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Effect of a plated Fe–Cr–Ni alloy layer for rapid nitriding of invar

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The nitriding rate in a plated invar with an Fe–Ni–Cr alloy (face-centred cubic) layer were compared by optical microscopy with the rate in an unplated invar. In the plated invar rapid nitrogen diffusion was discovered. The plated layer plays a role in enhancing the nitriding rate. The result gives a solution for an abnormal enhancement nitriding rate in austenitic stainless steels. The enhancement is explained from the viewpoint of non-equilibrium thermodynamics.

1. Introduction

Abnormal enhancement nitriding rates in an austenitic stainless steel were reported by Lebrun *et al.* [1] and later confirmed by Edenhofer [2]. They attributed the phenomenon to a $\gamma \rightarrow \alpha$ transformation in the nitrided layer. They considered that chromium as alloying element reacted with nitrogen atoms to form nitrides during the nitriding and the nitrided layer was then changed to the Fe–Ni binary system containing the nitrides with α-phase, and mentioned that the α-phase brought about the enhancement of the nitriding rate because the diffusion rate in α-phase is about 100 times greater than that in γ-phase at 773 K [3]. In 1985 Billon and Hendry [4] postulated that an enhanced rate in AISI 316 stainless steel was a result of microcracks formed in the nitrided layer. They mentioned the mechanism that these cracks allowed ammonia gas into the nitrided layer, since nitrogen atoms have a shorter diffusion path than the net nitrided layer. That is, the enhancement of the rate was a deceptive appearance. Today the cause of the phenomenon has still not yet been clarified. Recent authors have presented a model for understanding the enhancement nitriding of austenitic stainless steels [5, 6]. It is that the decomposition of a nitrogen-supersaturated solid solution formed in SUS304-type stainless steel (18Cr–8Ni steel) brings about the enhancement of the rate, and, after the decomposition, this solid solution is recovered by new diffused nitrogen atoms which are supplied by the dissociation of ammonia molecules at the surface of the steel. Repeating the decomposition and recovery, enhancement will continue in the steel. If this model is correct a thin austenite stainless steel layer plated on an alloy (e.g. invar) will bring about an acceleration of nitrogen diffusion, and this effect then ought to extend into the core of the alloy. The aim of this investigation was to verify this model experimentally.

2. Experimental

2.1. Preparation of specimens

An invar 22 mm in diameter (Ni 35.72%, Mn 0.57%, Si 0.14%, C 0.007%, Co 0.02% and Fe balance) was used. After hydrogen-annealing at 1173 K for 7.2 ks, discs of approximately 1 mm thickness were sliced out as specimens. These were polished on metallographic paper to a fineness of 1000 and degreased as follows: wiped with a cloth dipped in trichloroethane, washed in this vapour and finally treated in an ultra-supersonic bath with clean acetone. These discs were immediately plated with Fe–Cr–Ni ternary alloy in a plating bath according to the method of Takahashi *et al.* [7]. After plating these specimens were annealed again in hydrogen at 1423 K for 3.6 ks. The chemical composition of the plating bath used and plating conditions are shown in Table I.

Fig. 1 shows a typical scanning electron microscopy (SEM) micrograph of the as-plated invar, together with the line analysis image of Fe, Cr and Ni. Based on Fig. 1, a 3 μm layer is formed on the invar. From comparison of the count numbers of FeK_α, CrK_α and NiK_α X-rays between SUS304 steel and the plated layer upon measurement under the same conditions, it is shown that this layer consists of a composition near that of SUS304 steel. Fig. 2 shows an X-ray diffraction pattern of the layer plated on a low-carbon steel after annealing at 1273 K for 3.6 ks in hydrogen. Clearly, an austenitic phase is detected together with α-Fe. These results show that the plated layer consists of an austenite stainless steel layer.

2.2. Nitriding

All specimens were nitrided in the temperature range 723–873 K for 3.6–25.2 ks in an ammonia gas atmosphere after pretreatment by ammonium chloride vapour for surface activation of the alloy using a quartz reaction tube 40 mm in diameter fitted in a vertical electric furnace. The furnace temperature was controlled by an automatic thermocontroller. The temperature of the specimen was measured with a calibrated chromel–alumel thermocouple next to the specimen. After nitriding a section of the specimens

TABLE I Composition of plating bath used and plating conditions

Composition	(kmol m^{-3})	Conditions	
$CrCl_3$	0.50	Current density	2 kA m^{-2}
$FeCl_2$	0.15	Bath temperature	293 K
$NiCl_2$	0.15	pH	2.0
NH_4Cl	4.00	Plating time	180 s

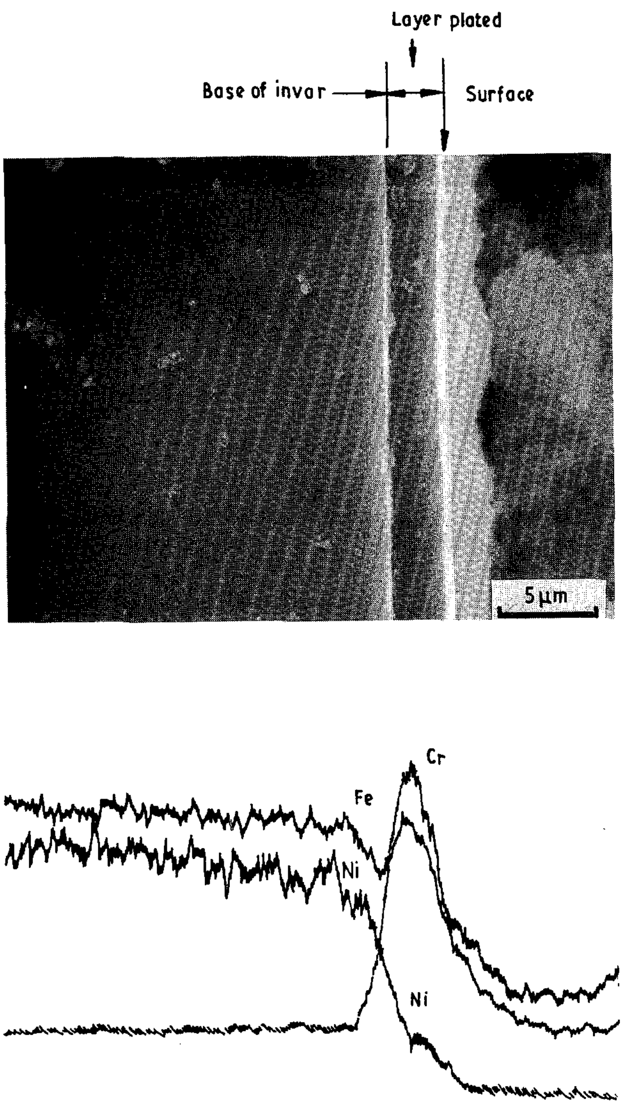

Figure 1 SEM micrograph of the Fe–Cr–Ni alloy plated invar with line analysis profiles of FeK_α, CrK_α and NiK_α X-rays.

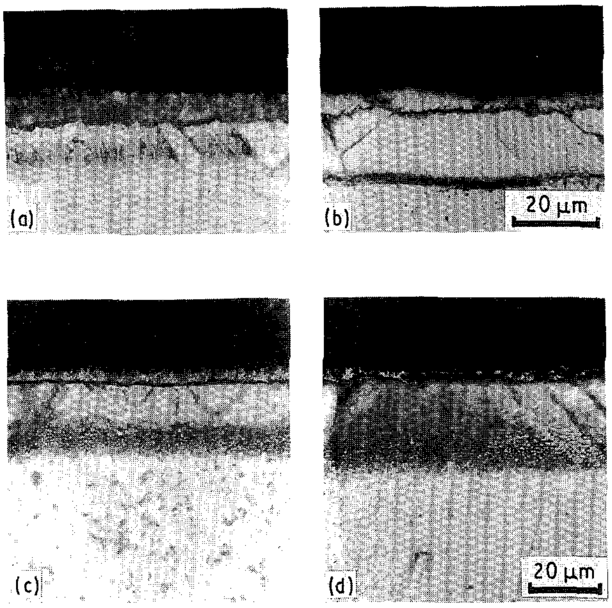

Figure 3 Micrographs of (a and c) unplated invars and (b and d) plated invars nitrided at 723 and 773 K for 10.8 ks. (a and b) Nitrided layers formed at 723 K, (c and d) those formed at 773 K.

treated metallographically was observed by optical microscopy. A diluted marble reagent (25 ml saturated aqueous $CuSO_4$ + 50 ml concentrated aqueous HCl) with ethanol was used as etchant. X-ray diffraction (XRD) analysis by use of a cobalt target was performed.

3. Results

Fig. 3 shows the optical microstructures of the nitrided specimens of the plated and unplated invar at 723 and 773 K for 10.8 ks, respectively. Fig. 3a and c shows the nitrided structure of the unplated invar, and Fig. 3b and d that of the plated invar. The nitrided layer shown in a and b were formed at 723 K, and those shown in c and d at 773 K. These layers consist of duplex layers. A primary layer is formed under the alloy surface and a secondary layer is formed beneath the primary layer. It is clearly shown that the thickness of total nitrided layers formed in the plated invar was thicker than that formed in the unplated invar. In

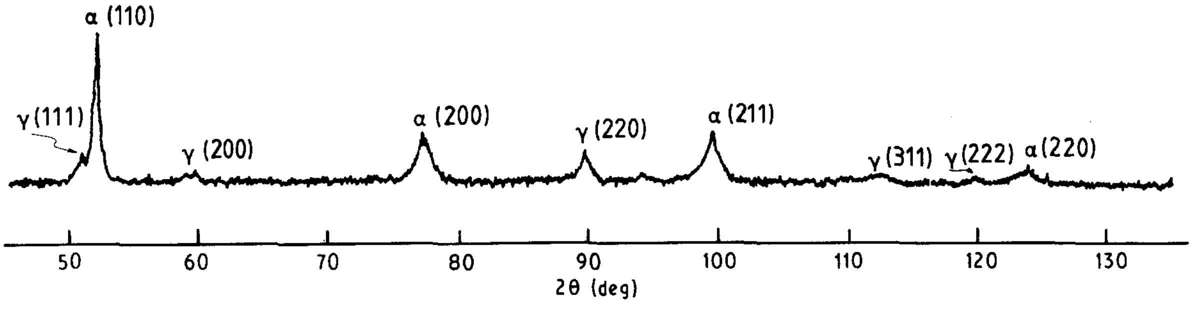

Figure 2 XRD pattern obtained from an Fe–Cr–Ni layer plated on a low-carbon steel after hydrogen annealing at 1423 K for 3.6 ks.

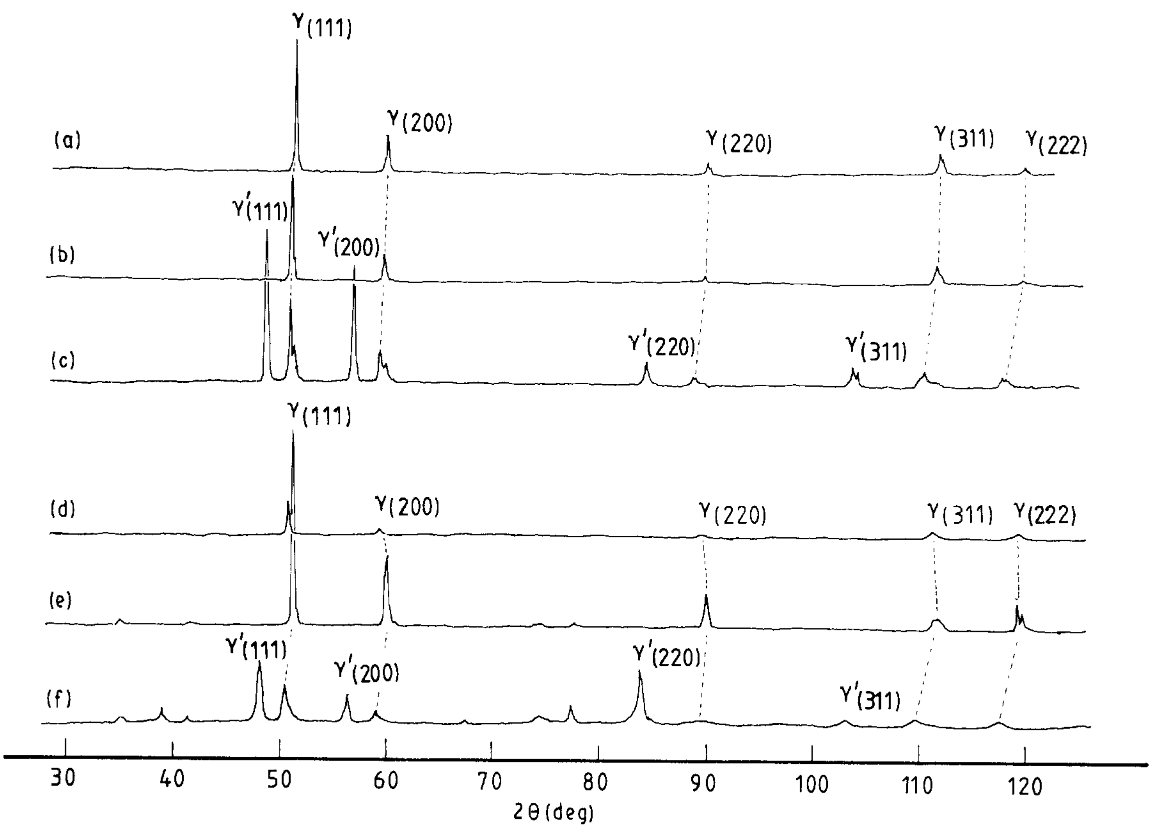

Figure 4 XRD patterns obtained from the surfaces of various invar specimens. (a) As-received invar, (b) hydrogen-annealed specimen of (a), (c) nitrided specimen (b), (d) plated invar, (e) hydrogen-annealed specimen of (d) and (f) nitrided specimen of (e).

the thickness of the secondary layer this contrast was more clearly seen. Fig. 4a to f shows XRD patterns obtained from the surface of various specimens. Fig. 4a is a result obtained from the as-received invar. An austenitic phase was detected. Fig. 4d was obtained from a plated invar. An austenitic phase was again detected but the diffracted X-rays were weakened. Hydrogen annealing causes the appearance of an austenitic phase as shown in Fig. 4e. The nitriding causes two effects in both specimens, as shown in Fig. 4c and f; one is the formation of an γ'-(Fe_4N)-type nitride and the other is a shift of the austenite peaks to the lower-angle side of the 2θ co-ordinate. In Fig. 4f the peaks diffracted from the γ'-(Fe_4N) and the austenite are broadened in width and shifted to the lower-angle side more than the peaks shown in Fig. 4c. Thus, γ'-(Fe_4N) and austenite phases were detected in Fig. 4f, but no chromium nitrides (Cr_2N and CrN) were detected. Other peaks in Fig. 4f may be from diffraction from oxides formed by the cooling process.

Figs 5 and 6 show the change in the thickness of the total nitrided layer, ξ, against the nitriding times, t, for the plated and unplated invar in temperature range 723–873 K, respectively. Upon nitriding at 723 K for 25.2 ks, a layer of thickness 29 μm is formed in the plated invar whereas one of thickness only 18 μm is formed in the unplated invar. Layers 94 and 91 μm thick are also formed in these specimens at 873 K for 25.2 ks, respectively. This result shows that the plated layer on the invar has an acceleration effect for nitrogen diffusion in the alloy. This effect appears more distinctly at low-temperature nitriding at 723 K.

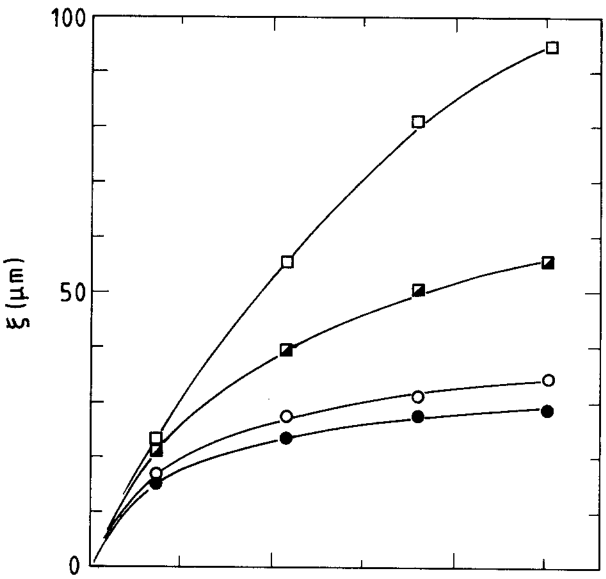

Figure 5 Total thickness of the nitrided layer versus nitriding times for the plated invar nitrided at 723–873 K in ammonia: (●) 723, (○) 773, (◪) 823 and (□) 873 K.

Fig. 7 shows the change in the total thickness of the nitrided layer plotted against the square root of the nitriding times, $t^{1/2}$, for both specimens. In the figure two different types of parabolic rate mechanism are shown for both specimens at times < 10.8 and > 10.8 ks. At > 10.8 ks both rates are decreased.

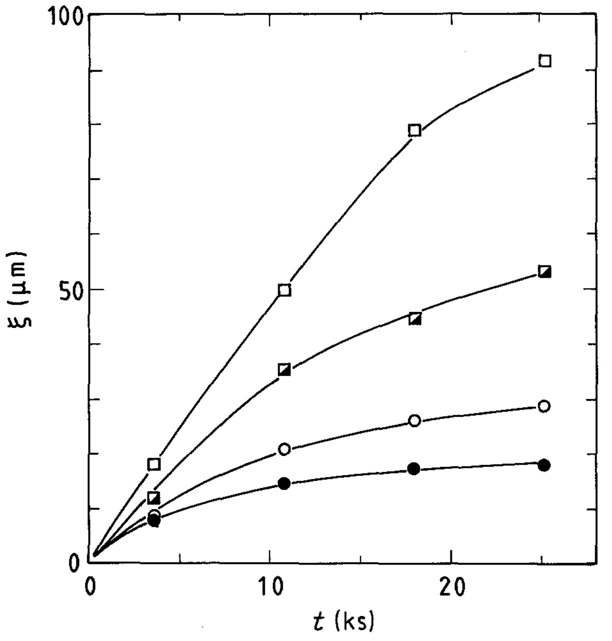

Figure 6 Total thickness of the nitrided layer versus nitriding times for the unplated invar nitrided at 723–873 K in ammonia: (●) 723, (○) 773, (◪) 823 and (□) 873 K.

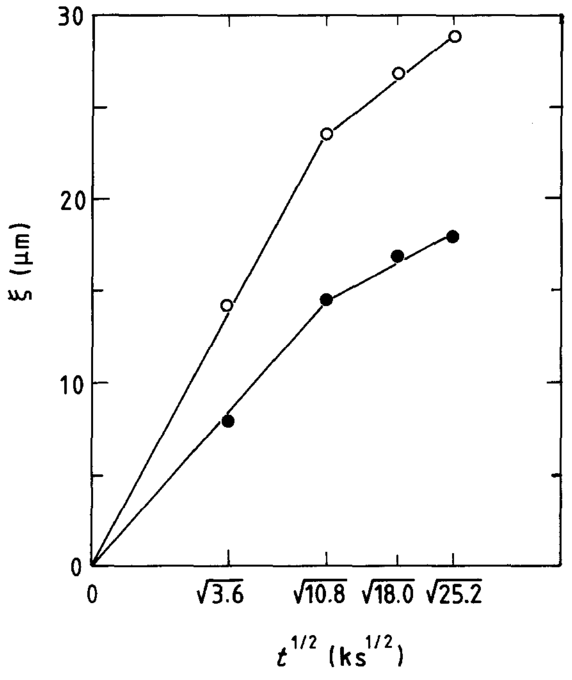

Figure 7 Total thickness of the nitrided layer versus square root of nitriding times for (●) the unplated and (○) the plated invar which were nitrided at 723 K for 3.6–25.2 ks in ammonia.

Similar decreasing have been reported in the nitriding of some austenitic stainless steels [8, 9], but no reasons have been given for the decrease. In this work the acceleration of nitrogen diffusion in the plated invar was discovered, and this result gives an understanding of the abnormal enhancement nitriding rate in austenitic stainless steels from that based on the presented model described previously.

4. Discussion

Symbolizing by $D^{\mathrm{N}}_{\mathrm{PLT}}$ and $D^{\mathrm{N}}_{\mathrm{INV}}$ the diffusion coefficients of nitrogen in a plated layer and bulk of invar, respectively, and by ξ_{PLT} and ξ_{INV} the thickness of the nitrided layer formed in a plated and unplated specimen under the same conditions, respectively, $D^{\mathrm{N}}_{\mathrm{PLT}} > D^{\mathrm{N}}_{\mathrm{INV}}$ naturally brings the result $\xi_{\mathrm{PLT}} > \xi_{\mathrm{INV}}$, but a difference of $\Delta\xi$ ($= \xi_{\mathrm{PLT}} - \xi_{\mathrm{INV}}$) will always be less than the thickness of the plated layer. Only when $D^{\mathrm{N}}_{\mathrm{PLT}} = \infty$ will $\Delta\xi$ be able to have the same thickness as the plated layer, because the delay of nitrogen diffusion in the layer becomes zero. However, there will be no such case in actuality. On the other hand, when $\Delta\xi$ has a greater width than the thickness of the layer (for example, the result shown in Fig. 7), it is suggested that an immediate cause for the effect exists in the plated layer. Recently the formation of a very high nitrogen content layer, which contained as much as 33–38 at % nitrogen, was reported in the low-temperature nitriding of austenitic stainless steels [5, 6, 10]. With respect to the layer, it was established by thermogravimetry and gas chromatography that this layer discharged a considerable amount of nitrogen gas at a temperature of approximately 673 K, and by X-ray diffractometry that the layer decomposed into CrN and γ'-(Fe,Ni)$_4$N phases [6]. Under nitriding, repeating the decomposition and recovery of the nitrogen-supersaturated solid solution in the plated layer as described previously, the free energy of the decomposition will bring about local temperature rises in the nitrided layer. If there is some coprecipitated nitrogen atoms which are discharged as nitrogen gas, as noted above, a portion of the free energy will contribute to the activation of these atoms. This mechanism will turn the atoms into an abnormal supersaturated state, because CrN and γ-(Fe,Ni)$_4$N phases hardly solute the nitrogen atoms. Under such abnormal conditions these atoms will be carried into a very high entropy level with some disturbances (precipitation, local temperature rises, lattice distortion, etc.). This condition is a particular state in comparison with the general diffusion control system for interstitial atoms. Based on non-equilibrium thermodynamics theory, all disturbances that are brought about by irreversible processes always accompany entropy production [11, 12]. It is possible to add the entropy to the term of activation entropy in the Arrhenius equation for the diffusion process. In the following section the enhancement of the interstitial diffusion is discussed from viewpoint of the activation entropy rising.

4.1. Entropy production and activation entropy for diffusion

Based on Wert and Zener [13], the relationship between the diffusion coefficient and temperature for the soluted atoms in the solid metals is given by

$$D = n\alpha a^2 \nu \exp(\Delta S/R) \exp(-\Delta H/RT) \quad (1)$$

where n and α are constants determined by the given lattice, a is the lattice constant, ν is the frequency of thermal vibration of the solute atoms in the interstitial positions, R is the gas constant, and ΔS and ΔH denote the activation entropy and enthalpy for the diffusion, respectively. In a given crystal lattice n, α, a and ΔH are constants and these are hardly influenced by chemical reactions such as precipitation in the nitrided layer. ΔS and ν are generally treated as constants in a narrow temperature range. However they will be influenced by the reaction as noted above. In the nitriding of the austenitic stainless steels, the nitrogen diffusion coefficient in the steels, $D^{\mathrm{N}}_{\mathrm{AUS}}$, was estimated to be a factor of about 100 higher than in γ-iron [3, 4]. In this diffusion process, supposing ν to be hardly influenced by the reaction, the increase of $D^{\mathrm{N}}_{\mathrm{AUS}}$ depends on the increase of ΔS.

In the nitriding of the invar, the following equation can be applied for the growth of the nitrided layer on the basis of Equation 1:

$$D^{\mathrm{N}}_{\mathrm{INV}} = A\exp(\Delta S_{\mathrm{ACT}}/R)\exp(-\Delta H/RT) \quad (2)$$

where $D^{\mathrm{N}}_{\mathrm{INV}}$ is the nitrogen diffusion coefficient in the nitrided layer formed in the invar and ΔS_{ACT} is the activation entropy for nitrogen diffusion in the layer. The term A is the product of n, α, a and ν. Equation 2 can also be applied to the growth of the secondary layer in the unplated invar as shown in Fig. 3a and c, but cannot be applied to the growth of the layers of the plated invar as also shown in Fig. 3b and d. Because the layers in Fig. 3b and d are thicker than in Fig. 3a and c, for such a growth mechanism of the layer in the plated invar, adding the entropy production, ΔS_{PRO}, to ΔS_{ACT} in Equation 2, gives

$$D^{\mathrm{N}}_{\mathrm{PLT}} = A\exp[(\Delta S_{\mathrm{ACT}} + \Delta S_{\mathrm{PRO}})/R]\exp(-\Delta H/RT) \quad (3)$$

where $D^{\mathrm{N}}_{\mathrm{PLT}}$ is the nitrogen diffusion coefficient in the plated invar. ΔS_{PRO} being estimated from all disturbances taking place in the plated layer under nitriding as mentioned previously. It is therefore considered that Equation 3 can be applied for the nitriding of the plated invar. In the carburizing of steels the depth of the carburized layer, ξ_c, is generally estimated from [14, 15]

$$\xi_c^2 = 4D_c t \quad (4)$$

where D_c is the diffusion coefficient of carbon in the carburized layer.

A similar relationship can be applied for the nitriding process in this experiment. Then

$$\xi^2_{\mathrm{INV}} = 4D^{\mathrm{N}}_{\mathrm{INV}}\,t \quad (5)$$

$$\xi^2_{\mathrm{PLT}} = 4D^{\mathrm{N}}_{\mathrm{PLT}}\,t \quad (6)$$

are introduced. From these relationships a rough estimate for ΔS_{PRO} from the measurement of ξ_{INV} and ξ_{PLT} is made as follows:

$$\begin{aligned}\xi^2_{\mathrm{PLT}}/\xi^2_{\mathrm{INV}} &= 4D^{\mathrm{N}}_{\mathrm{PLT}}t/4D^{\mathrm{N}}_{\mathrm{INV}}t \\ &= D^{\mathrm{N}}_{\mathrm{PLT}}/D^{\mathrm{N}}_{\mathrm{INV}} \quad (7)\end{aligned}$$

Substituting Equations 2 and 3 into $D^{\mathrm{N}}_{\mathrm{INV}}$ and $D^{\mathrm{N}}_{\mathrm{PLT}}$

$$\begin{aligned}(\xi_{\mathrm{PLT}}/\xi_{\mathrm{INV}})^2 &= \exp[(\Delta S_{\mathrm{ACT}} + \Delta S_{\mathrm{PRO}})/R)]/ \\ &\exp(\Delta S_{\mathrm{ACT}}/R) = \exp(\Delta S_{\mathrm{PRO}}/R) \quad (8)\end{aligned}$$

therefore

$$\Delta S_{\mathrm{PRO}} = 2R\ln(\xi_{\mathrm{PLT}}/\xi_{\mathrm{INV}}) \quad (9)$$

Now, denoting the average thickness of the secondary layer formed in the plated and unplated invar as ξ_{PLT} and ξ_{INV}, respectively, at 723 K $\xi_{\mathrm{PLT}} = 10.8\ \mu$m and $\xi_{\mathrm{INV}} = 6.4\ \mu$m are obtained from Fig. 2. At 773 K $\xi_{\mathrm{PLT}} = 26.9\ \mu$m and $\xi_{\mathrm{INV}} = 20.0\ \mu$m are also obtained. Substituting these values into Equation 9, ΔS_{PRO} are calculated as approximately 2.1 cal $\mathrm{deg}^{-1}\,\mathrm{mol}^{-1}$ at 723 K and 1.1 cal $\mathrm{deg}^{-1}\,\mathrm{mol}^{-1}$ at 773 K.

In the above treatment, although the increase in ν is omitted, all disturbances induced by the chemical reaction in the nitrided layer are included in ΔS_{PRO}.

Guiraldenq [16] enumerated some forced diffusions and interpreted them briefly. These are enhanced by an influence of the electric field, a temperature and chemical potential gradient, etc. In contrast with these factors the enhancement of nitrogen diffusion observed in the present experimental results is clearly taking place due to a new factor; that is, an effect of the plated layer. Furthermore, there is no paper on the effect that a plated layer on metals and alloys plays a role in the acceleration of the interstitial diffusion of atoms (e.g. nitrogen and carbon). It is therefore concluded that the abnormal enhancement of nitriding rate in austenitic stainless steels is also taking place because of the same factor. Furthermore, it is evaluated that nitrogen diffusion rates in these stainless steels are too fast in comparison with the enhanced rate by the enumerated factors [16]. From these viewpoints, this phenomenon must be classified as a new kind of enhancement diffusion.

5. Conclusion

In nitriding of plated invar with an Fe–Cr–Ni alloy (fcc) layer, an acceleration of nitrogen diffusion was observed. This verifies the model that a cyclic mechanism of formation and decomposition of the nitrogen-supersaturated solid solution in the austenitic stainless steels brings about the abnormal enhancement nitriding rate. Furthermore, no papers have been published on the phenomenon of nitrogen diffusion in an alloy being accelerated by such a plated layer. This phenomenon must be classified as a new kind of enhancement diffusion and must be explained on the basis of the theory of non-equilibrium thermodynamics. In the theory, this phenomenon can be discussed from the concept of entropy production, and the contribution of the entropy for the acceleration of nitrogen diffusion in a plated invar can be estimated experimentally to make a comparison between the thickness of the nitrided layers formed in the plated and unplated invar. The approximate values of the entropy production at two temperatures were calculated in this paper.

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