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Kazuhide Ishii
Senior Researcher,
Coating Lab., Technical Res. Labs.

Masaaki Kohno
Senior Researcher,
Electrical Steel Lab.,
Technical Res. Labs.

Susumu Satoh
Dr Eng., General Manager, Stainless Steel Lab., Technical Res. Labs.

Synopsis:

River Lite 20–5USR(20%Cr-5%Al) stainless steel foil, which contains small amounts of La and Zr, possesses excellent oxidation resistance, and has been widely applied to catalytic converters of automobiles. To clarify the mechanism of improvement in oxidation resistance by La and Zr addition, the oxidation behavior of 50 μm thick 20%Cr-5%Al steel foils containing small amounts of La, La + Ti and La + Zr was examined. The addition of La decreased the growth rate of both Al_2O_3 layer, which grew until Al in the foil had been depleted, and Cr_2O_3 layer, which formed between the Al_2O_3 layer and the substrate after the depletion of Al. The addition of an adequate amount of Zr to alloys containing La made the growth rate of both oxide layers still lower, while the addition of Ti did not. The segregation of La and Zr at grain boundaries in the Al_2O_3 was observed with TEM. However, Ti segregation was little detected. The reduction in the growth rate of the Cr_2O_3 layer indicates that the oxygen diffusion rate in the Al_2O_3 layer is reduced. It is considered that La and Zr segregation suppresses oxygen diffusion via the Al_2O_3 grain boundaries with the result of decreasing the growth rate of the Al_2O_3 and Cr_2O_3 layers.

1 Introduction

Automobiles that have a gasoline engine are equipped with a catalytic converter in which a honeycomb substrate supports noble metal catalysts such as Pt and Rh that clean exhaust emissions. Although ceramic substrates have mainly been used, in recent years the use of metallic substrates made from stainless steel foil has been increasing in order to cope with the tightening of emission standards. This is because metallic substrates have many advantages such as low exhaust back pressure due to small wall thickness and good start-up performance resulting from a low thermal capacity. Since the substrate is heated to above 900°C by high-temperature exhaust, 20%Cr-5%Al stainless steel foil, which has good oxidation resistance, is used in the metallic substrate.

Oxidation of 20%Cr-5%Al steels results in the formation of an Al_2O_3 layer on the surface. This layer becomes a protective film, providing good oxidation resistance. An Al_2O_3 layer formed in pure Cr-Al steels has poor adhesion to the substrate metal and spalls off easily during cooling; in actual steels, therefore, small amounts of reactive elements (REM, Ti, Zr, etc.) are added to prevent this[1–3)]. Furthermore, in the foil the surface-to-volume ratio is small and the depletion of Al by oxidation occurs. For this reason, not only the scale adhesion, but also a reduction in the oxidation rate is important.

Therefore, the effect of various elements on the oxidation rate was investigated. It was found that La is effective in lowering the oxidation rate[4)], and on this basis R20-5SR (20%Cr-5%Al-0.08%La-0.08%Ti) was developed[5)]. After that, it was found that the combined addition of La and Zr further lowers the oxidation rate[6)] and R20-5USR (20%Cr-5%Al-0.08%La-0.03%Zr) has been commercially produced since 1992. This steel is widely used in catalytic substrates for its excellent oxidation resistance.

In this report, oxidation tests and observation of oxide

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Table 1 Chemical compositions of experimental heats

(mass%)

	Cr	Al	La	Ti	Zr
La added steels	19.6～20.6	5.0～5.1	Tr.～0.18	Tr.	Tr.
La and Ti/Zr added steels	19.9～20.2	4.9～5.1	0.07～0.12	Tr.～0.16	Tr.～0.24

layers using a transmission electron microscope were conducted for 20%Cr-5%Al steel foil which contains La, La and Ti, or La and Zr, and the mechanism of improvement of oxidation resistance by combined La-Zr addition was investigated.

2 Experimental Procedure

The steels used in the experiment have the basic composition of 20%Cr-5%Al, with La alone totaling to 0.18%, or 0.07–0.12% when used in combination with Ti or Zr. These steels were melted in a vacuum induction furnace having a capacity of 10 kg and rolled to 50 μm thick foil by hot rolling and cold rolling. The chemical compositions of these steels are shown in **Table 1**. These foils were annealed at 950°C for 60 s in hydrogen gas and, then were polished to eliminate the effect of annealing, which decreases the oxidation rate[7]. After that, 20 × 30 mm coupons were prepared and subjected to oxidation tests.

In the oxidation tests, a coupon suspended from a Cr-Al steel wire on a holder was put in a box-type electric furnace heated to test temperature and taken out at given time intervals. The weight of the coupon was measured after cooling. Since the oxide layer in the foil with no addition of La spalled off during cooling, it was measured for continuous oxidation using thermogravimetric analysis. The tests were carried out in air at 1 373 K and 1 473 K.

The present authors have reported[4] that the oxidation of La- or Ce-added foil proceeds in the three stages shown in **Fig. 1**.

(1) The Al_2O_3 layer grows until all Al in the foil is depleted by oxidation. At the end of this stage the mass gain by oxidation is 0.8×10^{-2} kg/m^2. The color is gray.

(2) Cr_2O_3 grows between the Al_2O_3 layer and the substrate steel. The color is green.

(3) The formation of Fe oxides begins and the mass gain increases abruptly. The color changes to black.

In all foil samples except the foil without La addition whose appearance could not be observed, oxidation proceeded in the three stages, and the mass gain at the end of the first stage was about 0.8×10^{-2} kg/m^2, which corresponded to the mass gain at which all 5%Al in steel became Al_2O_3. In this report, therefore, the oxidation behavior was examined in three stages.

The transmission electron microscope (TEM) observation was conducted on the Al_2O_3 layers formed on 0.10%La, 0.08%La-0.05%Ti and 0.12%La-0.03%Zr foil samples oxidized at 1 473 K for 72 ks. The samples were prepared by mechanically grinding the oxidized foil from the metal side to near the oxide layer and then by ion-milling using Ar ions to obtain a thin film. Since ion-milling was carried out from both sides of a coupon, it was concluded that the portion observed was near the middle of the scale layer[8].

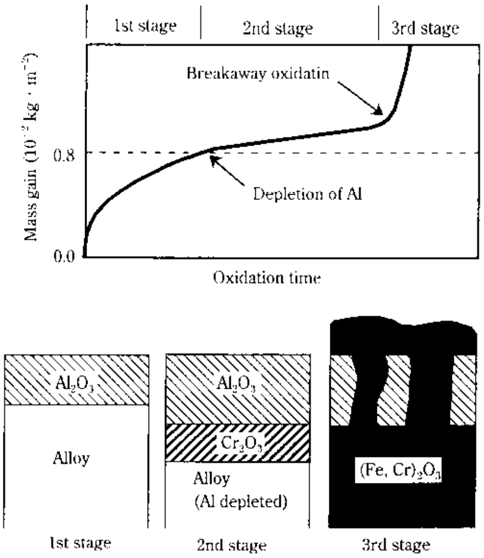

Fig. 1 Schematic illustration for oxidation behavior 50 μm thick 20Cr-5Al steel foil

3 Experimental Results and Discussion

3.1 Oxidation Tests

Figure 2 shows the mass gain curves of the 0.03%La foil, 0.10%La foil and 0.12%La-0.03%Zr foil at 1 373 K and 1 473 K as examples of the oxidation tests. At both temperatures, the mass gain become 0.8×10^{-2} kg/m^2 in the order of the 0.03%La foil, 0.10%La foil and 0.12%La-0.03%Zr foil, and it is clear that the growth rate of the Al_2O_3 layer was lowered by the combined addition of La and Zr. Furthermore, at 1 473 K the third stage began in this order, showing that the addition of La and Zr was effective in suppressing the start of the third stage.

The results shown in Fig. 2 are expressed in a double-logarithmic plot in **Fig. 3**. In the first stage the slope was about 0.4. This means that the oxidation deviated slightly from the parabolic rate law. In other foil samples as well, the mass gain was proportional to the 0.3–0.4

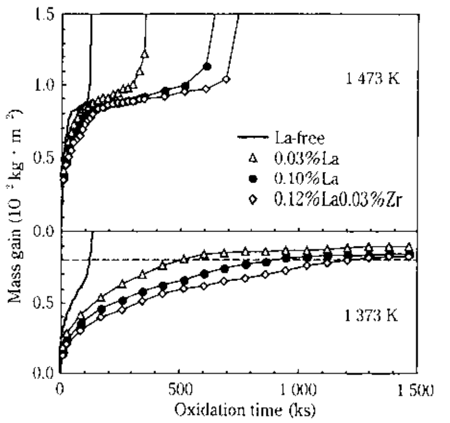

Fig. 2 Oxidation behavior of 50 μm thick foil samples without addition of La and with addition of La, La-Zr to 20Cr-5Al steel at 1 373 and 1 473 K in air

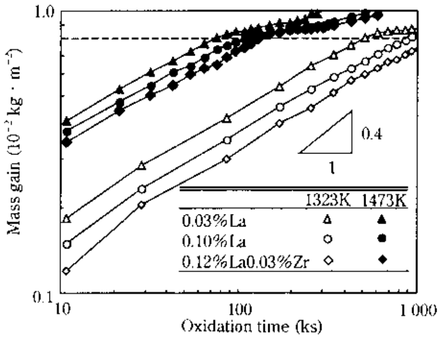

Fig. 3 Double-logarithmic plot of oxidation behavior of 50 μm thick 20Cr-5Al steel foils samples containing La or La-Zr in air

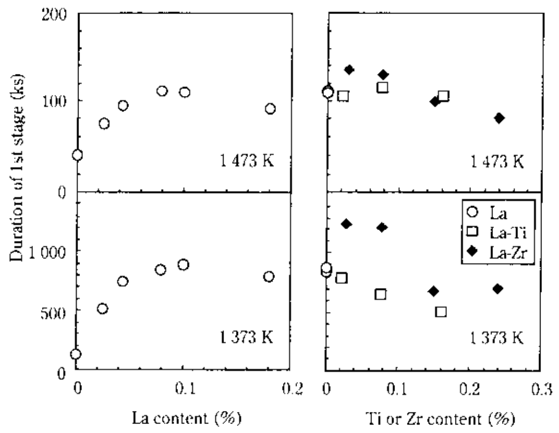

Fig. 4 Effect of La, Ti or Zr content on duration of first stage of oxidation of 50 μm thick 20Cr-5Al steel foil samples at 1 373 and 1 473 K in air

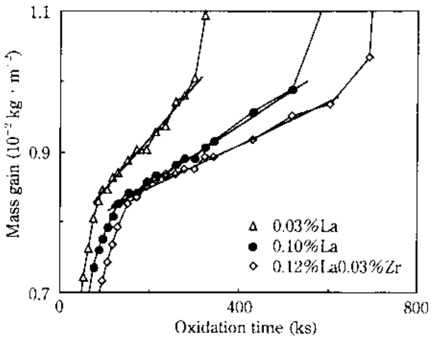

Fig. 5 Oxidation behavior in second stage for 50 μm thick 20Cr-5Al steel foil samples containing La or La-Zr at 1 473 K in air

power of oxidation time. Therefore, in this report, the growth rate of the Al_2O_3 layer was compared using the duration of the first stage instead of a parabolic rate constant. The oxidation time required for the mass gain to become 0.8×10^{-2} kg/m^2 was used as the duration.

Figure 4 shows the effect of the addition of La or Ti/Zr on the duration of the first stage at 1 373 K and 1 473 K. The duration increased as the content of La increased in the region below about 0.06%, but remained at approximately the constant value at content above 0.06%. Thus it is apparent that the addition of not less than 0.06%La is effective in lowering the growth rate of the Al_2O_3 layer.

With the addition of La-Ti/Zr, the duration of the first stage increased only in the foil to which Zr was added in an amount of 0.03% or 0.08%. This shows that the addition of an appropriate amount of Zr was effective in lowering the growth rate, although the addition of an excessive amount of Zr increased the growth rate. On the other hand, Ti increased the growth rate at 1 373 K although it did not affect the growth rate at 1 473 K.

Figure 5 is an enlarged view of the second stage at 1 473 K shown in Fig. 2. Oxidation was governed by the linear rate law, as it was in the other foil specimens.

Figure 6 shows the relationship between the La content or Ti/Zr content and the linear rate constant at 1 473 K. In the La-added foils the linear rate constant decreased with increasing La content. In the La-Ti/Zr added foils the liner rate constant decreased only in the 0.03%Zr foil and 0.08%Zr foil and increased markedly with increasing Ti content.

It has been reported[9-11] that in the Al_2O_3 layers formed in Cr-Al steels containing Y, Ti or Zr, oxygen ions diffuse through the grain boundaries of the layers and reach the layer/steel interface, where new Al_2O_3 is formed. In this case, the growth rate of the Al_2O_3 layer was controlled by the diffusion rate of oxygen ions. It is presumed that the foil samples used in this study, the Al_2O_3 layer in the first stage also grew by this mechanism and the addition of La and Zr decreased the growth rate of the Al_2O_3 layer by suppressing the diffusion of oxygen ions. In general, it is difficult to directly measure

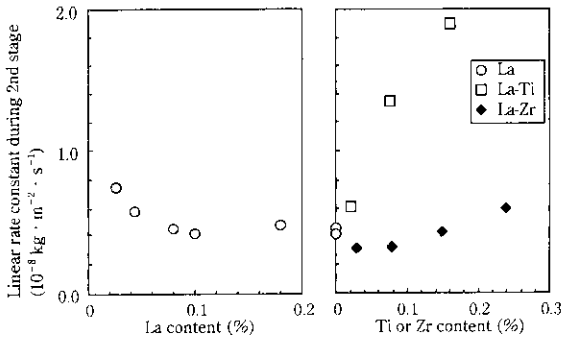

Fig. 6 Effect of La, Ti or Zr content on linear rate constant during second stage of oxidation of 50 μm thick 20Cr-5Al steel foil samples at 1 473 K in air

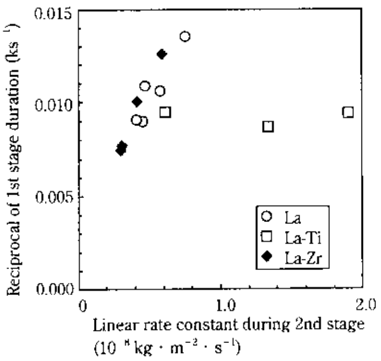

Fig. 7 Relationship between linear rate constant during second stage and duration of first stage in oxidation of 50 μm thick 20Cr-5Al foil samples at 1 473 K in air

the diffusion rate of oxygen ions. However, the present author has reported[4] that in an La-added foil, the growth of the Cr_2O_3 layer in the second stage is caused by oxygen ion migration through the Al_2O_3 layer formed in the first stage, thus the linear rate constant is proportional to the diffusion rate of oxygen ions in the Al_2O_3 layer. Therefore, the relationship between the growth rate of the Al_2O_3 layer and the diffusion rate of oxygen ions was examined using this relationship.

Figure 7 shows the relationship between the linear rate constant of the second stage and the inverse number of duration of the first stage. Since the mass gain at the end of the first stage was 0.8×10^{-2} kg/m^2 in all foil samples, the growth rate of the Al_2O_3 layer was obtained by dividing $(0.8 \times 10^{-2}$ kg/m$^2)^2$ by the duration of the first stage if the parabolic rate law was valid. Although the oxidation behavior deviated slightly from the parabolic rate law in the present samples, the inverse number of duration in the first stage was used here as the growth rate for simplification. With the exception of the Ti-added foil, the inverse number of duration in the first stage decreased with decreasing linear rate law. This indicates that a decrease in the growth rate of the Al_2O_3 layer is caused by a decrease in the diffusion rate of oxygen ions. Because the linear rate constant also is proportional to the diffusion rate of oxygen ions in the Al_2O_3 layer as mentioned above, it is believed that the addition of La or an appropriate amount of Zr lowers the growth rate of both the Al_2O_3 layer in the first stage and that of the Cr_2O_3 layer in the second stage by suppresing the diffusion of oxygen in the Al_2O_3 layer. Furthermore, because the linear rate constant is large in excessively Zr-added foil samples whose first-stage duration is short, it is presumed that the addition of an excessive amount of Zr promotes the diffusion of oxygen in the Al_2O_3 layer, increasing the growth rate. In the Ti-added foil, no relation was observed between the linear rate constant in the second stage and the duration of the first stage, as will be discussed later.

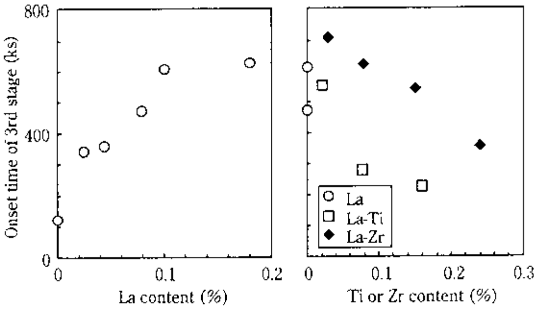

Fig. 8 Effect of La, Ti or Zr content on onset time of third stage in oxidation of 50 μm thick 20Cr-5Al steel foil samples at 1 473 K in air

Figure 8 shows the effect of the addition of La or Ti/Zr on the onset time of the third stage. While the addition of La delayed this onset time, the addition of La-Ti/Zr delayed the onset time only in the 0.03% and 0.08% Zr foils. Since the third stage began at almost the same mass gains (i.e., 0.9–1.0 × 10^{-2} kg/m^2), in all samples except the foil without La addition the decrease in the linear rate constant of the second stage was attributed to the delay.

3.2 Results of TEM Observation and X-Ray Diffraction

The TEM image of a grain boundary in the Al_2O_3 layer formed on the 0.10%La foil is shown in **Photo 1**. No grain-boundary phase is apparent. At the grain boundaries of the Al_2O_3 layer formed on the 0.10%La, 0.08%La-0.08Ti and 0.12%La-0.03%Zr foils no grain-boundary phase was observed.

The results of an EDX analysis of the grain boundaries of the Al_2O_3 layer of each foil sample are shown in **Fig. 9**. La segregated at the grain boundaries in each sample. In the Zr added foil, Zr also segregated at the grain boundaries. In contrast, the segragation of Ti was slight. As shown in Fig. 4, the duration of the first stage

Table 2 Results of X-ray diffraction analysis for foils oxidized at 1 473 K

Alloy	Oxidation time (ks)	Mass gain ($\times 10^{-2}$kg·m^{-2})	Strong peak	Weak peak
0.09%La-0.16%Ti	72	0.63	α-Al_2O_3	
	216	1.06	α-Al_2O_3, Cr_2O_3	TiO_2
0.12%La-0.03%Zr	54	0.60	α-Al_2O_3	
0.07%La-0.24%Zr	54	0.68	α-Al_2O_3	ZrO_2

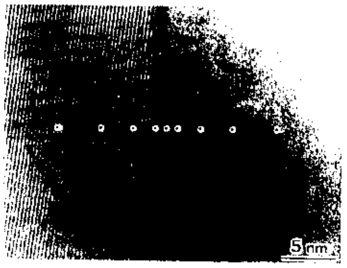

Photo 1 TEM image of a grain boundary in Al_2O_3 layer formed on foil containing 0.10% La after oxidation at 1 473 K. White circles indicate the EDX analysis points.

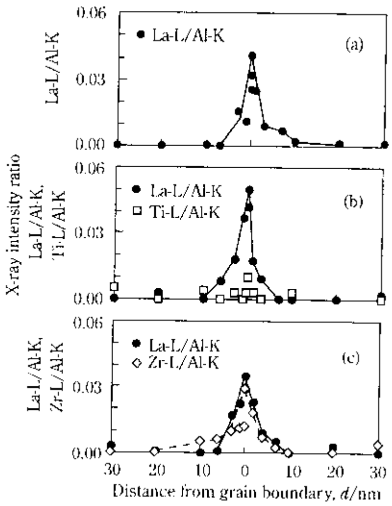

Fig. 9 X-ray intensity ratio of (a) La-L, (b) La-L, Ti-L and (c) La-L, Zr-L to Al-K in EDX spectrum across grain boundaries in Al_2O_3 layer formed on foils containing 0.10%La, 0.08%La-0.08%Ti and 0.12%La-0.03%Zr after oxidation at 1 473 K, respectively

was longer in the 0.10%La foil than in the foil without La addition, and was much longer in the 0.12%La-0.03%Zr foil, while the 0.08%La-0.08%Ti foil had a duration which was equal to or less than that of the 0.10%La foil. Thus there is a correspondence between the segragation at the grain boundaries and the oxidation rate. This indicates that in the La-Zr-added foil, La and Zr segragated at the grain boundaries of Al_2O_3 and suppressed the diffusion of oxygen in the Al_2O_3 layer, with the result that a decrease in the growth rate of the Al_2O_3 layer and Cr_2O_3 improved oxidation resistance.

Table 3 Equilibrium dissociation pressure of various oxides at 1 473 K

Oxide	Equilibrium dissociation pressure (Pa)
Fe_2O_3	3.3×10^{-11}
Fe_3O_4	2.7×10^{-12}
FeO	1.1×10^{-12}
Cr_2O_3	1.4×10^{-18}
TiO_2	8.4×10^{-25}
Al_2O_3	3.3×10^{-29}
ZrO_2	6.7×10^{-30}
La_2O_3	3.3×10^{-33}

Table 2 shows the results of X-ray diffraction analyses of the oxide layers formed on the 0.09%La-0.16%Ti and 0.07%La-0.24%Zr foils. In the 0.09%La-0.16%Ti foil, only Al_2O_3 was detected in a sample oxidized at 1 473 K for 72 ks, whereas TiO_2 was detected together with Al_2O_3 and Cr_2O_3 in a sample oxidized at 1 473 K for 216 ks. The EPMA analysis revealed that Ti was present mainly in the Al_2O_3 layer. This demonstrates that in the first stage of this foil, only the Al_2O_3 layer was formed and that in second stage the Ti in steel was oxidized and mixed into the Al_2O_3 layer as TiO_2. From this it is concluded that in the Ti-added foil, the mixing-in of TiO_2 made oxygen diffuse easily in the Al_2O_3 layer, causing the growth rate of the Cr_2O_3 layer in the second stage to increase (Fig. 6).

Because the Al_2O_3 layer in the second stage was thus different from the Al_2O_3 layer in the first stage, it might explain why no relation was observed in the Ti-added foil between the linear rate constant in the second stage and the duration of the first stage, as shown in Fig. 7. ZrO_2 was detected in the foil containing 0.07%La-0.24%Zr, an excessive amount of Zr. The EPMA observation revealed that ZrO_2 mixed into the Al_2O_3 layer. As described above, the oxidation rate increased in this foil because an Al_2O_3 layer having a large oxygen diffusion rate was formed. Therefore, it appears that, as suggested by Okabe[12], ZrO_2 provided a short-circuit diffusion passage of oxygen, increasing the oxygen diffusion coefficient.

The equilibrium dissociation pressures of various oxides at 1 473 K are shown in **Table 3**[13]. The dissociation pressure of TiO_2 is higher than that of Al_2O_3 but is lower than that of Cr_2O_3; this means that Ti is less apt to be oxidized than Al but more apt to be oxidized than Cr. This order of oxidation is attributed to the formation of

TiO_2 in the second stage, when the Al in foil was depleted and the formation of Al_2O_3 came to an end. On the other hand, the dissociation pressure of ZrO_2 is lower than that of Al_2O_3 meaning that Zr is more apt to be oxidized than Al. For this reason, ZrO_2 formed in the Al_2O_3 layer of the excessive-Zr foil.

4 Conclusion

In order to investigate the mechanism of improvement in the oxidation resistance of R20–5USR (20%Cr-5%Al) stainless steel foil by the combined addition of La and Zr, oxidation tests were conducted at 1 373 K and 1 473 K on 50 μm thick 20%Cr-5%Al stainless steel foil samples to which La, or La plus Ti, or La plus Zr was added. The following results were obtained:

(1) Oxidation proceeded by the formation of an Al_2O_3 layer until all the Al in the foil had been depleted. It then proceeded by the formation of a Cr_2O_3 scale between the Al_2O_3 layer and the substrate. The addition of La lowered the growth rate of both the Al_2O_3 layer and the Cr_2O_3 layer. When an appropriate amount of Zr was added with La, the growth rate of these oxides decreased further and oxidization resistance was improved. However, the addition of Ti was not effective in lowering the growth rate.

(2) Using a TEM, the segregation of La at the grain boundaries of Al_2O_3 layer was observed in the La-added foil and that of La and Zr at the grain boundaries was observed in the La-Zr foil. In the La-Ti foil, however, the segregation of only La at the grain boundaries was observed and that of Ti was slight.

(3) It appears that La or Zr suppressed the diffusion of oxygen in the Al_2O_3 layer by segregating at the grain boundaries of Al_2O_3 and lowering the growth rate of the Al_2O_3 and Cr_2O_3 layers, thus improving oxidation resistance.

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