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Isothermal decomposition behavior of the high nitrogen concentration γ-Fe[N] prepared from pure iron

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ABSTRACT

The isothermal decomposition characteristic of the homogeneous high nitrogen austenitic samples prepared by a new multi-stage nitriding process was investigated by SEM and TEM in this paper. Lamellar-structure precipitations arranged on the decomposed austenite grain boundaries (GBs) and the flaky γ′ particles and network-structure precipitations appeared inside of the γ matrix. The extra high Vickers hardness more than 800 HV was found in the 5-h aged samples, which was different from those of the bainitic/martensitic structures in Fe–C alloys. The SAED analysis indicates the γ′ has the coherent relation with the parent γ-Fe[N] phase and the interstitial nitrogen atoms are inclined to aggregate on {1 1 0}γ′/γ planes, which also contributes to the hardness of the matrix.

1. Introduction

Dissolved nitrogen atoms in austenitic stainless steels can stabilize the austenite grains and bring them high strength, good impact toughness, excellent corrosion resistance and other benefits [1]. Although new techniques such as high-pressure melting and powder metallurgy methods have been developed for many years, the production of high nitrogen steels (HNSs) has a major obstacle of its low solubility of nitrogen in liquid Fe (<0.045 wt.% at atmospheric pressure) [2,3]. The difficulties in preparing the HNSs samples also greatly restrict the experimental researches on their mechanical, thermal or corrosion properties. Simultaneously, the decomposition mechanisms of high nitrogen austenite are still somewhat unclear, especially the nucleation mechanism of the nitride precipitation from the parent phases and the growth of the ferrite lath on the austenitic grain boundaries (GBs) [4–9].

In the present work, two specially designed contrastive gas-nitriding processes were carried out at an elevated temperature higher than that used in traditional gas-nitriding process to prepare high nitrogen concentration austenite samples. Microstructure observations and hardness analysis were performed on both the as-quenched and the aged samples to investigate the decomposition behavior of the high nitrogen concentration austenite.

2. Experimental

Pure-iron samples with the thickness of 100 μm were annealed in the hydrogen protection atmosphere at 1100 °C for 8 h, and then nitrided in the quartz tube furnace with the inner diameter of 45 mm at 645 °C. The nitriding atmosphere consists of the gaseous ammonia and the gas mixture of nitrogen and hydrogen, which decomposed from other ammonia gas source. In process one, the annealed samples were single-stage nitrided in the atmosphere of 15 vol.%NH_3 + 64 vol.%N_2 + 21 vol.%H_2 for 3 h and then oil quenched. In process two, other samples were two-stage nitrided: (1) in the atmosphere as the former gas content for 6 h, and (2) in the atmosphere of 5 vol.%NH_3 + 72 vol.%N_2 + 23 vol.%H_2 for another 2 h. After nitriding, these samples were isothermally aged at 225 °C in the salt bath for different durations and then water quenched.

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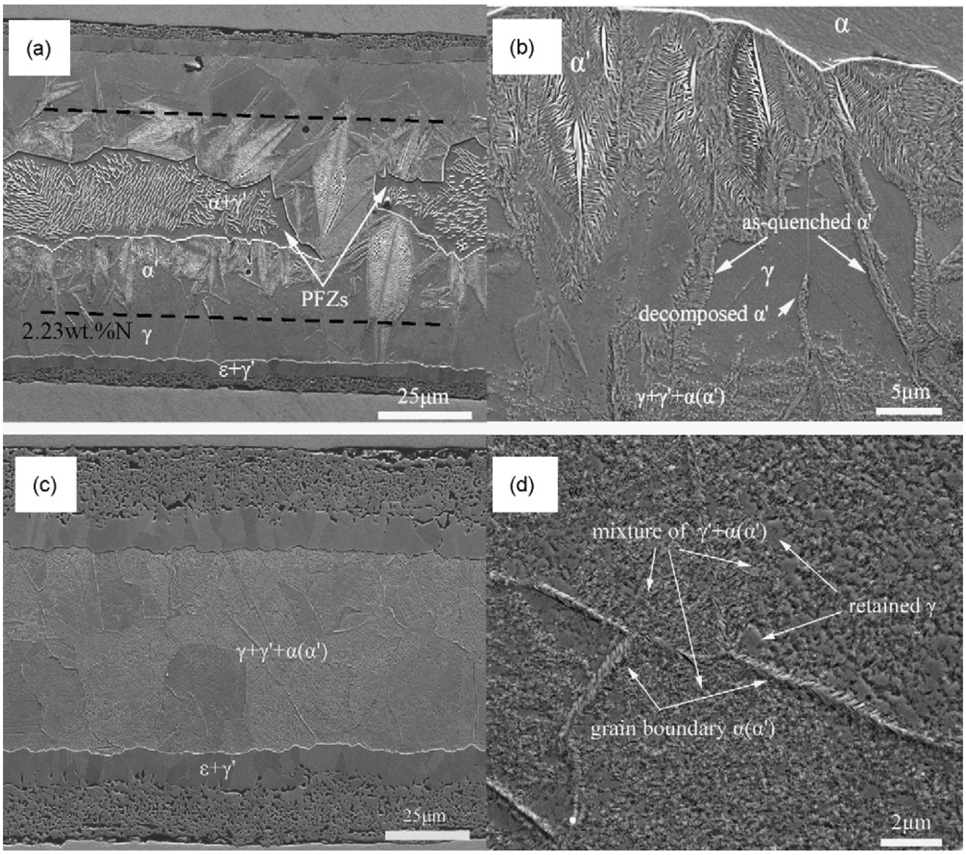

Fig. 1. SEM micrographs of the aged Fe–N samples. (a) Cross-section of the single-stage nitrided and 5-h aged sample; (b) austenite region in single-stage nitrided sample; (c) cross-section of the 6 + 2-h nitrided and 5-h aged sample; (d) austenite region in two-stage nitrided sample.

Microstructures of the nitrided or the aged samples were observed by the scanning electron microscope (Philips FEI Quanta 200), and their microhardness was tested by the Vickers hardness tester (MH-6). The aged samples were prepared to thin foils, electric polished in the solution of 10% perchloric acid and 90% acetic acid at the room temperature, and observed by the transmission electron microscope (JEOL JEM-2010 200 kV). Some aged austenite samples were also determined by X-ray diffraction apparatus (D/Max-2200 Cu Kα 40 kV).

3. Results and discussion

3.1. Preparation and ageing process of high nitrogen austenite

The conventional gas nitriding is usually carried out within the temperature range between 500 and 550 °C, however in this work, pure-iron foils (Fe $>$ 99.97 wt.%) were nitrided at 645 °C which is much higher than the eutectoid austenitic temperature (590 °C) of the Fe–N alloy [10]. The designedly elevated temperature brings an additional austenitic transformation to this gas–solid reaction and diffusion process. To obtain the single-phased and homogenous austenite layer, the two-stage nitriding process was put forward. At the first so-called "boost-nitriding" stage, the pure-iron samples were held in the atmosphere with higher Nitrogen potential (N_p) [11]; while at the second so-called "diffusing" stage, the N_p value was decreased to a lower level by adjusting the volume ratio of NH_3 as mentioned above. The higher N_p value in the first stage helps to offer plenty of free nitrogen atoms into the surface layer and accelerate the nitrogen diffusing. However, the lower one in the second stage slows the growth of the nitride layer and homogenize the nitrogen distribution in the γ matrix.

Fig. 1 shows the clear SEM micrographs of the separated layers relative to the different Fe–N phases obtained from the nitrided and the aged samples. The surface nitride layer in Fig. 1(a), i.e. the so-called white layer, consists of the ε-$Fe_{2-3}N$ and γ′-Fe_4N compounds and keeps growing thicker during the nitriding process. The γ-Fe[N] grains nucleate on the interface of the white layer and the original ferrite layer and form a new austenite layer between them. With the moving of the γ/α interface, this new γ layer grows thicker and makes the ferrite layer shrinking to the center.

Bell [12] has given out a relationship between the martensite transformation start temperature (M_s) and nitrogen content (N_c) as: M_s (°C) = 533−228N_c (wt.%). According to this formula, the suppositional boundaries which divide the γ layer into the high-N and low-N regions can be marked out as 2.23 wt.%N lines. The low-N austenite region adjacent to α phase has sheared to α′-Fe[N] martensite when it was oil-quenched to the room temperature(25 °C) after nitriding, while the high-N region adjacent to the surface still remains the austenitic state.

In the low-N austenite region, the plate martensite of α′-Fe[N] has decomposed into the tempered martensite after aged in the salt bath for 5 h, as shown in Fig. 1(b). At the same time, the high-N region decomposed into the dispersed α and γ′ precipitates, which nucleated both inside of the matrix and on the GBs. Their shapes and grain sizes are much different from those of the as-quenched plate martensite.

Fig. 1(c) shows the SEM micrograph of the single-phased austenite with the white layers in a two-stage nitrided sample. The α-Fe[N] grains have completely disappeared and the γ grains have encountered at the center and homogenized due to the nitrogen diffusing. The nitrogen content of γ phase is about 2.5 wt.%

acquired by the XRD technique, which is much higher than that of high nitrogen stainless steels prepared by other metallurgy methods. The lamellar decomposing products on the austenite GBs have the size of 200 nm in length after aged for 5 h, as shown in Fig. 1(d). The tiny precipitates inside of the matrix have much smaller size than those on the GBs, and they grow up more slowly. So we believe that two different phase transformation mechanisms exist in the decomposition of high nitrogen austenite, although this is hard to be explained with the common experience in the bainite transformation of Fe–C system.

3.2. Micro-hardness analysis

Hardness profiles were obtained by the Vickers hardness tester with a load of 50 gf. Line-1 and Line-2 in Fig. 2(a) are the hardness profiles of the two-stage and single-stage nitrided samples, respectively. The hardness values of $\varepsilon + \gamma'$ (white layer) and γ phases in Line-1 are slightly higher than those in Line-2, and it can be attributed to the solid solution strengthening of supersaturated nitrogen atoms. The average hardness of the martensite formed in the low-N austenite region is about 460 HV, which is much higher than that of the adjacent high-N austenite and retained ferrite regions (220 and 160 HV, respectively).

Two-stage nitrided samples with fully austenite phase were aged for 1, 3 and 5 h respectively, and their hardness were tested and listed in Fig. 2(b). For each case, hardness values change little from the surface to the center, that indirectly proves the γ-Fe[N] phase has the homogeneous nitrogen distribution. The average hardness of the γ matrix has slightly increased from 270 HV(as-quenched) to 310 HV(aged for 1 h) and to 400 HV(aged for 3 h). Interestingly, the hardness quickly increases to more than 800 HV after aged for 5 h, which has been doubled during the last two-hour ageing process. The strengthening mechanism of this phenomenon is still unclear and to be investigated in the following study.

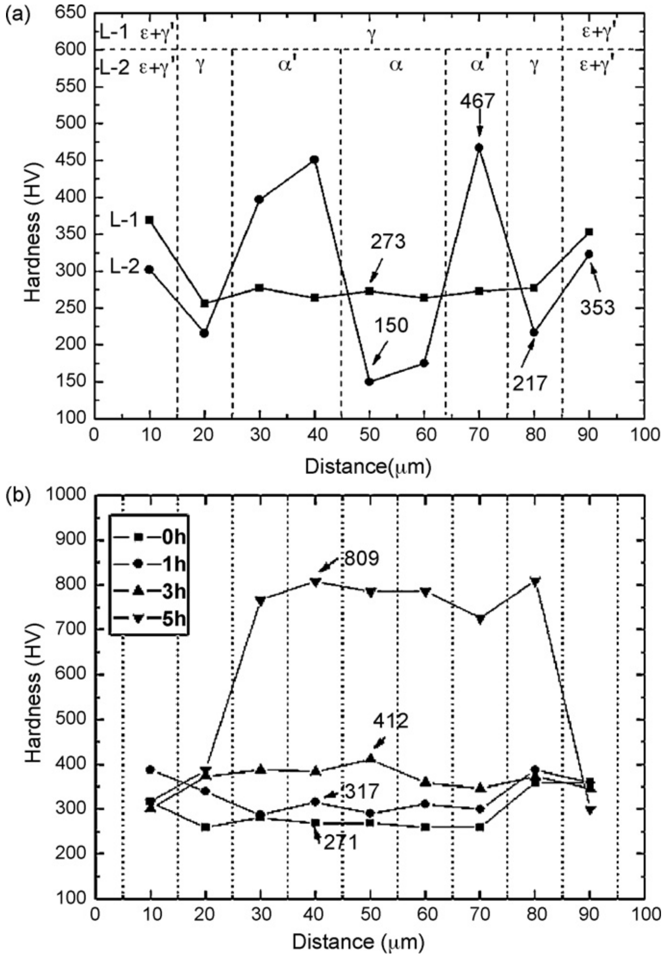

Fig. 2. Hardness profiles of the nitrided and aged samples: (a) hardness distribution of the samples in as-quenched state, L-1: two-stage nitrided sample and L-2: single-stage nitrided sample; (b) hardness profiles of the aged samples.

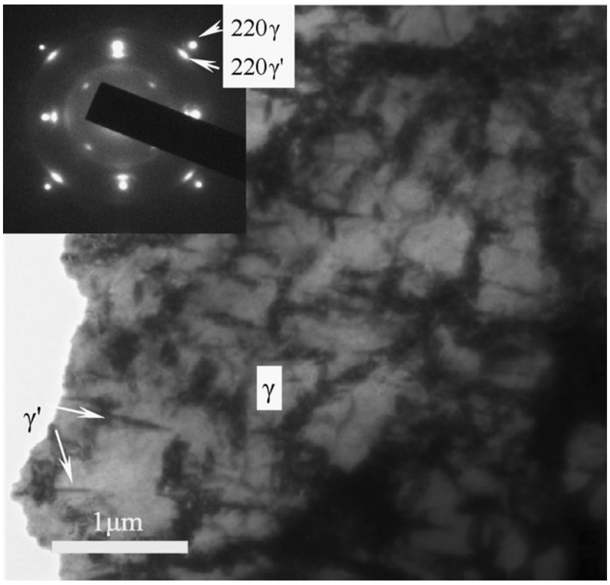

Fig. 3. TEM observation of the aged γ-Fe with both the particle and network, insert picture: SAED pattern of the γ' nitride and the γ matrix with the zone axis of [0 0 1]γ.

3.3. TEM and XRD observations on the aged samples

Fig. 3 shows the TEM micrograph of the 3-h aged high nitrogen γ matrix of the two-stage nitrided sample. The plate particles of γ' (see arrows) arrange on the planes of {1 0 0}γ, their shape is similar to what addressed by Foct et al. [4]. They regarded this kind of particles as the plate γ'-Fe_4N precipitation formed by a shear mechanism. Interestingly, network-structure precipitations were found surrounding the retained γ phase. Jiao et al. [13] indicated the network structure is something like the bainitic clusters which nucleate on the dislocations.

Selected-area electron diffraction (SAED) analysis has found out the coherent relationship between the γ' precipitations and the primary γ matrix with the zone axis of [0 0 1]γ. The spots located at the outer side of the diffraction pattern (see insert in Fig. 3) originate from the γ matrix, and those at the inner side come from the γ' precipitation. It is well understood that the γ and γ' have the same fcc structure, and their only difference is the arrangement of the interstitial nitrogen atoms in the ferrite lattices. When the octahedral interstitials of γ lattice cell are regularly occupied by nitrogen atoms, the γ cells are expanded and turned to γ' cells. Simultaneously, super-lattice spots in the set of γ' pattern appear at some special positions as a reflection of the ordering of the nitrogen atoms. In the pattern of γ', extra spots appear at {1 1 0}γ' and their intensity is higher than those at {1 0 0}γ', which indicates that more interstitial nitrogen atoms aggregate to {1 1 0}γ' planes. Therefore, the chemical formula of γ' precipitation here should be γ'-Fe_4N_{1-x} better than γ'-Fe_4N because of the lack of nitrogen atoms on some other planes.

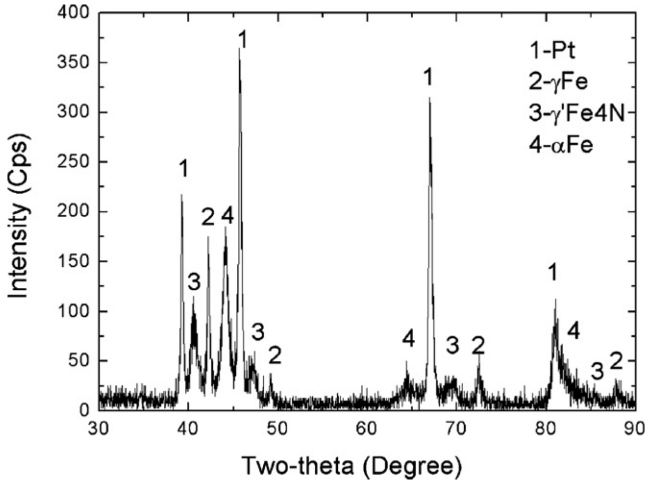

Fig. 4. XRD spectrum of the 2-h aged sample. Pt peaks are induced by the stage carrier.

Fig. 4 shows the X-ray diffraction spectrum of the 2-h aged sample. The peak series1 is the diffraction of platinum which is induced by the stage carrier. Series2 is the peaks of retained γ-Fe[N] whose intensity has decreased greatly after 2-h ageing process. The peaks of decomposed products of γ'-Fe_4N and α-Fe are denoted as series3 and series4, respectively. Their changes of peak shape and shifts of 2θ degrees all accord with the SEM and TEM observations. The more details can be obtained from Ref. [14].

4. Conclusions

The two-stage nitriding process provides an economical and useful way to produce the high nitrogen austenitic alloys in thin-foil shape instead of the metallurgy methods. Our investigation shows that the decomposition products of high nitrogen concentration austenite consist of lamellar precipitations on the austenite GBs, plate γ′ precipitation and network-structure precipitations inside of the matrix, while the γ′ precipitates are coherent with the parent γ-Fe[N] and the interstitial nitrogen atoms are inclined to aggregate on {1 1 0}γ′ planes. We believe that the strengthening mechanism of the aged high nitrogen austenite cannot be simply considered as a solid solution and precipitation strengthening. It may also be attributed to the coherent relation between precipitations and parent phase, and the short range ordering of the interstitial nitrogen atoms.

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