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Beneficial effects of Y_2O_3 dispersion on Al_2O_3 protective coating

Y. Ikeda and M. Yata

National Research Institute for Metals, 1-2-1, Sengen, Tsukuba, 305, Japan

Abstract. — We have studied the mechanism by which dispersed Y_2O_3 exerts beneficial effects on the oxidation protection of an Al_2O_3 coating (film) on the basis of the following models: 1) Y_2O_3 suppresses surface segregation of S by trapping it in the alloy matrix and accordingly suppresses spalling of the Al_2O_3 film; 2.1) The diffusion of alloying elements into the Al_2O_3 film is retarded by dispersed oxide particles, probably through formation of a diffusion barrier at the Al_2O_3 /alloy interface; 2.2) The diffusion in Al_2O_3 film is retarded through incorporation of Y_2O_3 into the film; 3) Y_2O_3 acts as an adhesive at the Al_2O_3 /alloy interface; 4) Y_2O_3 incorporated into the Al_2O_3 film suppresses the spalling by increasing the plasticity of the film. We reached the following conclusions: 1 is very important, 2 is also significant but 3 and 4 are negligible.

1. Introduction.

We found that scale spalling is promoted by S segregated at the scale/alloy interface but suppressed by trapping S as a stable sulfide of REM (rare earth metal) within alloy matrix [1]. Our results are supported by subsequent researches [2-5]. This trapping effect of REM is, however, perturbed by other factors such as interfacial voids, the keying effect, growth stress etc., which differ from sample to sample. Thus we applied this S trapping effect model to an Al_2O_3 coating film-alloy system, where the Al_2O_3 coating was made under controlled conditions. The S trapping effect of REM was revealed much more clearly for coating film-alloy systems than oxide scale-alloy systems [6]. Because a simulation experiment with a coating film-alloy system is useful in understanding the mechanism of oxide scale spallation, we employed similar systems in this work to elucidate the Y_2O_3 dispersion effect, in order to examine the following models independently.

1.1 MODEL 1. S TRAPPING EFFECT. — High temperature AES (Auger electron spectroscopy) measurements and cyclic oxidation tests on some Al_2O_3 coating film-alloy systems suggest very strongly that dispersed Y_2O_3 traps S in the alloy matrix [6]. The first object of this work is to obtain further evidence for the S trapping using other Al_2O_3 -alloy systems and to detect S trapped by dispersed oxide with analytical electron microscope.

1.2 MODEL 2. RETARDED DIFFUSION IN Al_2O_3 COATING FILM ON ODS (OXIDE DISPERSION STRENGTHENED) ALLOYS. — Diffusion of alloying elements such as Mn and Cr into the Al_2O_3 coating film will cause degradation of the film. According to earlier works on the oxidation of ODS alloys [7], anion diffusion prevails in the oxide scale on ODS alloys. Thus we considered, supported by our preliminary results [8], that cation diffusion may be retarded also in the Al_2O_3 coating film on ODS alloys.

1.2.1 Diffusion in Al_2O_3 coating film on ODS alloys. — Several alloys with and without Y_2O_3 dispersion were coated with Al_2O_3 and heated at 1200 K. Then the concentration profiles in the Al_2O_3 film were compared on the cross-sections.

1.2.2 Diffusion barrier. — As shown later, AES measurement detected slight enrichment of Y at the surface of ODS alloys. This implies that a diffusion barrier containing Y can be formed at the interface between the Al_2O_3 coating film and ODS alloys. A simulation experiment using a very thin Y_2O_3 undercoat was made to examine the barrier effect model.

1.2.3 Diffusion In Al_2O_3 doped with Y_2O_3 . — In expectation of retardation of diffusion, an Al_2O_3 coating film doped with Y_2O_3 was prepared by simultaneously sputtering Al_2O_3 and Y_2O_3 . Diffusion measurement was made as described above.

1.3 MODEL 3. ADHESIVE EFFECT. — On alloys containing a fine precipitate of TiC, the TiC is enriched at the Al_2O_3 coating-alloy interface and acts as an adhesive [9]. In analogy with TiC, Y_2O_3 was considered to act as an adhesive. We examined the effect of Y_2O_3 undercoat on the adherence of Al_2O_3 coating film.

1.4 MODEL 4. PLASTICITY OF Al_2O_3 DOPED WITH Y_2O_3 . — Some authors reported that Y incorporated in the Al_2O_3 scale increases the plasticity of the Al_2O_3 [10, 11]. Thus it can be expected that the Al_2O_3 coating doped with Y_2O_3 also has greater plasticity than Y_2O_3 -free Al_2O_3 and therefore greater resistance to spalling during thermal cycling.

2. Experimental.

2.1 SAMPLE. — The chemical composition of alloys used in this work is given in table I. Most of samples were prepared in the same manner as described earlier [6]. Type 304- Y_2O_3 steel was prepared through ball milling of 304 steel and Y_2O_3 powders for 3.6 ks (1 h), pressing at 500 MPa (50 kg mm^{-2}), sintering at 1573 K for 3.6 ks and hot-rolling. All alloys were cut into coupons of about $10 \times 10 \times 1 \text{ mm}$, polished with diamond slurry, washed with acetone and dried.

2.2 AES. — Surface segregation study was carried out in an AES apparatus in a similar manner as earlier [1, 6]. Surface concentration was measured at 1100 K up to 86.4 ks (24 h).

2.3 Al_2O_3 COATING. — Al_2O_3 coating was performed by magnetron sputtering in the same manner as described earlier [6]. The coating condition is given in table II.

3. Results and discussion.

3.1 MODEL 1. TRAPPING OF S. — Figure 1 shows the surface segregation rate measured with AES on ODS alloys and a reference alloy without Y_2O_3 dispersion. Figure 2 shows the surface feature of alloys coated with Al_2O_3 and heated cyclically. Comparing these figures, it is clear that the spalling of the Al_2O_3 film is very extensive on alloys which fail to suppress the surface segregation of S. Even a moderate amount of Y_2O_3 (3%) can not suppress the spalling, unless it suppresses the S segregation. This is probably because of unsuccessful dispersion. This result suggests very strongly that S weakens the Al_2O_3 -alloy bonding, and that the Y_2O_3 particle suppresses the surface segregation of S by trapping it.

Table I. — *Chemical composition of alloys. (mass%).*

Alloy	S	Mn	Cr	Al	Fe	Ni	Y_2O_3	Other
321	0.005	1.06	17.3	—	Bal.	9.91	—	
310S	0.035	1.05	25.9	—	Bal.	20.0	—	MM=0.045
310S-La	0.003	1.09	25.5	—	Bal.	20.0	—	La=0.15
MA957	0.006	0.08	14.16	—	Bal.	0.11	0.27	
MA956	0.004	0.093	19.76	4.60	Bal.	—	0.52	Ti
MA754	0.0007	0.002	19.55	0.33	0.33	Bal.	0.57	
MA758	0.0014	0.004	29.32	0.25	0.67	Bal.	0.60	
MA6000	0.002	0.004	14.9	4.09	—	Bal.	1.1	Ti, Ta etc.
TMO-2	0.003	0.004	5.9	4.2	—	Bal.	1.1	W, Ta, Co
304-181S	0.0181	1.48	18.49	—	Bal.	10.04	—	
304-10S	0.001	1.49	18.83	—	Bal.	9.39	—	
304- Y_2O_3							3	

MM = Misch metal (70Ce-30La)

Fig. 1. — Surface segregation of S on ODS and a dispersion free steel measured with AES at 1100 K.

In fact, the previous XPS study [12] gave evidence to show that the bonding was weakened by S.

In this work we tried to detect S trapped by dispersed Y_2O_3 particles with the aid of an analytical electron microscope. On a specimen of MA956 alloy prepared through ion milling some particles and the alloy matrix were analysed. The result of analysis is given in table III

which shows that S concentration on the particle is two orders of magnitude greater than that of basis chemical analysis (Tab. I). The above four results; AES, spalling, XPS and analytical TEM, show consistently that the beneficial effect of Y_2O_3 dispersion is greatly attributed to the trapping of S.

Table II. — Al_2O_3 depositing condition.

Target	Sintered Al_2O_3 (99.9%)
Sputter gas	Ar (99.999%)
RF power density	$51 \text{ kW} \cdot \text{m}^{-2}$
Ar sputtering pressure	0.5 Pa
Substrate temperature	Ambient
Sputtering time	7.2 ks
Film thickness	ca. $2 \mu\text{m}$

Fig. 2. — Surface feature of the same alloy as figure 1, which were coated with Al_2O_3 and heated cyclically. (SEM images) a) 310S : 1100 K, 10 ks $\times$ 3 cycles; b) 304- Y_2O_3 : 1200 K, 86.4 ks $\times$ 1 cycle; c) MA758 : 1200 K, 86.4 ks $\times$ 12 cycles; d) TMO-2 : 1100 K, 10 ks $\times$ 20 cycles; e) MA6000 : 1100 K, 10 ks $\times$ 20 cycles; f) MA956 : 1100 K, 10 ks $\times$ 36 cycles.

Table III. — Local concentration of MA956 alloy measured by analytical electron microscope(*). (mass%).

	Fe	Al	Si	P	S	Ti	Mn	Cr	Y
Dispersed particle	61.4	8.0	2.1	3.9	0.3	0.5	0.3	16.6	6.8
Matrix	73.1	5.6	0.6	0.0	0.0	0.4	0.4	19.9	0.0

(*) oxygen can not be analyzed with this apparatus

Fig. 3. — Concentration profiles with EPMA on alloys which were coated with Al_2O_3 and heated at 1200 K for 86.4 ks in O_2 .

3.2 MODEL 2. RETARDED DIFFUSION IN Al_2O_3 COATING FILM ON ODS ALLOYS.

3.2.1 Diffusion in the Al_2O_3 coating on ODS alloys. — The concentration profiles after diffusion-annealing are shown in figure 3. Mn and Cr diffused to the surface of the Al_2O_3 coating on alloys without Y_2O_3 dispersion, and an alloy with a small quantity Y_2O_3 dispersion (MA957). On the other hand, diffusion of Mn and Cr into the Al_2O_3 film was suppressed on ODS alloys.

Fig. 4. — AES spectrum on TMO-2 alloy heated at 1100 K for 86.4 ks.

3.2.2 Diffusion barrier. — AES measurement revealed the surface enrichment of Y on TMO-2 alloy after heating at 1100 K (Fig. 4). The above EPMA and AES results suggest that a diffusion barrier enriched in Y is formed on ODS alloys. In order to obtain supporting evidence for the retardation of diffusion by a barrier, an Y_2O_3 undercoating was made on type 310S-0.15La steel which does not contain dispersed Y_2O_3 but suppresses surface segregation of S. This steel was chosen in order to avoid the diffusion retardation arising from insufficient contact between Al_2O_3 and other substrates which could not suppress the S segregation. Y_2O_3 undercoating was made in a similar manner as shown in table II but the coating time was 8 to 120 s and a Y_2O_3 target was used instead of Al_2O_3 . The undercoated surface was analyzed with AES. As seen in figure 5 Fe peaks arising from the substrate remains clearly after 23 s of coating and a small peak of Y is also recognized. Fe peaks remained in the trace after 120 s of coating.

Then the undercoated specimens were coated with Al_2O_3 in the same manner as shown in table II and diffusion-annealed at 1200 K for 86.4 ks. The concentration profiles taken with EPMA are represented in figure 6 which indicates that the undercoating with Y_2O_3 suppresses the diffusion of alloying elements into the Al_2O_3 film on a Y_2O_3 -free steel also. The undercoating experiment affords further evidence for the suppression of diffusion through the formation of a barrier on ODS alloys.

3.2.3 Diffusion in Al_2O_3 doped with Y_2O_3 . — Y_2O_3 doping was made through simultaneous sputtering of Al_2O_3 and Y_2O_3 . For this purpose Y_2O_3 thin plates ($10 \times 10 \times 1$ mm) were placed on the Al_2O_3 target (50 mm ϕ). The other coating conditions were the same as shown in table II. Type 310S-0.15La steel was employed as the substrate. According to the EDX result the atomic ratio of Y to the other metallic elements in Al_2O_3 - Y_2O_3 film was 0.7 for the

Fig. 5. — AES spectra on the surface undercoated with Y_2O_3 .

Fig. 6. — Penetration of Mn and Cr into Al_2O_3 film on 310S-0.15La steel with and without Y_2O_3 undercoating.

film through one piece of Y_2O_3 plate and 2.0 for three pieces. Coated specimens were heated at 1200 K for 86.4 ks and concentration profiles were taken on the cross-section (Fig. 7). Comparing the profiles in figure 7 with profiles on Y_2O_3 -free systems in figures 3 and 6, it is seen that the diffusion of Mn and Cr in Al_2O_3 film is retarded with Y_2O_3 doping.

Fig. 7. — Penetration of Mn and Cr into Al_2O_3 film doped with Y_2O_3 . Diffusion annealed at 1200 K for 86.4 ks.

3.3 MODEL 3. ADHESIVE EFFECT. — In analogy with TiC, we considered that surface enriched Y may act as an adhesive at the Al_2O_3 film/alloy interface. This idea leads to the expectation that the Y_2O_3 undercoat as stated in Model 2 may suppress the spalling of Al_2O_3 film, even on alloys which can not suppress the surface segregation of S. Thus specimens double-coated as described in Model 2 were cyclically heated at 1100 K in O_2 . Contrary to the expectation, the adherence was not improved at all on type 304-181S steel on which the surface segregation of S is extensive. The adhesive effect of Y_2O_3 is considered to be negligible. It is the suppression of S segregation that is important to improve the adherence.

3.4 MODEL 4. PLASTICITY OF Al_2O_3 DOPED WITH Y_2O_3 . — Al_2O_3 films doped with Y_2O_3 were made in the same manner as described in Model 2.3. Cyclic heating of the samples at 1100 K shows that the spalling of the Al_2O_3 film could not be suppressed through Y_2O_3 doping on type 304-181S steel which gives rise to extensive surface segregation of S. This is further evidence for the importance of the suppression of S segregation.

4. Conclusions.

- 1) Trapping of S is the most important effect that dispersed Y_2O_3 exhibits.
- 2) The diffusion of Mn and Cr into Al_2O_3 film is effectively suppressed by dispersed Y_2O_3 .
- 3) The simulation experiment using Y_2O_3 undercoating did not support the expectation that the dispersed Y_2O_3 may act as an adhesive at the Al_2O_3 /alloy interface.
- 4) Y_2O_3 doping into the Al_2O_3 film did not suppress the oxide film spalling.

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