Anomalous Nitrogen Solubility in Gradient Nanostructured Layer Formed in the Surface of Bulk Iron by Severe Plastic Deformation under Friction

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Abstract

By means of friction nitriding (FN) the deformation-induced structure, which includes section of nano-sized grains and that of submicro-sized grains, was formed at the top surface of pure Fe sample. Nitrogen content in bcc-Fe[N] solid solution of ultra fine grains enhanced dramatically compared to that obtained for large-grained iron subjected to conventional nitriding in furnace. When grain/cell size was limited to less than 1 μm nitrogen content reaches the value of about 0.3 wt.% that is even by 3 times higher than that appointed by binary system Fe–N for bcc–Fe[N] solid solution at the temperature 863 K at which nitrogen solubility is the highest, i. e. 0.1 wt.%.

Introduction

Nitriding the iron and steel is used widely for improvement of the tribological properties, the fatigue endurance and the corrosion resistance. The microstructural revolution due to ultra grain refining by severe plastic deformation (SPD) results in a lot of novel properties including high strength and hardness as well as other excellent customer characteristics [1], making them attractive for different engineering applications and for upgrading conventional manufacturing processes. Several SPD–based techniques capable for providing the effective grain refinement of bulk metals and alloys up to nano- and submicro-meter scales were developed nowadays and compiled in [1]. They can be grouped into two types, i.e. technique for grain refining in volume of material [1] and that in surface layer of material [2]. Nevertheless, there are only a few evidences referred to ultra grain refining the grain structure of nitriding layer [3].

This paper aims to study microstructural features of gradient surface layer on iron formed by SPD forced by directional mass transfer of nitrogen that occurs during FN process. The effect of ultra grain refining the grain structure on nitrogen solubility in the bcc–Fe[N] solid solution is the main objective too.

Experimental Procedures

An iron cylindrical–shaped sample (8 mm in diameter and 50 mm in height) with a purity 99.97 wt. % was used in experimentation. To obtain homogeneous large grains about 80 - 100 μm in size samples were annealed at the temperature about 1223 K

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during 180 min. Then, annealed samples were subjected to friction under strait flow of ammonia-gas (NH_3). This route was developed originally for high efficiency of nitriding process and called "friction nitriding" (FN) [4]. However, it was clarified recently [3] that FN process is especially viable for ultra fine refining the grain structure up to nano-metre scale due to severe plastic deformation being forced additionally by directional mass transfer of dopant element. Therefore, new technique termed "sever plastic deformation forced by diffusion flow" (SPDD) became available for the subject matter.

Fig. 1 shows a schematic presentation of the apparatus used in the present study. Main parts of this apparatus are as follow: (1) chamber that can be closed hermetically when gas atmosphere distinct to air was used; (2) system for gas inputting and pressure control; (3) system for gas outputting; (4) system for sample rotation that is equipped by spindle with chuck for holding the one side of cylindrical sample; (5) two blocks forced to sample surface; (6) system for temperature control by chromel–alumel thermocouple. Ammonia-gas was inputting the chamber through the hole (2) whereas other hole (3) was used for outputting NH_3-gas partly dissociated due to reaction at sample surface.

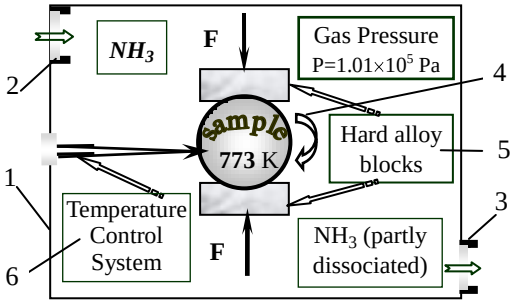

Figure 1. Schematic presentation of the apparatus for FN process: (1) chamber; (2) system for gas inputting and pressure control; (3) system for gas outputting; (4) system for sample rotation; (5) two blocks forced to sample surface; (6) system for temperature control.

Sample was heated by friction occurred due to its rotation between hard alloy (WC-8%Co) blocks being pressed to sample surface by certain force *F*, which ensured the unchanged temperature of 773 K during exposition time about to 60 min. Rotation speed was about 3,000 r.p.m. (50 turnovers per one second). After treatment samples were cooled down to room temperature and, then, they were exposed by visual control.

XRD line profile analysis was performed using X–ray diffractometer (20kV) with Fe radiation. Electrochemical etching the treated surface was used to remove layer-by-layer, so that the evolution of nitrogen content and microstructural features along the depth from the top surface to the strain–free matrix was studied.

Cross–section of samples was observed using powerful optical microscope Neophot–21 (resolution up to 0.4 μm). Furthermore, TEM images and selected area electron diffraction (SAED) patterns were performed to study the structure of refined surface layer. The average grain size was found by observation of TEM images.

Results and Discussion

Fig. 2 shows the structure of nitriding layer on the surface of iron treated by FN process. The results of XRD analysis and cross-sectional observation of treated Fe sample showed that thin layer of Fe_4N nitride (Fig. 2, section 1) of about 10 μm is formed at the top surface of the sample. Then, the layer of Fe_4N nitride is followed by thick section (up to 250μm) of bcc-Fe[N] that exhibits gradient-grained structure of different scale. Several structural sections (2-5) are visible within deformation region (Fig. 2). However, optical microscopy was inadequate to recognise in details the grain structure of ultra fine-grained sections (2, 3). So, the results of TEM observation were used to recognise the grain scale of sections above.

Section (4) of aquiaxed micrometer grains follows the section (3). At least at the last sections (5) adjacent to the strain-free matrix (6) exhibits the banded structure of micrometer grains with inclination to cylindrical surface (Fig. 2). Proper SPD evidences are seen by optical microscopy of this section.

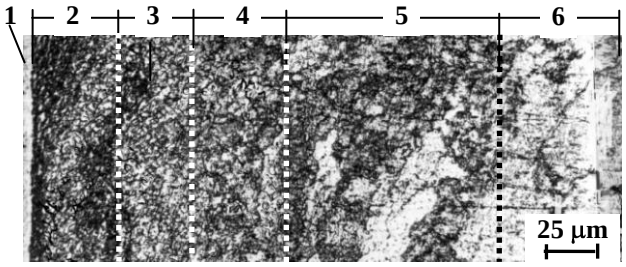

Figure 2. Optical micrograph of nitriding layer on the surface of iron treated by FN process: 1 – layer of Fe_4N nitride; 2 – nanostructured section; 3 – submicrostructured section; 4 – section of aquiaxed micro scale structure; 5 – section of micro scale banded structure; 6 – strain-free matrix.

It is noticed that processing conditions of conventional nitriding are more favourable for stimulating the nitrogen diffusion since exposition temperature about 823 K is higher and typical exposition time of 6 hours is greater than those exploited by FN route. Despite of this extension of nitriding layer formed by FN process is dramatically greater than that obtained typically by conventionally nitriding (Fig. 3).

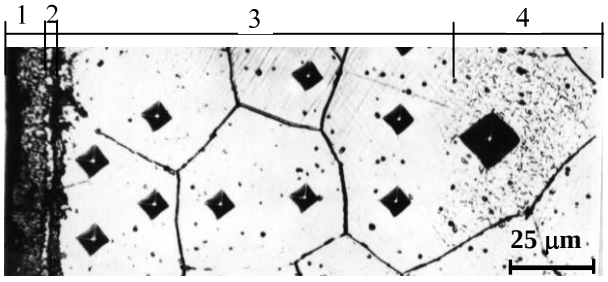

Figure 3. Optical micrograph of nitriding layer on iron sample treated by conventional nitriding in furnace: 1 – layer of $Fe_{2-3}N$ nitride; 2 – layer of Fe_4N nitride; 3 – layer of α-Fe[N]; 4 – α-Fe

(matrix).

Significant acceleration of atomic nitrogen mass transfer through ultra fine grain structure is confirmed additionally by almost full disappearance of undesirable layer of $Fe_{2-3}N$-nitride being usually formed at the top surface of iron subjected to conventional nitriding, as shown in Fig. 3.

TEM images shown in Fig. 4 demonstrate the dominated features for deformation-induced structure of bcc-Fe[N] subjected to FN process.

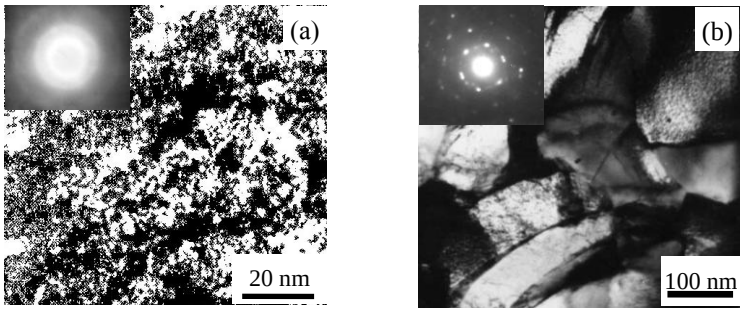

Figure 4. Bright-field TEM images obtained in Fe samples treated by FN process: (a) in nano-sized section (15 μm in deep) and (b) in submicro-sized section (50 μm in deep).

Nano-sized grain/cells with random crystallographic orientation appears in nano-sized section (2) (at the top surface) of bcc–Fe[N] *(*section*)* (up to 50 μm in deep), as indicated by SAED pattern in Fig. 4 (a). Dislocation density in this section is still high. Dislocations are preferably accumulated in tangles (DT) and dense dislocation walls (DDW), which are randomly arranged, as seen in Fig. 4 (a). In the submicro-sized section (3) grains (or subgrains) are orientated randomly and separated by DDW, as evidenced by Fig. 4 (b). It is notable that these grains are divided additionally into smaller equiaxed cells separated by DDW, DT or subboundaries. Also, inside grains one can see evident contrast of high density of lattice dislocations. The results obtained in the present study and those published previously [3] show that grain/cell size increases gradually along the depth from 10 nm at the top surface of nano-sized section to 700 nm at the submicro-sized section. Furthermore, dislocation density decreases gradually from the 10^{12} within nano-grained section to 10^{9} cm/cm^3 in submicro-grained section when Fe-sample was treated by friction.

Fig. 5 (a) exhibits the variation of lattice parameter "a" for bcc–Fe[N] determined along the depth from the top surface to strain-free matrix.

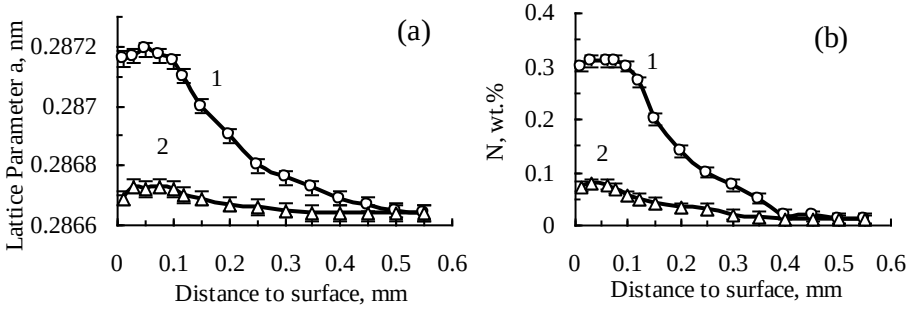

Figure 5. Data for (a) lattice parameter "a" of bcc-Fe[N] and (b) nitrogen content in bcc-Fe[N]

via distance to surface treated (1) by FN process and (2) by conventional nitriding.

Following to Paranjipe et al. [5], who published the correlation *vs.* N wt. % in bcc-Fe[N] solid solution, nitrogen content in refined nitriding layer was obtained, as shown in Fig. 5 (b). Experimental results shown in Fig. 5 (b) clearly demonstrate that nano- and submicro-grained structure of high dislocation density causes nitrogen content in bcc–Fe[N] solid solution to increase dramatically. The amount of nitrogen becomes higher by 10^2 times than that recorded in micro grained bcc–Fe[N] obtained by conventional nitriding and it is even by 3 times higher compared to that appointed by binary system Fe-N for bcc–Fe[N] solid solution at the temperature 863 K at which nitrogen solubility is the highest, i. e. 0.1 wt.%.

Conclusion

The effective refinement of nitriding layer up to nano- and submicro-meter scales has been demonstrated experimentally. The grains of bcc–Fe[N] have been refined up to 10 nm at the top of nano-sized section and they achieved 700 nm at the most within submicro-sized section. Ultra grain refining the grain structure of nitriding layer provides for anomalous high solubility of nitrogen in bcc–Fe. The amount of nitrogen becomes higher by 10^2 times than that recorded in micro grained bcc–Fe[N] obtained by conventional nitriding and it is even 3 times higher compared to that appointed by binary system Fe-N for bcc–Fe[N] solid solution at the temperature 863 K at which nitrogen solubility is the highest, i. e. 0.1 wt.%.

Acknowledgements

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References

1. Noskova N.I., Mulyukov R.R. *Submicrostructural and Nanocrystalline Metals and Alloys.* Ekaterinburg: UrO RAS , 2003, p. 279.
2. Tao N.R., Wang Z.N., Tong W.P. et al. *Acta Mater*. 50 (2002), 4603–4616.
3. A.I. Yurkova, A.V. Belots'ky, and A.V. Byakova et al. "Nanocrystallization in Iron Alloys Induced by Friction Treatment and Nitrogen Diffusion" *Metallic Materials with High Structure Efficiency,* ed. O.N.Senkov et. al. Kluver Academic Publishers, 2004, 113–118.
4. Bilots`ky A.V., Yurkova A.I. *Technologiya i Organizatziya Proizvodstva* 2 (1988), 40–41.
5. V.G.Paranjipe, M.Cohen, M.B.Bever, and C.F.Floe. *J. Metals*., **182**, no. 2, (1950), 261–267.