A Method to Obtain Fine Cr Carbides in High Carbon Martensitic Stainless Steel

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Abstract

As the hardness of high carbon martensitic stainless steels is very high, they are used for cutlery and bearings, etc. However, as huge Cr carbides larger than 20 μm in diameter are formed in these steels, knife edges are easily chipped and fatigue cracks during rolling are initiated from these huge Cr carbides. In this paper, the effect of the nitrogen addition to obtain fine Cr carbides in Type 440A SS (Fe-16.5%Cr-0.65%C) has been studied, and the effect of nitrogen content on both mechanical properties and the corrosion resistance has been investigated. The main results are summarized as follows: The addition of nitrogen more than 0.25% suppresses the crystallization of eutectic Cr carbides during casting, and fine Cr carbides can precipitate after hardening heat treatment. As a result, the impact toughness of hardened and tempered sheets is improved, the maximun hardness shows more than HRC60, and the cold workability, the resistance to temper softening and the corrosion resistance are comparable to conventional low nitrogen steels.

Riassunto

Gli acciai inossidabili martensitici ad alto contenuto di carbonio vengono utilizzati per la coltelleria, i cuscinetti, ecc., a causa della loro notevole durezza. In tali materiali si formano, però, carburi di Cr molto grossi, di diametro superiore a 20 μm, che determinano la facile scheggiatura delle lame dei coltelli e rotture di fatica nei cuscinetti a rotolamento. Il presente documento esamina l'effetto dell'aggiunta di azoto per ottenere carburi Cr fini nell'acciaio inossidabile Tipo 440A (Fe-16,5%-Cr0,65%C) e l'effetto della presenza di tale elemento sia sulle proprietà meccaniche che sulla resistenza alla corrosione. I risultati principali si riassumono come segue: l'aggiunta di più dello 0,25% di azoto elimina la cristallizzazione dei carburi Cr autettici durante la solidificazione e i carburi Cr fini possono precipitare dopo il trattamento termico di tempra. La resistenza all'impatto degli acciai temprati e rinvenuti risulta quindi migliorata, la durezza massima supera HRC60 e la deformabilità a freddo, la resistenza all'addolcimento e alla corrosione sono paragonabili a quelle degli acciai tradizionali a basso contenuto di azoto.

Key Words

High carbon martensitic stainless steel, high nitrogen stainless steel, eutectic Cr carbide, Cr nitride, pitting corrosion, spheroidizing heat treatment.

Introduction

As high carbon martensitic stainless steels like Type440 SS (Fe-17%Cr-0.6/1.2%C) have very high hardness and the good resistance to corrosion[1]), they are used for cutlery and bearings, etc. Although their hardness and corrosion resistance are enhanced by the increase of the content of Cr and C, eutectic Cr carbides crystallize at proeutectic austenite grain boundaries during casting of high Cr and high C SS. After hot rolling and spheroidizing heat treatment, the maximum diameter of eutectic Cr carbides is observed to be 20 μm. These retained huge Cr carbides after final hardening heat treatments deteriorate their mechanical properties. For example, knife edges are easily chipped in cutlery and fatigue cracks tend to start from large Cr carbides in bearings. Although several studies have been reported[2)3)] to control the eutectic crystallization of Cr carbides and to obtain fine Cr carbide precipitates in high C martensitic SS, no effective method has been found yet. In this paper, the effect of nitrogen content on not only the nucleation behavior of eutectic Cr carbides in Type 440A SS, but also mechanical properties and the corrosion resistance has been studied. As a result of this study, a method to obtain fine Cr carbide precipitates was developed in high carbon martensitic stainless steels.

Experimental Procedure

Specimens

The basic chemical composition of specimens is Fe-16.5%Cr-0.65%C, and the nitrogen content is changed from 0.015% to 0.45%, as shown in Table 1. The steels of less than 0.105%N were melted in a 10Kg vacuum induction melting (VIM) furnace, and those of higher nitrogen were melted in pressurized nitrogen atmospheres. In order to change the nitrogen content in Fe-16.5%Cr-0.65%C, the pressure of nitrogen gas in VIM fumace was controlled by Eq(l) and reciprocal

$$[N] = \frac{\exp\{2.303\cdot(-518/T-1.063)\}}{\exp\{2.303\Sigma\, e_N\,[I\%]\}}\, P_{N2} \qquad (1)$$

where [I%] is element content, T is temperature and PN is the pressure of nitrogen gas.

TABLE 1 - Chemical composition of speciments (mass%)

	C	Si	Mn	P	S	Cr	Ni	T.N	T.O
0,02%N	0,667	0,532	0,471	0,003	0,006	16,37	0,244	0,0152	0,0123
0,06%N	0,643	0,484	0,606	0,003	0,006	16,24	0,255	0,0653	0,0154
0,10%N	0,619	0,526	0,530	0,003	0,005	16,40	0,255	0,1052	0,0047
0,25%N	0,634	0,542	0,512	0,003	0,006	16,45	0,248	0,2680	0,0090
0,35%N	0,686	0,568	0,532	0,003	0,005	15,86	0,258	0,3420	0,0081
0,45%N	0,669	0,543	0,494	0,003	0,009	16,34	0,248	0,4320	0,0085

TABLE 2 - Reciprocal coefficient, e_N

C	Si	Mn	P	S	Al	Cr	Ni
0,1426	0,057	-0,0211	0,0475	0,0074	0,01056	-0,0497	0,01056

coefficients shown in Table 2. Ingots (9Omm thick, 90mm wide and l50mm long) were hot rolled to 3.0mm thick plates after heating at 1200 C for 30 min. Hot rolled plates were subjected to the spheroidizing heat treatment at 750 °C for 10h, and cold rolled to 1.5 mm thick sheets. These sheets were hardened by the heat treatment at a temperature from 900°C to 1200°C for 10 min., and tempered at a temperature from 50 °C to 700 °C for 1 h.

Analysis of precipitates and other tests

In order to clarify the effect of nitrogen content on the morphology of Cr carbides, microstructures of ingots and hardened sheets, heat treated at 1000 °C or at 1050 °C were observed by an optical microscope.

Precipitates in as cast ingots and hardened plates were extracted by SPEED (Selective Potentiostatic Etching by Electrolytic Dissolution) method[4], and they were examined by X-ray and electron diffraction method. The mechanical properties of Type 440A SS were measured on tensile properties of annealed plates after hot rolling and the hardness after the hardening and after the tempering heat treatments. The effect of nitrogen content on the corrosion resistance of Type 440A SS was examined by anodic polarization curves measured in 5.0%H_2SO_4 and 3.5% NaCl solutions.

Results and Discussion

The effect of nitrogen content on the morphology of precipitates

(i) As cast ingots

As the cross sectional microstructures at the central part of as cast ingots of Type 44OA SS with different nitrogen contents are shown in Fig. 1, eutectic Cr carbides are observed to crystallize at proeutectic austenite grain boundaries in steels with the lower nitrogen content than 0.10%. The volume fraction of these eutectic Cr carbides is observed to decrease with the increase of the nitrogen content. On the other hand, eutectic Cr carbides disappeared from proeutectic austenite grain boundaries, and the lamellar type of precipitates was observed to form around proeutectic austenite grain boundaries in steels with the higher nitrogen content than 0.25%. The volume fraction of these precipitates is observed to increase with the nitrogen content in steels. As the analyzed results of extracted precipitates of different nitrogen bearing alloys by X-ray diffraction method are shown in Fig.2, the lamellar type of precipitates in the steels with more than 0.25%N are found to be $(Cr,Fe)_{23}C_6$ and $(Cr,Fe)_2N$, and the volume fraction of $(Cr,Fe)_2N$ is increased with the increase of the nitrogen content. From the above mentioned results, the eutectic crystallization of Cr carbides at proeutectic autenite grain boundaries seems to be suppressed by the addition of nitrogen. As the phase diagram[5] of Fe-17%Cr-C steel is shown in Fig.3, Type 44OA SS is solidified on the line of $L \rightarrow L + \alpha \rightarrow L + \alpha + \gamma \rightarrow L + \gamma \rightarrow L + \gamma + \eta \rightarrow \gamma + \eta$, where η is $(Cr,Fe)_7C_3$ type of eutectic Cr carbides, and eutectic Cr carbides crystallize at proeutectic austenite grain boundaries. As the addition of nitrogen or the increase of the nitrogen content spreads the range of austenite monophase[6)7)] to the higher temperature, it is considered that the proeutectic grains become the full austenite phase. As solubilities of carbon and nitrogen are higher in the austenite phase than in the ferrite phase, it is considered that η phase does not crystallize in the steels with more than 0.25% nitrogen during the solidification. After that, carbon and nitrogen supersaturated in the austenite phase precipitate as lamellar type of $(Cr,Fe)_{23}C_6$ and $(Cr,Fe)_2N$ around proeutectic austenite grain boundaries during cooling.

(ii) Heat treated sheet

As microstructures of Type 440A SS with the different content of nitrogen are shown in Fig.4, large Cr carbides whose maximum diameter is more than 10 μm are observed to precipitate in the sheet of the lower nitrogen content than 0.10%, heat treated at 1050°C where the maximum hardness is obtained. On the other hand, only fine precipitates can be observed in the sheets with the higher nitrogen content than 0.25%. These fine precipitates are identified to be spheroidal $(Cr,Fe)_{23}C_6$ and stick-shaped $(Cr,Fe)_2N$, as it is clearly seen in Fig.5.

From the above mentioned results, it is considered that eutectic Cr carbides of $(Cr,Fe)_7C_3$, crystallized at proeutectic grain boundaries in as cast ingots are related to form huge Cr carbides of $(Cr,Fe)_{23}C_6$. And it is also considered that eutectic Cr carbides crystallized in as cast ingots with the lower nitrogen content than 0.10% cohere by hot rolling and spheroidizing heat treatment and they form huge $(Cr,Fe)_{23}C_6$. As the steels of higher nitrogen content than 0.25% do not crystallize eutectic Cr carbides during casting, it is considered that huge Cr carbides are not formed. Lamellar type of $(Cr,Fe)_{23}C_6$ and $(Cr,Fe)_2N$ precipitated around proeutectic austenite grain boundaries are broken finely by hot rolling. As fine spheroidal $(Cr,Fe)_{23}C_6$ newly precipitates at different sites of $(Cr,Fe)_2N$ by spheroidizing heat treatment, fine Cr carbides and Cr nitrides can be obtained.

The effect of nitrogen on mechanical properties

As a lot of Cr carbides and nitrides are precipitated in Type 44OA SS after spheroidizing heat treatment, cold workabilities, especialy cold rollability and cold drawability, are very bad. It is predicted that the cold workability is decreased by the increase of the nitrogen content compared with conventional low nitrogen SS. The effect of nitrogen content on tensile properties of spheroidizing heat treated plates is evaluated. The results are shown in Fig.6. The tensile strength and 0.2% proof stress of these steels gradually increase with the increase of the nitrogen content below 0.35%. On the contrary, they decrease above 0.35% nitrogen. The elongation and the reduction of area are almost same regardless of the nitrogen content. The cold rolling test showed that the cold rollability of these steels was almost same regardless of the nitrogen content.

As it is reported that the austenite phase is stabilized and Ms point is decreased by the increase of the nitrogen content in Type 44OA SS[8]), it is predicted that the retained austenite after hardening heat treatment is increased and the maximum hardness is decreased with the increase of the nitrogen content.

Fig.7 shows the effect of the nitrogen content on the hardness after hardening heat treatment. When these steels are heat treated at hardening temperature from 900 - 1000°C, the maximum hardness of each steel is more than HRC60 regardless of the nitrogen content, and the hardness is the most suitable for cutlery and bearings. Although the hardness of each steel is increased by the increase of the austenitizing temperature, it is, recognized that the hardness of the steels heat treated above the austenitizing temperature to obtain the maximum hardness rapidly decreases with the austenitizing temperature. Although the austenitizing temperature to obtain the maximum hardness in 0.015%N steel is 1100 °C, it decreases with the increase of the nitrogen content. It is reported that $(Cr,Fe)_2N$ is dissolved in the austenite matrix at the lower temperature than $(Cr,Fe)_{23}C_6$[7]). If the amount of (C+N) dissolved in the martensite matrix at the maximum hardness is constant, it is considered that the austenitizing temperature to obtain the maximum hardness decreases with the increase of the nitrogen content, because the content of nitrogen dissolved in austenite is higher in high nitrogen steels than in low nitrogen steels. As the nitrogen content dissolved in austenite of the steel more than 0.25%N below 1000 °C is saturated, the austenitizing temperature to obtain the maximum hardness in the steel with more than 0.25% nitrogen becomes constant.

The effect of nitrogen content on the resistance to temper softening of Type 440A SS is shown in Fig.8. Although the hardness of the steels tempered at the temperature below 500 °C gradually decreases with the increase of the tempering temperature regardless of the nitrogen content, the superior resistance to temper softening is observed. The martensite phase is transformed to the ferrite phase at the temperature above 600 °C, so that the hardness of the steels is rapidly decreased with the increase of the tempering temperature.

Fig.9 shows the effect of nitrogen on the impact toughness of the steels heat treated at the temperature where the maximum hardness is obtained and tempered at 200°C. The impact toughness of the steels with the higher nitrogen content than 0.25% is higher than that of 0.06%N steel in which huge Cr carbides are formed. The impact toughness of the steels with more than 0.25% nitrogen is decreased with the nitrogen content. It is considered that the toughness deteriorates by the increase of the precipitation of stick-shaped $(Cr,Fe)_2N$.

The effect of nitrogen content on electrochemical properties

Fig.10 shows anodic polarization behaviors of plates with different nitrogen contents spheroidizing heat treated at 750 °C for 10h and temper heat treated at 200°C after hardening heat treatment in 5.0% H_2SO_4

solution. Active dissolution current densities of the steels with the higher nitrogen content than 0.25% are lower than that of 0.06% N steel. This tendency of tempered sheets is more remarkable than in speroidized plates. However the reason is not clarified. Although the current density of spheroidized plates at the passive state is increased with the increase of the nitrogen content, those of tempered sheets are almost constant regardless of the nitrogen content.

Fig.ll shows the effect of nitrogen content on anodic polarization curves in 3.5% NaCl solution. Because pitting corrosion potentials of spheroidized plates is observed to decrease with the nitrogen content, it is considered that the chromium content in the ferrite matrix are decreased by the precipitation of $(Cr,Fe)_2N$ in the higher nitrogen bearing steels. On the other hand, the corrosion resistance of tempered sheets with the higher nitrogen content than 0.25%N is superior to that of 0.06%N sheet.

From the above mentioned results, the corrosion resistance of spheroidized sheets is deteriorated by the increase of the nitrogen content, but that of tempered sheets with higher nitrogen content than 0.25% is almost same or superior to low nitrogen steels.

Conclusion

The effect of the nitrogen addition to obtain fine Cr carbides in Type 440A SS has been studied, and the effect of nitrogen content on both mechanical properties and the corrosion resistance has been investigated. The obtained results are as follows:

(1) In as cast ingots with the lower nitrogen content than 0.10%, eutectic Cr carbides crystallize at proeutectic austenite grain boundaries. On the other hand, in those with higher nitrogen content than 0.25%, eutectic Cr carbides are not observed to crystallize.

(2) In hardened sheets with the lower nitrogen content than 0.10%, the maximum diameter of Cr carbides is observed to be 20 μm. On the other hand, in hardened sheets with the higher nitrogen content than 0.25%, huge Cr carbides are not observed and fine Cr carbides and nitrides are identified to precipitate.

(3) Cold workability is found to be almost same regardless of the nitrogen content.

(4) Although the austenitizing temperature to obtain the maximum hardness is decreased with the nitrogen content, the maximum hardness is more than HRC60 regardless of the nitrogen content. The resistance to temper softening is almost same regardless of the nitrogen content.

(5) Impact toughness of hardened and tempered sheets is improved by the addition of nitrogen more than 0.25%, but it is gradually decreased by the increase of the nitrogen content.

(6) Although the corrosion resistance of spherodized plates is deteriorated by the increase of the nitrogen content, that of hardened and tempered sheets with the higher nitrogen content than 0.25% is almost same with that of conventional low nitrogen steels.

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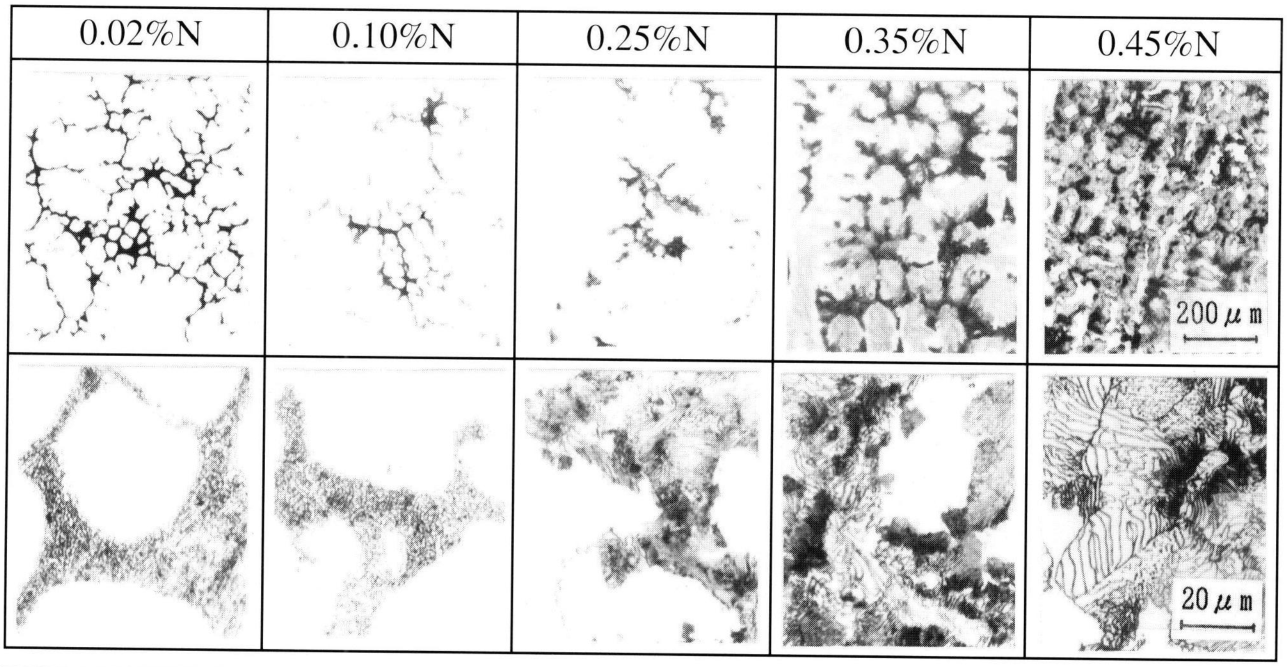

Fig. 1:
Changes in as cast structure of Type 440A SS with N content.

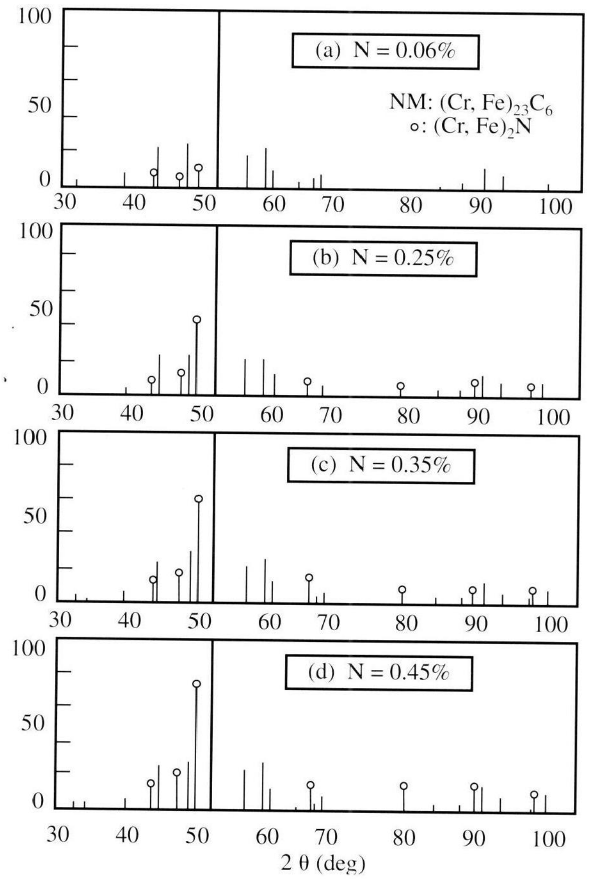

Fig. 2:
X-ray spectrum of precipitations
extracted from casting ingots

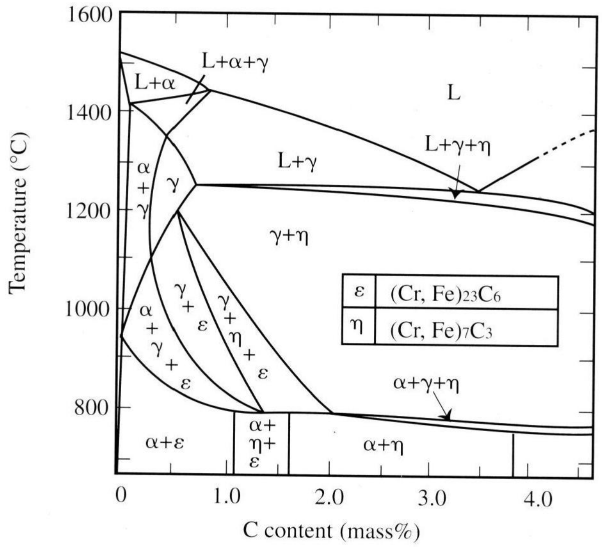

Fig. 3:
Phase diagram of Fe-17% Cr-C steel

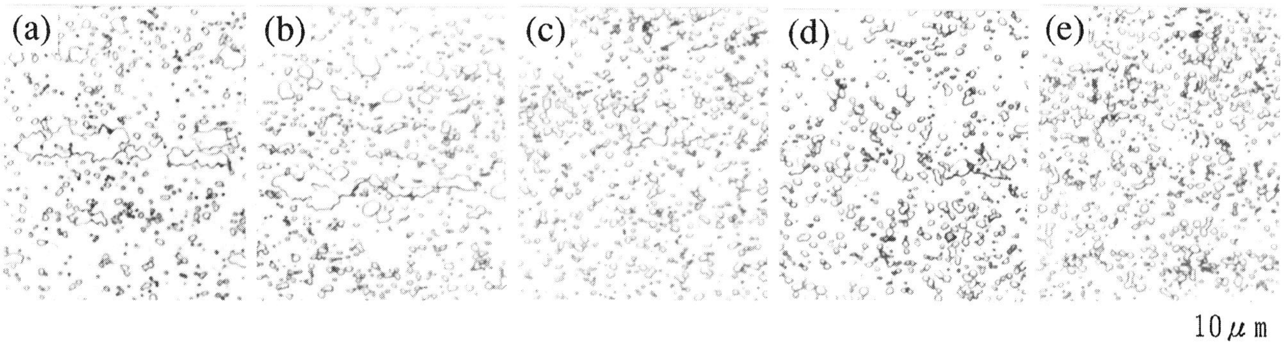

Fig. 4:
Changes of hardened structure of Type 440A SS with N content.
(a) 0,02%N and (b) 0,10%N steel heat treated at 1050 °C
(c) 0,25%N, (d) 0,35%N and (e) 0,45%N steel heat treated at 1000 °C

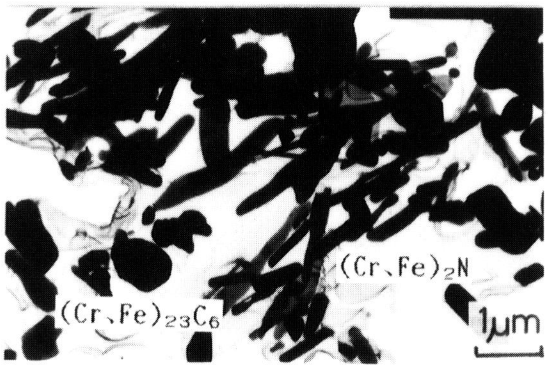

Fig. 5:
Transmission electron micrograph
of precipitations extracted from annealed plate
of Type 440A SS added 0,25%N

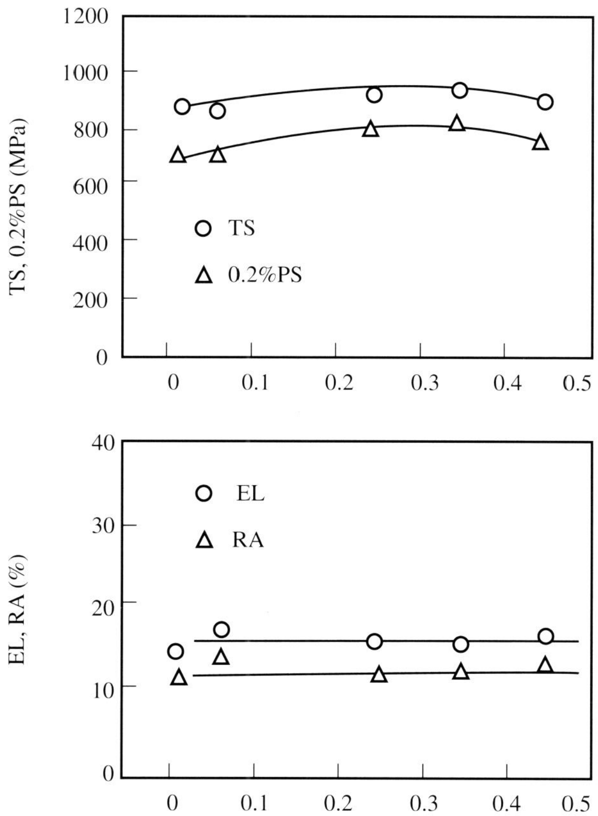

Fig. 6:
Effect of N content on tensile properties

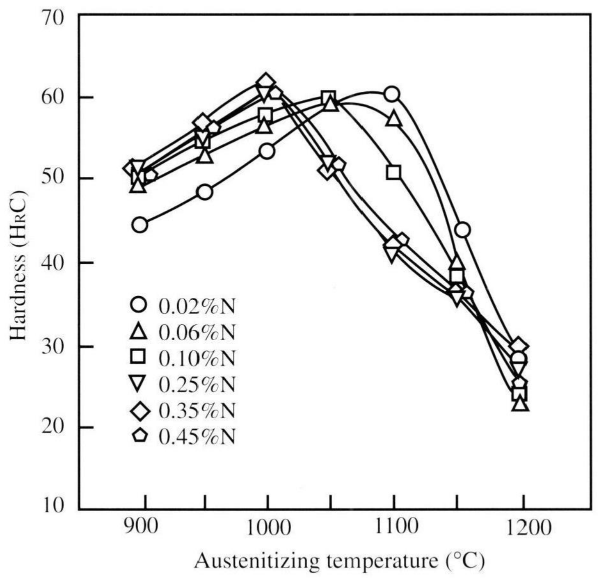

Fig. 7:
Changes in hardening behavior with N content

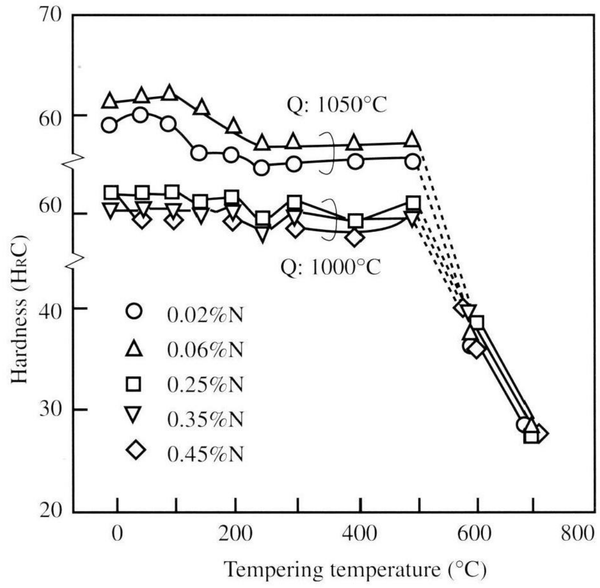

Fig. 8:
Changes in temper softening behavior with N content

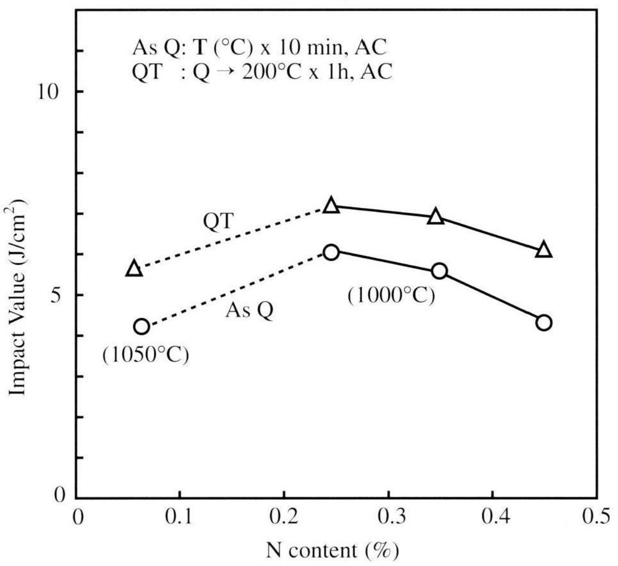

Fig. 9:
Effect of N content on impact value

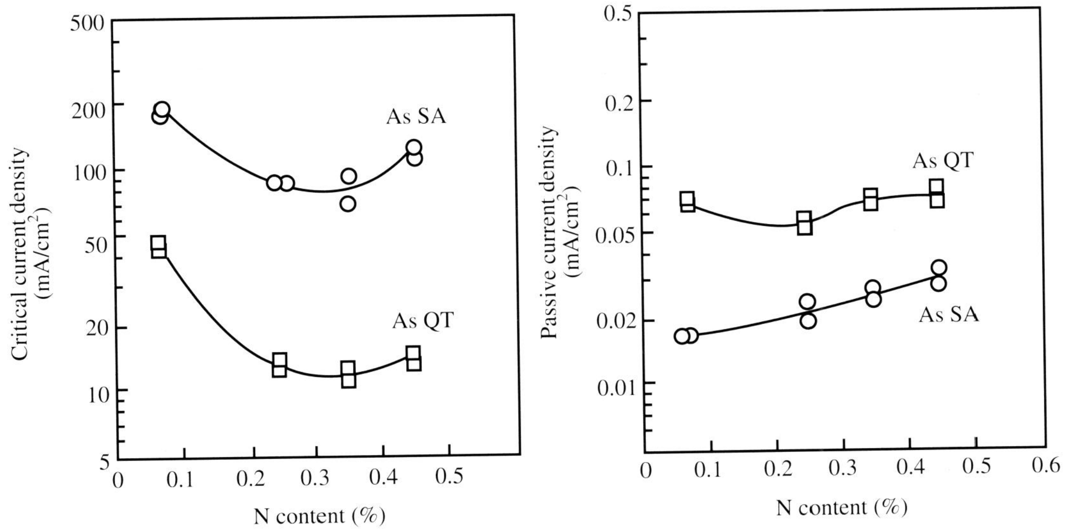

Fig. 10:
Effect of N content on anodic polarization properties

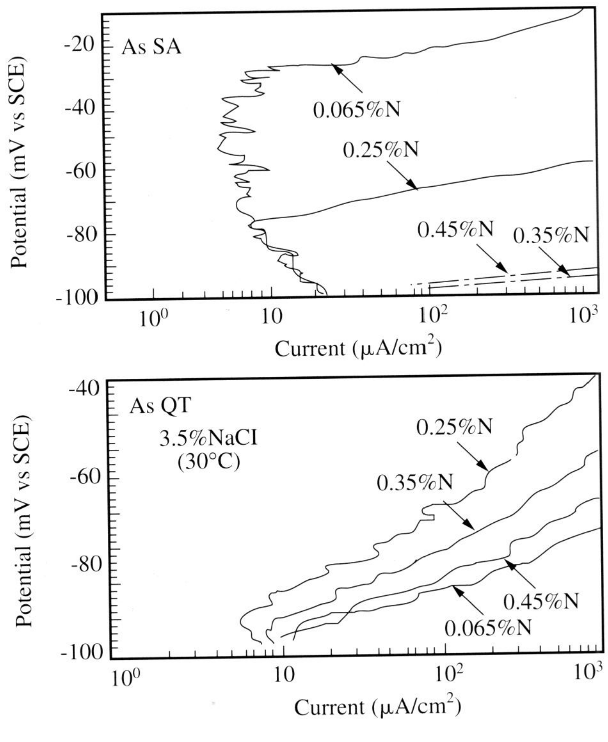

Fig. 11:
Effect of N content on pitting
corrosion resistance