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Phase transformations in low-temperature chromized 0.45 wt.% C plain carbon steel ☆

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Abstract

The phase transformations occurring in a 0.45 wt.% C plain steel subjected to plasma nitriding at 540–560 °C for 5.5 h, followed by a salt bath thermoreactive deposition and diffusion (TRD) chromizing process at 500 °C or 550 °C (a process referred to as low-temperature chromizing or duplex chromizing) was investigated by means of optical microscopy(OM), scanning electron microscopy(SEM), X-ray energy dispersive spectroscopy(EDS), and X-ray diffraction. It was found that a CrN compound layer with an average thickness of 7.4 μm and an average microhardness of 1476 $HV_{0.01}$ was formed in the prior plasma nitrided compound layer by low-temperature chromizing at 550 °C for 6 h. The chromized coating as a whole was found consisting of three sub-layers, namely the outer CrN layer, the intermediate diffusional layer, and the inner residual nitrided compound layer, all formed in the prior nitrided compound layer, and with the inner sub-layer vanishing by prolonging the chromizing time. The intermediate diffusional layer formed at the initial stages of TRD was seen "black" under OM (hence is called "black zone"), and found consisting of α-Fe as a major phase. The self-exhaustion of the "black zone" promoted the chromium atom diffusion deeper into the substrates. The transformation paths involved in the decomposition of the prior nitrided compound layer was likely to be $\varepsilon\text{-Fe}_{2-3}\text{N} \rightarrow \gamma'\text{-Fe}_4\text{N} \rightarrow \alpha\text{-Fe}$; and the high hardness of the chromized coating was attributed to a large amount of nano-sized and evenly distributed CrN grains generated in the compound layer.

1. Introduction

As a widely used surface coating technology, chromizing is employed to economically develop corrosion- and/or wear-resistant layer on metal or alloy substrates [1]. Due to the limited diffusivity of chromium at low temperatures, however, all the conventional chromizing processes are usually conducted at temperatures above 1000 °C for a duration of 6–10 h [2]. In view of the susceptibility of the substrate microstructure to coarsening and deteriorating at such high temperatures, a lower temperature chromizing process was developed by the authors in order to avoid these negative effects of the conventional chromizing processes on microstructure, and to promote the application of chromizing techniques to various substrate materials.

Duplex surface technique [3], involving the consecutive application of two or more established surface engineering techniques to a component, so as to produce a surface layer with multiple properties which can not be obtained by any single technique, is gaining increasing attentions in surface modification engineering. There is a duplex process which combines nitriding or nitrocarburizing with thermoreactive deposition and diffusion (TRD) process. Chicco et al.[4] assessed the effects of various pre-treatments (gas nitriding, liquid nitrocarburizing, or liquid carburizing) on the TRD of vanadium on AISI H13 steel at 1000 °C. High temperature TRD performed above 700 °C and low-temperature TRD conducted below 700 °C are classified in the present study, based on the A_{c1} critical temperature of the steel. In the high temperature TRD processes, carbide-forming elements such as chromium, niobium, titanium, and vanadium, while reacting with carbon diffusing from the

interior of the substrate, are deposited on the surface of substrates by a thermo-chemical process. A 4–7 μm thick carbide layer is produced in 10 min to 8 h [5], depending on the bath temperature and the type of steels used. For a low-temperature coating, however, a rather long time is needed to form a significant carbide layer because of the lower diffusivity of carbon at low temperatures, so that a plain TRD process is useless for the practical purposes. However, Arai et al. [6] pointed out that compound layer consisting of iron nitrides produced by nitriding is very effective in producing a vanadium carbonitride layer with adequate thickness at 550–700 °C for practical applications.

There is at present some evidence that a hard coating consisting of nitride or carbonitride of chromium may be produced at temperatures below 700 °C by a duplex process involving nitriding and low-temperature TRD. Arai et al. [7] claimed that a CrN layer of about 8 μm in thickness was formed on a nitrided substrate after the nitrided substrate was further chromized at 570 °C for 50 h in a fluidized bed reactor. King et al. carried out nitrocarburizing plus a fluidized bed low-temperature TRD process on AISI H13 [8] and plain carbon steels [9] at 570 °C, and found that a "cover layer" consisting of porous iron nitride was formed during the nitrocarburizing which significantly influenced the microstructure of the Cr(N,C) coating, thus suggesting using a higher temperature or prolonging the treatment time to achieve a thicker Cr deposition. Fabijanic et al. [10] developed a duplex process involving a precursor nitrocarburizing plus a fluidized bed low-temperature TRD on AISI H13 at 575 °C, claiming that while producing a good chromized coating, the low-temperature treatment did not alter the properties of the substrate interior.

A chromizing process conducted in a salt bath at temperatures ranging from 500 to 550 °C via TRD with specimens subjected to a precursor plasma nitriding at 540–560 °C is referred to as low-temperature chromizing or simply as duplex chromizing. To the authors' knowledge, little has been reported in the literatures regarding the duplex chromizing of steels at temperatures below 550 °C. Therefore, the purposes of this study are to further explore the duplex process, and to clarify the transformations occurring in the prior plasma nitrided compound layer during the low-temperature chromizing process, based on the previous studies [11,12].

2. Experimental procedures

2.1. Duplex chromizing process

The duplex chromizing process developed in the present study consists of a precursor plasma (ion) nitriding and a subsequent salt bath chromizing conducted via a low-temperature TRD. Annealed commercial 0.45 wt.% C plain carbon steel was cut into discs of 15 mm in diameter and 8 mm in thickness. All the discs were first polished with SiC polishing paper of up to 900 grade, degreased by annealing them at 270 °C for 30 min, and ultrasonically cleaned, before they were plasma nitrided at 540–560 °C for 5.5 h in a vacuum furnace, and furnace cooled in vacuum. All the specimens to be inves-

Table 1
Low-temperature chromizing procedures employed in the present study

Group	Precursor plasma nitriding	Low-temperature chromizing
A	At 540–560 °C for 5.5 h	At 500 °C for 1.5 h, 3 h, 6 h, 12 h
B	At 540–560 °C for 5.5 h	At 550 °C for 0.5 h, 1 h, 1.5 h, 3 h, 6 h, 12 h, 24 h, 48 h
C	At 540–560 °C for 5.5 h	At 550 °C for 1.5 h, 3 h, 6 h, 12 h, 24 h, 48 h

tigated were plasma nitrided together in a single batch to ensure an even nitrided layer throughout the specimens, and ultrasonically cleaned again before chromizing in a salt bath composed of BaCl$_2$ (analytically pure, AP), CaCl$_2$ (AP), NaCl (AP), CrCl$_3$·6H$_2$O (AP) and Cr–Fe powders (200 mesh) at 500 °C or 550 °C for a certain period of time, followed by quenching in water.

The duplex chromizing procedures employed in the present study are listed in Table 1. Specimens of group A were used to study the initial transformation process in plasma nitrided compound layer subjected to chromizing treatment, and those of groups B and C were treated with the same procedures, except that a slightly higher chromizing temperature was employed, to eliminate the random scatterings in microstructure and property.

2.2. Characterizations of the chromized layer

All the specimens were ultrasonically cleaned in acetone before characterizations. Cross-sectional specimens for characterization were prepared from the chromized discs by polishing with 2.5 μm diamond paste, and etching with 3% nital. The Vickers micro-hardness across the coating was measured on a 401MVA™ micro-hardness tester with an applied load of 10 gf and a dwelling time of 15 s.

X-ray diffraction spectra were recorded on a PHILIPS X' Pert MPO Pro X-Ray diffractometer operating with Cu K$_\alpha$ radiation at 40 kV and 40 mA. Both the conventional Bragg diffraction (CBD) and sample tilting diffraction (STD) modes were used for phase identification.

The cross-sectional microstructure of the coatings were observed using an optical microscope and a LEO1530VP scanning electron microscope equipped with a back-scattered electron detector, the chemical composition of various sublayers determined by EDS, and the profiles of chromium, iron, nitrogen and carbon across the coating characterized by X-ray line scanning.

3. Results and discussions

3.1. Thermodynamic calculations

Chromium dichloride(CrCl$_2$) is the active species in the chloride system for chromizing, which reacts with the iron-base substrates to form the activated [Cr] [13]. Since pure chromium dichloride is extremely hygroscopic, the chromium dichloride in the present study was in situ made from the dehydrated 6-

water chromium chloride($CrCl_3 \cdot 6H_2O$) and chromium powders by following the reactions:

$$2CrCl_3 + Cr(powders) \rightarrow 3CrCl_2 \qquad (1)$$
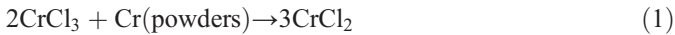
The nitrogen resources needed to form chromium nitrides resulted from the decomposition of iron nitrides [9]:

$$2\varepsilon - Fe_2N \rightarrow \gamma' - Fe_4N + 2[N] \qquad (2)$$

$$\gamma' - Fe_4N \rightarrow 4\alpha - Fe + [N] \qquad (3)$$

And, the chromium nitrides were formed via the following reactions [14]:

$$2[Cr] + [N] \rightarrow Cr_2N \qquad (4)$$

$$[N] + Cr_2N \rightarrow 2CrN \qquad (5)$$

The changes in Gibbs free energy for the above reactions were calculated according to the equation: $\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ$, which is an approximation of the simplified Gibbs–Helmholtz equation: $\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$ [14]. The calculations were performed in terms of the thermodynamic data by Kubaschewski et al.[14] and Dean [15]. The data for N atoms in solid state refer to that of $1/2N_2$ in gas state.

Fig. 1 shows the calculated Gibbs free energy changes, ΔG_T°, varying with temperature. It is clear from Fig. 1 that all the above reactions are thermodynamically possible in the temperature range of 500 °C to 550 °C, which was employed for the low-temperature chromizing in this study, due to the negative values of the Gibbs free energy change for each of the reactions. It is in addition seen from Fig. 1 that the thermodynamic driving force for the decomposition of ε-Fe_2N (reaction 2) is greater than that for the decomposition of γ'-Fe_4N (reaction 3), thus suggesting that there would be un-decomposed γ'-Fe_4N remaining in the nitrided compound layer, as is confirmed in Fig. 2. Meanwhile, since CrN is more stable than Cr_2N, the

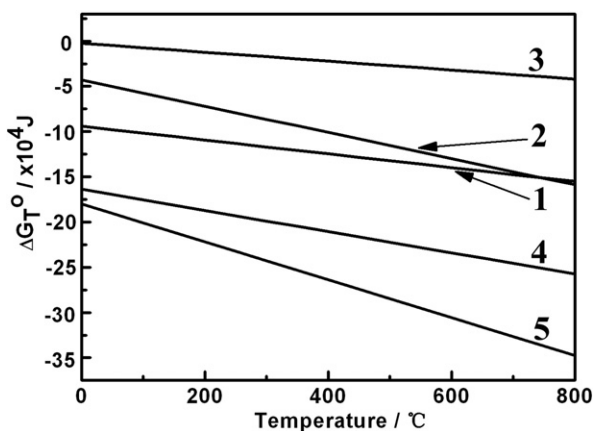Fig. 1. Calculated Gibbs energy change, ΔG_T° for reactions 1, 2, 3, 4, 5. 1: $2CrCl_3 + Cr$ (powders) $\rightarrow 3CrCl_2$, 2: 2ε-$Fe_2N \rightarrow \gamma'$-$Fe_4N + 2[N]$ 3: γ'-$Fe_4N \rightarrow 4\alpha$-$Fe + [N]$, 4: $2[Cr] + [N] \rightarrow Cr_2N$, 5: $[N] + Cr_2N \rightarrow 2CrN$.
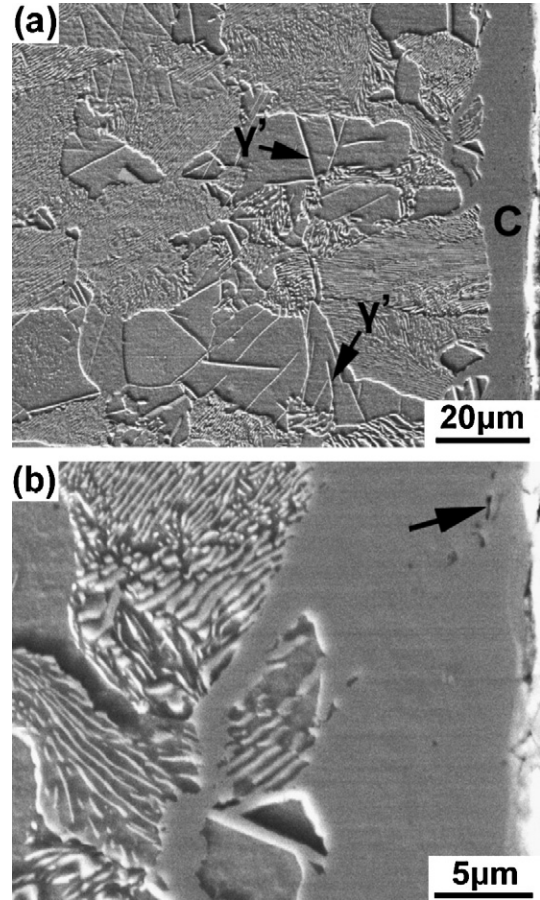
Fig. 2. Microstructure of 0.45 wt.% C plain carbon steel plasma nitrided at 540–560 °C for 5.5 h. (a) γ'-Fe_4N precipitated in the proeutectoid ferrite colonies, (b) Voids occasionally found in the nitride compound layer, secondary electron SEM images.

former may become the major phase in the coating layer, if there are adequate quantities of [Cr] and [N] atoms supplied to forming the chromium nitride. Furthermore, the calculated negative ΔG_T° for reaction 1 indicates that the reaction can proceed from left to right spontaneously in the temperature range of 500–550 °C, to form the active species $CrCl_2$. Therefore, the activity of $CrCl_2$ can be adjusted by changing the weight fractions of $CrCl_3$ and Cr in the salt bath. In the present study, the ratio of $CrCl_3$: Cr was taken as 2:1 for all groups of specimen, with the Cr fraction being 10 wt.% for group A, and 20 wt.% for groups B and C.

3.2. Characterization of the plasma nitrided layer

Fig. 2(a) shows the cross-sectional microstructure of a specimen which was plasma nitrided at 540–560 °C for 5.5 h. On the outer surface of the specimen was a compound layer (marked C) which consisted mainly of ε-$Fe_{2-3}N$ and γ'-Fe_4N (confirmed by near-surface XRD). Underneath the compound layer was the diffusional layer with needle-shaped γ'-Fe_4N precipitated within the proeutectoid ferrite colonies. The plasma nitriding procedures were carefully formulated so as to reduce the porosity on the outer surface of the specimen, and hence to

avoid subsequent grinding process. As is seen from Fig. 2(b), although minor voids were formed at the position 1–2 μm below the surface, no striking porous layer was produced with the plasma nitriding procedures used in this study. Thus, no subsequent grinding process was needed to remove the surface porosity, if any.

3.3. Transformations occurring in the prior nitrided compound layer during chromizing at 500 °C

The thermodynamic calculations shown in Subsection 3.1 provide two methods to control the chromizing rate, one being the temperature, i.e. chromizing process can be slowed down by lowering the treating temperature; the other being the activity of $CrCl_2$ in salt bath, i.e. the chromizing rate can be reduced by reducing the Cr fraction in salt bath. Fig. 3 shows the cross-sectional microstructure of specimens chromized at 500 °C and with a bath containing 10 wt.% Cr. The curved boundary between the chromium nitride layer (arrowed and marked C1 in Fig. 3(a)) and the un-decomposed nitrided compound layer (marked C2), indicates that the chromizing process at 500 °C was a diffusional one. In addition, discrete patches (marked L) were seen formed inside the compound layer adjacent to the chromium nitride layer (Fig. 3(b)). The same grey color of these patches as that of the outer chromium nitride layer displayed in
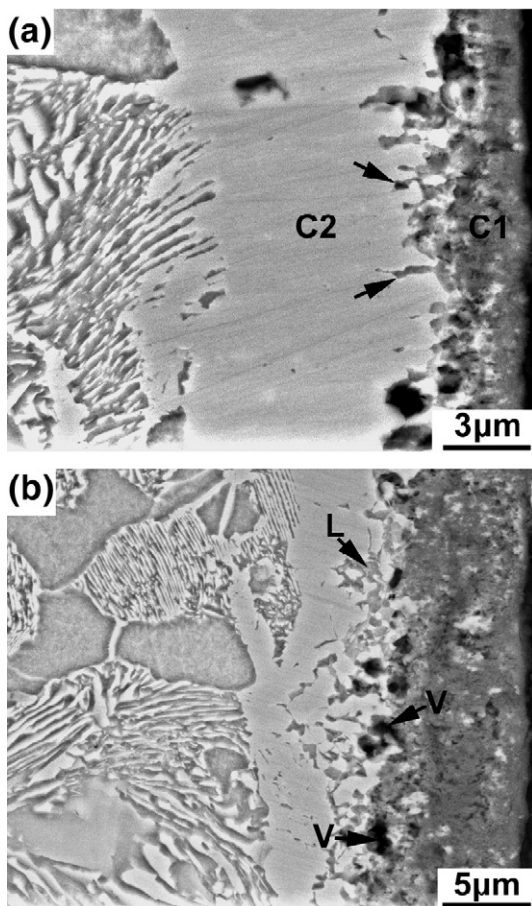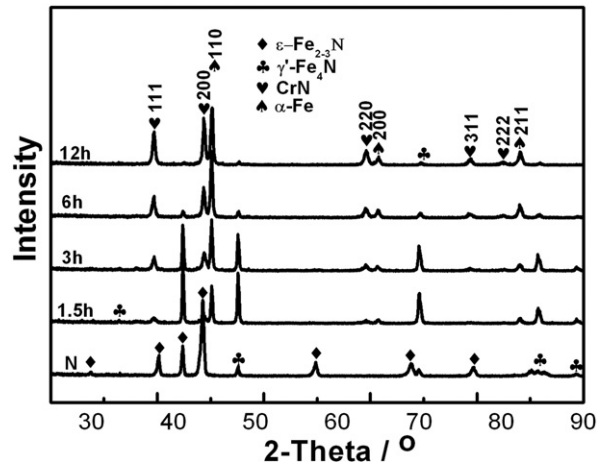

Fig. 4. Phase structure evolving in low-temperature chromizing at 500 °C. 'N' for specimen plasma nitrided at 540–560 °C for 5.5 h; '1.5 h' for specimen chromized for 1.5 h; and the other plots have similar meanings, determined by conventional Bragg diffraction.

this backscattered electron SEM image which confirmed that these patches were chromium nitride nucleated and grown within the compound layer. This result was similar to those by King et al. [9], Fabijanic et al.[10] and Wu et al. [12], although they were obtained at temperatures slightly higher than that used in the present study. Obviously, the active nitrogen atoms needed for forming the chromium nitride did result from the decomposition of the prior nitrided compound layer via re-actions 2 and 3. There were voids (marked V in Fig. 3(b)) formed underneath the chromium nitride layer; and they seemed to be consistently accompanying the formation of the chromium nitride layer, not disappearing even when the near-surface layer of the nitrided specimen was removed by grinding before chromizing. It is therefore believed that the formation of the voids was associated with the aggregation of the vacancy flux from the outer surface into the substrate. The vacancy flux was formed due to a mismatch in the diffusion rates of Cr and N at such a low temperature, and a mass transfer imbalance resulted from the mismatch [16].

Fig. 4 illustrates the phase structure evolution with chromizing time. It is clear from Fig. 4 that the intensity of ε-$Fe_{2-3}N$ and γ′-Fe_4N diffraction is decreasing while that of the CrN increasing with increasing the chromizing time, in agreement with what is shown in Fig. 3, i.e. the thickness of the nitrided compound layer is decreased and that of the chromium nitride layer is increased with increasing the chromizing time. It is thus apparent that the formation of CrN layer is at the expense of iron nitrides.

3.4. Transformations occurring in the prior plasma nitrided compound layer during chromizing at 550 °C

In view of the ambiguous tendency of the microstructure evolutions with chromizing time at 500 °C, the chromizing temperature was then increased to 550 °C in order to accelerate the process. Fig. 5 shows the cross-sectional microstructure and element distributions varying with chromizing time at 550 °C
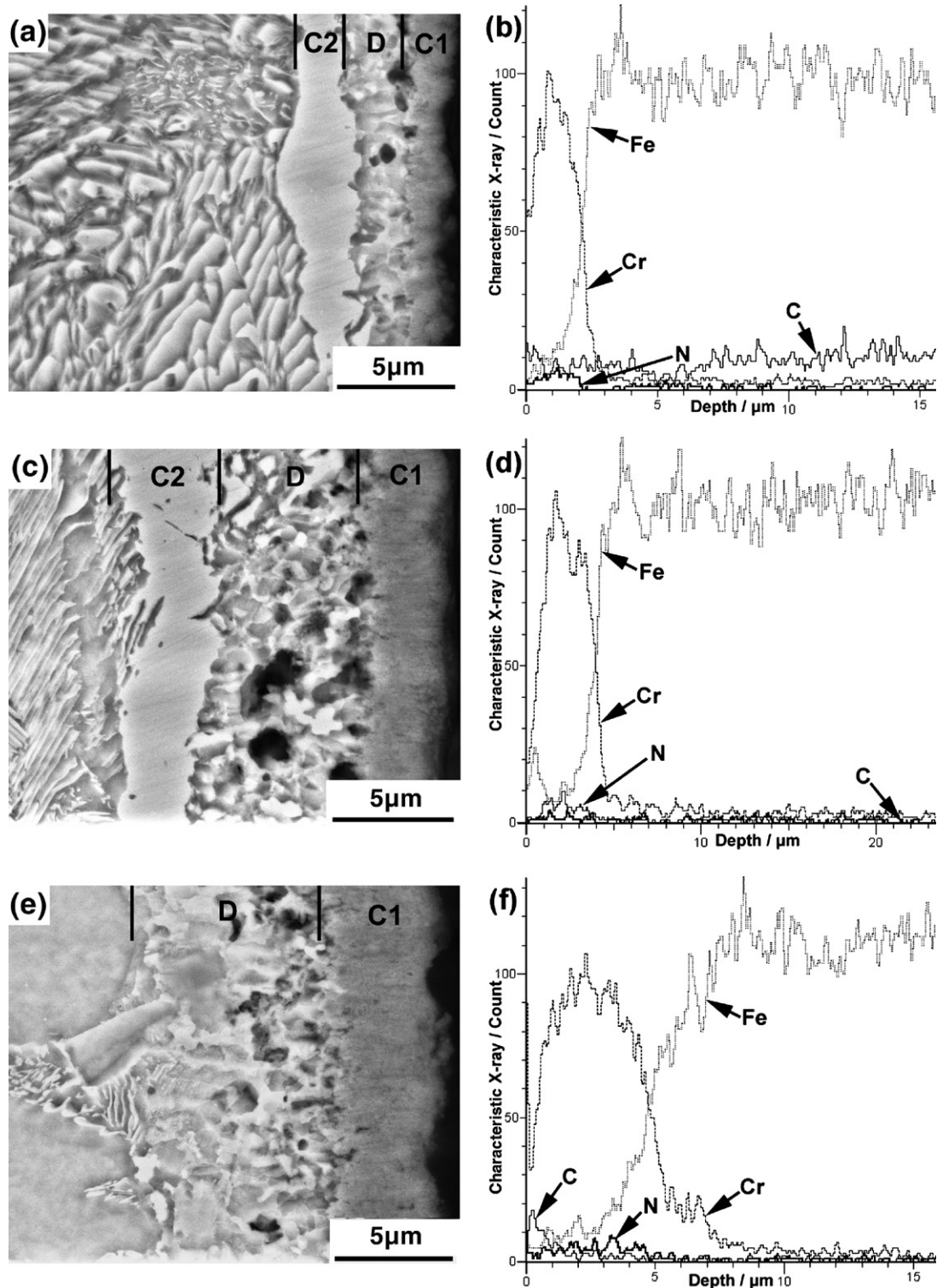

Fig. 3. Microstructure of transformations occurring in the prior nitrided compound layer during chromizing at 500 °C for (a) 6 h; (b) 12 h.

Fig. 5. Microstructure of specimens of group B chromized at 550 °C for (a) 0.5 h; (c) 1 h; and (e)1.5 h, all backscattered electron SEM images. (b), (d) and (f), the corresponding EDS line scanning for (a), (c) and (e), respectively.

for the specimens of group B. The chromizing time for Fig. 5 (a, c, e) were 0.5 h, 1 h and 1.5 h respectively and Fig. 5 (b, d, f) are the corresponding EDS line scanning profiles of chromium, iron, nitrogen and carbon. Fig. 5 (a, c) indicate that the duplex chromized layer formed at the initial stages of chromizing consists of three sub-layers, namely the outer chromium nitride layer (marked C1), the intermediate diffusional layer (marked D), and the inner residual plasma nitrided compound layer (marked C2).This result is in agreement with that by Wu et al. [12] who found three sub-layers in the chromized layer on AISI H13 duplex chromized in salt bath at 590 °C for 6 h. As is seen in Fig. 5 (e), however, the inner layer vanished after a 1.5 hour-
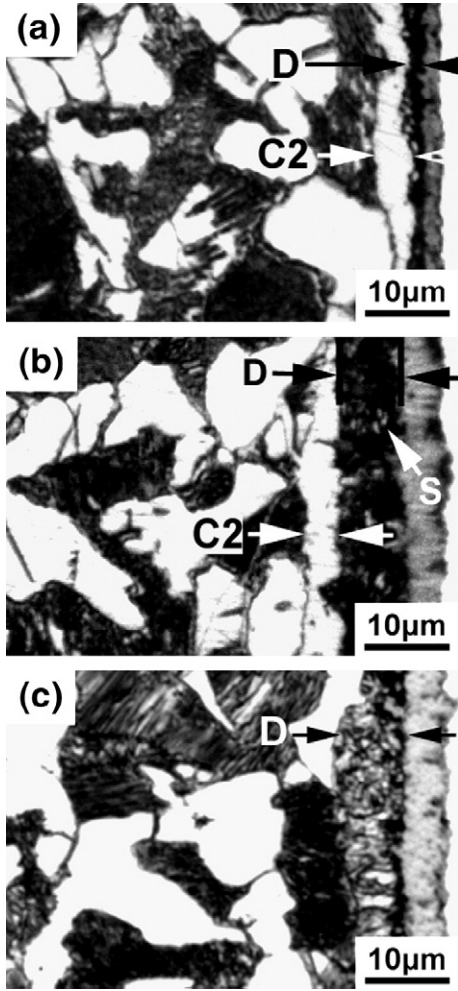
Fig. 6. Microstructural evolutions in the "black zone" for specimens chromized at 550 °C for (a) 0.5 h; (b) 1 h; and (c) 3 h.

indicating that the D layer in Fig. 5(a) is different from that in Fig. 5(c, e) in microstructure and composition. Fig. 6 shows more details of such D layer as those shown in Fig. 5(a, c, e). The entire D sub-layer(Fig. 6 (a)) was preferentially etched and turned "black" under optical microscope at the initial stages of TRD(treated at 550 °C for 0.5 h), and hence is also called "black zone". In the later stages, however, a corrosion-resistant phase constituent (Fig. 6(b), marked S) seemed to have been precipitated in the previous "black zone", and the latter narrowed and disappeared by prolonging the chromizing time (Fig. 6(c)). It is likely that the chromium atoms diffusing into the zone from the outer surface to combine with the nitrogen atoms diffusing to the zone from the residual plasma nitrided compound layer are responsible for the precipitation of these phase constituents, and thus for the CrN compound layer, layer thickening with increasing chromizing time. The diffusion in of chromium atoms by a substitutional mechanism is confirmed by the secondary Fe peak detected at the depth of $0-1$ μm in Fig. 5 (d), that is produced by the surplus Fe atoms resulting from the inward diffusion of chromium atoms. From this viewpoint, the

chroming at 550 °C. It is therefore assumed that the three sub-layer chromized layer is not the final microstructure of the plasma nitrided compound layer subjected to duplex chromizing, instead, it is formed due to an incomplete chromizing process. As is seen in Fig. 5 (e), the chromium nitride layer could be thickened by prolonging the chromizing time until the inner nitrided compound layer is ultimately consumed. From this point of view, the three sub-layers presented by Wu et al. [12] may result from an activity of $CrCl_2$ which was too low to consume all the plasma nitrided compound layer with a chromizing treatment at 590 °C for 6 h, and it is likely that the nitrided compound layer would also disappear by increasing the treatment duration in Wu et al.'s study.

It is seen from Fig. 5 that the chromium peaks present in Fig. 5 (b, d, f) are located in almost the same depth as the nitrogen peaks are, while the location of the carbon peak is strikingly mismatched relative to the chromium peak (Fig. 5(f)), thus suggesting that the compound layer (C1 layer) consists of chromium nitride. Fig. 5 (b) shows a nitrogen depleted zone at a depth of about $2-3$ μm, and the diffusion of nitrogen from this zone towards the outer surface is responsible for this depletion. However, there is no such N-detected zone in Fig. 5 (d, f), thus
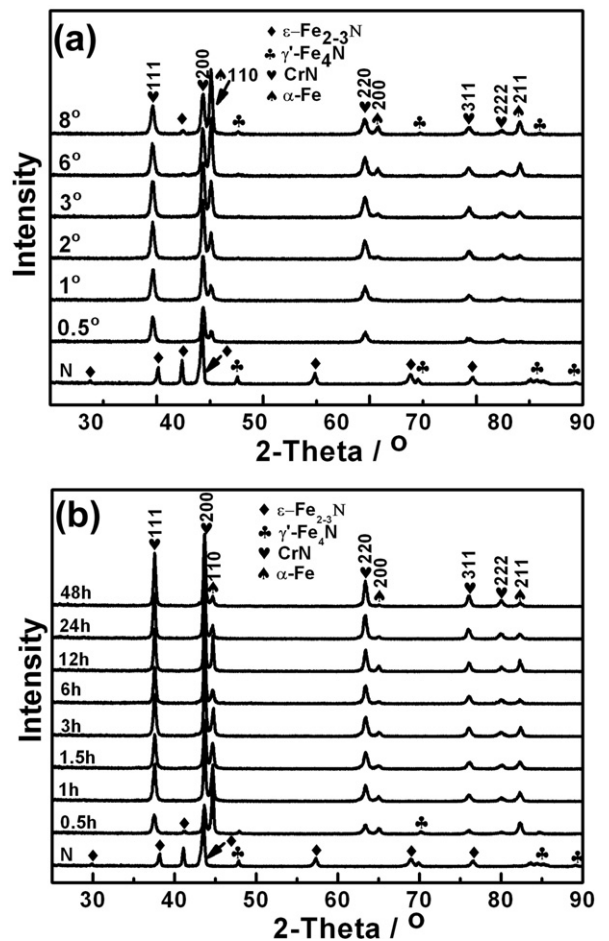

Fig. 7. Phase structure evolving in low-temperature chromizing at 550 °C. (a) Phase structure in the "black zone" for specimen chromized at 550 °C for 0.5 h, determined by sample tilting diffraction, (b) Phase structure evolving with increasing the chromizing time, determined by conventional Bragg diffraction, 'N' for plasma nitrided specimen; Angle "0.5°" means the tilted angle $\alpha_0 = 0.5°$; and the other angles have similar meanings. All, except 'N', were from specimens of group B.

"black zone", which is usually considered as a microstructural defect in other duplex processes [17,18], can instead promote the chromium atom diffusion deeper into the substrates.

In order to clarify the phase structure of the "black zone", the sample tilting diffraction (STD) mode of X-ray scanning was employed, in which the effective penetration depth of X-ray can be adjusted by varying the tilting angle, α_0 [19]. Fig. 7 (a) shows the phase structure varying with the depth on the specimen chromized at 550 °C for 0.5 h. The intensity of α-Fe increased with increasing the penetration depth, and exceeded that of CrN when α_0 reached 6°, thus suggesting that the major phase in the "black zone" in Fig. 6 was α-Fe, and the decomposing transformation path of the plasma nitrided compound layer is ε-Fe$_{2-3}$N $\rightarrow \gamma'$-Fe$_4$N $\rightarrow \alpha$-Fe. It is therefore concluded that the CrN was the major phase of the chromium nitride layer, and the ε-Fe$_{2-3}$N and γ'-Fe$_4$N shown up at 6° was from the residual plasma nitrided compound layer ("C2" layer in Fig. 5).

Fig. 7(b) shows a similar but more striking phase structure evolution than that revealed in Fig. 4. However, no detectable diffraction peaks were found from "C2" layer shown in Fig. 5 (c), possibly due to the thin and discontinuous residual plasma nitrided compound layer which is difficult to be identified by means of XRD. No new type of chromium nitrides phase, besides the CrN, was identified by prolonging the chromizing time until 48 h. It is therefore believed that the low-temperature chromizing process proceeded by a unique mechanism in the temperature range of 500–550 °C.

3.5. Properties of the duplex chromized layer formed at 550 °C

It was found that the microstructure and property of the duplex chromized specimens were well reproducible, since specimens of both group A and group B, which were chromized with the same procedures except for a slightly higher temperature for group B, yielded almost the same microstructure and phase structure. Optical microscopic results indicated
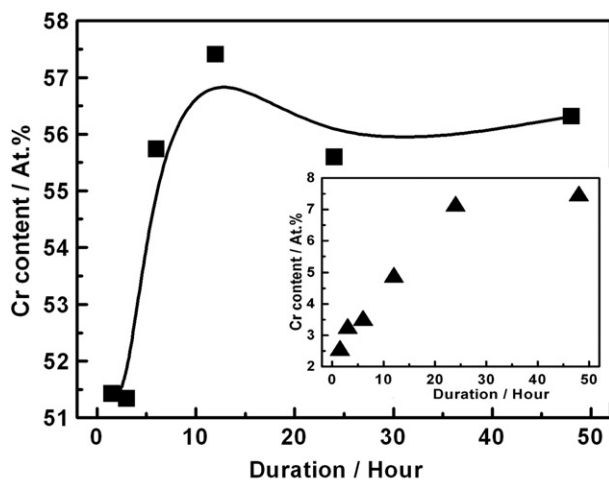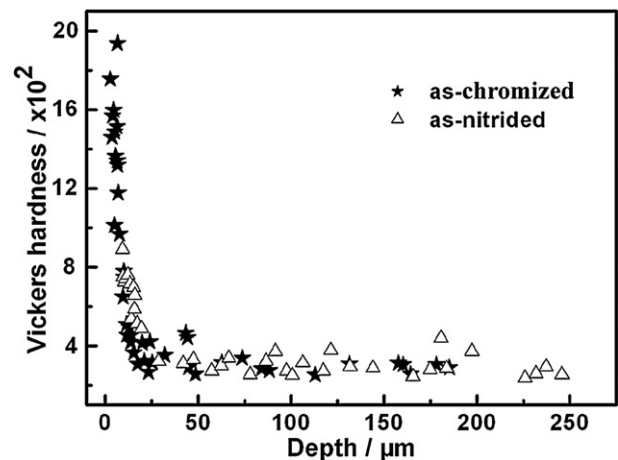

Fig. 9. Hardness profile across the coatings. '★' specimens of group B chromized at 550 °C for 6 h; 'Δ' specimens plasma nitrided at 540–560 °C for 5.5 h.

that the thickness of the CrN layer was hardly increased by further prolonging the chromizing time after the plasma nitrided compound layer had been consumed, suggesting that the major nitrogen source for forming the CrN layer was supplied by the decomposition of the plasma nitrided compound layer. The average thickness of the CrN layer was about 7.4 μm for chromizing at 550 °C for 6 h.

As is illustrated by Fig. 8, the average chromium content of about 55.5 at.% in the CrN layer kept nearly unchanged when the specimens were chromized at 550 °C for over 6 h. The chromium content values in Fig. 8 were quoted in atomic fraction, for there was an inherent error produced if the values were quoted in weight percentage, and this error became quite significant for dilute solutions [13]. As shown by the inserted plot in Fig. 8, the average chromium content in the diffusional layer gained a continuous increase until the chromizing process was ended.

Fig. 9 shows the Vickers hardness profiles across the specimens which were plasma nitrided at 540–560 °C for 5.5 h, followed by low-temperature chromizing at 550 °C for 6 h. The essentially identical hardness profiles from 25 μm to 250 μm for the 2 sets of specimens indicate that the property (hardness) in the interior of the specimen kept unchanged during the chromizing treatment. The average hardness of the CrN layer was 1476 HV$_{0.01}$, and that of the diffusional layer was 629 HV$_{0.01}$.

According to C.P. Luo et al.'s [20] TEM observations, the CrN compound layer was composed of evenly distributed nano-sized (50–70 nm) CrN grains the formation of which was promoted by (1) the high thermodynamic driving force for CrN formation (Fig. 1), (2) the high nucleation rate resulting from the ample supply of Cr and N atoms in the near-surface layer, and (3) the difficult growth of the CrN grains due to the low diffusivity of the atoms at relatively low temperatures. These nano-sized and evenly distributed CrN grains were definitely responsible for the high hardness of the CrN compound layer and hence for the chromized coating as a whole. Detailed TEM observations are to be undertaken in the short future.

Fig. 8. Cr content in the CrN layer formed by low-temperature chromizing at 550 °C. '■' means Cr content in CrN compound layer, '▲' means Cr content in diffusional layer. All from specimens of group C.

4. Conclusions

A CrN layer with a thin diffusional layer formed underneath was coated on 0.45 wt.% carbon plain steel via plasma nitriding at 540–560 °C for 5.5 h, followed by a salt bath low-temperature chromizing at temperatures ranging from 500 to 550 °C, which is named as duplex chromizing as a whole. Based on the above results and analysis, the following conclusions are drawn.

(1) The chromized layer formed at the initial stages of the duplex chromizing process consisted of three sub-layers, namely the outer CrN layer, the intermediate diffusional layer and the inner residual plasma nitrided compound layer. The residual nitrided compound layer vanished by prolonging the chromizing duration. The activity of $CrCl_2$ in salt bath and the chromizing temperature appreciably influenced the chromizing rate.

(2) The intermediate diffusional layer formed at the initial stages of TRD was seen "black" under OM (hence is called "black zone"), and found consisting of α-Fe as a major phase. The self-exhaustion of the "black zone" by chromium atoms diffusing into the zone to combine with the nitrogen diffusing from the residual plasma nitrided compound layer promoted the chromium atom diffusion deeper into the substrates.

(3) The CrN layer was formed at the expense of the decomposition of the prior plasma nitrided compound layer by following the transformation path ε-$Fe_{2-3}N \rightarrow \gamma'$-$Fe_4N \rightarrow \alpha$-Fe.

(4) The thickening of the CrN layer almost ceased when the prior plasma nitrided compound layer was completely consumed. However, the chromium content in the diffusional layer kept slightly increasing until the end of the chromizing process. A CrN layer with an average thickness of 7.4 μm was formed on the specimens by chromizing at 550 °C for 6 h. A high average micro-hardness of 1476 $HV_{0.01}$ was attained in the CrN layer, which was believed to result from a large amount of nano-sized and evenly distributed CrN grains generated in the layer.

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