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A new perspective for rapid nitriding in high Cr austenitic steels

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1. Introduction

Anomalous nitriding behaviour in austenitic stainless steels has been investigated by many metallurgists [1–14]. The anomalies can be summarized as follows:

(i) a decrease of the nitriding rate between approximately 873 and 923 K [1–3].
(ii) a rapid nitriding between the 773 and 873 K [1, 2].
(iii) a change in rate kinetics at approximately 700 K [4, 7, 8].
(iv) a decrease in the temperature dependence of the rate below 700 K [7, 8].

In addition, a novel and important experimental result for the understanding of the rapid nitriding has been reported. It was found that a plated Fe–18Cr–9Ni layer on an invar yielded a deep nitrogen migration in the substrate, thicker than that in an unplated invar under the same nitriding conditions [9]. The phenomenon is illustrated in Fig. 1A–C, using results obtained by a new experiment. The maximum nitrogen migration depth is clearly seen in the specimen C. On the other hand, the migration depth in the invar with Fe–10Cr–10Ni plating is thin, less than that in unplated invar. Fig. 1A–C indicates that nitrogen atoms diffused with different velocities at the same temperature in the same crystal lattice of the invar. Therefore a driving force to accelerate the nitrogen diffusion appears to be associated with the Fe–18Cr–9Ni plating layer. On the other hand, the Fe–10Cr–10Ni layer appears to provide no such force. In general, the nitrogen migration depth in the substrate invar with the plated layer would always be expected to be less than that in unplated invar because there is a time-lag associated with a diffusion path through the plated layer. The results shown in Fig. 1 are contrary to the prediction of the theory.

In another experimental result, an austenitic Fe–Cr–Ni alloy containing up to 16 mass% Cr was aoso found to exhibit show rapid nitriding. When the Cr content was less than 13%, the thickness of the nitrided in these steels layer was found to be not only thinner than that in the 16 mass% Cr steel but was inversely proportional to the Cr content. This results is consistent with internal nitiding theory [12].Thus different nitriding mechanisms, the rapid nitriding and the internal nitriding, were observed in austenitic Fe–Cr–Ni alloys between 13 and 16% Cr.

What are the nitrogen diffusion kinetics in the nitrided layer of high Cr austenitic steels? In our previous paper the rapid nitriding was discussed from the standpoint of the contribution of entropy production to activation entropy in terms of Arrhenius equation [9]. To further this investigation, new experimental results are shown in Fig. 2. The thickness of nitrided layer (ξ) vs temperature (T) in various high Cr high M austenitic steels (M = Ni, Mn & Pt) and a dual phase stainless steel showed all the anomalies summarized above in spite of the austenite former elements are different. In particular, the initial temperature of the rapid nitriding agreed closely at 740 K even in the dual phase steel, however the temperature of the Pt alloying steel was shifted to just below 800 K. It is noted that 740 K approaches the intersection temperature (T_c; 703 K) of the free energies of Cr_2N and CrN on a $T - \Delta G^\circ$ diagram. Thus it is clear that the Cr will play a major role in the rapid nitriding and for all the anomalies. At present there are a number of theories which address the rapid nitriding [1–3, 5, 8], however, these are not satisfactory to explain all the phenomena (i)–(iv).

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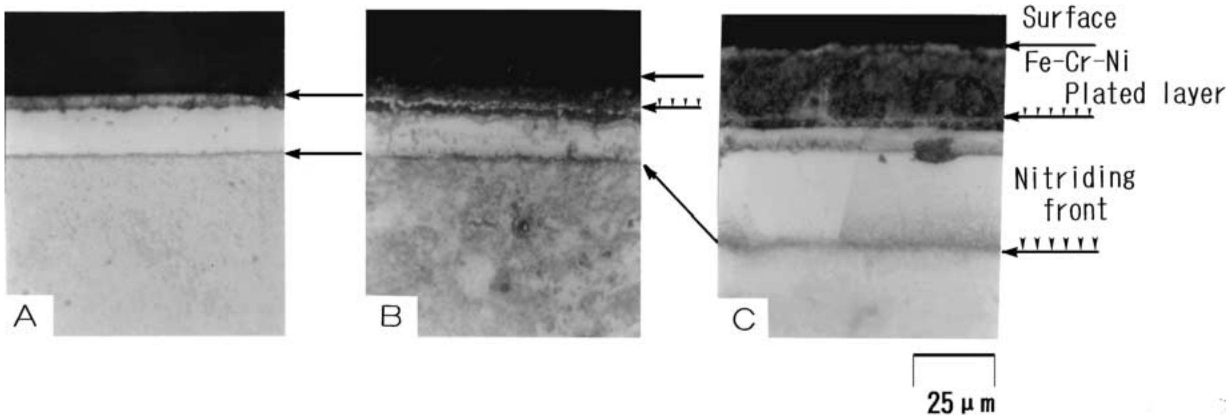

Figure 1 Optical microphotographs of unplated and the austenitic Fe–Cr–Ni plated invars nitrided at 823 K for 18.0 ks. (A) unplated invar, (B) the Fe–10Ni–10Cr plated invar, (C) the Fe–18Cr–9Ni plated invar.

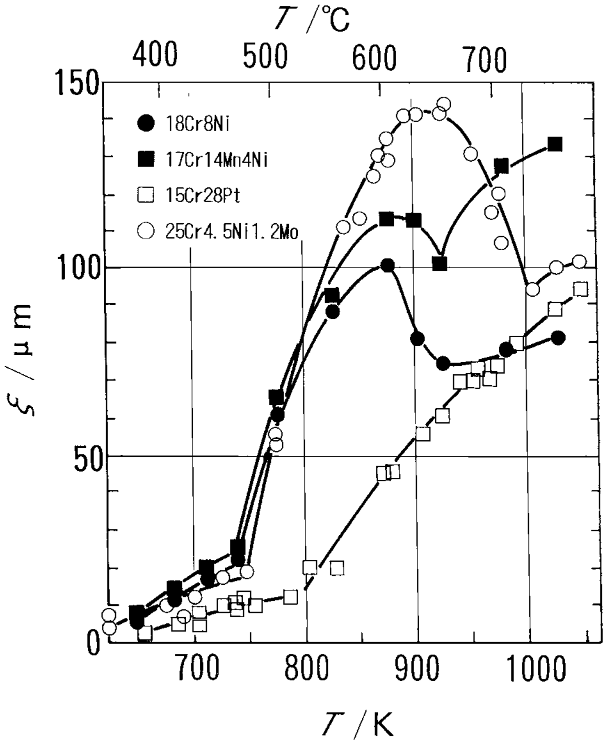

Figure 2 Temperature dependence of nitrided layer thickness formed in various high Cr austenitic steels. ●; 18Cr–8Ni steel (a type 304 stainless steel), ■; 17Cr–14Mn–4Ni steel (a non-magnetic steel), □; 15Cr–28Pt steel (an argon arc smelted specimen) ○; 25Cr–4.5Ni–1Mo steel (a dual phase stainless steel).

In the temperature range below the T_c, a face centered crystal phase (γ_{SN}) with an extremely high nitrogen concentration of 30–38 atomic% has been found to be stable [6], and the rate of nitriding showed a slowing down with rising temperature. Thus the nitriding mechanism of the austenitic stainless steels changes suddenly at the Tc in the manner of a phase transition.

The γ_{SN} phase may also form as a metastable phase in the area of the rapid nitriding at a temperature of 773 K [7]. In this paper the kinetics of the rapid nitriding are discussed from accumulated and established experimental results reported by many investigators. The important results are summarized as follows;

1. A nitride-free phase with an extremely high nitrogen content (approximate 30–38 atomic%) and a face centered lattice is formed stably on the surface of the austenitic stainless steels below 700 K [6, 7, 14].
2. This phase is also formed meta-stably as a solid solution (meta-γ_{SN}) between the temperatures of 773 and 873 K in which the rapid nitriding is taking place [6, 7, 12].
3. The formation of the meta-γ_{SN} is confined to the surface during the nitriding in an ammonia atmosphere [7, 12].
4. Ammonia gas has a giant fugacity of nitrogen evaluated as approximately 10^{5-6} MPa (calculated from the equilibrium constant of ammonia at 773 K [15–18]).
5. Under the nitrided surface the meta-γ_{SN} phase is cut off from ammonia, and CrN and $\gamma' - M_4N(M = Fe, Ni)$ are precipitated in the layer in the temperature range of 723 to 873 K [1, 5, 7].
6. The meta-γ_{SN} phase is adequately stabilized as a face centered lattice by the diffused nitrogen because nitrogen is a very strong austenite-forming element.

Here, two important relations are noted for further discussion. The first is that between the giant fugacity of ammonia and the formation of the meta-γ_{SN} phase; the second is between the nitriding temperature and the precipitating tendency in the meta-γ_{SN} phase cut off from the ammonia.

2. Theoretical background and metallugical phenomena

2.1. Inverted population of nitrogen in the meta-γ_{SN} phase

Haken has discribed the phenomenon of lasing (i.e., light amplification by stimulated emmision) as a system lying on the borderline between a natural system and a man-made device based on the concept of synergetics [19]. An inverted population of atomic electrons lying in energy levels above the ground state leads to the laser phenomenon. The laser can be described as a system far from thermal equilibrium. A supersaturated state in a solid solution is also such a system, because a precipitation would take place under thermodynamic equilibrium. Therefore the state is looked as a kind of inverted population in chemical potential, and the precipitation is taking place spontaneously from a high potential to an equilibrium state. This change terminates in only one irreversible step.

On the other hand rapid nitriding is known to proceed continuously during the gas and plasma nitriding, that is, the rapid nitrogen diffusion mechanism is maintained in the meta-γ_{SN} phase under the processsing. These continual kinetics are dealt with in this paper from a new viewpoint of synergetics.

For understanding the continuity, "Rückbildung" defined as reversion in age hardening alloys [20, 21], is here introduced as a key phenomenon for the rapid nitriding. The reversion is known as redissolution of the Guinier–Preston zone (G. P. zone) by reheating near/below a solvus of the alloys. Quenching the redissolved state once more, a new G. P. zone is formed again in the alloys [22, 23]. The cycle of reheating and quenching yields repetition of the redissolution and formation of the G. P. zone. On the other hand, the meta-γ_{SN} phase is always elevated into a thermodynamic state in which not only nitirides of chromium and iron but also their G. P. zones are formed. At the same time the state will allow the redissution of the G. P. zones due to the surrounding of extremely high nitrogen concentration at nitriding temperatures such as 823 K.

When a high chromium austenitic alloy is exposed under a giant nitrogen fugacity, the fugacity will always act as a strong pump suppling nitrogen to the surface of the alloy, and form the meta-γ_{SN} phase with a N content of 30 atomic% and up. Under these conditions, precipitation and redissolution of the G. P. zone will be take place cyclically in the phase during the nitriding. This is a model presented for the rapid nitriding of the austenitic stainless steels.

Fig. 3 shows an inverted population model for the nitrogen potential in the nitrided layer, analogous to a laser model. Electron energy levels are discontinuous in an atom; however, the nitrogen potential in the meta-γ_{SN} phase will change continuously and gradually in the shadowed area in Fig. 3. The potential is always maintained by pumping of the giant fugacity of ammonia. A ground state of the potential refers to the austenitic steel equilbriated to 0.1 MPa of nitrogen pressure (1 atm of N_2; $\mu N = 1$). From this background a concept of the inverted population of nitrogen potential is here developed. Reactions in Fig. 3 are written as follows;

$$[\text{Fe–18Cr–9Ni}]_{\text{AUS}} + \text{NH}_3 \rightarrow [\gamma_{\text{SN}}]_{\text{META I}} \qquad \Delta h_1 \qquad (1)$$

$$[\gamma_{\text{SN}}]_{\text{META I}} + \text{NH}_3 \rightarrow [\text{Cr–N}]_{\text{CLUS}} \qquad \Delta h_2 \qquad (2)$$

$$h[\text{Cr–N}]_{\text{CLUS}} + \text{i}\underline{\text{N}} \rightarrow \text{j}[\text{Cr–N}]_{\text{cri}}(h > 2,\ h > i) \qquad \Delta h_3 \qquad (3)$$

$$j[\text{Cr–N}]_{\text{cri}} \rightarrow [\text{Cr} \cdot \text{N}]_{\text{GP}} + \text{x}\underline{\text{N}}^* \qquad \Delta h_4 \qquad (4)$$

$$[\text{Cr} \cdot \text{N}]_{\text{GP}} + \underline{\text{N}} \rightarrow [\text{Cr–N}]_{\text{CLUS}} \qquad \Delta h_5 \qquad (5)$$

$$[\text{Cr} \cdot \text{N}]_{\text{GP}} + \underline{\text{N}} \rightarrow [\gamma_{\text{SN}}]_{\text{META II}} \qquad \Delta h_6 \qquad (6)$$

$$[\text{Cr} \cdot \text{N}]_{\text{GP}} \rightarrow \text{CrN} + \gamma' - \text{M}_4\text{N} + \text{z}\underline{\text{N}}^* \qquad \Delta h_7 \qquad (7)$$

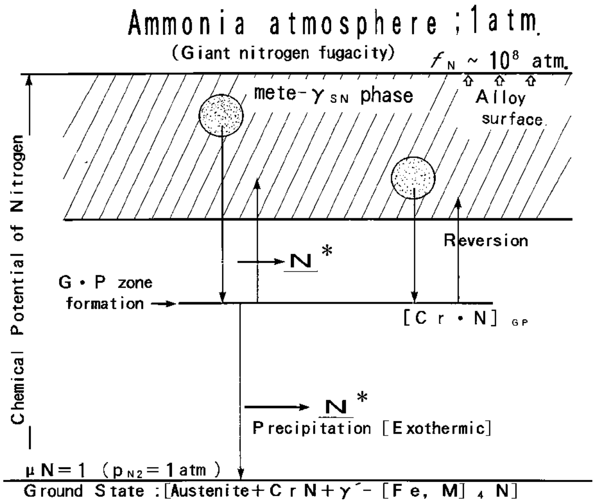

Figure 3 A model for rapid nitriding of austenitic stainless steel in 1 atm. (0.1 MPa) of ammonia, illustrated by analogy with a simple mode of laser action. Nitrogen concentration at the surface of the alloy is elevated from a ground state of the alloy's matrix to a remarkable nitrogen supersaturated state (the meta-γ_{SN} phase up to 30 atomic%N) by pumping of the giant nitrogen fugacity of ammonia. The fugacity maintains steadily the phase (shadowed zone). At the same time G. P. zones, $[\text{Cr} \cdot \text{N}]_{\text{GP}}$, are formed locally and randomly in the shadowed area. The high chemical potential at the local portion will drop to a lower level such as precipitating the G. P. zone with accompanying generation of a $\underline{N}^*$ as shown in the figure. The $\underline{N}^*$ is excited thermally because the formation of a G. P. zone is generally exothermic. At the step, the G. P. zones are recovered by reversion to a new meta-γ_{SN} phase. At the moment of the reversion, a simultaneous formation of new G. P. zones will take place at different portions in the phase. Thus presuming the giant nitrogen fugacity of ammonia, and the inverted population of chemical potential of nitrogen on/below the surface of the alloy, and further reversion of the G. P. zones formed in the phase, the rapid nitriding in austenitic stainless steels is analogous to sipmle model of laser action.

where $[\text{Fe–18Cr–9Ni}]_{\text{AUS}}$ and $[\gamma_{\text{SN}}]_{\text{META}}$ show type 304 austenitic steel and the meta-γ_{SN} phase, respectively. The subscript number of the $[\gamma_{\text{SN}}]_{\text{META}}$ gives an individual nitrogen concentration. $[\text{Cr–N}]_{\text{CLUS}}$ means a cluster of Cr–N_X ($x > 1$) formed in the meta-γ_{SN} phase. Formula (4) is just the reaction for the rapid nitriding; $[\text{Cr–N}]_{\text{cri}}$ means the cluster has reached a critical condition to decompose itself into a G. P. zone, $[\text{Cr} \cdot \text{N}]_{\text{GP}}$, with $\underline{N}^*$.The $\underline{N}^*$ is a some of nitrogen atom precipitated around the $[\text{Cr} \cdot \text{N}]_{\text{GP}}$. Since N contents of 30 atomic% and up in the meta-γ_{SN} phase are stoichiometric excess over the $[\text{Cr} \cdot \text{N}]_{\text{GP}}$, a small amount of x$\underline{N}^*$ is probably generated exothermically with Δh_4 . Hence the $\underline{N}^*$ will be excited by the enthalpy, and will diffuse rapidly. Among reaction (1) and (3), nitrogen potential in the layer is greatly elevated by pumping of the giant nitrogen fugacity of ammonia from a ground state to the meta-γ_{SN} phase. The state is maintained just under the surface of the layer involving a driving force of the precipitation of nitrides during the nitriding. The driving force proceeds via reactions (4) and (7), and the $\underline{N}^*$ will be generated. Reactions (5) and (6) are of the reversion. Reaction (7) is precipitation of nitrides in the inner area of the layer with z$\underline{N}^*$, however, the reaction is irreversible. New experimental results on the growth of a nitrided layer on type 304 steel have been obtained. The dependence of the nitrided layer growth rate on NH_3 (pNH_3) on type 304 steel in a NH_3–H_2 atmosphere is shown in Table I. The rate was proportional to the pNH_3. The data show that the nitriding rate constant was highly dependent on the pNH_3 at constant temperature. This is an important result to understand the rapid nitriding in the austenitic stainless steels reported by Lebrunet *et al.* [1] and Edenhofer [2]. If plasma nitriding had been carried out under various

TABLE I Dependence of nitrided layer growth on $p\mathrm{NH_3}$ for SUS304 austenitic steel in $\mathrm{NH_3}$–$\mathrm{H_2}$ mixtures

	$p\mathrm{NH_3}$ (kPa)				
Nitriding; 823 K for 14.4 ks	0.5	1.0	3.0	5.0	10.0
Thickness of nitrided layer; $\xi(\mu\mathrm{m})$	5	9	22	31	68

nitrogen potentials, a thinner nitrided layer would have been observed at same temperature. Therefore the maximum thickness of the layer must be formed in 100% $\mathrm{NH_3}$. Thus the diffusion constant of nitrogen in γ-iron is unsuitable as a reference value for the rapid nitriding. Indeed Fig. 1 shows that the nitrogen diffused with a different velocity at the same temperature through the same invar sample.

The result in Table I is noticeable for the relation between the $p\mathrm{NH_3}$ (the activity of an adsorbed nitrogenous intermediate on the alloy surface) and the diffusion rate of nitrogen. It is estimated theoretically that the parabolic rate constant is proportional to the activity of the solute atom adsorbed on the surface of metals. The growth of the nitrided layer in austenitic stainless steels follows the parabolic rate law [5, 7]. Although carburizing of steels also follows the law, rapid carbon diffusion is hardly observed because the maximum activity (α) of carbon adsorbed on the steel surface is always $\alpha = 1$. Compared to the carburizing, the nitriding rate constant estimated from Table I clearly depended on the nitriding potential on the surface, related to the nitrogen fugacity of ammonia. This phenomenon is a rare and noticeable example.

Since chromium has a strong affinity for nitrogen, a cluster between these elements will be formed in the meta-γ_{SN} phase similar to the Al–N cluster formed in a steel pointed out by Darken [24]. Let us consider a number of a Cr–N cluster formed in the phase. The number will be proportional to the concentration of chromium in the steel. We will discuss the mechanism of the rapid nitriding based on the above considerations and experimental results.

2.2. Laser mode analogy for the rapid nitriding mechanism

As discussed above, the rapid nitriding will result from reaction (4). Namely, the generation of the $\underline{\mathrm{N}}^*$ determines the rate of the nitriding, however, the clustering of the $\mathrm{Cr}\cdot\mathrm{N_X}$ will be ahead of the generating of the $\underline{\mathrm{N}}^*$. Let us discuss the rapid nitriding considering the speed of formation of $[\mathrm{Cr–N}]_{\mathrm{cri}}$ from reaction (3) in analogy to the simple model of the laser [19]. Consider one chromium atom put under a diffusion flow of nitrogen in the meta-γ_{SN} phase as shown in Fig. 4. The nitrogen atoms passing by the Cr atom are attracted around the latter atom, and one cluster, Cr–N_X ($x > 1$), is formed. Aggregation of these clusters will make a certain $[\mathrm{Cr–N}]_{\mathrm{cri}}$ in the meta-γ_{SN} phase randomly. It is considered that the velocity of the formation of the $[\mathrm{Cr–N}]_{\mathrm{cri}}$ is proportional to the total number of the $[\mathrm{Cr–N}]_{\mathrm{CLUS}}$. The number must be proportional to the concentration of Cr and nitrogen in the meta-γ_{SN} phase. After all the generating velocity of the $\underline{\mathrm{N}}^*$ is proportional to the number

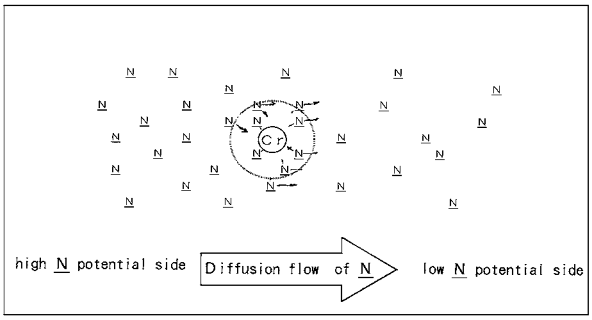

Figure 4 Illustration of clustering model of Cr–N_X ($x > 1$) under diffusion flow of $\underline{\mathrm{N}}$ in the meta-γ_{SN} phase; a dotted circle shows the cluster of Cr–N_X. $\underline{\mathrm{N}}$ atoms which flow near a Cr atom are attracted by the Cr, and a cluster of Cr–N_X is formed (gain). Some $\underline{\mathrm{N}}$ atoms in the cluster far from the Cr are often released from the attractive force, and these will flow away to the lower $\underline{\mathrm{N}}$ potential side of the core of the alloy (loss).

of the $[\mathrm{Cr–N}]_{\mathrm{cri}}$ in the phase. Consider the formation of the $[\mathrm{Cr–N}]_{\mathrm{CLUS}}$ given the symbol G_{CLUS}, as "gain".It is defined as

$$G_{\mathrm{CLUS}} = gc_{\mathrm{Cr\cdot Nx}} \cdot d_{\mathrm{N}} \cdot V_{\mathrm{N}} \tag{8}$$

where g is a coefficient of the gain, $c_{\mathrm{Cr\cdot Nx}}$ is number of $[\mathrm{Cr–N}]_{\mathrm{CLUS}}$, and d_{N} and V_{N} are of the density and diffusion velocity of nitrogen near the Cr atoms, respectively. The nitrogen which leaves the Cr is also proportional to the d_{N} and V_{N}. Thus "loss" of the $[\mathrm{Cr–N}]_{\mathrm{CLUS}}$ (symbol L_{CLUS}) is given as

$$L_{\mathrm{CLUS}} = \lambda d_{\mathrm{N}} \cdot V_{\mathrm{N}} \tag{9}$$

where λ is a coefficient of the loss. The velocity of formation of the $[\mathrm{Cr–N}]_{\mathrm{CLUS}}$ is written as

$$\begin{aligned} d[\mathrm{Cr–N}]_{\mathrm{cri}}/\mathrm{d}t &= G_{\mathrm{CLUS}} - L_{\mathrm{CLUS}} \\ &= gc_{\mathrm{Cr\cdot Nx}} \cdot d_{\mathrm{N}} \cdot V_{\mathrm{N}} - \lambda d_{\mathrm{N}} \cdot V_{\mathrm{N}} \end{aligned} \tag{10}$$

Setting the total number of $c_{\mathrm{Cr\cdot Nx}}$ before generating the $\underline{\mathrm{N}}^*$ as $c^0_{\mathrm{Cr\cdot Nx}}$, the decrease of the $c_{\mathrm{Cr\cdot N_x}}$, Δc becomes

$$\Delta c = c^0_{\mathrm{Cr\cdot Nx}} - c_{\mathrm{Cr\cdot Nx}} \tag{11}$$

The critical decomposing condition of the $[\mathrm{Cr–N}]_{\mathrm{cri}}$ is considered to be an inverted population state; such a state is released by generating the $\underline{\mathrm{N}}^*$ based on the system's tendency toward precipitation. Since the tendency is strengthened with increasing the nitrogen concentration, Δc is proportional to the d_{N} and V_{N}

$$\Delta c = \beta d_{\mathrm{N}} \cdot V_{\mathrm{N}} \tag{12}$$

where β is a constant. From Equations 10, 11 and 12,

$$\begin{aligned} d[\mathrm{Cr–N}]_{\mathrm{cri}}/\mathrm{d}t &= gc_{\mathrm{Cr\cdot Nx}} \cdot d_{\mathrm{N}} \cdot V_{\mathrm{N}} - \lambda d_{\mathrm{N}} \cdot V_{\mathrm{N}} \\ &= \left(gc^0_{\mathrm{Cr\cdot Nx}} - \lambda\right) d_N \cdot V_{\mathrm{N-g}} \beta d_{\mathrm{N}}^2 \mathrm{d} V_{\mathrm{N}}^2 \end{aligned} \tag{13}$$

Since $d_{\mathrm{N}} \cdot V_{\mathrm{N}}$ is the estimated diffusion flux of nitrogen, f_{N}

$$\begin{aligned} d[\mathrm{Cr—N}]_{\mathrm{cri}}/\mathrm{d}t &= -\left(\lambda - \mathrm{g}c^0_{\mathrm{Cr\cdot Nx}}\right) f_{\mathrm{N}} - \mathrm{g}\beta f_{\mathrm{N}}^2 \\ &= -\kappa f_{\mathrm{N}} - \kappa_1 f_N^2 \end{aligned} \tag{14}$$

$$\kappa = -\left(\lambda - \mathrm{g}c^0_{\mathrm{Cr\cdot Nx}}\right), \quad \kappa_1 = \mathrm{g}\beta \tag{15}$$

When $(\lambda - gc^0_{\mathrm{Cr}\cdot\mathrm{Nx}}) > 0$, $d[\mathrm{Cr{-}N}]_{\mathrm{cri}}/\mathrm{d}t < 0$, and the clustering becomes unstable. Hence no $[\mathrm{Cr–N}]_{\mathrm{cri}}$ is formed. As a result, no $\underline{\mathrm{N}}^*$ is generated [19]. On the other hand $(\lambda - gc^0_{\mathrm{Cr}\cdot\mathrm{Nx}}) < 0$ defines $d[\mathrm{Cr{-}N}]_{\mathrm{cri}}/\mathrm{d}t > 0$, because the formation of the $[\mathrm{Cr–N}]_{\mathrm{cri}}$ is warranted, and the rapid nitriding will take place. Clearly the $c^0_{\mathrm{Cr}\cdot\mathrm{Nx}}$ depends on the Cr concentration in the austenitic alloys. This agrees the experimental results shown in the Fig. 1B and C. In addition it was confirmed that a transition of mechanism between the internal and the rapid nitriding lies between about 13 and 16 mass% Cr in the high Cr austenitic steels [12]. Thus treating the rapid nitriding in the austenitic stainless steels based on synergetics gave a good agreement between experimental results and theory. Now even though the threshold of $(\lambda - gc^0_{\mathrm{Cr}\cdot\mathrm{Nx}}) < 0$ is satisfied by enough Cr concentration, the threshold will be inverted when the $p\mathrm{NH}_3$ is reduced to very low pressures because the terms $c^0_{\mathrm{Cr}\cdot\mathrm{Nx}}$c and f_{N} are highly dependent upon the NH_3. Table I suggests the relation. Further precision measurement are expected to add details to this model.

3. Conclusion

This paper examined the rapid nitridings anomaly in high Cr austenitic steels. There are two factors which affect the rapid nitriding, temperature and Cr concentration. It has been suggested that the transition temperature (Tc) of ΔG° of $\mathrm{Cr_2N}$ and CrN is a parameter which separates the normal and the rapid nitriding behavior steels. The transition to rapid nitriding takes place suddenly at temperatures over the Tc . The γ_{SN} phase is stable below the Tc . Above the Tc, this phase becomes unstable and is formed as the meta-γ_{SN} phase on the surface the austenitic stainless steels.

Nitriding dependence on Cr concentration was evident in the shift from internao nitriding to rapid nitriding as Cr concentration increased from 13 to 16 mass%. Since Tc refers to a critical temperature for the formation of Cr nitrides, the anomalies in the austenitic Fe–Cr–Ni alloys resulted from the presence of the Cr in the steels.

From this view point, the rapid nitriding was examined using a simple model of the laser based on synergetics [19] as follows. The γ_{SN} phase of at least 30 atomic%N was treated as a state with an invarted population in nitrogen chemical potential. A metastable phase is formed above Tc and maintained by the giant nitrogen fugacity of ammonia during nitriding. The formation of a G. P. zone co-generating the $\underline{\mathrm{N}}^*$ was considered with reversion to the G. P. zone in the mata-γ_{SN} phase. From the many experimental results the reversion of the G. P. zone during nitriding was considered as new aspect for theoretical treatment of the rapid nitriding.

The cyclic combination of these new aspects has highlighted the role played by Cr concentration in determining whether or not rapid nitriding takes place. The parameter clearly affects the rapid nitrogen diffusion in the plated invar shown in Fig. 1C, as well as the transition of the nitriding mechanism as the Cr concentration changes between 13 and 16 mass%Cr in the austenitic high Cr steels [12].

Up to now, no papers have been published on the mechanism of the rapid nitriding in terms of a "laser" (i.e., population inversion) model. In brief a continuously formed of a nitrogen supersaturated state (meta-γ_{SN} phase) is produced by pumping of the giant nitrogen fugacity of ammonia, in analogy to the pumping of electrons in the laser phenomenon. In this inverted population state of chemical potential, a spontaneous precipitation and a reversion of the G. P. zone are take place, simultaneously. This refers to the releasing of the inverted chemical potential exothermically with precipitation of the $\underline{\mathrm{N}}^*$ analogous to the emmision of a photon in a laser. Thus the anomalous nitriding behaviors in the austenitic stainless steels are treated from a new stand point of synergetics.

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