Ion-nitriding of an Fe–19 wt % Cr alloy

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The ion-nitriding behaviour of an Fe–18.75 wt % Cr alloy was investigated at 803 K under constant plasma conditions. Both a thin surface layer of γ'-Fe$_4$N and an internal-nitriding layer were observed. The nitride formed in the internal-nitriding layer was found to be CrN, rather than Cr$_2$N. The hardness of the nitriding layer rises to Hv = 1200 due to small CrN precipitates. The growth rate of the internal nitriding layer, in the present alloy is controlled by a nitrogen diffusion process in the matrix metal, α-iron. Because such ion-nitriding behaviour is analogous to that of internal-oxidation, the growth rate of nitriding was discussed according to the rate equation to that of internal-oxidation. The nitrogen diffusion in the present alloy is scarcely affected by the CrN precipitates.

1. Introduction

There have been few investigations [1–4] of the ion-nitriding of iron alloys compared with the number of investigations of gas nitriding [5–7]. The mechanism of ion-nitriding has still not been made clear, because most investigations so far have focused on either the hardening behaviour of the morphology or the nitride formed.

In the ion-nitriding of iron alloys, nitrogen in the plasma forms a surface layer of iron nitride on the specimen surface. Another layer can be also seen beneath the surface layer, this is called the internal-nitriding layer. It is here that the small nitride particles precipitate out in the metal matrix. Thus, these two layers are analogous to those formed in internal oxidation. Many investigators [1–3] have dealt with the ion-nitriding of alloys containing a low alloying element content. However, there is little information available on the ion-nitriding behaviour of iron alloys with a high alloying element. Iron alloys with a high chromium content, such as type 430 stainless steel, are difficult to nitride using gas-nitriding methods, because a protective oxide film forms on the surface and separates them from the gas.

The present study aims to make clear the mechanism of the ion-nitriding of Fe–19 wt % Cr alloy, type 430 stainless steel, by application of the rate equation for internal-oxidation, which has been discussed in detail theoretically as well as experimentally [8–10]. Special attention has been paid to the effect of the high alloying element content on the nitriding behaviour. For this purpose, the thickness of the nitriding layer and the hardness of the nitrided alloy were measured, and the nitride and the concentration of nitrogen and chromium in the nitrided alloy were examined.

2. Experimental procedure

The Fe–19 wt % Cr alloy used in the present study was prepared by vacuum-melting and swaging. The chemical composition of the alloy is listed in Table I. Specimens of about 10 mm × 10 mm × 5 mm were annealed for 1.8 ksec at 1373 K and quenched in iced water, giving a grain diameter of 430 μm. After being polished with an abrasive paper of # 1500, the specimens were cleaned in trichloroethylene using an ultrasonic cleaner prior to nitriding.

A mixture of nitrogen and hydrogen at a total pressure of 1 torr was placed in a vacuum chamber with a d.c. potential of 1 kV applied between the work (cathode) and the grounded metal vacuum enclosure (anode). In order to control the nitriding temperature of the specimen, an external heater was also used, resulting in a temperature control of within ±4 K. The ion-nitriding conditions were as follows: nitriding temperature, T_N, 803 K; glow-current density, 11 A m^{-2}; gas ratio of N_2 to H_2, 0.25.

Specimens were carefully cut into halves parallel to one face of the specimen surfaces. The cross-sections, polished with alumina powders, were etched in a ferric chloride solution (FeCl$_2$, 5 g; HCl, 50 ml; C$_2$H$_5$OH, 100 ml). The feature and thickness of the nitriding layer as well as the hardness were measured with a microhardness tester. To determine the nitrides formed on the specimen surface and the internal-nitriding layer, X-ray diffraction experiments were carried out on the surface of the specimen subjected to ion-nitriding.

An electron probe microanalyser (EPMA, Hitachi X-650) was used to determine the concentration profiles of both nitrogen and chromium in the nitrided specimens. The operating conditions were as follows: accelerating voltage, 15 kV; crystals used, LiF for Cr$K\alpha$ and Fe$K\alpha$, and STE for N–K; take-off angle, 0.66 rad (38 deg).

TABLE I Chemical composition of the alloy used (wt %)

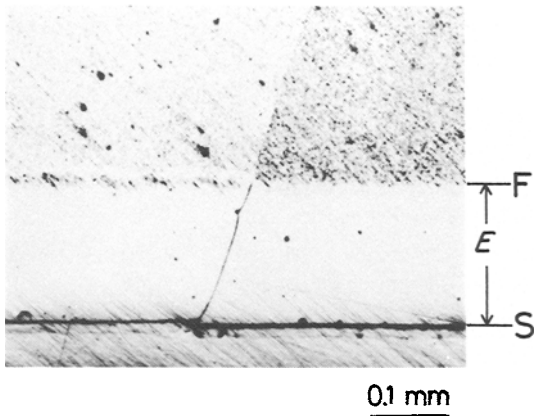| Alloy	Cr	C	Si	Mn	P	S
Fe–19Cr	18.75	0.0013	0.27	0.24	0.001	0.004

Figure 1 Typical microstructure of the Fe–19 wt % Cr alloy ion-nitrided for 57.6 ksec at 803 K. S and F indicate the specimen surface and the nitriding front, respectively.

3. Experimental results
3.1. Observation of microstructure
A typical microstructure of Fe–19 wt % Cr alloy ion-nitrided for 57.6 ksec at 803 K is shown in Fig. 1, where S indicates the specimen surface and F the nitriding front. On the specimen surface a thin surface layer of a few micrometres thick was observed. A region between S and F, called the internal-nitriding layer in which small nitride particles were dispersed, was also formed. E in Fig. 1 indicates the thickness of the internal-nitriding layer. The nitriding front was parallel to the specimen surface. A similar microstructure has been reported in iron alloys with a low alloying element content [2, 3]. In the high temperature oxidation of some alloys, two analogous oxide layers are formed [11, 12]: one is the surface oxide layer, called scale or the external oxidation layer; the other one a layer where small oxide particles of the alloying element are precipitated, called subscale or the internal-oxidation layer.

3.2. Growth rate of internal-nitriding layer
Fig. 2 shows the square of the thickness of the internal-nitriding layer, E^2, as a function of nitriding time, t. One can easily see a parabolic rate law

$$E^2 = K_p t \qquad (1)$$

where K_p is the rate constant. This result suggests that the internal-nitriding is controlled by a diffusion

process [8–10]. The value obtained for K_p is $1.81 \times 10^{-13}\ \mathrm{m^2\,sec^{-1}}$ at 803 K in the present alloy.

3.3. Hardness of the nitriding layer
A typical hardness profile of Fe–19 wt % Cr alloy nitrided for 57.6 ksec at 803 K is given in Fig. 3. The hardness in the nitriding layer (Hv) increases up to about 1200, and remains almost constant throughout the layer. The value of 1200 is much higher than those reported in other dilute iron alloys subjected to nitriding [2, 3] and close to that obtained in an Fe–18 wt % Cr–8 wt % Ni alloy, austenitic stainless steel [4]. The Hv value markedly drops to 176 in the base metal. The location at which such a drastic change in Hv occurs, corresponds to the nitriding front determined by optical microscopic observation, as shown in Fig. 1. However, in such a hardness profile the indentation near the nitriding front crosses both the internal-nitriding layer and the unnitrided region, so that Hv is an average of the hardness in both regions.

A nitrided specimen was mechanically polished by about 20 μm, resulting in a cross-section of the internal-nitriding layer. Fig. 4 shows the result of X-ray diffraction on the cross-section of the nitrided alloy. One can easily see that CrN as well as α-iron are present in the nitriding layer of this alloy. Similar CrN precipitates have been observed in an Fe–0.1 wt % Cr alloy [1] and an Fe–18 wt % Cr–8 wt % Ni alloy [4] ion-nitrided in the α-phase and γ-phase regions, respectively. Thus, the chromium nitride formed in Fe–Cr alloys by ion-nitriding is CrN, not Cr_2N. The X-ray diffraction experiments on the surface of the nitrided specimen show that the surface nitrided layer is mainly γ'-Fe_4N in the present alloy. No ε-Fe_{2-3} peak was detected. These results are in good agreement with those obtained in dilute iron alloys [2, 3].

Fig. 5 shows typical concentration profiles of nitrogen, chromium, and iron in the Fe–19 wt % Cr alloy nitrided for 57.6 ksec at 803 K. One can see that the nitrogen concentration, as well as those of chromium and iron, change sharply at the nitriding front, indicating that nitrogen penetrates to the front and that the CrN is precipitated in the nitriding layer. Furthermore, the nitrogen concentration remains constant throughout the nitriding layer. This shows that the volume fraction of CrN in the layer is unchanged there. The fluctuation of the X-ray intensity of
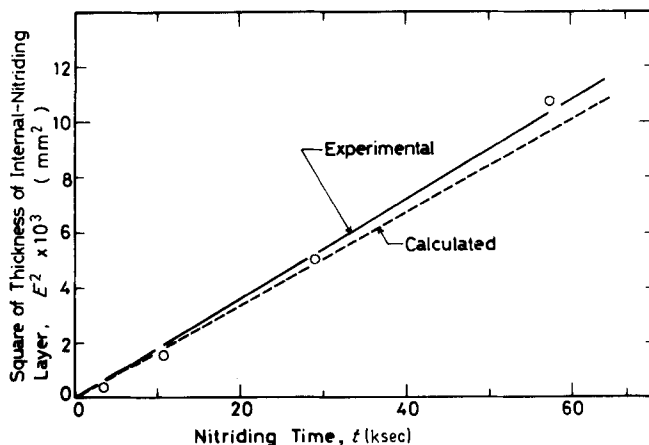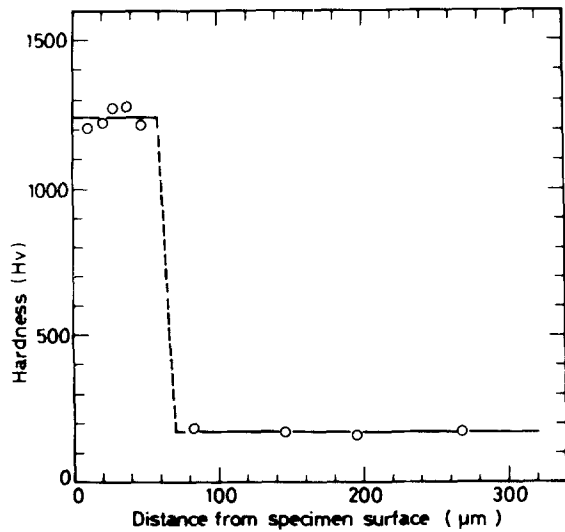

Figure 2 Square of the thickness of the internal-nitriding layer as a function of nitriding time. The solid line was determined using the experimental data by the least square method. The dotted line represents the line calculated according to Equation 3. $T_N = 803$ K.

Figure 3 Typical hardness profile of the Fe–19 wt % Cr alloy ion-nitrided for 57.6 ksec at 803 K.

chromium and nitrogen is also found to be small as shown in Fig. 5. If the CrN precipitates are large enough to be detected by electron microprobe of about 2 μm in diameter, the intensities of chromium and nitrogen would have their peaks at the position where CrN precipitates exist, and large fluctuations in the X-ray intensity could be observed. Therefore, the present result, as shown in Fig. 5, indicates that there are a great number of small CrN particles. The intensities of chromium and iron in the nitriding layer are lower than those in the unnitrided region, the bulk alloy. This is because the nitrogen atoms presenting mainly as CrN are introduced into the layer by the ion-nitriding and the relative atom fraction of chromium or iron subsequently decreases.

4. Discussion

The ion-nitriding behaviour of the present alloy is analogous to the internal-oxidation behaviour of alloys: two different layers are formed and the inner layer advances holding a parabolic rate law. Therefore, in this investigation, the ion-nitriding kinetics is discussed according to the rate equation for internal-oxidation [8, 9, 13].

The surface layer of γ'-Fe$_4$N is in thermodynamic equilibrium with the matrix metal, α-iron, in the internal-nitriding layer. This indicates that the concentration of dissolved nitrogen, N_N^S, at the specimen surface

of the internal-nitriding layer, which corresponds to the concentration at the interface between the surface-nitriding and the internal-nitriding layers, can be determined by the nitrogen solubility in α-iron. Thus, N_N^S is 3.68×10^{-3} at 803 K according to the data on nitrogen solubility [14].

The rate equation for ion-nitriding is given by modifying that for internal-oxidation [8, 9, 13]

$$E^2 = \frac{2N_N^S D_N^{app}}{\nu N_B} t \tag{2}$$

Here, ν is the atom ratio of nitrogen to the alloying element, B, in the nitride, N_B is the concentration of B in the nitriding layer, and D_N^{app} is the diffusion coefficient of nitrogen in the nitrided layer in which small CrN particles are precipitated.

We have indicated that N_B is larger than the original concentration of B, N_B^0, due to its outward-diffusion from the bulk alloy to the oxidation front in the internal-oxidation of some iron alloys [13]. In such cases N_B should be determined by calculation or experiments. In Fe–Si alloys [13], N_B is calculated using the diffusion coefficient of B. However, in the present alloy, the counter-diffusion of chromium hardly occurs, as shown in Fig. 5, indicating that N_B is equal to N_B^0. In the present alloy the nitride of CrN gives $\nu = 1$. We found that most of the chromium content in the Fe–18 wt % Cr–8 wt % Ni alloy was nitrided by ion-nitriding [4]. We, therefore, assume that the whole chromium content is completely nitrided. Thus, the rate equation for the ion-nitriding of the Fe–19 wt % Cr alloy can be rewritten as

$$E^2 = \frac{2N_B^S D_N^{app}}{N_B^0} t \tag{3}$$

Assuming that D_N^{app} is equal to the diffusion coefficient of nitrogen in α-iron [15], the relationship between E and t can be predicted using Equation 3. The calculated line, indicated by the dotted line in Fig. 2, is in good agreement with the experimental results, shown as a solid line. This indicates that the ion-nitriding kinetics of this alloy can be explained in terms of nitrogen diffusion in α-iron. In addition, the nitrogen diffusion coefficient in the nitriding layer is scarcely affected by the existence of nitride particles. This is in contrast to internal-oxidation of iron alloys [13], in which the apparent diffusion coefficient of oxygen in the oxidation layer is enhanced by the
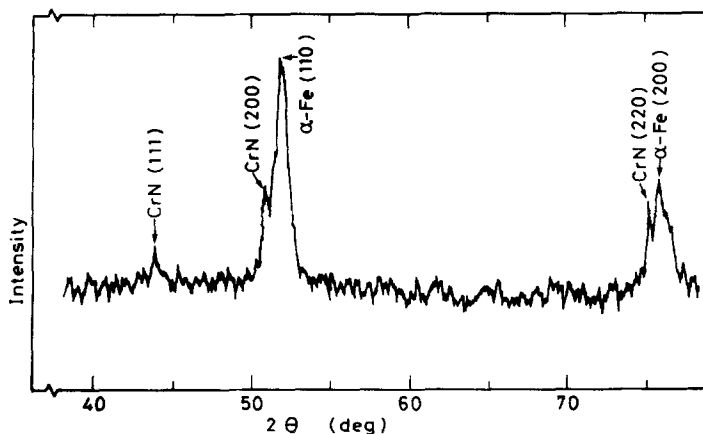

Figure 4 X-ray diffraction pattern of the nitriding layer of the Fe–19 wt % Cr alloy ion-nitrided for 57.6 ksec at 803 K.
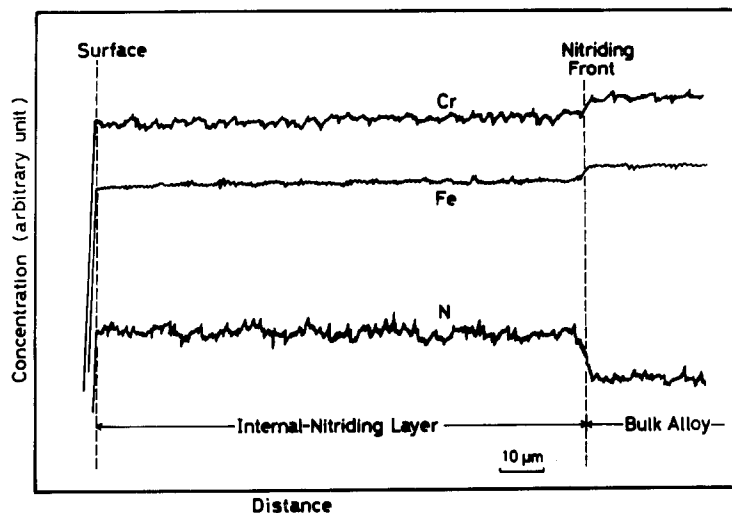
Figure 5 Concentration profiles of nitrogen, chromium, and iron for the Fe–19 wt % Cr alloy ion-nitrided for 28.8 ksec at 803 K. The thickness of the nitriding layer, determined by optical microscopic observation, is 70.6 μm.

presence of oxide particles. Further discussion on these subjects needs more detailed experiments.

Acknowledgements

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