Effect of La$_2$O$_3$ particles on microstructure and cracking-resistance of NiO scale on electrodeposited nickel films

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Abstract

The effect of La$_2$O$_3$ particles on the microstructure and cracking-resistance of thermally grown NiO scale, formed at 900 and 1000°C, on electrodeposited nickel films has been investigated through in situ acoustic emission (AE) testing in conjunction with SEM and TEM/EDX. NiO scale formed on electrodeposited films of pure nickel, has a porous duplex layered structure, which exhibits a more brittle behavior than the scale on films with the addition of La$_2$O$_3$ particles. They played a profound role in the procrastination of the occurrence of scale cracking and reduction of the cracking events. Upon the comparison of the microstructure of NiO scale on the nickel film with the NiO scale on the LaO-containing film, several points can be concluded. For example, the stresses in NiO scale on the film with La$_2$O$_3$ very partly released by a non-destructive means, such as scale plastic deformation due to La$_2$O$_3$-induced formation of a single-layered and fine-grained NiO scale. Also, it is believed that the particles reduced the size of the defects at the scale–metal interface and probably enhanced the cohesion between NiO grains and the adhesion between the scale–metal interface by retardation of the inward diffusion of nickel vacancies. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that growth stress is developed in oxide scales during oxidation whereas, thermal stress is generated at the scale–metal interface during cooling. Growth stress is mainly associated with the origin of the Pilling–Bedworth ratio (PBR), a change in volume as the metal is converted into oxide. The thermal stress is a consequence of mismatching coefficients of thermal expansion (CTE) between the scale and the metal substrate. The stresses in the scale are associated with a complex summation of the growth stress, the thermal stress, and stress relaxation. If relaxation through creep does not operate and/or if the scale stress (usually being compressive) is highly significant, scale damages (decohesion, formation of micro-cracks, buckling, and spalling, etc.) will take place. The critical stress, $\sigma_c$, for scale decohesion is given by Hancock et al. [1] as follows,

$$\sigma_c = \frac{K_{ic}}{\sqrt{\pi a}}$$

where, $K_{ic}$ is the critical stress intensity factor and $a$ the half–length of a defect at the scale–metal interface. Similarly, Eq. (1) is applicable for the evaluation of the critical stress for cracking within the scale. Following Eq. (1), the value of $\sigma_c$, is strongly dependent on the defect size in the scale. The latter, in most cases, is determined by growth-related scale microstructure. Any factor that changes scale microstructure will have an effect on the mechanical behavior of the scale. For example, reactive element (RE) addition into metals usually leads to the formation of a perfect scale mi-
crostructure, which prevents its breakdown. Although mechanisms of the RE effect on scale mechanical properties have been proposed for different scale-metal systems [2,3], it seems to be generally agreed upon that RE addition can reduce the number and size of defects in the scale by the following ways: (1) RE addition provides sites for vacancy sink, causing reduction in the extent of interfacial voiding; (2) RE addition decreases the activity of detrimental segregants such as sulfur and consequently increases the interfacial toughness, etc.

For the Ni-NiO system, impurities can result in the formation of a duplex-layered NiO scale with outer columnar crystals and inner equiaxial grains [4-7]. Defects like porosity, microchannels, and cracks have been found in the outer columnar layer [4,5,7]. Stress in the scale can be relaxed to a degree by the generation of defects and the creep within the scale or the metal, if it can operate at the processing temperatures. Some work has shown that RE addition has no observable effect on the formation of the duplex-layered scale. For instance, several decades ago, ThO₂ particles were introduced into nickel by mechanical alloying [8]. The ThO₂-dispersion-strengthened nickel is so-called the first generation of the commercial ODS alloy, TDNi. According to Petit and Felten [9], ThO₂ particles do not substantially change the double-layered structure of NiO scale formed and the oxidation kinetics. Our recent work [10] revealed that the similar double-layered scale, which was formed on electrodeposited films of pure nickel, has cracks appearing during thermal cycling. While La₂O₃ particles dispersed in nickel by co-electrodeposition favor the formation of a more protective NiO scale composed of finer grains, which has a slow growing rate and good cracking resistance. As a result, the electrodeposited Ni-La₂O₃ composite was applied as a protective coating for materials such as TiAl intermetallic [11].

Upon comparing the electrodeposited film of pure nickel with the film containing La₂O₃, it was found that there are no apparent differences in the composition of the two films (including impurities), with one exception, the film without La₂O₃ additions. Hence, the difference in oxidation resistance can be presumed to be associated with the role that La₂O₃ particles played during oxidation. As is evident, a comparative study which was done on the relations of microstructure and mechanical property in NiO scale formed on the two nickel films is helpful to elucidate how RE addition has an influence on the scale stress build up and the scale cracks development as well. Although X-ray diffraction and deflection measurements have been employed to analyze the stress development in the scale [12-16], these techniques do not have the capability to detect when and where cracks appear in the scale. In this study, a highly sensitive in situ technique, acoustic emission (AE) [17-20], was coupled with SEM and TEM/EDX in order to investigate when and where cracks are appearing in the scale.

2. Experimental

Cold rolled pure nickel (>99.9%) was cut into 10 × 10 × 1 mm pieces and then abraded using 300 grit SiC waterproof paper. Once the samples were abraded, the nickel samples were used as a negative electrode, onto which La₂O₃-containing nickel films were electrodeposited from a La₂O₃ particle (>99.98%) containing nickel electrolyte (250 g l⁻¹ NiSO₄ · 7H₂O, 15 g l⁻¹ NH₄Cl, 15 g l⁻¹ H₂BO₃, and 0.1 g l⁻¹ Cl₆H₁₂NaSO₄). The microstructure of the codedeposited nickel films has been reported in our previous work [10]. In this study, 2.2 wt.% La₂O₃-containing films with a thickness of 10 μm were prepared for experiment. For comparison, electrodeposited nickel films without La₂O₃ particles were also prepared in the same electrolytic bath without La₂O₃ additions.

Acoustic emission is a phenomenon of the emission of sound waves, which are generated due to sudden changes in the local elastic strain situation as a result of damage development in solid materials. Thus, AE measurements are very effective for monitoring the generation of cracks in brittle oxide scales. AE data has been used in the past, as an indication of the appearance of cracks in the scales. Fig. 1 is a schematic representation of the experimental set-up used for in situ measurement of AE events in the damage development of the NiO scale. One of the four secondary faces of the specimen
Fig. 2. Dependence of the AE counts being recorded with time for samples of nickel metal (a), the electrodeposited nickel film (b) and the film with La$_2$O$_3$ addition (c) during cooling after 5-h oxidation at 1000°C, showing the occurrence of scale cracking in NiO scale (hanging inside furnace) was spot-welded onto one end of a $\Phi$1 mm Pt wire (serving as an acoustic wave-guide to an AE sensor). The other end of the wire was spot-welded to the head of a stainless-steel cone (positioned outside furnace) and a transducer was attached to the bottom. First, the transducer output signals were sent to a pre-amplifier and were then recorded by an AE system (4101-type, made in China). The samples were isothermally oxidized at high temperatures (900 or 1000°C) in a vertical furnace tube and then cooled to room temperature by furnace cooling or cyclically oxidized between the oxidation temperature and a lower temperature. The cooling rate was calibrated by a thermocouple. AE counts (ring down counts) were used to analyze the AE signals. The cracking events that occur have a response of a sudden increase in AE counts. To ensure that all AE signals came from the scale cracking process, the transducer with a resonant frequency of 150 kHz was used. The pre-amplifier has an amplification of 40 dB. The total amplification of the 4101 AE system was 94 dB, with a threshold voltage of 1 V. After the AE testing was complete, the fracture sections of the scale and its morphologies at the inner interface were investigated using a Philip XL40FE GL-6900-type scanning electron microscopy (SEM/EDX) coupled with a Phillips EM 420 type TEM/EDX (operated at 100 kV).

3. Results

3.1. AE monitor

During AE measurements, AE signals were only very slightly detected during the isothermal oxidation stage, however, during the cooling period the signals were very evident. These results indicate that thermal stresses play a determined role in the emission of the AE signals. Fig. 2 depicts the dependence of the collected AE counts on time during the furnace-cooling after 5 h of exposure at 1000°C. Using the same cooling rate, AE events that were recorded obviously differed with different samples. For the electrodeposited nickel film and the pure nickel metal, AE events began to be recorded when the furnace was cooled from the exposure temperature to approximately 740°C. However, AE events were not detected after the furnace temperature was reduced below 200°C. The electrodeposited La$_2$O$_3$-containing nickel film displayed AE events, which were delayed at a lower temperature. The temperature range AE events were recorded was 440–400°C (see Fig. 2c).

Fig. 3 is the curve of cumulative AE counts vs. $\Delta T$. From this curve, it is evident that the AE events are remarkably lower for the scale formed from the La$_2$O$_3$-containing film rather than being made from the pure nickel film and from the nickel metal. For the latter sample, the dependence of the AE counts on $\Delta T$ can be divided into two sequential stages. In stage I, the AE counts increased smoothly. According to Kippender and Schütze [19], growth of voids and other defects probably occurs during stage I, whereas the through-scale cracks are probably created during stage II, which gives rise to a steeper increase in AE counts. In the work, the scale formed on all the samples did not spall. Thus, it is believed that the AE events correspond to the development of cracks in the scale, which were observed by SEM or TEM. This can also be seen from
Fig. 3, where the scale-cracking events were obviously higher for the pure nickel film with respect to the nickel metal.

During the 15-h isothermal oxidation and then eight cycles of cyclic oxidation between 900 and 1500°C (2-h exposure per cycle), almost all the AE signals were recorded during cooling (some weak AE signals were recorded during re-heating and the isothermal oxidation stage of the electrodeposited film of pure nickel). The dependence of the cumulative collected AE counts on time during the thermal cycling after a 15-h oxidation is illustrated in Fig. 4. This figure shows that the AE counts total 1 400 000 for the nickel film and only 18 000 for the La₂O₃-containing film. Evidently, the crack-resistance of the scale on the La₂O₃-containing film was greatly improved.

3.2. SEM/EDX and TEM/EDX analyses

Fig. 5 is a SEM cross-section of the NiO scale on the electrodeposited nickel film, which was used above for the AE testing after the metal had been dissolved away. The scale is double-layered with the outer coarse columnar grains and the inner fine equiaxed crystals, as has been reported previously [10]. Through-thickness crack and porosity were observed in the outer layer. Part of inner oxides was probably peeled off during the metal dissolution because the inner layer appears to be more porous and cracked (see Fig. 7 and literature [21]).

NiO scale formed on the La₂O₃-containing nickel film is single-layered and significantly fine-grained. The grains close to gas-scale interface are smaller compared with those near the scale-metal interface, as seen in Fig. 6a. In addition, the surface scale is somewhat convoluted and cracks were invisible. Large voids were sometimes found within the scale close to the scale-metal interface (see Fig. 6b). It is unlikely that such voids were created due to the interface decohesion (or buckling) because below the voids, oxides did appear. Hence, it can be presumed that the voids may form due to the scale plastic deformation.

When observing the bottom of the scale, the scale formed on the nickel film exhibits a number of large interfacial voids (see Fig. 7a). Around the voids, some cracks can be observed with a high magnification as presented in Fig. 7b. For comparison, the scale on the La₂O₃-dispersed nickel film was generally flatter and lacked large interfacial voids. However, small voids at some GB triple-points can be observed, as shown in Fig. 8. The voids can be clearly seen under TEM observation.

Fig. 9 is a TEM bright-field image of a section close to the metal (parallel to the scale-metal interface) of the scale on the La₂O₃-containing film. Voids and microcracks, dislocation pile-ups, were clearly observed. However, the oxides near the scale surface appear to be
Fig. 6. Cross-sectional morphologies of NiO scale on the nickel film with La₂O₃ after 5-h exposure at 1000°C, showing that the scale is convoluted. The oxide grains are much finer at place as indicated by S near surface than at B-marked place in the vicinity of the inner interface, where large voids as being arrowed were sometimes observed (B).

coherent, as seen in Fig. 10, in which the defects appeared in the area near the metal were not visible. For comparison purpose, the EDX microanalysis in the TEM was applied to analyze the chemical compositions at the grain boundaries of the oxides on both areas. We analyzed the composition of several areas located at and near a grain boundary of NiO along a line normal to the boundary. In the region near the scale surface, segregation of lanthanum in NiO grain boundary was frequently observed. Fig. 11 is a statistical result, based on ten measurements at different grain boundaries, of the dependence of the X-ray intensity ratio of La to Ni on spots with a distance from the grain boundary. While in the region near the metal, the segregation of lanthanum could not be frequently detected. Thus, the increase of the cohesion between oxide grains in the area near the surface may be as a result of the segregation of lanthanum to the oxide grain boundaries. By comparing Figs. 9 and 10, it can be seen that the size of the oxide grains near the surface is generally below 1 μm. This size is smaller than that in the area which was close to the metal, where the size of the oxide grains range from 1 to 5 μm.

Fig. 7. The plan views of NiO oxide from the bottom of the scale after 5-h oxidation of the nickel film at 1000°C, where many large voids appear (a) and in higher magnification cracks indicated by arrows can be observed around the voids (b).

Fig. 8. The plane views of NiO oxide at the bottom of the scale after 5-h oxidation at 1000°C of the La₂O₃ containing film. Many fine voids can be found at the grain boundaries.
La O particles were sometimes observed within the scale. Most particles are in a spherical shape and less than 200 nm. Concentration gradient of La was detected from some doped fine particles. One example is presented in Fig. 12, where a particle is indicated in position 2. A number of Ni gathered during the EDX analysis because of the small size of the particle and a relative large beam spot size of the probe in the TEM. From Fig. 12, La concentration at the grain boundary (in position 'S') is also higher than that found on the

Fig. 11. EDX microanalytical results of the change of La concentration on spots with distances away from the grain boundary.

Fig. 10. TEM bright-field image of NiO scale near the surface.

Fig. 12. TEM bright-field image of a particle doped in a NiO grain (a) and the corresponding microanalytical results (b) of lanthanum atomic percentage at the different marked spots.
Fig. 13. Pits exhibited within a surface NiO grain on the nickel film after air-cooling from 48-h oxidation at 900°C.

other area located away from the grain boundary. No voids or micro-cracks were observed around these upper particles. Accordingly, the small particle, which is deep in the scale, is unlikely to be an assistant source for the onset of cracking due to stress concentration.

4. Discussion

4.1. Effect of La$_2$O$_3$ particles on scale microstructure

NiO scale formed on the electrodeposited nickel film is double-layered. It could be interpreted by a model that the formation of the outer columnar layer is due to the outward diffusion of nickel cations and the inner layer grows as a result of the inward diffusion of molecular species of oxygen through microchannels in the outer layer [4, 5]. In contrast to the morphology and microstructure of NiO scale on the nickel film, the scale formed on the La$_2$O$_3$-containing nickel film is single-layered, which is more dense and fine-grained. The scale microstructure is believed to be a result of an association with that La$_2$O$_3$ addition, which causes the change in the mechanism of scale growth.

For nickel oxidation, NiO growth was controlled by outward cation diffusion. In this case, there is a reaction at the gas–scale interface [22]

\[ O_{ad} \rightarrow O^+_\infty + V^-_{\infty} \]  
(2)

and a reaction

\[ V^-_{\infty} + 2h^+ + Ni \rightarrow Ni_{ad} \]  
(3)

at the scale–metal interface. That is, accompanying the outward diffusion of nickel cations during the scaling process is a concentration gradient of $V^-_{\infty}$ which, builds up between the interface of the scale–gas and of scale–metal. The $V^-_{\infty}$ at the gas–scale interface will, in most cases, condense at grain boundaries or at the oxide–metal interface. During cooling, these condensed vacancies will coalesce into voids [23, 24]. The oxidation of the electrodeposited film of pure nickel is very fast [10, 21]. Meaning that a number of $V^-_{\infty}$ will diffuse into and condense at the inner interface to form large interfacial voids. This may be proven by the result that a number of pits within the surface NiO grains appeared not on the nickel metal but on the pure nickel film after 48 h of oxidation at 900°C (see Fig. 9 in reference [21]). A high magnification of such pits is presented in Fig. 13. The symmetrical configuration of such pits may be proof of the coalescence of excess $V^-_{\infty}$ during rapid cooling. The oxidation of electrodeposited nickel films is faster than nickel metal oxidation [10, 21]. Hence, more $V^-_{\infty}$ will be produced at the surface scale during oxidation of the nickel film. When condensation of vacancies at the interface or at other location in the scale suddenly become inactive during cooling, vacancies at the gas–scale interface will be saturated. Then, they will coalesce into pits (the super-saturation of oxygen vacancies ($V^o_{\infty}$)) at the surface can cause the formation of pits in the surface scale. However, if the spots developed from $V^o_{\infty}$ were true, it would be difficult to interpret why no pits with such a high density were exhibited on the surface scale of the nickel metal [21].

In contrast to the microstructure of the NiO scale on the electrodeposited nickel film, the scale formed on the La$_2$O$_3$-containing nickel film appeared as a denser, fine-grained, and single-layered structure. As is evident, La$_2$O$_3$ particles played a profound role in modifying the scale microstructure. In the work, segregation of La ions at the NiO grain boundaries was detected, particularly at the grain boundaries near the scale surface (see Fig. 11). This may be one of the reasons causing the change in the scale microstructure. For example, the segregation of La ions at grain boundaries can reduce the inward flux of $V^-_{\infty}$ by suppressing the 'short circuit' diffusion of cation oxidation, leading to a reduction in the formation of defects such as voids at the scale interface and within the scale. The La ions segregation can also play roles in inhibiting the grain growth by the 'solute-drag' effect [25] or decreasing the growth rate of oxide grains during oxidation [10] and consequently give rise to formation of fine oxide grains. This may be a reason that the oxide grains close to the scale surface are finer than those near the metal. In addition, it is noteworthy that the La$_2$O$_3$ particle itself may act as the nucleus for NiO oxide and as the sinkage site for vacancy. Therefore, it may favor the formation of a fine-grained and dense oxide scale.

It has been reported that ThO$_2$ particle addition into nickel did not substantially change the double-layered scale structure and also oxidation kinetics [9]. The reason may result from the ThO$_2$ particles added into nickel by mechanical alloying are much larger than the size of La$_2$O$_3$ particles introduced into nickel by
electrodeposition. In electrodeposited nickel films, La₂O₃ particles are in general smaller and below 500 nm. Particles below 5 nm have also been observed in the film by HREM [10]. The fine La₂O₃ particles, especially those that are nanometer in size, may be susceptible to dissolve partially at high temperatures. Once partially dissolved, they may provide a resource for creation of La ions, which can segregate to grain boundaries of the scale. In this case, the concentration of the segregated La ions at oxide grain boundaries maintained a value-limit at which the outward growth of oxide was effectively blocked and the oxidation rate was remarkably reduced [10,21]. The segregation phenomenon in the NiO scale has been observed for oxidation of Ni-1.6wt.%Cr alloy [26]. However, the NiO scale formed on the alloy was duplex-layered. This may be related to several factors. For example, the Cr in the alloy can not provide a site for NiO nucleation as the La₂O₃ particle did during the onset of oxidation. Also, the concentration of the segregated Cr⁺⁺ ions can not be maintained as high as would be expected for blocking the rapid diffusion of nickel ions along the scale grain boundaries.

4.2. Mechanical property of NiO scale with and without La₂O₃

Almost all AE counts were recorded during cooling. It indicates that scale cracking is a result of the development of the thermal stresses, compared with which, the growth stresses may be smaller and can be accommodated by NiO scale. Thus, if not considering the differences in mechanisms of the stress relaxation, it can be presumed that the stresses developed in both the scales on the nickel film and the La₂O₃-containing nickel film are almost in the same magnitude. However, AE testing results showed that the scale formed on the electrodeposited film is more susceptible to cracking than that on the La₂O₃-dispersed nickel film. The possible reason for this decreased susceptibility is believed to be associated with the addition of La₂O₃ that led to the changes in the scale's microstructure and consequently in the releasing mechanism of the stresses developed in the scale.

As discussed above, the V₉, will condense at the scale-metal interface and form the interfacial voids in the case of oxidation of electrodeposited nickel films. The interfacial flaws led to the separation of the scale from the metal. According to Evans [24], the latter is a prerequisite for a scale buckling as a result of introduction of a driven force such as tensile stresses and shear stresses into the perimeter of the separation under compressive stresses, which are usually developed in the NiO scale during oxidation and cooling. Although there is no obvious morphological evidence confirming that buckling occurred, it can not exclude that part of

AE counts result from buckling-related damage. Also, the development of tensile stresses and shear stresses along the scale-metal interface is responsible for the formation and growth of the cracks. Cracking was frequently observed at the interface between the scale and the nickel film (see Fig. 7 and the literature [21]). The reason for this is believed to be the formation of a number of interfacial voids in large sizes. In this case, the defect length in Eq. (1) can be considered as an effective value being composed of voids whose individual stress fields overlap noticeably [1,27]. Based on the morphological evidence, the sizes of some composite defects at the scale-metal interface are as large as over 20 μm at some regions. From Eq. (1), the calculated critical stresses for the scale fracture, σ_c, are below 280 MPa (Taking a K_c value as 1.6 MN m⁻¹² [28]). As is evident, the stress value is not difficult to reach for tensile stresses or shear stresses developed in the scale.

Similarly, at the grain boundary within the scale where the V₉n condenses, micro-cracks may be initiated and extended by shear stresses which appeared in the NiO scale or by slight tensile stresses (which developed in outer layer of NiO scale as has been suggested by Liu et al. [13]). The stable growth of micro-cracks during oxidation may become unstable though cracking during cooling when the value of the compressive shear stresses generated and the size of micro-cracks extended satisfy Eq. (1). The sudden scale cracking may be a critical factor causing strong AE signals. In addition, according to Liu et al. [17] the formation of large interfacial voids (see Fig. 7) will lead to thermal transfer barriers and cause tensile stresses when temperature changes. The latter is sometimes large enough to give rise to rupture of the oxide.

Compared to AE testing on the nickel film, cracking events were profoundly reduced from the scale formed on the La₂O₃-containing nickel film. The reason is that La₂O₃ additions changed the scale microstructure significantly, giving rise to a change in the mechanism of stress relaxation. Based on SEM and TEM investigation, two factors are induced by the La₂O₃ additions, which are responsible for improving the scale-cracking resistance. One of these factors is that the number and size of the defects in the scale are reduced. The other factor is that the scale is significantly fine-grained.

As described above in detail, La₂O₃ additions suppressed the inward flux of V₉, and result in a decrease in the number and size of defects embedded in the scale at both the oxide grain boundary and the scale-metal interface. La₂O₃ additions also increase the cohesion between the oxides, i.e., the fracture toughness of the scale. According to Eq. (1), the results will cause an increase in the critical stress for scale fracture.

In addition, the oxide grain size of the scale on the La₂O₃-added nickel film is profoundly fine-grained and generally below 1 μm at most regions, especially at or
near the surface layer, i.e. about one order lower than the columnar oxide grains. Hence, the doped oxide is so fine that the superplastic behavior becomes operable at temperatures as has been suggested [29]. The relation of the flow stress, $\sigma_f$, for plastic and superplastic deformation to the strain rate $\varepsilon$ and grain size $d$ for ceramic materials can be given as follows [29].

$$\sigma_f = \left[ \frac{4A}{\pi} \varepsilon d^p \right]^{1/n} \exp(Q/RT)$$

(4)

where $A$ is a constant, $Q$ the activation energy, $R$ the gas constant, and $T$ the temperature. Under the same strain, the value of $\sigma_f$ obviously depends on the grain size, i.e. $\sigma_f \propto d^p$ ($p$ is 2 or 3). The flow behavior for the thermally grown NiO oxides has not been reported so far. The reason that they have not been reported is that the oxide grains are often as large as around 10 $\mu$m. In this case, the operation of oxide creep or grain boundary sliding seems to be difficult.

Using Eq. (4), the plastic flow can be represented by the flow curve as illustrated in Fig. 14. Fig. 14 demonstrates that as the stress is increased below the transition temperature, $T$, it will reach the fracture stress before the flow stress. When it is over $T$, it will reach the flow stress first. From Fig. 3, the onset of scale cracking being recorded by AE is at 740$^\circ$C or after about 12 min of cooling for the undoped scale, while for the La-doped scale cracking events appears at 440$^\circ$C or after almost 40-min cooling, i.e. the transition temperature from ductile to brittle for the doped scale is decreased.

In summary, from Fig. 14, the mechanical property of the scale that was modified after La$_2$O$_3$ additions was attributed to the following factor. The flow curve is lowered due to fine-grained scale formed on the film with La$_2$O$_3$, and the fracture curve is lifted due to the segregation of La$^{3+}$, which leads to a reduction in the size of defects or an increase in the fracture toughness of the scale.

Here, it is worthy to point out that when the concentration of segregated La at the grain boundary is reduced to a level below the critical value for blocking the outward diffusion of Ni ions, the scale lateral growth occurs. The induced elastic strain within oxides may cause scale wrinkling. Yet, wrinkling seldom happens to NiO scale. However, for the fine-grained NiO scale grown on electrodeposited La$_2$O$_3$-added nickel films, convolution of the surface scale is sometimes observed (see Fig. 6b or elsewhere [10,11,21]. The results account for the fact that lateral stress can be released by wrinkling the fine-grained NiO oxides.

For the fine-grained NiO scale, voids were also observed at triple points of oxide grain at the scale–metal interface. The voids are apparently different from the interfacial voids formed in the case of oxidation of nickel film. They are more like wedge voids, which may generate due to oxide creep. The formation of these voids may initiate generation of micro-cracks along the grain boundary. However, for the fine-grained scale, superior plastic scale property makes the growth of the micro-cracks stable. The formation of the voids and the stable growth of the micro-cracks will cause a stress reduction. However, the energy released is too small to produce an AE response. In contrast to the appearance of voids in the scale close to the metal, the voids did not appear at the area next at the surface layer (see Fig. 10). One reason is that the segregated La ions are maintained at a certain concentration level, which is so high that it can be detected by the FDX microanalysis (see Fig. 11). The other reason is that the scale stresses generated are always lower at near the surface than at the regions near the scale–metal interface.

Also, the sulfur in the film may weaken the interface and make the scale cracking an easier process. However, La$_2$O$_3$ may act as sulfur gettering and as a result increase the chemical bonding between the scale and the metal, as has been proposed elsewhere [30,31].

Based on the results observed from the TEM, the stress concentration of the La$_2$O$_3$ particles that appeared in the scale was extremely low, definitely not enough to cause the formation of voids or micro-cracks at the particle–oxide interface. One reason may be related to the spherical shape and the small size of the particles that appeared in the scale. Our previous results have shown that a diffusion reaction occurred between the small doped particle and NiO forming an intermediate phase (analogous to Ni$_x$La$_{1-x}$O, spinel) [10]. Thus, as proposed by Ramnarayanan et al. [32], the interface of La$_2$O$_3$ and NiO is unlikely to be a location for triggering cracks. Contrarily, it should inhibit the germination and propagation of cracks, even if it appeared at the grain boundary. From this point of view, the particle

![Fig. 14. Dependence of plastic deformation and fracture of scale on temperature [29]. $T$ represents the transition temperature from brittle to ductile.](image-url)
5. Summary

The AE counts associated with the occurrence of cracking of the NiO scale are used to evaluate the mechanical properties of NiO on the nickel film with and without the addition of La$_2$O$_3$ particles during the process of exposing and cooling. Almost all the AE counts were recorded during cooling, which indicated that the creation of cracks was a result of thermal stress. AE counts are profoundly lower on the La$_2$O$_3$-containing nickel film than on the pure nickel film. At the same time, the onset of cracking for the La-doped scale on the former film was evidently delayed during cooling. Therefore, the NiO scale on the pure films of nickel exhibits brittleness. However, in contrast, the scale on the La$_2$O$_3$-containing nickel film was more ductile. Based on the SEM and TEM investigations during the oxidation of the La$_2$O$_3$-containing nickel film, La$_2$O$_3$ particles may play a major role in supplying nuclei for oxide formation and in providing the lanthanum ions, which are segregated to the scale grain boundary for suppressing the oxide grain growth. This will consequently lead to the formation of a dense single-layered and fine-grained scale instead of the porous and double-layered NiO scale formed on the electrodeposited nickel film. Therefore, it is proposed that the superior cracking resistance of the scale formed on the nickel film with La$_2$O$_3$ may attribute to the roles of La$_2$O$_3$. Which are as follows, (1) increasing the plastic behavior of the scale through thinning the oxides; (2) suppressing inward diffusion of vacancies and thereafter reducing the interfacial flaws and increasing the scale fracture toughness, as a result, making the interface decohesion more difficult. Prevention from sulfur segregation at the interface may be an additional factor for the La$_2$O$_3$ role in which it can improve the scale mechanical behavior and make the scale decohesion a more difficult process.

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