer cracks and spalls, and Al content of CoAl outside layer (the side close to coating surface) decreases correspondingly with the formation of self-healing oxide film. The Al amount in CoAl outside layer gets less and less with prolonging oxidation time. When Al content reduces to below the concentration at balance between CoAl and α -Co, α -Co phase

will precipitate. With oxidation going on, Al will continue to penetrate the generated α -Co phase to participate in oxidation at oxide scale, and the total α -Co phase will expand unceasingly.

It is discovered by Irving^[7] that the critical contents of Al to form protective α -Al₂O₃ on surface of Co-Al alloy are 7% ~ 10%, 10% ~ 13% and 13% (mole fraction) respectively at 800, 900 and 1 000 °C. However, Al content in α -Co formed by CoAl degradation is less than 8% (in Table 2) which is below the critical content, so Al₂O₃ formed by solid solution of α -Co in the coating lacks the stable condition at this time, and the accelerated oxidation like that of matrix will appear after all CoAl transforms to α -Co. Since the time for thorough degradation lessens successively, the time to reach the accelerating stage from the stationary oxidation gets longer successively too.

The higher the temperature, the greater the effect both of growth stress and thermal stress exerting on oxide scale^[8, 9], the more the micro-cracks in oxide layer, and the more the Al depletion for oxide scale healing and α -Co phase arising. As to the coating with Ti, Al concentration is relatively low, so CoAl degradation is heavier and α -Co phase is formed more too. Therefore, under the same oxidation condition, α -Co phase formed at the outside increases in proper order of Coating- I, II and III. Besides, the action of Ti on oxide scale growth, namely, the formation of Ti oxide with different crystal lattices from that of Al^[10], will also cause the same results.

As contents both of Co and Al at two sides of the carbide layer differ notably, the mutual diffusion of elements will take place at high temperature, so α -Co phase will also form within

CoAl phase near the carbide layer. The structure variation of metal phase shown in Fig. 4 indicates that, at the same temperature for the same time, α -Co phase caused by diffusion degradation at inner side of CoAl phase grows in quantity in proper order of Coating- I, II and III, and the remained CoAl phase decreases successively. One reason is that the lower the Al concentration, the easier the depletion, and the other is that the addition of Ti probably enlarges the diffusion coefficients of Al and Co within CoAl phase. The lower the temperature, the less the diffusion, and it can not be found at inner side of coatings even after aging at 900 °C for 2 000 h. When the aging time at a high temperature prolongs, the CoAl degradation caused by diffusion at inner side increases.

It may also be discovered from Table 2 that, because of high temperature effect, the content of Ni in CoAl of the coatings improves so high as to approach two times of the concentration in matrix, but that of Cr is much less. However, in α -Co caused by CoAl degradation, Ni content and Cr content are close to those of the matrix roughly. That is because of the mutual elemental diffusion and the definite solid solubilities possessed by different elements at a certain temperature, meanwhile, the compositions of α -Co at various positions are all the same.

To sum up, the stability of CoAl phase is the factor that controls the coating phase transformation. Since Al in CoAl phase of the coating depletes by its diffusion outward and inward, the

total coating always takes the phase transformation of " $\text{CoAl} \rightarrow \text{CoAl}(\text{majority}) + \alpha\text{-Co} \rightarrow \alpha\text{-Co}(\text{majority}) + \text{CoAl} \rightarrow \alpha\text{-Co}$ ". The appearance of α -Co marks the beginning of degradation, and the degradation will end when all CoAl changes into α -Co. Besides, the addition of Ti promotes the above course of phase transformation and makes the coating depleting over in advance.

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