Nitriding of nanocrystalline pure Fe induced by surface mechanical attrition treatment

Yuzhu Fu[1,2], Weiping Tong[1,a], Mengying Gong[1], Haizhi Li[1], and Liqing Chen[3]

[1] Key Laboratory for Electromagnetic Processing of Materials (Ministry of Education), Northeastern University, 3-11 Wenhua Road, Shenyang 110819, PR China
[2] Liaoning Petrochemical Vocational and Technical College, 2-4 Beijing Road, Jinzhou 121001, PR China
[3] State Key Laboratory of Rolling and Automation, Northeastern University, 3-11 Wenhua Road, Shenyang 110819, PR China

Abstract. Properties of nanocrystalline (nc) materials are different from, and often superior to those of conventional coarse-grained counterparts. Unfortunately, it is still difficult to obtain "ideal" (e.g. full-density, residual stress-free, flaw-free, porosity-free and contamination-free) nc bulk sample by using the present preparation methods. Recently, a new technique named surface mechanical attrition treatment (SMAT) was developed. SMAT enables the fabrication of an nc surface layer on various bulk metals. The nc layer is free of contamination and porosity because the nanocrystallization process is induced by the severe plastic deformation at very high strain rates. In this work, a pure Fe plate was subjected to the SMAT and its microstructure were characterized. The effect of the surface nanocrystalline layer on the gas nitriding process at a lower temperature was also investigated by using structural analysis. The surface nanocrystallization evidently enhances nitriding kinetics and promotes the formation of an ultra-fine polycrystalline compound layer. The results of the investigation showed that this new gas nitriding technique can effectively increase the hardness of the resulting surface layer in comparison with conventional nitriding, demonstrating a significant advancement for materials processing.

1. Introduction

Nitriding is a widely used chemical treatment to form surface nitrides. This technique is of great industrial interest as it forms a unique composite structure with a hard surface (nitride compounds layer) and tough interior so that the global mechanical performance and wear/corrosion resistance of alloys and steels could be greatly improved [1]. However, nitriding processes are performed at high temperatures (above 773 K) for a long duration ($20 \sim 80$ h) and may induce serious deterioration of the substrate for many material families.

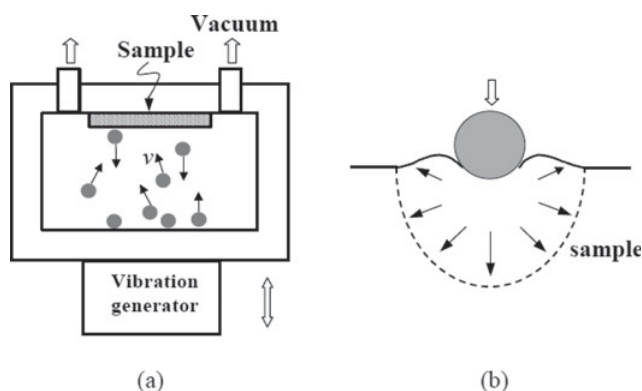[a] Corresponding author: `wptong@mail.neu.edu.cn`

Figure 1. Schematic illustration of the SMAT technique (a) and the localized plastic deformation zone induced by the vibrating ball (b).

To accelerate the chemical reaction of a material surface, a change of the surface microstructure by means of grain refinement is one option [2]. It is known that nanocrystalline (nc) materials possess ultrafine grains with a large number of grain boundaries that may act as fast atomic diffusion channels. Significantly enhanced atomic diffusivities in nanocrystalline materials relative to their conventional coarse-grained counterparts have been experimentally observed. A large number of grain boundaries with various kinds of non-equilibrium defects also constitute a high excess stored energy that may further facilitate their chemical reactivity. It has been demonstrated experimentally that chemical reaction (or phase transformation) kinetics are greatly enhanced during mechanical attrition of solids in which the grain size is significantly reduced into the nm scale and structural defects are created due to the severe plastic deformation [3]. Nitriding of iron was observed when Fe powders were in situ processed by ball-milling in a nitrogen-containing atmosphere at nominal ambient temperature [4], although a considerable transient temperature rise (as high as a few hundred degrees) is always accompanied by the impacts of the milling balls and may have contributed to an enhanced chemical reactivity.

In recent years, we studied enhanced chemical reaction kinetics at lower temperatures when the surface layer of a metal is transformed into nanocrystalline structure, using the nitriding of Fe as an example. The experimental observations clearly show that surface nanocrystallization greatly facilitates the nitriding process and it provides an alternative approach to surface modification of metallic materials.

2. Surface mechanical attrition treatment (SMAT)

A surface layer with nanocrystalline grains can be produced on a bulk metal by using a recently developed surface mechanical attrition treatment (SMAT) [5]. The basic principle of the treatment is the generation of plastic deformation in the top surface layer of a bulk material by means of repeated multidirectional impacts of flying balls onto the sample surface (Fig. 1a). The plastic deformation in the surface layer with a large strain and a high strain rate results in a progressive refinement of coarse grains into the nanometer regime. GCr15 steel balls (with a diameter of 8 mm) were placed at the bottom of a cylinder-shaped vacuum chamber attached to a vibration generator. Because of the high vibration frequency of the system (50 Hz in this work), the sample surface under treatment was impacted repetitively by a large number of balls within a short period of time that the sample surface can be severely plastically deformed (Fig. 1b). As a consequence, grains in the surface layer (can be as much as $10 \sim 50\,\mu$m thick) are effective refined into the nanometer scale.

A pure iron (70 mm × 100 mm × 100 mm in size) was treated to achieve a nanostructured surface layer and the average grain size was about 10 nm (Fig. 2). Prior to the treatment, the samples were
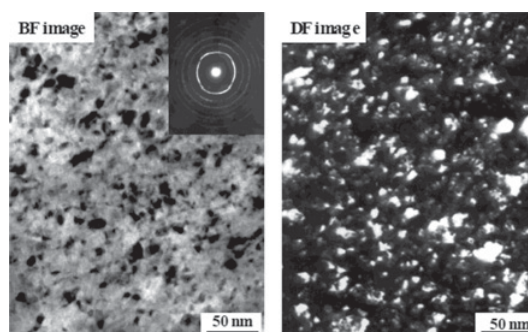
Figure 2. TEM images showing planar microstructures of the top surface layer in the SMAT Fe sample.

annealed at 1223 K for 120 min to eliminate the effect of mechanical polishing on the surface structure and to obtain homogeneous, coarse grains of the α-Fe phase ($\sim$100 μm). The samples were treated in vacuum for 60 min at room temperature. After the treatment, the samples surface are free of fractures and mirror-like smooth (the surface roughness less than 1 μm), which are comparable to the original samples. Positron annihilation spectroscopy experiments indicated that the surface layers of the as-treated samples are free of porosity. A detailed microstructural characterization of the nanostructured surface, together with an underlying nanocrystallization mechanism during the SMAT in terms of the severe plastic deformation mode of bulk materials, can be found in Ref. [5].

Experiments showed that apparent grain growth of the nanocrystalline α-Fe phase in the surface layer may occur at 773 K or above, and the average grain size of the α-Fe nanophase was measured to be about 40 nm at 723 K after 9 h, indicating a rather weak grain growth tendency at this temperature. These results make it possible to investigate nitridation of nc iron and steels at lower temperature.

3. Effect of surface nanocrystalline layer prepared by means of SMAT on gas nitriding

3.1 Gas nitriding SMAT Fe at lower temperatures

Both an untreated and treated Fe samples were nitrided in a flowing high-purity ammonia gas (NH_3) at 573 K for 9 h. After nitriding, a continuous dark-gray surface layer of about 10 μm thick was observed on the SMAT Fe sample (Fig. 3b) which is not seen on the original (Fig. 3a) [1]. Measured nitrogen profiles (Fig. 3c) showed that nitrogen concentration is very high (about 10 wt.%) in the dark-gray layer and it gradually drops with increasing depth beneath the dark-gray layer. For the original sample, the nitrogen concentration is negligible from the top surface to the substrate.

TEM observations combined with electron diffraction verified that the dark-gray layer is composed of ultrafine polycrystalline ε-Fe$_{3\sim2}$N and γ'-Fe$_4$N compounds, as well as a small amount of α-Fe phase (as in Fig. 4a and 4c). The constitution is identical to the compound layer formed during the conventional nitriding of coarse-grained Fe at high temperatures. Underneath the compound layer is a mixture of nitrides and α-Fe solid solution, as indicated in Fig. 4b. Clearly, the nitride (ε-Fe$_{3\sim2}$N) phase forms at the grain boundaries (or junctions) of the ultrafine-grained α-Fe phase. With increasing depth, the volume fraction of nitrides in the mixture layer decreases. XRD analysis confirmed presence of iron nitrides (ε-Fe$_{3\sim2}$N and γ'-Fe$_4$N) in the SMAT sample after nitriding (Fig. 4d), which differs from that in the original Fe sample where no nitride was detected.
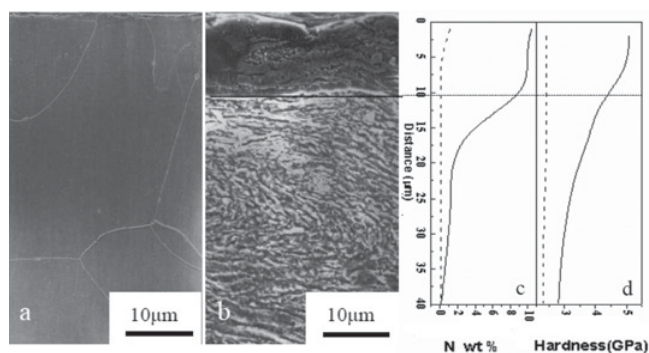
Figure 3. Cross-sectional observations of the original coarse-grained (a) and the SMAT Fe samples after nitriding at 573 K for 9 h (b). The measured nitrogen concentration by using electron probe (c) and microhardness using nanoindentation (d) along the depth from the top surface layer for the original Fe sample (dashed lines) and the treated one (solid lines), respectively.
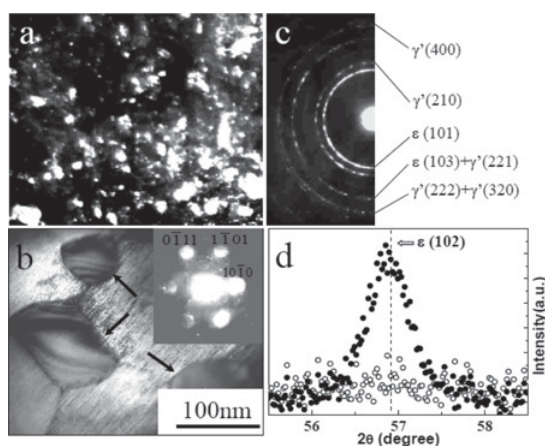

Figure 4. (a) A dark-field TEM image and the corresponding (c) electron diffraction pattern for the compound layer. (b) A TEM image for the microstructure beneath the compound layer. Indicated by arrows are ε phase particles, as confirmed by electron diffraction pattern (insert), formed at grain boundaries and junctions of α-Fe phase. (d) An XRD profile of ε (102) peak for the SMAT Fe sample (solid circles) and the original sample (open circles) after nitriding at 573 K for 9 h. The dashed line indicates the tabulated 2θ position for ε (102) peak.

3.2 Enhanced gas nitriding kinetics by means of grain refinement

The farther structural analysis of the untreated and treated samples nitrided at different temperatures and durations revealed similar results after nitriding. The XRD spectra for the SMAT samples nitrided at 573 K, 623 K, 673 K and 723 K during 4 h respectively are shown in Fig. 5. It can be seen that in all cases, the XRD pattern can be indexed by γ'-Fe$_4$N and ε-Fe$_{3\text{-}2}$N, with peaks of α-Fe phase from substrate material.

These observations confirmed the presence of iron nitrides (ε-Fe$_{2\sim3}$N and γ'-Fe$_4$N) in the SMAT samples after low-temperature nitriding, which differs from the original Fe samples in which no nitrides form when the nitriding temperature is below the critical value (673 K).

Figure 6 shows the gaseous nitriding kinetics for both the untreated and treated samples at lower temperatures. At the nitriding temperature of 723 K a compound layer for treated sample about 18 μm thickness was evidently formed after nitriding for 4 h, while the thickness of compound layer for
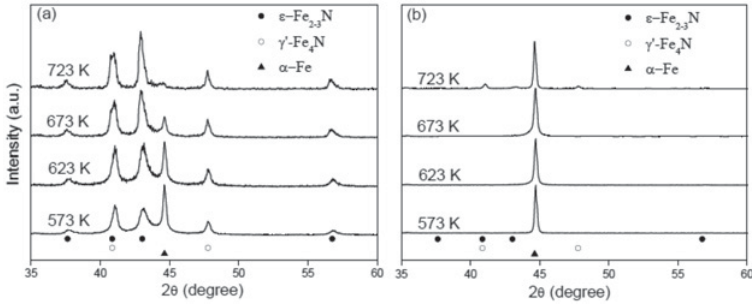
Figure 5. X-ray diffraction patterns of the nanocrystalline Fe (a) and the coarse-grained Fe (b) nitrided at different temperatures for 4 h as indicated.
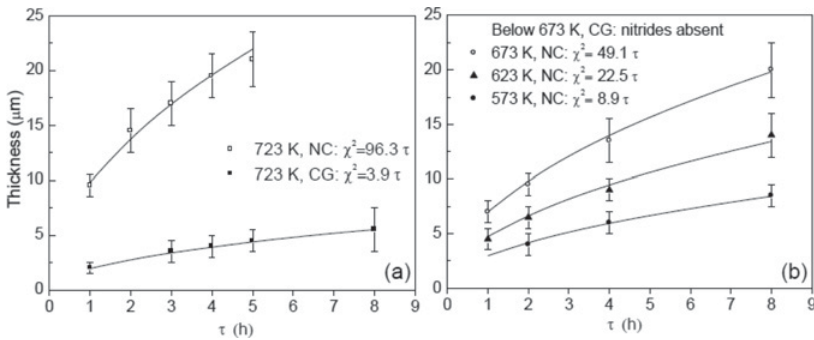

Figure 6. Thickness of compound layer as a function of nitridation duration at different temperatures as indicated for the nanocrystalline Fe (NC) and the coarse-grained Fe (CG).

untreated sample was only 3∼4 μm at the same condition. SEM observations at the nitriding temperature of 573 ∼ 673 K show that the SMAT samples form a continuous compound layer, but the untreated samples do not possess any nitrides, which accord with results of XRD analysis.

The subsequent nitriding kinetics of the as-treated iron with the nanostructured surface layer is greatly enhanced so that the nitriding temperature can be reduce to 573 ∼ 673 K regions, and the ultrafine polycrystalline ε-Fe$_{2\sim3}$N and γ'-Fe$_4$N compounds layer were formed in nanocrystalline grains layer. The ultrafine-grained structure provides a high volume fraction of grain boundaries, roughly about 30 vol.% for an average grain size of 10 nm, which may serve as numerous fast diffusion "channels" for nitrogen atoms [6].

To investigate the nitriding kinetics wherein the nitrogen transport proceeds in composite nanocrystalline ε-Fe$_{2\sim3}$N and γ'-Fe$_4$N compounds, a diffusion model has been established. Based on the Fick's law the model can be expressed as:

$$\chi^2 = 2\Omega\Delta c[D_0 \exp(-Q_{eff}^N/RT)]\tau \qquad (1)$$

where T is the temperature and D_0 as well as R are constants respectively. The effective activation energy for diffusion of nitrogen in composite nanocrystalline ε-Fe$_{2\sim3}$N and γ'-Fe$_4$N nitrides layer can be calculated from the temperature dependence of compound layer thickness ($\tau = 4$h), as shown in Fig. 7, in comparison with that for the coarse-grained Fe nitrides at high temperature (above 773 K). The obtained value of activation energy for diffusion being about 54.39 kJ/mol, is evidently smaller than that for coarse-grained ε phase (80.7 kJ/mol) and γ' phase (88.3 kJ/mol).
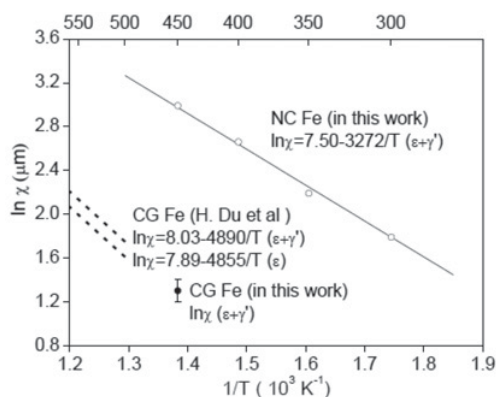
Figure 7. Temperature dependence of the thickness for composite nanocrystalline nitrides layer (NC), in comparison with those for the coarse-grained nitrides layer (CG).

4. Discussions

The gas nitriding results revealed the fact that nitriding kinetics of the SMAT samples with the nanostructured surface layer is greatly enhanced so that the nitriding temperature can be reduced as low as $573 \sim 673$ K. The lowered nitriding temperature may be attributed to enhanced nitrogen diffusion and the driving force for nitride formation in the nanocrystalline surface layer relative to the coarse-grains. The experimental results are further confirmed that the mechanical-induced surface nanocrystallization of Fe created a considerable amount of stored energy in the surface layer that constitutes an effective driving force for the nitriding process at low temperature.

On the other hand, formation of compound phase is a process of nucleation and growth. Grain boundaries are preferable heterogeneous nucleation sites for ε-$Fe_{3\sim2}N$ and γ'-Fe_4N phases, of which the activation energy barrier is much lower than that for homogeneous volume nucleation in the α-Fe lattice.

In this paper it is shown that a nanostructured surface layer on pure Fe samples can be obtained by means of a surface mechanical attrition treatment (SMAT). The subsequent gas nitriding kinetics of the SMAT samples with the nanostructured surface layer was found to be greatly enhanced. Effective nitriding can be performed at temperature as low as 573 K for iron which is much lower than conventional nitriding temperature [7]. The much lowered nitriding temperature for the SMAT samples can be attributed to nano-scale grains sizes with a large amount of defects such as grain boundaries. These defects not only provided more nucleation sites for nitrides, but also greatly enhanced atomic diffusion that facilitates the nitriding process.

5. Conclusions

The microstructure in the surface layer of a pure Fe plate was refined at the nanometer scale by means of a surface mechanical attrition treatment (SMAT) that generates repetitive severe plastic deformation of the surface layer. The subsequent gas nitriding kinetics of the SMAT samples along with the nanostructured surface layer was found to be greatly enhanced. Effective nitriding can be performed at temperature as low as 573 K for iron, which is much lower than conventional nitriding temperature. The investigation results showed that this new gas nitriding technique can effectively increase the hardness of the resultant surface layer in comparison with conventional nitriding. This enhanced processing method demonstrates the technological significance of nanomaterials in improving traditional processing techniques and provides a new approach for selective surface reactions in solids.

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