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A phenomenological model for lifetime design of Ni_2Al_3/Ni hybrid coating formed on creep resistant ferritic steels

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Abstract: The phase layer transformation kinetics in the Ni_2Al_3/Ni hybrid coating formed on creep resistant steel P92 has been studied via a series of prolonged isothermal annealing experiments at 650 °C. All the intermediate phase layers of NiAl, Ni_5Al_3 and Ni_3Al formed in the coating by interdiffusion during isothermal annealing process. The phase layers of NiAl and Ni_3Al formed at the very beginning of isothermal annealing at the interface between Ni_2Al_3 and Ni, but the Ni_5Al_3 phase layer formed at the interface between the NiAl and Ni_3Al phase layer only at an annealing time at which the outer Ni_2Al_3 phase layer was completely consumed. The growth and consumption of the Ni_2Al_3 and NiAl phase layers and the growth of the Ni_3Al_5 phase layer were all parabolic, but the growth of the Ni_3Al phase layer obeyed the power rate law $d = kt^{1/n}$. The growth kinetics of an intermediate phase layer was found to be faster than the kinetics of its subsequent consumption. The rate constants in both the growth and consumption kinetics need to be determined for each of the intermediate phase layers at a particular temperature. The lifetime of the coating with an outer Ni_2Al_3 phase layer of any specified initial thickness and a sufficiently thick inner Ni layer can then be estimated using the lifetime design model delineated in this study.

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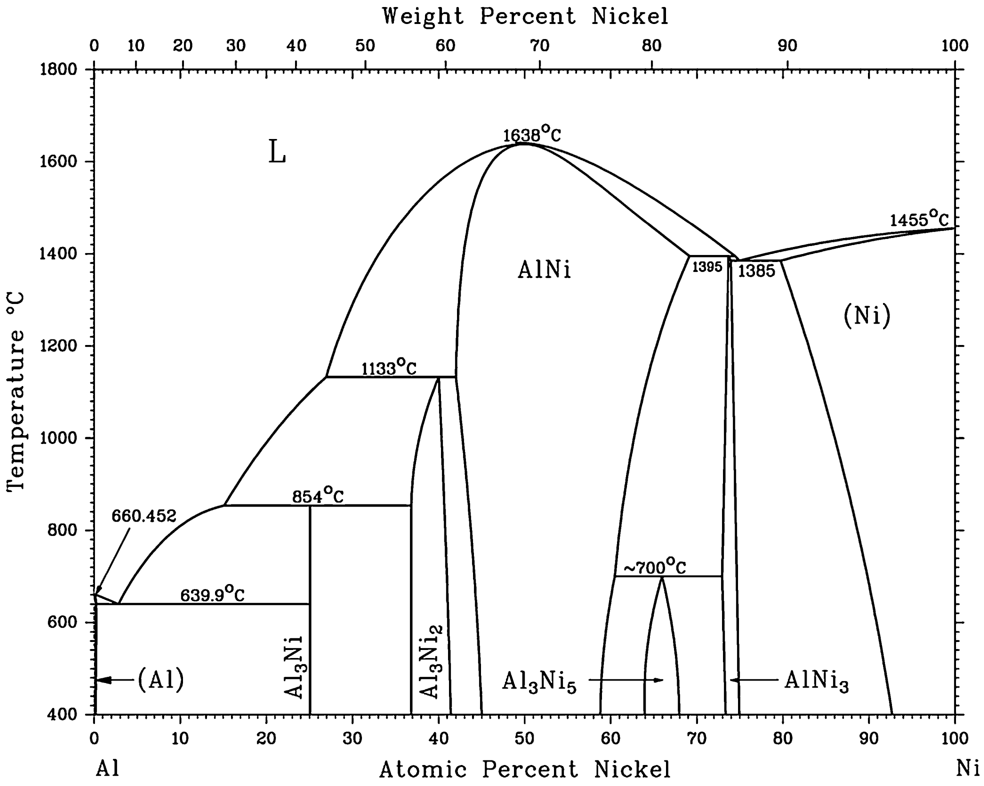
Introduction

Nickel aluminide coatings with a hybrid structure consisting of an outer nickel aluminide layer (either Ni_2Al_3 or NiAl) and an inner Ni layer have been considered recently for applications in protecting creep resistant steels against steam oxidation at temperatures up to 650 °C [1–3]. This type of coatings can be formed on steels' surface by firstly nickel plating to form a high purity nickel layer and then by partially aluminising the nickel layer at a temperature below 700 °C [1]. For creep resistant steels, it is of critical importance to minimise the aluminising temperature so that their microstructure and hence creep resistance are not affected by the aluminising process [4–9]. The conditions necessary to facilitate the coating formation in such a low temperature range has been further validated and rationalised recently [10, 11]. The outer nickel aluminide layer formed normally is Ni_2Al_3 under such low temperature conditions. The oxidation resistance of the coating is provided by the outer Ni_2Al_3 layer. If the inner Ni layer is made sufficiently thick, it can act as a barrier zone to prevent Al reaching the steel substrate and as a bonding layer that provides good adhesion between coating and substrate. For such a coating, its lifetime is controlled not by oxidation but by interdiffusion between the outer Ni_2Al_3 layer and inner Ni layer, i.e. by interdiffusion in the diffusion couple Ni_2Al_3/Ni. In such a diffusion couple, the alloy composition at the Ni_2Al_3 side changes progressively with time but remains constant at the Ni side. According to the Ni–Al phase diagram (Fig. 1) [12], the interdiffusion in such a diffusion couple will consume Ni_2Al_3 and lead to the growth and subsequent consumption of NiAl, Ni_5Al_3 and Ni_3Al phases at temperatures below 700 °C. Once the Al content in the coating reduces to a critical level, the coating will no longer be protective. In engineering applications, the

Fig. 1 Al–Ni phase diagram



lifetime of the coating at a specified temperature needs to be predicted from any initial thickness of the outer Ni_2Al_3 phase layer in the coating. To do so requires knowing not only the rate constants for the growths of different phase layers but also how these phases evolve with time in the coating. However, layer growth data for the diffusion couple Ni_2Al_3/Ni are still too sporadic particularly in the temperature range of 600–700 °C, which is important for ultrasupercritical steam turbine applications. The only piece of systematic work reported in the literature is that of Janssen and Rieck who studied the layer growth kinetics in a similar diffusion couple in the temperature range of 655–1000 °C, but used only short diffusion times, lasting not more than 300 h in total at the longest [13]. In addition, in nearly all previous studies on diffusion couples in the Ni–Al alloy system, the so-called bulk diffusion couples are used in which alloy compositions of the two members of the diffusion couple do not change with diffusion time [13–20]. Such a steady boundary condition differs from a situation in which the alloy composition of the outermost surface changes progressively with time as encountered in the present Ni_2Al_3/Ni hybrid coating with a thick inner Ni layer formed on creep resistant steels. Therefore, in this study, a series of extended isothermal annealing is undertaken to determine the sequence and kinetics of phase layer growth in the Ni_2Al_3/Ni hybrid coating at 650 °C and based on the results obtained a phenomenological model is formulated for lifetime design for this type of coatings.

Experimental details

A coating with a hybrid layer structure consisting of a 33 μm outer Ni_2Al_3 layer and a 140 μm inner Ni layer was formed on the commercial creep resistant steel P92 (Fig. 2); the nominal chemical composition of the steel substrate was Fe–9Cr–1.8W–0.5Mo–0.1C wt%. The coating was produced by firstly electroplating to form a high purity nickel layer and then by pack aluminising at 650 °C for 8 h in a power pack 4Al–2$AlCl_3$–94Al_2O_3 wt%; the detailed coating formation procedures were reported previously [1]. The coating was isothermally annealed in a horizontal tube furnace at 650 °C under high purity argon (99.99%). At different intervals, the coating was taken rapidly out of the furnace and cooled at room temperature. A small portion of the coating specimen was then cut off and the cross-section was polished. It was then analyzed using techniques of scanning electron microscopy (SEM) (FEI Quanta200) and energy dispersive X-ray spectroscopy (EDS) (Oxford INCA).

Results and discussions

According to the Ni–Al phase diagram, the composition ranges in which Ni_2Al_3, NiAl, Ni_5Al_3 and Ni_3Al can exist at 650 °C are 58.9–63.1, 40–55.6, 33.4–34.8 and 25–26.6 at.% Al, respectively, which correspond to the ranges of Al

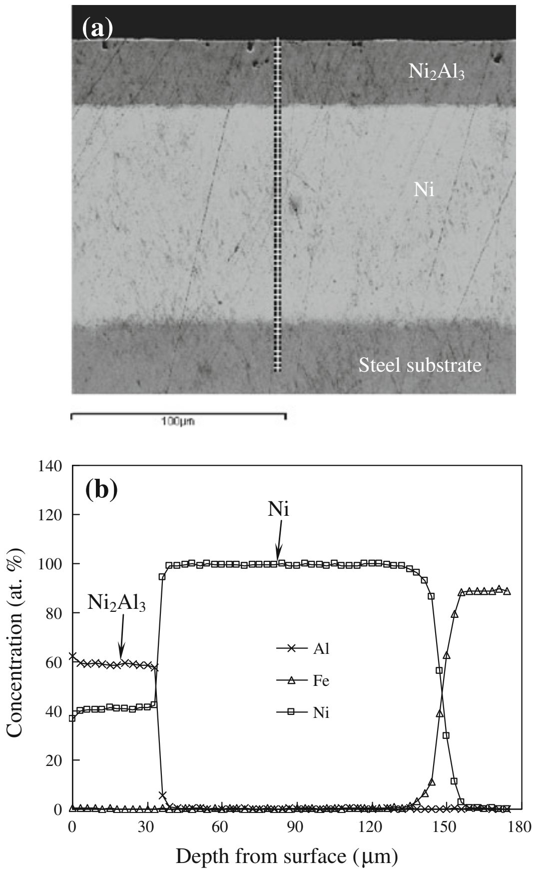


Fig. 2 Cross-sectional SEM image and depth profiles of major elements in the Ni_2Al_3/Ni coating formed on steel P92 by firstly electro Ni plating and then pack aluminising at 650 °C for 8 h

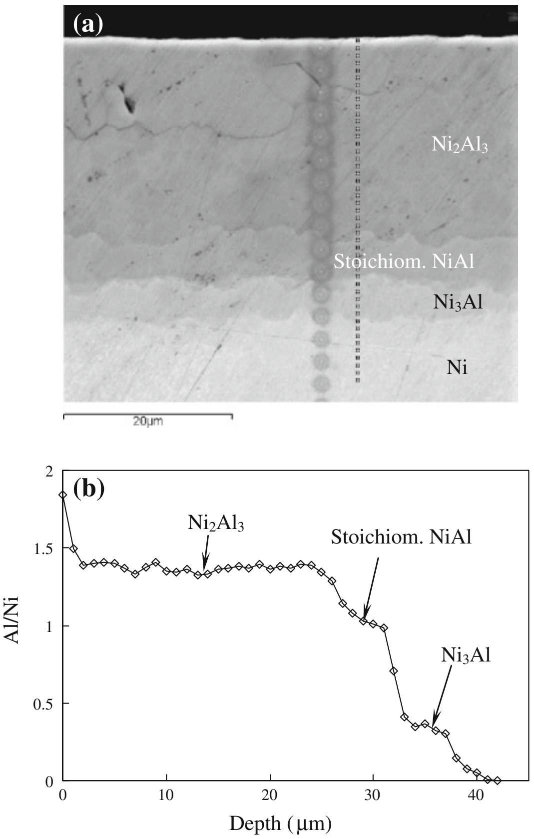


Fig. 3 Cross-sectional SEM image and depth profile of atomic ratio of Al to Ni in the coating after isothermal annealing at 650 °C for 24 h

to Ni atomic ratios of 1.71–1.43, 1.25–0.67, 0.53–0.5 and 0.36–0.33, respectively. These atomic ratio values were used as reference for identifying the respective phase layers inside the coating after different periods of isothermal annealing by EDS analysis.

Evolution sequence of different phase layers

The phase layers of NiAl and $NiAl_3$ started to form and grow at the expense of the outer Ni_2Al_3 phase layer at the very beginning of isothermal annealing as illustrated in Fig. 3 for the coating at 24 h annealing. As described previously the original thickness of the outer Ni_2Al_3 phase was approximately 33 μm, but at 24 h annealing, it was reduced to approximately 27 and both of the NiAl and Ni_3Al phase layers grew to a thickness of approximately 6 μm. The Ni_3Al_5 phase layer was not observed at this stage. This phase layer became only identifiable in the coating after more than 800 h annealing and growth of this phase layer was extremely slow. An example of the presence of this phase layer in the coating is shown in Fig. 4 for an annealing time of 3555 h. In this example, a thin Ni_3Al_5 phase layer with a thickness of only approximately 6 μm on average was present between the nickel rich NiAl and Ni_3Al phase layer; the original Ni_2Al_3 outer layer had been totally consumed and the two forms of the NiAl phase, i.e. stoichiometric NiAl and nickel rich NiAl, could be identified both on the SEM image and on the depth profile of Al to Ni atomic ratio; the stoichiometric NiAl phase layer was on the outermost surface. With further increase in annealing time, the newly formed outermost stoichiometric NiAl phase layer was totally consumed and the coating was transformed to a phase layer structure consisting of an outer nickel rich NiAl phase layer, a middle Ni_3Al_5 phase layer and an innermost Ni_3Al phase layer. Such a phase layer structure remained in the coating at annealing times up to 10898 h as shown in Fig. 5.

Growth and consumption kinetics of different phase layers

Consumption and growth of Ni_2Al_3, NiAl and Ni_3Al_5 phase layers

The consumption of the Ni_2Al_3 phase layer, growth and subsequent consumption of the NiAl phase layer and

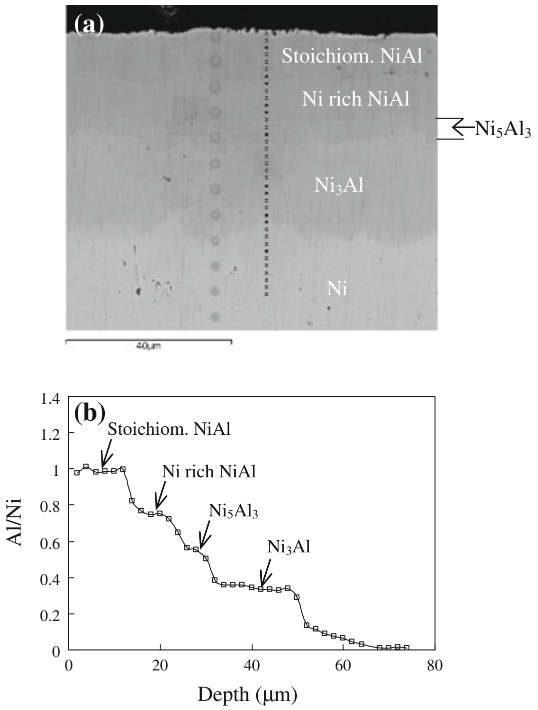


Fig. 4 Cross-sectional SEM image and depth profile of atomic ratio of Al to Ni in the coating after isothermal annealing at 650 °C for 3555 h

growth of the Ni_3Al_5 phase layer were plotted as a function of the square root of annealing time in Fig. 6, which shows that they were all parabolic. It also reveals that the Ni_3Al_5 phase layer started to form only at an annealing time when the outer Ni_2Al_3 layer was completed consumed; it was also a time when the NiAl phase layer reached its maximum thickness and began to be consumed. This phenomenon is indicated by the dashed vertical line in Fig. 6. For the consumption of Ni_2Al_3 phase layer, the kinetics determined by the least squares fit was:

$$d^{-}_{\mathrm{Ni_2Al_3}} = -1.37t^{1/2} + 33.25 \tag{1}$$

where $d^{-}_{\mathrm{Ni_2Al_3}}$ is the thickness in μm of the Ni_2Al_3 phase layer and t is the annealing time in h; it can be noted that the offset value in the equation above is close to the initial Ni_2Al_3 phase layer thickness as expected. Thus, the parabolic rate constant for the consumption of the Ni_2Al_3 phase was 1.37 μm $h^{-1/2}$.

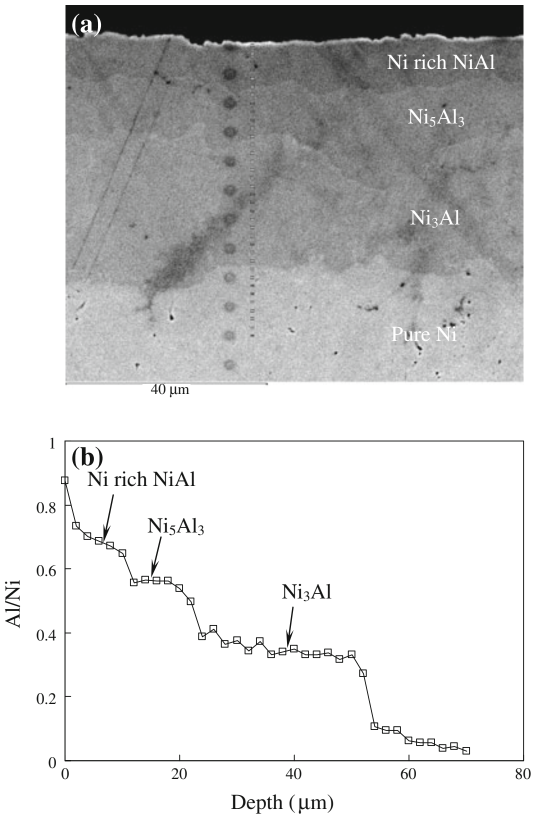


Fig. 5 Cross-sectional SEM image and depth profile of atomic ratio of Al to Ni in the coating after isothermal annealing at 650 °C for 10898 h

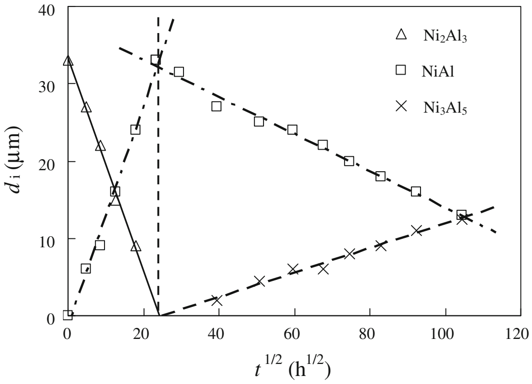


Fig. 6 Growth and consumption kinetics of different phase layers in the coating at 650 °C

For the growth and consumption kinetics of the NiAl phase layer, the least squares fit gives:

$$\text{for growth}, d^{+}_{\mathrm{NiAl}} = 1.42t^{1/2} - 1.25 \tag{2}$$

$$\text{for consumption}, d^{-}_{\mathrm{NiAl}} = -0.239t^{1/2} + 37.89 \tag{3}$$

where d^{+}_{NiAl} and d^{-}_{NiAl} are thickness in μm of the NiAl phase layer at the growing and consuming stage, respectively. Thus, the parabolic rate constant for the growth of the NiAl phase layer was 1.42 μm $h^{-1/2}$, which was approximately 5.9 times that for its subsequent consumption (0.239 μm $h^{-1/2}$). The small offset value in Eq. 2 indicates that there was a short incubation period of approximately 0.9 h for the growth of the NiAl phase layer. The offset value in Eq. 3 is the maximum thickness that the NiAl phase layer reached when the original outer Ni_2Al_3 phase layer was completely consumed in the coating.

The growth kinetics of the Ni_3Al_5 phase layer determined by the least squares fit was

$$d^{+}_{Ni_5Al_3} = 0.159t^{1/2} - 3.596 \quad (4)$$

where $d^{+}_{Ni_5Al_3}$ is the thickness in μm of the Ni_3Al_5 phase layer at its growing stage in the coating. Thus, it can be estimated that the incubation period for the growth of the Ni_3Al_5 phase layer was approximately 511 h. The extremely slow growth of this phase layer is reflected by the low parabolic rate of 0.159 μm $h^{-1/2}$, which was the reason for the fact that this phase layer was not easily identifiable in the coating at annealing times shorter than 800 h as described previously.

Growth of the Ni_3Al phase layer

The Ni_3Al phase layer started to form at the expense of the outer Ni_2Al_3 layer at the very beginning of isothermal annealing and continued to grow with increase in annealing time throughout the entire isothermal annealing period of 10898 h studied. However, the growth of this phase layer was not parabolic with time, but, a straight line was obtained on a log–log plot of $d^{+}_{Ni_3Al}$ versus t (Fig. 7a); the least squares fit gives

$$\log d^{+}_{Ni_3Al} = 0.279 \log t + 0.397 \quad (5)$$

where $d^{+}_{Ni_3Al}$ is the thickness in μm of the Ni_3Al phase layer at its growing stage. Rearranging above gives

$$d^{+}_{Ni_3Al} = 2.5t^{1/3.58} \quad (6)$$

Growth of Al penetration depth in the coating

The Al penetration depth is defined in this study as the distance from the outermost surface to a depth at which the Al concentration becomes zero. It can be estimated from the Al depth profile measured by EDS. As stated previously, the coating before isothermal annealing had an outer Ni_2Al_3 phase layer thickness of approximately 33 μm; but the Al penetration depth in the coating was approximately 39 μm (Fig. 2), which increased continuously with annealing time at 650 °C. The increment in the Al penetration depth Δx_{Al} is defined as $\Delta x_{Al} = d^{t}_{Al} - d^{0}_{Al}$, where d^{t}_{Al} and d^{0}_{Al} are the Al penetration depth at annealing time t and at 0 h, respectively. When the values of Δx_{Al} in μm are plotted against $t^{1/2}$ in $h^{1/2}$, a linear relationship was revealed as shown in Fig. 8 where the straight line is the best fit to the data points by setting the intercept at the origin, which gives:

$$\Delta x_{Al} = 0.272t^{1/2} \quad (7)$$

The continued increase in the Al penetration depth indicates that the consumption and growth of all the intermediate phase layers were predominantly facilitated by the inward Al diffusion in the coating at the temperature studied.

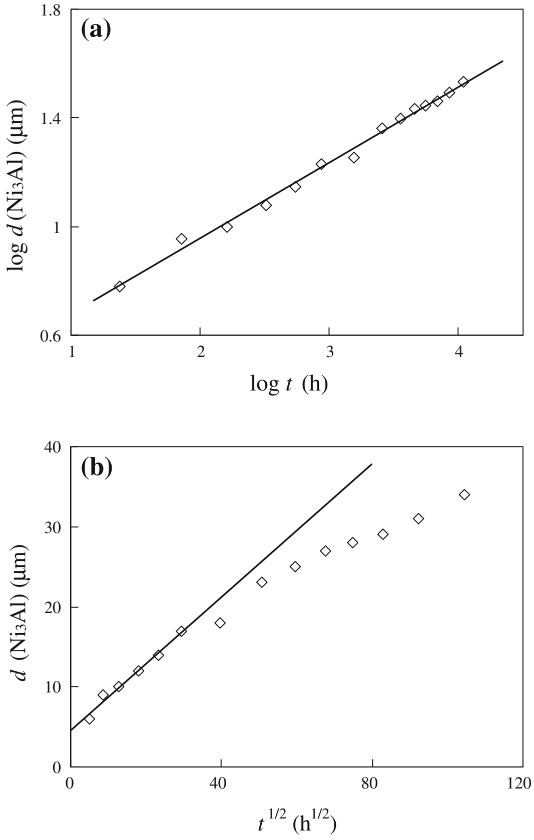


Fig. 7 Growth kinetics of the Ni_3Al phase in the coating at 650 °C

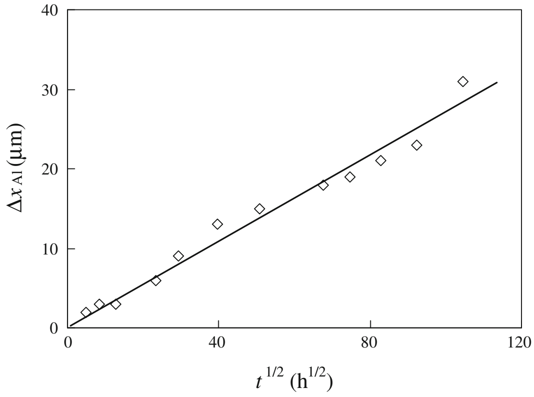
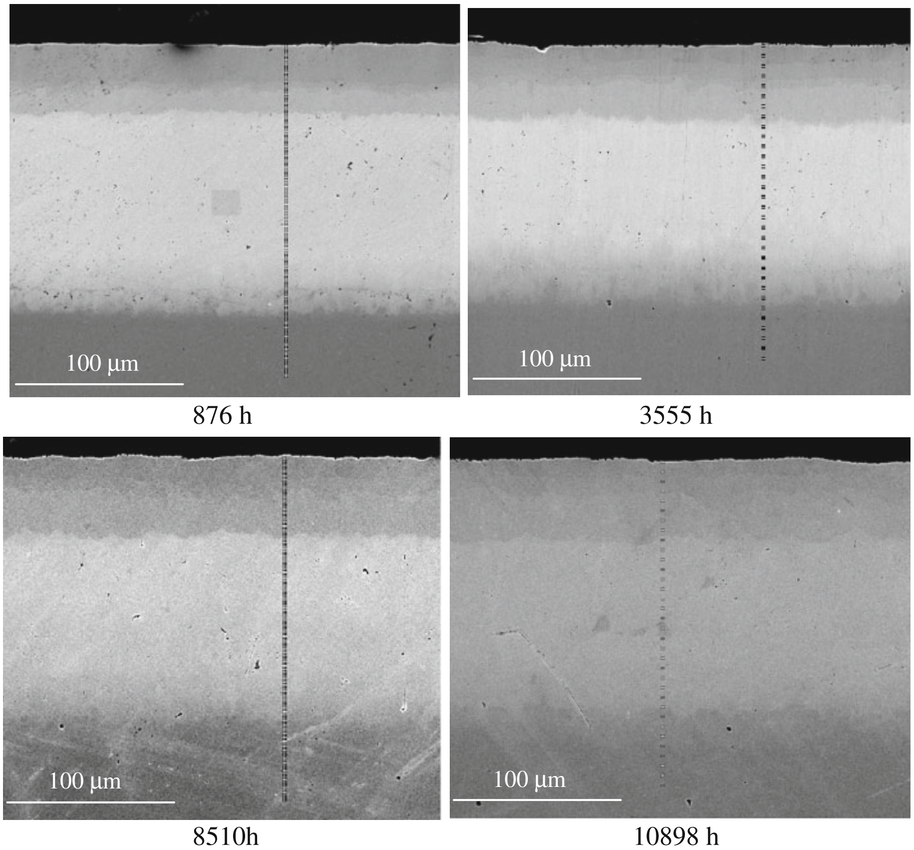


Fig. 8 Increment in Al penetration depth in the coating versus annealing time at 650 °C

Integrity of the coating during isothermal annealing

The coating maintained its integrity during the entire isothermal annealing periods studied with no signs of spallation. This is demonstrated in a series of cross-sectional



876 h 3555 h

8510h 10898 h

Fig. 9 Cross-sectional SEM images of the coating at different annealing times at 650 °C

SEM images shown in Fig. 9 for the coating at different annealing times up to 10898 h.

Discussion

Consumption and growth kinetics of phase layers

It was observed that the consumption of the Ni_2Al_3 phase layer was parabolic with a rate constant of 1.37 μm $h^{-1/2}$. This was more than one magnitude lower than those extrapolated to the same annealing temperature from the growth data reported by Jung et al. [14] and by Janssen and Rieck [13]; such extrapolations made by the present authors were 35.22 and 53.72 μm $h^{-1/2}$, respectively. Whereas the difference in the data of previous investigators may be attributed to the difference in methods used to prepare the diffusion couples, the same consideration cannot be applied to the large difference between the value determined in this study and those extrapolated from previous studies. It indicates that the growth of the Ni_2Al_3 phase layer is much faster than that of its subsequent consumption by interdiffusion. Further evidence supporting such a conclusion comes from the data reported by Hickl and Heckel [21]. For example, the present authors estimated from their reported data that the parabolic rate constant for the growth of the Ni_2Al_3 phase layer formed on nickel in an aluminising process was 68.3 μm $h^{-1/2}$ at 870 °C, which was much higher than 26.0 μm $h^{-1/2}$ for its subsequent consumption in an isothermal annealing process at the same temperature that transformed the Ni_2Al_3 phase layer to β-NiAl.

The growth of the NiAl phase layer was much faster than its subsequent consumption in the coating as evidenced by the much higher parabolic rate constant for its growth (1.42 μm $h^{-1/2}$) than for its subsequent consumption (0.239 μm $h^{-1/2}$). Although the consumption kinetics of the Ni_3Al_5 and Ni_3Al phase layer have not been determined in this study, it may be reasonable to conclude al least that the rate constant for the growth of a phase layer differs from that of its subsequent consumption by interdiffusion.

The parabolic rate constant for the growth of the Ni_3Al_5 phase layer was extremely low, being approximately 0.159 μm $h^{-1/2}$. Although as far as the present authors are aware no such data have been reported in the literature, the extremely low growth rate of the Ni_3Al_5 phase layer observed in this study was consistent with the observations of other investigators on the bulk Ni–Al alloys in the two phase region of NiAl and Ni_3Al [22–25]. Ootoshi et al. [25] studied the diffusion couple Ni-24Al/Ni-45Al (at.%) at 650 °C and from their data presented in Fig. 4 of [25] the present authors estimated that the parabolic rate constant for the growth of the Ni_5Al_3 phase layer in their diffusion couple was approximately 0.262 μm $h^{-1/2}$, which is higher than, but comparable to, the one determined in this study.

The growth of the Ni_3Al phase layer was not parabolic but followed a power rate law of growth of the form $d^{+}_{Ni_3Al} = k^{+}_{Ni_3Al} t^{1/n}$, where $k^{+}_{Ni_3Al}$ is the rate constant at the growth stage of the Ni_3Al phase layer. This is in contrast to the results of previous studies, which all showed that the growth of the Ni_3Al phase layer was parabolic [13]. The difference is almost certainly due to the difference in the lengths of annealing time used to measure the kinetics; an annealing time of 10898 h was used in this study to measure the kinetics whereas annealing times lasting only 300 h at the longest were used in previous studies. At short annealing times the parabolic kinetics appeared to be obeyed as illustrated in Fig. 6b, where the straight is the least squares fit to the data points at annealing times up to 548 h.

Lifetime design model of the coating

The phase layer growth and consumption phenomena observed may be applied to formulate a model for the lifetime design of the coating with any specified initial outer Ni_2Al_3 layer thickness $d^{0}_{Ni_2Al_3}$ and a sufficiently thick inner Ni layer. The formulation can be made on the basis of three assumptions and three boundary conditions, which are listed below:

Assumptions:

(a) the rate constant for the growth of any phase layer differs from that of its subsequent consumption by interdiffusion;
(b) growth and consumption of the Ni_2Al_3, NiAl and Ni_3Al_5 phase layer are all parabolic, but the growth and consumption of the Ni_3Al phase layer obey the power rate law $d = kt^{1/n}$;
(c) the exponent n in the power rate law for the growth of the Ni_3Al phase layer is the same as for its subsequent consumption.

Boundary conditions:

(a) the Ni_5Al_3 phase layer starts to form at the interface between the NiAl and the Ni_3Al phase layer only when the initial outer Ni_2Al_3 layer is totally consumed by interdiffusion;
(b) at the moment when the outermost phase layer is completely consumed, the phase layer next to it reaches its maximum thickness and begins to be consumed;
(c) the last phase layer to be consumption by interdiffusion is Ni_3Al.

According to the results presented in the preceding sections, the assumption (a) is valid for all the phase layers in the coating; the assumption (b) is valid for the growth and consumption of the Ni_2Al_3 and NiAl layers and for the growth of the Ni_3Al_5 and Ni_3Al phase layers, but it remains to be verified for the consumption of the Ni_3Al_5 and Ni_3Al phase layers; further evidence is also required to confirm the validity of the assumption (c).

Nevertheless, on the basis of above assumption and boundary conditions, it can be derived that the time needed to completely consume the last phase layer (Ni_3Al) in the coating, designated as $t^{-}_{Ni_3Al}$, is given by (Appendix A):

$$t^{-}_{Ni_3Al} = \left(\frac{k^{+}_{Ni_3Al} + k^{-}_{Ni_3Al}}{k^{-}_{Ni_3Al}}\right)^{n} \times \left[\frac{k^{+}_{NiAl}k^{+}_{Ni_5Al_3} + k^{-}_{Ni_5Al_3}\left(k^{+}_{NiAl} + k^{-}_{NiAl}\right)}{k^{-}_{Ni_2Al_3}k^{-}_{NiAl}k^{-}_{Ni_5Al_3}} d^{0}_{Ni_2Al_3}\right]^{2} \tag{8}$$

where k^{+}_{i} and k^{-}_{i} are the rate constants for the growth and consumption of the phase layer i, respectively.

When the Ni_3Al layer is completely consumed, the coating will have been transformed to a layer consisting of two phases according to the Ni–Al phase diagram; one is Ni_3Al and the other the saturated solid solution of Al in Ni. The Al concentration at the outermost surface of the coating will be slightly less than 25 at.% and the coating will still be protective. Susan and Marder showed that, at 800 °C, the Al concentration in the Ni–Al coating needs to be above 12 at.% in order to maintain its ability to grow the alumina scale [26]. It is expected that the Al content needed in the coating for it to remain protective will be slightly lower at a lower temperature such as 650 °C concerned in this study. The lifetime of the coating at this remaining stage, designated by t^{-}_{r}, i.e. the time needed for the Al content in the coating to drop from a level slightly below 25 at.% to a level lower than 12 at.%, may be estimated using the model suggested by Susan and Marder [26]. Therefore, the lifetime of the coating $t^{lifetime}_{coating}$ can be given by:

$$t^{lifetime}_{coating} = t^{-}_{Ni_3Al} + t^{-}_{r} \tag{9}$$

Although Eq. 8 is derived on the basis of experimental phenomena observed at 650 °C, it is expected to be applicable at any temperatures below 700 °C because the phase transformation mechanisms in the coating in such a temperature range is not expected to differ from that at 650 °C, which is dominated by the inward Al diffusion [27]. At temperatures above 700 °C, the Ni_5Al_3 phase cannot form in the coating according to the Ni–Al phase diagram and thus Eqs. 8 and 9 will no longer be applicable. However, the phenomenological approach used to derive it is still expected to be valid at temperatures higher than 700 °C as long as it is not too high to change the phase transformation mechanisms in the coating.

Equation 8 is easy to use and all the rate constants in it can be determined at different temperatures by annealing experiments. Because the values of $k^{-}_{\mathrm{Ni_5Al_3}}$ and $k^{-}_{\mathrm{Ni_3Al}}$ have not been determined, it is not possible to give a numerical value for $t^{-}_{\mathrm{Ni_3Al}}$ at 650 °C for the coating used in this study, which had an outer $\mathrm{Ni_2Al_3}$ layer thickness of 33 μm. As discussed previously, the $\mathrm{Ni_5Al_3}$ phase layer starts to be consumed only when the NiAl phase layer is completely consumed. For the coating used in this study, the annealing time needed to completely consume the NiAl phase layer will be approximately 25133 h according to Eq. 3. By then, the $\mathrm{Ni_5Al_3}$ phase layer will have grown to a thickness of approximately 22 μm according to Eq. 4. Thus, even longer annealing times will be needed to determine the values of $k^{-}_{\mathrm{Ni_5Al_3}}$ and $k^{-}_{\mathrm{Ni_3Al}}$, which is not feasible in this study, but deserves further research. For this purpose, a coating with a much thinner initial $\mathrm{Ni_2Al_3}$ outer layer will make the experimental time needed more practically manageable. For instance, for a coating with an initial outer $\mathrm{Ni_2Al_3}$ layer thickness of 10 μm, it can be estimated that the annealing time needed to completely consume the NiAl layer at 650 °C is only approximately 2567 h (see Appendix), which is more viable for the determination of the values of $k^{-}_{\mathrm{Ni_5Al_3}}$ and $k^{-}_{\mathrm{Ni_3Al}}$ from the consumption processes of the $\mathrm{Ni_3Al_5}$ and then $\mathrm{Ni_3Al}$ phase layers.

Design of inner Ni layer thickness of the coating

Clearly, in the lifetime of the coating, it is desirable to prevent the Al penetration reaching the steel matrix. Thus, the initial inner Ni layer thickness d_{Ni} should not be less than the increment in the depth of Al penetration into the inner Ni layer. Since the growth of the increment in the Al penetration depth into the inner Ni layer of the coating is parabolic with time, d_{Ni} can be given by:

$$d_{\mathrm{Ni}} \geq k_{\mathrm{Al}}\left(t^{\mathrm{coating}}_{\mathrm{lifetime}}\right)^{1/2} \quad (10)$$

substituting Eq. 9 into the equation above gives:

$$d_{\mathrm{Ni}} \geq k_{\mathrm{Al}}\left(t^{-}_{\mathrm{Ni_3Al}} + t^{-}_{\mathrm{r}}\right)^{1/2} \quad (11)$$

where k_{Al} is the parabolic rate constant for the growth of the increment in the depth of Al penetration into the inner Ni layer of the coating. Its value at 650 °C is 0.272 μm $\mathrm{h}^{-1/2}$ as given in Eq. 7.

Conclusions

The phase layer transformation process in a coating with a thin outer $\mathrm{Ni_2Al_3}$ layer and a sufficiently thick inner Ni layer on creep resistant ferritic steel has been studied in a series of isothermal annealing experiments carried out in an argon atmosphere at 650 °C. All the intermediate phase layers between $\mathrm{Ni_2Al_3}$ and Ni in the Ni–Al phase diagram will form and then be consumed during the lifetime of the coating. The phase layers of NiAl and $\mathrm{Ni_3Al}$ will form at the very beginning of isothermal annealing; the $\mathrm{Ni_5Al_3}$ phase layer will form only at the interface between the NiAl and $\mathrm{Ni_3Al}$ phase layer at the moment when the outer $\mathrm{Ni_2Al_3}$ phase layer is completely consumed. The growth and consumption of the $\mathrm{Ni_2Al_3}$ and NiAl phase layers and the growth of the $\mathrm{Ni_3Al_5}$ phase are all parabolic, but the growth of the $\mathrm{Ni_3Al}$ phase layer is non-parabolic; it, instead, follows the power law kinetics of the form $d = k^{+}t^{1/n}$. The growth of an intermediate phase layer is normally faster than its subsequent consumption and the rate constants both in the growth and in the consumption kinetics need to be determined for each of the intermediate phase layers at a particular temperature. The lifetime of the coating with an outer $\mathrm{Ni_2Al_3}$ phase layer of any specified initial thickness and a sufficiently thick inner Ni layer can then be estimated using the lifetime design model proposed in this study.

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Appendix A

Derivation of the equation for calculating $t^{-}_{\mathrm{Ni_3Al}}$: for a coating with an outer $\mathrm{Ni_2Al_3}$ layer of an initial thickness $d^{0}_{\mathrm{Ni_2Al_3}}$, the consumption kinetics of this layer can be written as:

$$d^{-}_{\mathrm{Ni_2Al_3}} = -k^{-}_{\mathrm{Ni_2Al_3}}t^{1/2} + d^{0}_{\mathrm{Ni_2Al_3}} \quad (12)$$

where $d^{-}_{\mathrm{Ni_2Al_3}}$ is the thickness of the $\mathrm{Ni_2Al_3}$ phase layer at time t and $k^{-}_{\mathrm{Ni_2Al_3}}$ is the parabolic rate constant for the consumption of the $\mathrm{Ni_2Al_3}$ phase layer. Thus, the time needed to completely consume this layer, designated by $t^{-}_{\mathrm{Ni_2Al_3}}$, is:

$$t^{-}_{\mathrm{Ni_2Al_3}} = \left(\frac{d^{0}_{\mathrm{Ni_2Al_3}}}{k^{-}_{\mathrm{Ni_2Al_3}}}\right)^{2} \quad (13)$$

The NiAl layer starts to grow next to the outer $\mathrm{Ni_2Al_3}$ layer at the very beginning of isothermal annealing and it reaches its maximum thickness when the outer $\mathrm{Ni_2Al_3}$ layer is completely consumed. As the growth of the NiAl phase layer is parabolic, its kinetics can be written as:

$$d^{+}_{\mathrm{NiAl}} = k^{+}_{\mathrm{NiAl}} t^{1/2} \tag{14}$$

where d^{+}_{NiAl} and k^{+}_{NiAl} are the thickness and parabolic rate constant of the NiAl layer at its growing stage, respectively. The time limit in Eq. 14 is $0 \le t \le t^{-}_{\mathrm{Ni_2Al_3}}$. At $t = t^{-}_{\mathrm{Ni_2Al_3}}$, the NiAl layer stops growing and starts to be consumed. Its consumption kinetics is also parabolic with time and can be given by:

$$d^{-}_{\mathrm{NiAl}} = -k^{-}_{\mathrm{NiAl}} t^{1/2} + \frac{(k^{+}_{\mathrm{NiAl}} + k^{-}_{\mathrm{NiAl}})}{k^{-}_{\mathrm{Ni_2Al_3}}} d^{0}_{\mathrm{Ni_2Al_3}} \tag{15}$$

where d^{-}_{NiAl} and k^{-}_{NiAl} are the thickness and parabolic rate constant in the consuming stage of the NiAl layer, respectively. The second term on the right hand side of Eq. 4 is derived using the boundary condition that at $t = t^{-}_{\mathrm{Ni_2Al_3}}$, $d^{-}_{\mathrm{NiAl}} = d^{+}_{\mathrm{NiAl}}$. Thus, the time needed to completely consume the NiAl layer t^{-}_{NiAl} can be calculated using Eq. 15, which is

$$t^{-}_{\mathrm{NiAl}} = \left[\frac{(k^{+}_{\mathrm{NiAl}} + k^{-}_{\mathrm{NiAl}})}{k^{-}_{\mathrm{Ni_2Al_3}} k^{-}_{\mathrm{NiAl}}} d^{0}_{\mathrm{Ni_2Al_3}}\right]^{2} \tag{16}$$

The $\mathrm{Ni_5Al_3}$ phase layer starts to form next to the NiAl layer only at the moment when the outer $\mathrm{Ni_2Al_3}$ layer is totally consumed in the coating, i.e. at $t = d^{-}_{\mathrm{Ni_2Al_3}}$, and the growth of this phase layer is parabolic. By using the boundary condition that at $t = t^{-}_{\mathrm{Ni_2Al_3}}$, the thickness of this layer $d^{+}_{\mathrm{Ni_5Al_3}}$ is zero, the growth kinetics of the $\mathrm{Ni_5Al_3}$ phase layer in the coating can be written as:

$$d^{+}_{\mathrm{Ni_5Al_3}} = k^{+}_{\mathrm{Ni_5Al_3}} t^{1/2} - \frac{k^{+}_{\mathrm{Ni_5Al_3}}}{k^{-}_{\mathrm{Ni_2Al_3}}} d^{0}_{\mathrm{Ni_2Al_3}} \tag{17}$$

The thickness of the $\mathrm{Ni_5Al_3}$ layer reaches its maximum and starts to decrease at the moment when the NiAl layer is totally consumed, which means that at $t = t^{-}_{\mathrm{NiAl}}$, $d^{+}_{\mathrm{Ni_5Al_3}} = d^{-}_{\mathrm{Ni_5Al_3}}$, where $d^{-}_{\mathrm{Ni_5Al_3}}$ is the thickness of the $\mathrm{Ni_5Al_3}$ layer at its consumption stage. Using this boundary condition and assuming that the consumption process of the $\mathrm{Ni_5Al_3}$ phase layer will also be parabolic, one can derive the following kinetics for the consumption of the $\mathrm{Ni_5Al_3}$ layer:

$$\begin{aligned} d^{-}_{\mathrm{Ni_5Al_3}} = {} & -k^{-}_{\mathrm{Ni_5Al_3}} t^{1/2} \\ & + \left[\frac{k^{+}_{\mathrm{NiAl}} k^{+}_{\mathrm{Ni_5Al_3}} + k^{-}_{\mathrm{Ni_5Al_3}} (k^{+}_{\mathrm{NiAl}} + k^{-}_{\mathrm{NiAl}})}{k^{-}_{\mathrm{Ni_2Al_3}} k^{-}_{\mathrm{NiAl}}}\right] d^{0}_{\mathrm{Ni_2Al_3}} \end{aligned} \tag{18}$$

where $k^{-}_{\mathrm{Ni_5Al_3}}$ is the parabolic rate constant for the consumption of the $\mathrm{Ni_5Al_3}$ layer. Therefore, the time needed to completely consume the $\mathrm{Ni_5Al_3}$ layer $t^{-}_{\mathrm{Ni_5Al_3}}$ is given by:

$$t^{-}_{\mathrm{Ni_5Al_3}} = \left[\frac{k^{+}_{\mathrm{NiAl}} k^{+}_{\mathrm{Ni_5Al_3}} + k^{-}_{\mathrm{Ni_5Al_3}} (k^{+}_{\mathrm{NiAl}} + k^{-}_{\mathrm{NiAl}})}{k^{-}_{\mathrm{Ni_2Al_3}} k^{-}_{\mathrm{NiAl}} k^{-}_{\mathrm{Ni_5Al_3}}} d^{0}_{\mathrm{Ni_2Al_3}}\right]^{2} \tag{19}$$

The $\mathrm{Ni_3Al}$ phase layer forms at the very beginning of the isothermal annealing process and grows continuously in the coating as annealing time increases; its growth obeys the power law kinetics:

$$d^{+}_{\mathrm{Ni_3Al}} = k^{+}_{\mathrm{Ni_3Al}} t^{1/n} \tag{20}$$

where $d^{+}_{\mathrm{Ni_3Al}}$ is the thickness, $k^{+}_{\mathrm{Ni_3Al}}$ the rate constant and $1/n$ the exponent of the power rate law for the growth of the $\mathrm{Ni_3Al}$ layer. It is assumed that the exponent $1/n$ will remain the same in the subsequent consumption process of the $\mathrm{Ni_3Al}$ layer. Now, using the boundary condition that at $t = t^{-}_{\mathrm{Ni_5Al_3}}$, $d^{+}_{\mathrm{Ni_3Al}} = d^{-}_{\mathrm{Ni_3Al}}$, where $d^{-}_{\mathrm{Ni_3Al}}$ is the thickness of the $\mathrm{Ni_3Al}$ layer at its consumption stage, one can obtain:

$$d^{-}_{\mathrm{Ni_3Al}} = -k^{-}_{\mathrm{Ni_3Al}} t^{1/n} + (k^{+}_{\mathrm{Ni_3Al}} + k^{-}_{\mathrm{Ni_3Al}})(t^{-}_{\mathrm{Ni_5Al_3}})^{1/n} \tag{21}$$

where $k^{-}_{\mathrm{Ni_3Al}}$ is the power rate law constant for the consumption of the $\mathrm{Ni_3Al}$ layer. Thus, the time needed to completely consume the $\mathrm{Ni_3Al}$ layer $t^{-}_{\mathrm{Ni_3Al}}$can be given by:

$$t^{-}_{\mathrm{Ni_3Al}} = \left(\frac{k^{+}_{\mathrm{Ni_3Al}} + k^{-}_{\mathrm{Ni_3Al}}}{k^{-}_{\mathrm{Ni_3Al}}}\right)^{n} t^{-}_{\mathrm{Ni_5Al_3}} \tag{22}$$

Substituting Eq. 19 into Eq. 22 gives

$$\begin{aligned} t^{-}_{\mathrm{Ni_3Al}} = {} & \left(\frac{k^{+}_{\mathrm{Ni_3Al}} + k^{-}_{\mathrm{Ni_3Al}}}{k^{-}_{\mathrm{Ni_3Al}}}\right)^{n} \\ & \times \left[\frac{k^{+}_{\mathrm{NiAl}} k^{+}_{\mathrm{Ni_5Al_3}} + k^{-}_{\mathrm{Ni_5Al_3}} (k^{+}_{\mathrm{NiAl}} + k^{-}_{\mathrm{NiAl}})}{k^{-}_{\mathrm{Ni_2Al_3}} k^{-}_{\mathrm{NiAl}} k^{-}_{\mathrm{Ni_5Al_3}}} d^{0}_{\mathrm{Ni_2Al_3}}\right]^{2} \end{aligned} \tag{23}$$

For a coating with $d^{0}_{\mathrm{Ni_2Al_3}} = 10\ \mu\mathrm{m}$, by inserting respective $k^{+}_{\mathrm{Ni_2Al_3}}$, k^{+}_{NiAl}, k^{-}_{NiAl} values determined at 650 °C in this study into Eq. 16, the time needed to completely consume the NiAl phase is estimated to be approximately 2567 h.

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