Microstructure and Hardness of High Temperature Gas Nitrided AISI 420 Martensitic Stainless Steel

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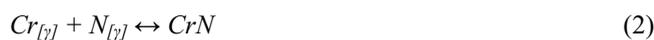
Abstract. This study examined the microstructure and hardness of as-received and nitrided AISI 420 martensitic stainless steels. High temperature gas nitriding was employed to treat the steels at 1200°C for one hour and four hours using nitrogen gas, followed by furnace cooled. Chromium nitride and iron nitride were formed and concentrated at the outmost surface area of the steels since this region contained the highest concentration of nitrogen. The grain size enlarged at the interior region of the nitrided steels due to nitriding at temperature above the recrystallization temperature of the steel and followed by slow cooling. The nitrided steels produced higher surface hardness compared to as-received steel due to the presence of nitrogen and the precipitation of nitrides. Harder steel was produced when nitriding at four hours compared to one hour since more nitrogen permeated into the steel.

1 Introduction

Nitriding is an established hardening technique to strengthen steels. Along with the derivative nitrocarburizing process, nitriding is used to produce many engineering components for example automotive and aircraft parts, bearings, turbine generation systems, and textile machinery [1]. Several nitriding techniques are available to produce steel with high nitrogen content and gas nitriding is one of them. It is a simple technique and does not require any special equipment [2]. This technique involved nitriding at high or low temperature. High temperature gas nitriding (HTGN) is achieved by exposing the sample in nitrogen atmosphere at temperature normally between 1000-1200°C and being held for certain duration of time. It was reported that nitriding at higher temperature had been successfully carried out [3]. Nitrogen gas is preferred in nitriding because this gas is neither toxic nor explosive. Nitriding involves diffusion of nitrogen interstitially into the steel and it is widely employed in improving the hardness of austenitic [4-7], ferritic [8-10], duplex [11], martensitic [12], and precipitation hardening stainless steels [13]. The works acknowledged that utilizing HTGN can diffuse nitrogen deeper into the steels compared to low temperature gas nitriding. Besides producing higher hardness, this process enhanced the impact resistance of the steel's core when applied to martensitic and martensitic-ferritic stainless steels [14]. The improvement of these steels properties were due to nitrides formation such as iron nitrides and other stable nitrides. The amount of permeated nitrogen in the steel influenced the microstructure of the nitrided steel. The microstructure may transform to austenite or martensite based on the amount of diffused nitrogen into the steel. The type

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of material, nitrogen partial pressure, process temperature, and nitriding time influenced the permeation of nitrogen [14]. Formation of nitrogen pearlite was observed when the nitrogen content exceeded its solubility in austenite [15]. Permeation of nitrogen in steel occurs through dissolution in austenite up to its solubility limit and this takes place according to reaction (1) [16]. Strong affinity between nitrogen and chromium at elevated temperature leads to formation of chromium nitrides. These precipitates are formed according to reaction (2) and (3) [16]. They were responsible for the hardening but at the same time, their presence impaired the corrosion resistance of steel [8, 14].

$$\frac{1}{2} N_2(gas) \leftrightarrow N_{[\gamma]} \tag{1}$$

$$Cr_{[\gamma]} + N_{[\gamma]} \leftrightarrow CrN \tag{2}$$

$$2Cr_{[\gamma]} + N_{[\gamma]} \leftrightarrow Cr_2N \tag{3}$$

Martensitic stainless steels are widely used as automotive components, boilers, cutting tools, dental and surgical instruments, machinery components, and structural parts due to their good mechanical properties [9, 17]. Even though nitrided austenitic stainless steels have established themself in many industrial applications, nitrided martensitic stainless steels remain a good choice for low temperature applications and mildly corrosive environments [12]. Besides, these steels have the highest strength among the stainless steels.

This investigation was attempted to study the effect of HTGN on microstructure and hardness of AISI 420 martensitic stainless steel. The comparison was made with as-received steel.

2 Experimental

2.1 Materials

AISI 420 martensitic stainless steel in the form of 20 mm diameter rod manufactured by Böhler Edelstahl GMBH & Co KG, Austria was selected for this study. The chemical composition of as-received steel (in weight percent) is 0.38% C, 14.25% Cr, 0.45% Mn, 0.70% Si, 0.20% V, and Fe (balance). The steel was cut into 1.5 mm thickness using electrical discharge machining (EDM) wire cut to obtain consistent thickness. The steels were ground using silicon carbide abrasive so that after nitriding only a little grinding and polishing are required to produce a good surface finish without removing too much of nitrided layer. Then, the steels were ultrasonically clean with acetone and dried with a hot-air dryer to remove contaminant on the surface.

2.2 Nitriding

The HTGN was carried out in a Carbolite alumina horizontal tube furnace in nitrogen atmosphere. The steels were placed in alumina boat and inserted into the heating zone. Before heating, the air in the furnace was purged with nitrogen for 15 minutes to prevent oxidation of the steels and this was observed by formation of bubbles in the Drechsel bottle. Heating at 5oC/min was started immediately after the purging completed. The nitrogen pressure was set to 75 mmHg and the nitrogen gas was flown into the furnace with constant flowrate of 1000cm3/min when the temperature reached 1200oC. The dwelling time was varied for one hour and four hours. Upon completion of the nitriding, the steels were cooled to room temperature in the furnace.

2.3 Characterization and hardness test

The steels were cross-sectioned using abrasive disc cutter. Then, they were ground with silicon carbide abrasive and polished with 1 μm diamond paste to a mirror like finish. After that, the steels were etched using Nital reagent with a mixture of 5 ml of nitric acid and 100 ml ethanol (95%) to enable microstructural observation [18]. The microstructure was observed and captured using Leica DMLM optical microscope. Elemental analysis was carried out on the cross section of the steels using energy-dispersive x-ray spectroscopy (EDX) attached to Zeiss Supra 55 VP field-emission scanning electron microscope (FESEM). Glancing incidence x-ray diffraction (GIXRD) analysis was performed by Bruker D8-Advance to identify phases present in the surface layers by employing Cu-Kα radiation

in the range of glancing angles of 15-90° with 0.02° interval step mode. The hardness assessment was carried out on the surface of the steels using LECO LM247 AT micro hardness tester. The equipment's indentation hardness scale is in Vickers. The dwelling time and load scale were set to 15 seconds and 100 g_f (HV 100), respectively. Ten measurements were taken on each surface and the hardness mean values were used for the analysis.

3 Results and discussion

After nitriding, the one hour and four hours nitrided steels turned into dark grey and slight grey, respectively. The microstructures of the as-received and nitrided steels are shown in Figure 1. The as-received steel contained coarse and globular carbides in ferrite matrix. The grain size of the nitrided steels enlarged after nitriding as shown in Figure 1b and 1c. It was inevitable to prevent the grain growth when it involved high process temperature such as HTGN followed by slow cooling to room temperature. Since the process temperature was set to 1200°C, the steel experienced heating above its recrystallization temperature. After recrystallization, some of the grains had boundaries and lattice orientation where the growth was more favourable than others. The process continued by atomic migration from grain across a grain boundary to a nearby grain with larger size. The smaller grains shrunk to accommodate the growth of the larger grain. The driving force for this growth was the reduction in total free energy as a result of decreased in boundary area per unit volume due to increase in grain size (i.e., in the high energy grain boundaries and number of relatively high stress) [19]. The microstructure retained this structure since furnace cooled was employed instead of quenching. From the previous work, the single phase austenitic grains enlarged after nitriding. The work also disclosed the refining effect of the martensitic transformation of the soft X4CrNiMo165 martensitic steel produced smaller grain size in the core after quenching [5].
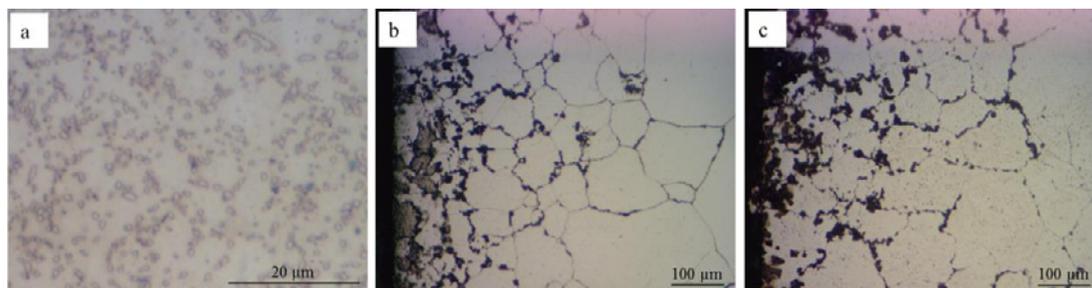

Figure 1. Optical micrographs of (a) as-received, (b) one hour nitrided, and (c) four hours nitrided.

The nitriding process produced precipitates that were concentrated in the grain boundary of the outmost surface area because this region contained the highest amount of nitrogen (Figure 1b and 1c). The nitrogen content at the surface was related to the nitride precipitation rate and nitrogen uptake reaction. At longer nitriding time, precipitation of chromium nitride was the controlling reaction and this highly depended on the chromium diffusion in austenite [14]. Upon GIXRD confirmation as can be seen in Figure 2b and 2c, the precipitates in one hour and four hours nitrided steels were Fe_2N and Cr_2N. There was no evidence found for formation of other phase within the sensitivity of the technique. Fe_2N and Cr_2N have hexagonal lattice systems. The formation of nitrides can be described as follows. When the temperature of steel during nitriding was increased, the crystalline structures of the steel began to vibrate around their discrete lattice points. The vibration occurred at molecular and atomic level. Since nitrogen has smaller size compared to iron, it migrated via interstitial sites in the iron-based lattice structure. This type of atom migration required lower activation energy compared to exchange of location between adjacent atoms or motion of vacancies in the lattice structure of the materials. The nitrogen then combined with iron to form iron nitrides as well as other stable nitrides and in this case, chromium nitride was formed due to strong affinity between chromium and nitrogen [20]. The degree of nitrogen interaction with steel's alloying elements influenced the type of nitride precipitation. A strong interaction was observed in steel containing elements like Al and Ti. Steel with

higher chromium content (more than 5.6 mass percent) presented strong interaction characteristics with nitrogen [17]. Therefore, 14.25wt% Cr in the steel was high enough for interacting with nitrogen to form chromium nitride. The similarity was found in the previous work for formation of nitrides. At low tempering temperature, MN type nitrides were precipitated in martensitic stainless steel, while M_2N nitrides were precipitated at a high tempering temperature, where M signifies a metallic element, specifically either Cr or Fe [9]. The possible reason behind the formation of Fe_2N could be due to the presence of high carbon content (0.38wt%) [12]. No carbides were detected in the nitrided steels since most of them were dissolved when austenitizing at 1200°C. The alloy content increased and martensite transformation range decreased due to the dissolved carbides. This increased the likelihood for formation of retained austenite after cooling [21]. From the EDX analysis on the precipitates, they contained high chromium content especially in four hours nitrided steel with the maximum concentration of 29.9 wt%. The consumption of chromium to form precipitates reduced the chromium content in the surface matrix as low as 3.28 wt%. This made the steels susceptible to intergranular corrosion and decreased their toughness [8, 14].
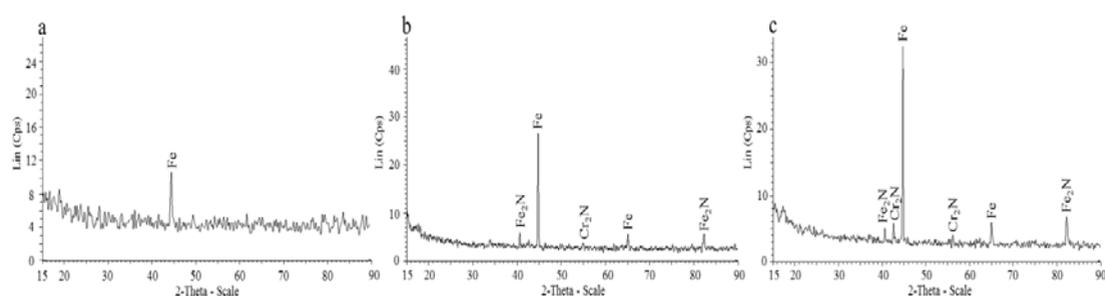

Figure 2. X-ray diffractograms of (a) as-received, (b) one hour nitrided, and (c) four hours nitrided.

Nitrided steels produced higher hardness compared to as-received steel (Figure 3). As-received steel had a hardness of 203 HV and it was increased to 331 HV when nitriding at one hour. When nitrogen diffused into the steel, it induced elastic distortion in the crystal lattice and increased the internal friction causing the movement of dislocation became more difficult. As a result, the strength of the steel was enhanced. Diffusion of nitrogen into the steel involved non steady-state condition which obeys Fick's second law of diffusion where it was affected by temperature and time. The hardness increased with longer nitriding time due to more nitrogen dissolved in the steel which can be seen in four hours nitrided steel that contained more precipitates compared to nitriding at one hour. It was reported that the precipitation of nitrides influenced the increase in hardness of the steels [9, 17]. Therefore, nitriding the steel for four hours produced higher hardness was associated to its higher nitrogen content and more precipitates. However, the increase in hardness between one hour and four hours nitrided steels was not significant since the values did not differ too much since longer nitrided steel produced 363 HV of hardness with the increase of 32 HV only.
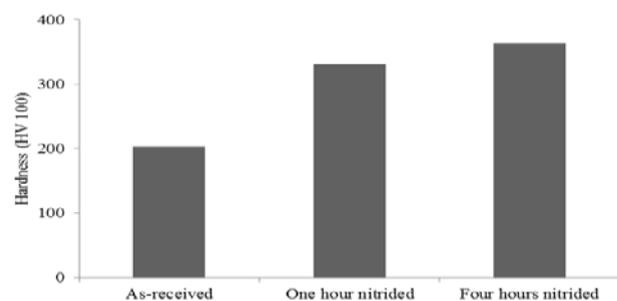

Figure 3. Surface hardness values of as-received and nitrided steels.

4 Conclusions

In conclusion, nitrided AISI 420 martensitic stainless steels were obtained using HTGN with predominantly Fe2N and Cr2N on the surface. Since nitriding above the recrystallization and slow cooling to room temperature were employed, the grain size of the steels enlarged. The precipitates were concentrated at the outmost surface area of the steels due to high nitrogen concentration at this region. The HTGN enhanced the surface hardness of the steels. The increase in hardness was contributed by the existence of the precipitates near the nitrided surfaces. Prolonging the nitriding time diffused more nitrogen into the steel, subsequently, improving the steel's hardness.

Acknowledgements

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