Growth of nitrided layers on Fe–Cr alloys

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Abstract

Chromium is an important alloying element present in numerous commercial steels. A systematic study on the nitriding behavior of Fe–Cr alloys is helpful in predicting the properties of nitrided Cr-alloyed steels. Aspects such as microstructural evolution, growth kinetics, and mechanical properties should be particularly emphasized. Fe–Cr alloys containing 5, 10, and 20 wt.% Cr have been arc melted and subsequently plasma nitrided under a N2–80% H2 atmosphere. The microstructure of the resulting nitrided layers was characterized and the microhardness profiles evaluated. Thicker layers developed on low chromium alloys. Differences in hardness profiles were also observed as a function of chromium contents. Nitriding Fe–5% Cr alloys resulted in two discrete fronts, refereed to as the diffusion front and the transformation front. Transformed regions sustained a decrease in hardness from 1000 down to 600 HV, associated with the conversion of homogeneously dispersed fine precipitates into coarser needle like particles immersed in the ferritic matrix. Similar behavior was not observed for the other alloys, where both fronts developed simultaneously. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Ion nitriding consists in a surface hardening process widely employed in steels. It has been used in the fabrication of components for the automobile industry, metallurgical industry and tool manufacturing, among others. The approach allows stainless steel nitriding, which improves overall mechanical properties, especially surface wear resistance. Stainless steels are often difficult to nitride by conventional techniques, such as gas nitriding, due to the presence of a stable oxide layer that coats the surface of the alloy [1]. The intense bombardment of ionized nitrogen impinging on the surface of the material effectively removes the passivation layer, thus exposing the substrate to the nitriding plasma atmosphere [2]. Although, several studies have addressed nitride precipitation in chromium steels, the primary mechanism that rules the onset of the phenomenon has yet to be determined. This is mostly due to the inherent difficulty in investigating precipitation in complex matrices. The driving force to precipitation changes continuously with the concentration of solute elements. With respect to the precipitation of nitrides in chromium steels, such a scenario can be prevented adjusting the nitriding atmosphere and running the process isothermally for binary alloys [3]. Studies on Fe–Cr alloys have demonstrated that, in NH3 atmospheres, both the nitride composition and the mechanism of precipitation depend not only on the temperature but also on the activity of chromium and nitrogen in solid solution. Chromium, in its turn, reduces the activity of nitrogen in iron, improving its solubility and allowing a higher concentration of interstitial nitrogen atoms in solid solution. As a result, thinner nitrided layers are expected to form [4].
Ion nitriding is based on the interaction of a plasma atmosphere with the surface of the material [5]. Due to the complexity of such phenomena, no general model has been proposed to explain the ion-nitriding process [6]. Recent experimental evidences indicate that nitried and diffusion layers result from the saturation of a surface with nitrogen from the plasma atmosphere. Substrate atoms are sputtered and joined with plasma active species in the cathode fall region forming precursor compounds which are subsequently redeposited onto the substrate surface, where stable nitrides can be formed [7]. Nitrided layers generally consist of two distinct zones. An outer layer, referred to as the compound layer, may contain one or both forms of stable nitrides, i.e., $\varepsilon$-Fe$_2$N and $\gamma'$-Fe$_4$N [8]. The innermost zone is called the diffusion layer and consists of a solid solution of nitrogen in ferrite, including fine and dispersed nitride precipitates originated from the reaction of nitrogen with alloying elements.

There exist major differences between the nitriding mechanism of a gas-based process and ion nitriding. Therefore, although the former process has been well established, a systematic investigation of ion nitrided Fe–Cr alloys seems appropriate, in as much as plasma nitriding has been widely employed in industry, replacing conventional nitriding methods such as gas and salt bath. This work reports on plasma nitrided Fe–Cr alloys containing 5, 10, and 20 wt.% chromium. The alloys were ion-nitrided for different periods of time and the resulting features of the compound layers, such as hardness profile, penetration depth and microstructural aspects, have all been evaluated.

2. Materials and methods

Electrolytic iron (99.99%) and metallic chromium (Polisinter, Brazil) of composition 0.04C, 0.01S, 0.02P, 0.2Al, 0.5Si (in wt.%) were used in the preparation of the alloys. The materials were mixed to have three different compositions containing 5, 10, and 20 wt.% chromium. Chromium contents were representative of commercially available stainless steels. The starting powders were mixed together and the alloys are melted in a furnace evacuated to a pressure of approximately 1.0 Pa. The furnace was subsequently purged with argon to a pressure of $4 \times 10^4$ Pa and heated up. A Ti sponge was placed near the sample in order to prevent oxidation. As the sample was melted, the electrode was continuously moved both circularly and longitudinally in order to improve impurity extraction and alloy homogeneity. Further homogenization was obtained remelting the material twice. To assure the presence of a ferritic microstructure, the alloys were heat-treated at 800°C during 24 h under argon. Finally, pellets of 10 mm in diameter and 2 mm thick were cut, polished, bathed in acetone and nitrided.

The plasma nitriding reactor consisted of a Pyrex tube 400 mm high and 320 mm in diameter, yielding a working volume of 0.32 m$^3$. Further details on the experimental setup can be found elsewhere [9]. The alloys were nitrided under the conditions summarized in Table 1. Next, metallographic specimens were mounted, ground, and polished in 15 μm chromium oxide and 0.05 μm alumina slurry. Finally, the specimens were tint etched in 10% sodium thiosulfate. For microprobe analysis, etching was carried out in either marble reagent or 2% nital. Microhardness profiles were obtained from a Carl–Zeiss Jena mph100a tester. A load of 100 g was applied onto the samples in a winding pattern in order to assure that consecutive measurements were independent.

Samples were also characterized by X-ray diffraction in a Siemens D 5000 diffractometer using Cu Kα radiation and a 0.6° slit at both ends of the optical system. The samples were positioned on a spinner at 60 rpm to minimize the effects of the presence of non-homogeneous areas in the structure of the coating layers. Firstly, the range of 35 and 75° (2θ) was investigated at a uniform scan rate of 1° min$^{-1}$. Detailed scans from narrower intervals were also obtained using a step of 0.01° and a holding time of 2 s per point.

3. Results and discussion

Table 2 shows the thickness of the nitried layers deposited on Fe–Cr alloys. The growth kinetics of plasma nitried layers was similar to that observed for gas nitried alloyed steels, i.e. the thickness of nitried
Fig. 1. Penetration depth as a function of chromium content for different nitriding times.

Fig. 2. Microhardness profile of nitrided Fe–5% Cr alloys as a function of nitriding time.

Fig. 3. Microhardness profile of nitrided Fe–10% Cr alloys as a function of nitriding time.

Fig. 4. Microhardness profile of nitrided Fe–20% Cr alloys as a function of nitriding time.

layers increased with the square root of time and the inverse of the chromium contents [10]. Fig. 1 shows that the penetration depth also depended on the chromium concentration. The slope of the plot is lower for samples with relatively low chromium contents. Such trend can be rationalized in terms of microstructural aspects, and affected the microhardness profile of the sample.

Microhardness profiles of all three alloys investigated, featured distinctive characteristics. After some initial nitriding, the profile of the alloy containing 5% chromium (Fig. 2) exhibited a plateau around 750 HV near the surface. At deeper regions, the hardness slightly increased prior to undergoing an abrupt drop to bulk values. Increasing chromium contents to 10 and 20% (Fig. 3 Fig. 4, respectively) did not result in a similar trend. Hardness plateaus were only observed for samples nitrided over 2.5 h and their thickness increased with the nitriding time.

The presence of a low-hardness plateau has been reported in the literature [4]. There is evidence that gas nitriding Fe–Cr alloys for over 24 h at temperatures below 600°C produces a morphological transformation of the grains. The degree of transformation is time dependent and may involve entire grains. Untransformed areas retain relative high hardness, around 1000 HV, whereas transformed areas exhibit a decrease in hardness, down to values between 600 and 700 HV. Those areas have been studied by transmission electron microscope, and have been identified as CrN precipitates aligned in the [100] direction, according to Bäker–Nuting’s relation: (001) (001)CrN: [100]CrN [4]. It has been proposed that the drop in hardness values can be associated with the conversion of homogeneously dispersed fine precipitates into coarser needle like precipitates dispersed in the ferritic matrix [4].

It can then be inferred that nitrided layers present in Fe–5% Cr alloys are characterized by the presence of both transformed and untransformed areas, which
evolve via the movement of two fronts, i.e. a diffusion front represented by the borders of untransformed areas, and a morphological transformation front, represented by the borders of transformed areas. It should be noted, however, that the formation of coarse needle like CrN particles and, consequently, the development of transformed areas requires a lag time necessary to the diffusion of nitrogen towards neighboring chromium atoms. The non-existence of transformed areas after short processing times explains the fact that Fe–5% Cr samples nitrided for 1 h were characterized by higher hardness values than those nitrided over longer times, enough to form transformed areas. The existence of a diffusion front and a morphological transformation front can be visualized in Fig. 5, which shows an alloy containing 5% Cr nitrided for 3 h. Whereas the diffusion front runs parallel to the nitrided surface, the transformation front is oriented according to the grain boundaries.
where the solid solution becomes less effective. Such a stage precedes the one depicted in grain 3. There, fine needle-like precipitates can be observed, particularly in the vicinity of the nitrided surface, where hardness values are constant and around 750 HV, well below the hardness measured for untransformed grains.

Alloys containing 10 and 20% chromium showed similar microstructural aspects, such as that shown in Fig. 7. That image was obtained from a surface etched in Obenhofer solution, which dissolves Fe but not Fe-nitrides. EDS analysis revealed the presence of alternate nitrided layers. According to the ternary Fe–Cr–N phase diagram [11], the observed lamellae consist of alternate layers of CrN and Fe$_4$N. This result was confirmed by X-ray diffraction. XRD patterns were gathered for all three alloys nitrided for 3 h (Fig. 8). In addition to the presence of nitride phases, $\gamma'$-Fe$_4$N, $\varepsilon$-Fe$_{2-3}$N, and CrN, diffraction also revealed the presence the $\alpha$-Fe. Alloys having high chromium contents featured less intense $\gamma'$- and $\varepsilon$-peaks, suggesting thinner compound zones. The stabilization of ferrite by chromium inhibits the growth of both the compound zone consisting of $\gamma'$-Fe$_4$N, $\varepsilon$-Fe$_{2-3}$N and the diffusion zone. The affinity of chromium for nitrogen drives the formation of homogeneously dispersed fine CrN precipitates, which increases the hardness of the nitrided layer. Therefore, increasing the Cr contents decreases the thickness and increases the hardness of the nitrided layer with respect to bulk values, which results in sharper hardness profiles, such as those illustrated in Figs. 3 and 4.

Fig. 6 shows the different stages of the evolution of precipitates. In that image, grains to the left (grain 3) are in the early stages of transformation, i.e., they consist of a Fe–N solid solution containing dispersed precipitates. This can be confirmed by the decrease in microhardness values as the bulk of the sample come closer. Regions nearer the surface (grain 2), although featuring higher nitrogen contents, are characterized by scattered values of hardness, averaging values lower than that of grain 1. This corresponds to an offset point
4. Conclusions

1. The penetration depth depended but did not vary directly with the inverse of the chromium concentration.
2. The hardness profile of Fe–5% Cr alloys depicted a plateau around 750 HV formed after a lag time of 2.5 h. The depth of the plateau increased with nitriding time. At deeper regions of the sample, the hardness initially increased and then abruptly dropped to bulk hardness values.
3. Nitrided layers in Fe–5% Cr alloys are characterized by the presence of a front represented by the borders between transformed and untransformed areas. Increasing the chromium contents to 10 and 20% Cr did not result in similar behavior.
4. Alloys containing 10 and 20% chromium depicted similar microstructural aspects with the presence of alternate layers of CrN and Fe₄N.
5. Chromium stabilizes ferrite, which implies that alloys having high chromium contents featured less intense γ' and ε- diffraction peaks, suggesting the formation of thinner compound layers.

References