EXCERPT OF DISSERTATION

Nitriding Iron and 38CrMoAl Steel with a Nanostructured Surface Layer[*]

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Abstract The microstructure of the surface layer on a pure iron and a 38CrMoAl steel samples was refined into the nanometer scale by means of the surface mechanical attrition treatment (SMAT) that generates repetitive severe plastic deformation in the surface layer. The subsequent nitriding kinetics of the SMAT samples with a nanostructured surface layer is greatly enhanced so that the nitriding temperatures can be reduced to 300 ℃ for iron and about 400 ℃ for 38CrMoAl steel, respectively, which are much lower than the conventional nitriding temperatures (above 500 ℃). The novel nitriding process not only facilitates reduction of torsion of the treated samples, but also provides a new approach for selective surface reactions of solids.

Key words nanocrystalline materials, 38CrMoAl steel, iron, nitriding, surface mechanical attrition treatment

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1   Introduction

Most surface modification techniques for solid materials are based on various chemical reactions for obtaining optimised structure and properties in order to improve the global performance of the materials. Widespread uses of these techniques are frequently hindered by the reaction kinetics involved. For example, 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 500 ℃) for a long duration (20~80 h) and may induce serious deterioration of the substrate for many material families.

To accelerate the chemical reaction of a material surface, a change of the surface microstructure by means of grain refinement is one option. 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[2]. 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 constitutes 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.

We demonstrate enhanced chemical reaction kinetics at lower temperatures when the surface layer of a metal is transformed into nanocrystalline structure, using the nitriding of Fe and 38CrMoAl steel 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. 1(a)). 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. 1(b)). As a consequence, grains in the surface layer (can be as much as 10~ 50 μm thick) are effectively refined into the nanometer scale.

A pure iron and a 38CrMoAl steel plates (70 mm × 100 mm × 100 mm in size) were treated to achieve a
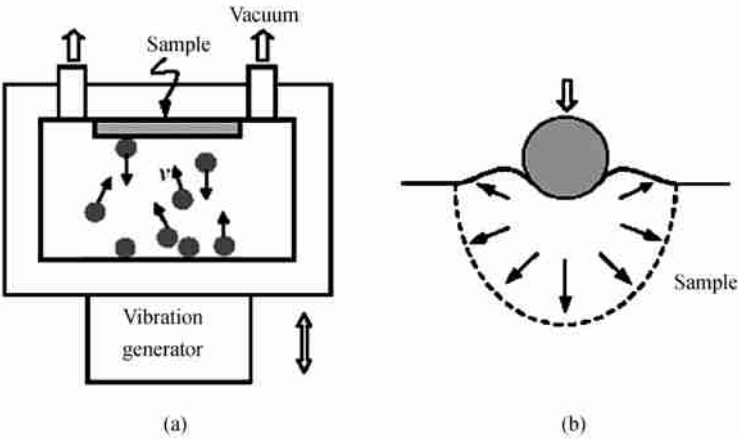

Fig. 1   (a) Schematic illustrations of the SMAT technique and
(b) Localized plastic deformation zone induced by the vibrating ball

nanostructured surface layer and the average grain size was about 10 nm (Fig. 2). Prior to the treatment, the samples were annealed at 950 ℃ 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 (•100 μm). The samples were protected by a high-purity argon atmosphere during the SMAT to avoid oxidation and after the treatment (duration of 60 min) the surfaces of the samples are free of fractures and mirror-like smooth (the surface roughness less than 1 μm), which are comparable to those of the original samples. Positron annihilation spectroscopy experiments indicated that the surface layer 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].
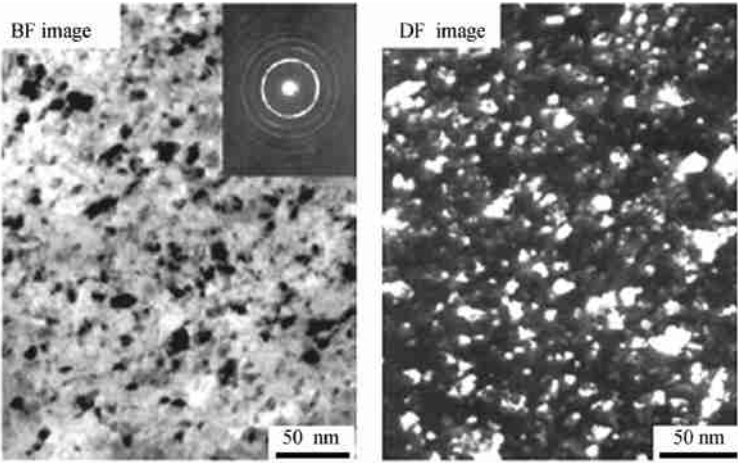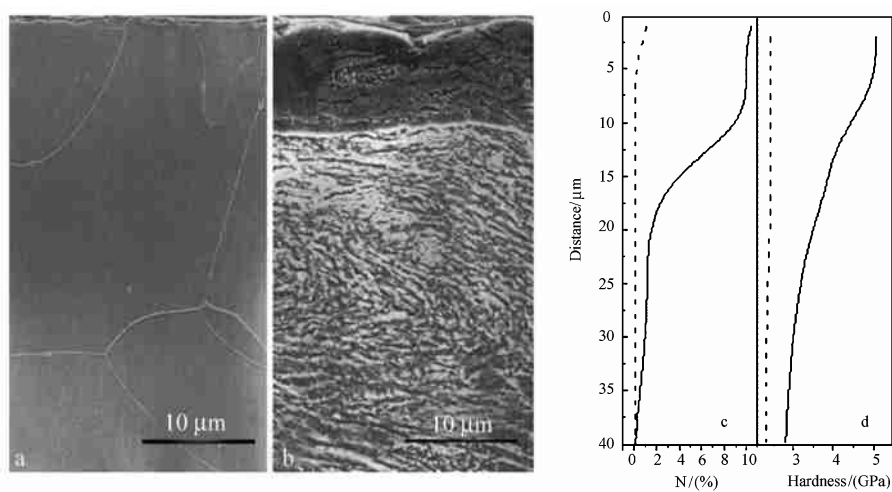

Fig. 2   TEM images showing planar microstructures of the top surface layer in the SMAT Fe sample

Experiments showed that apparent grain growth of the nanocrystalline α-Fe phase in the surface layer may occur at 500 ℃ or above, and the average grain size of the α-Fe nanophase was measured to be about 40 nm at 450 ℃ after 9 h, indicating a rather weak grain growth tendency at this temperature.
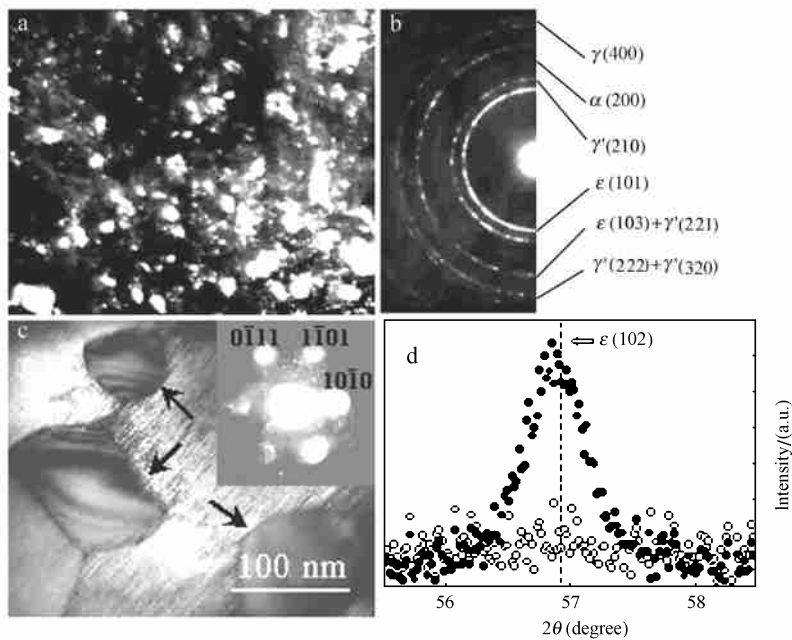
3   Effect of surface nc layer in pure Fe and 38CrMoAl steel on gas nitriding

3.1   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 300 ℃ 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)[6]. Measured nitrogen profiles (Fig. 3c) showed that nitrogen concentration is very high (about 10%) 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$_{3\sim 2}$N and γ'−Fe$_4$N compounds, as well as a small amount of α-Fe phase (as in Fig. 4a and Fig. 4b). The constitution is identical to that 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. 4c. Clearly, the nitride (ε-Fe$_{3\sim 2}$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$_{3\sim 2}$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.

Fig. 3   Cross-sectional observations of the (a) original coarse-grained and the (b) SMAT Fe samples after nitriding at 300℃ for 9 h, (c) and (d) are measured nitrogen concentration (by using electron probe) and microhardness (using nanoindentation) along the depth from the top surface layer for the original Fe sample (dashed lines) and the treated one (solid lines), respectively

Fig. 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 300℃ for 9 h, the dashed line indicates the tabulated two theta position for ε (102) peak

Nanoindentation measurements (Nanoindenter XP, MTS) indicated that the compound layer exhibits a much larger hardness (about 5.0 GPa, which is close to that for the conventional compound layer[1, 7]) than the substrate (•2.3 GPa), as depicted in Fig. 3d. The variation of hardness along depth agrees well with the structural and compositional analysis results. No hardness variation was noticed for the untreated sample after nitriding at this temperature. Tribological characterization of the samples after nitriding was performed by nanoindentation tests (standard nanoscratch tests) using a Berkovich diamond indenter having a tip radius of about 200 nm. The

coefficients of friction and penetration curves for both samples were measured by scratching a total distance of 400 μm under a constant load of 400 mN. Results showed that the coefficient of friction of the treated sample, was 0.38 ± 0.06 over the whole scratch length, is smaller than that for the original sample 0.52 ± 0.03 (which is close to that of the coarse-grained Fe without nitriding treatment). Profiling the scratch surface showed the penetration depth on the nitrided SMAT Fe sample is less than 1 μm while it is about 2.5 ± 0.5 μm for the untreated sample under the same load. The nanoscratch experiments were repeated for several times and very consistent results were obtained, indicating that the wear and friction resistance of the surface layer following SMAT and nitriding is enhanced.

Corrosion resistance of the nitrided Fe sample after SMAT is considerably increased relative to the original Fe sample, as indicated by the measured corrosion rate (current) as a function of immersion time for both samples with a polarization voltage of ±40 mV in a 3.5 % NaCl solution at ambient temperature. The corrosion current is about 0.11 ± 0.01 mA/cm^2 for the original Fe sample during the whole tested immersion time scale (120 h), while it is only 0.03 ± 0.01 mA/cm^2 for the nitrided SMAT Fe sample with the compound surface layer. Once the compound layer was fully corroded after about 65 h immersion, the corrosion rate gradually increased and approached the value of the coarse-grained Fe sample.

3.2　The formation of ε-Fe$_{3\sim2}$N phase in a SMAT Fe

During nitriding iron and steels, compound layers are formed via thermochemical treatment in an NH$_3$ containing atmosphere. The nitrides consist mostly of γ'-Fe$_4$N and/or ε-Fe$_{3\sim2}$N phases, the exact composition of which depends on the nitriding temperature and the nitrogen potential[1]. At a given nitriding temperature, a critical nitrogen potential exists, below which no nitride can be formed. The compound layer consisting of γ'-Fe$_4$N and/or ε-Fe$_{3\sim2}$N phases is formed when the nitrogen potential exceeds the critical value.

In this work, we investigated the formation of ε-Fe$_{3\sim2}$N phase in a nc pure Fe sample. Formation of ε-Fe$_{3\sim2}$N phase in the nc α-Fe was observed when the nitrogen potential is below the critical value for the coarse-grained Fe[8]. Nitriding of the SMAT Fe sample was performed in a flowing high-purity ammonia at a total pressure of 1 atm. The decomposition percentage of ammonia (with an accurate of ±1%) was controlled by adjusting the dissociation temperature and the flux of ammonia. The nitriding treatments were carried out at two temperatures of 400 ℃ and 450 ℃, respectively, with a duration of 6 h and different nitrogen potentials.

XRD spectra for the SMAT samples nitrided with different nitrogen potentials show that at both nitriding temperatures, with a decreasing nitrogen potential, diffraction peaks of ε-Fe$_{3\sim2}$N phase reduce gradually and those of γ'-Fe$_4$N and α-Fe phase obviously increase, indicating a substantial decrease of the volume fraction of ε-Fe$_{3\sim2}$N phase. At 450 ℃, for a nitrogen potential of 2.17 atm$^{-1/2}$, the XRD pattern can be indexed by γ'-Fe$_4$N and α-Fe phase, with rather weak peaks of ε-Fe$_{3\sim2}$N. With a further decrease of the nitrogen potential to 1.70 atm$^{-1/2}$, ε-Fe$_{3\sim2}$N phase can not be identified from the XRD pattern. Therefore, this nitrogen potential (1.70 atm$^{-1/2}$) can be regarded as a lower bound to form detectable ε-Fe$_{3\sim2}$N phase at 450 ℃ in the nc α-Fe by using XRD experiments of which the detection sensitivity is about 5% volume. Apparently, this nitrogen potential is much smaller than that for the coarse-grained α-Fe at the same temperature (~ 2.80 atm$^{-1/2}$). XRD results of the SMAT sample nitrided at 400 ℃ showed similar results. The lower bound of nitrogen potential for ε-Fe$_{3\sim2}$N phase formation in the nc α-Fe is about 4.83 atm$^{-1/2}$, comparable to 6.80 atm$^{-1/2}$ for the coarse-grained form.

Figure 5 summarizes the experimental measurements of the ε-Fe$_{3\sim2}$N phase formation in the nc Fe sample. One may clearly find that ε-Fe$_{3\sim2}$N phase can be formed at lower temperatures or with a smaller nitrogen potential for the nc α-Fe compared to that in the coarse-grained form. This phenomenon may be understood in terms of the numerous amounts of grain boundaries in the nanostructured surface layer generated by means of SMAT.

3.3 Nitriding SMAT 38CrMoAl steel at lower temperatures

38CrMoAl steel was a typical nitriding steel, with chemical compositions of (wt.%) 0.37 C, 0.32 Mn, 1.80 Cr, 0.20 Mo, 0.98 Al and bal. Fe. Both an untreated and treated 38CrMoAl steel samples were cut to 7 mm × 10 mm × 10 mm plates, washed carefully using acetone and absolute alcohol, then immediately carried out gaseous nitriding in a flowing high-purity ammonia gas at 400 ℃ for 30 h.

The SEM observations for both 38CrMoAl steel samples after nitriding (Fig. 6) shown that SMAT processes had a significant influence on the kinetics of compound layer formation[9]. The nitrided layers produced at lower temperature include a black-gay compound layer (upper part) and a diffusion zone (lower part) induced by nitrides precipitation. As it can be seen, original 38CrMoAl steel sample (left) after nitriding at 400 ℃ for 30 h in ammonia gas have no continuous compound layer. Only uneven nitrides layer can be observed. However, for the sample that was pre-treated (right), at the same condition, a continuous black surface compound layer of about 20~30 μm thick was observed, which shows the diffusion of nitrogen in surface nc layer is faster than that in coarse-grained sample.

These microhardness profiles (using the MVK-H300 microhardness testing machine with a load 50 g) for the cross-sections of nitrided layers are shown in Fig. 7(a), which can be used to estimate the diffusion zone depths. In the case of SMAT sample nitrided for 30 h, there is a peak hardness of 13.40 GPa at the surface and the hardness decreases slowly with

Fig. 5   Correlation of nitriding temperature and nitrogen potential for formation of ε-Fe$_{3-2}$N determined by means of XRD experiments from the nc α-Fe phase in the SMAT Fe sample (ε/γ' (nc) solid line) in comparison with that for the coarse-grained Fe reported by Lehrer[8] (dashed line)

Fig. 6   Cross-sectional observations of (a) the original coarse-grained and (b) the SMAT 38CrMoAl samples after nitriding at 400 ℃ for 30 h

the distance from the surface. The diffusion zone depth, defined by the distance from the surface to the point where the microhardness was 0.50 GPa higher than that in matrix, was 200 μm. For the original 38CrMoAl steel sample nitrided at same condition the hardness is also greater at the surface (10.15 GPa), but decreases much more rapidly with the distance from the surface, the diffusion zone depth being about 50~60 μm. Obviously, the SMAT processes can significantly increase the thickness and hardness of nitrided layer.

Sliding wear test results (using a SRV reciprocating sliding machine with a WC balling of 10 mm diameter, at a sliding speed 0.1 m/s, under a normal load of 50 N) showed that gas nitriding in the investigated temperature range can significantly increase the wear resistance of the materials. Fig. 7(b) summarizes the result for various
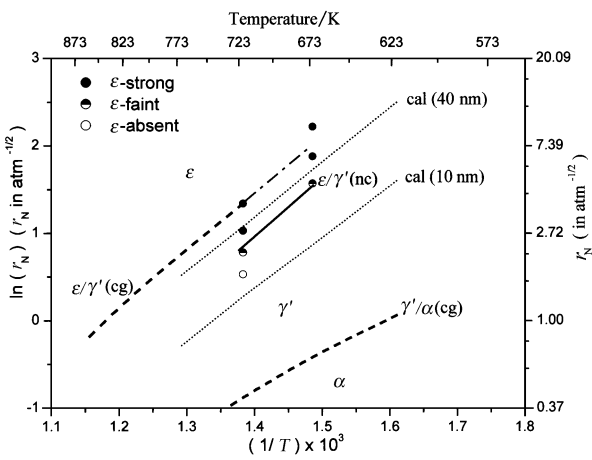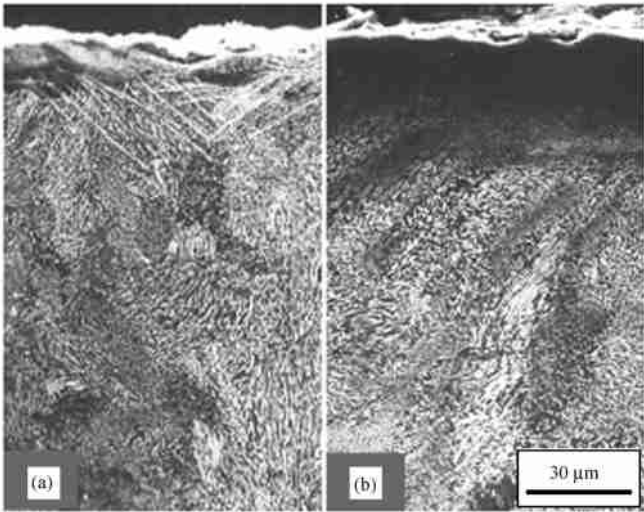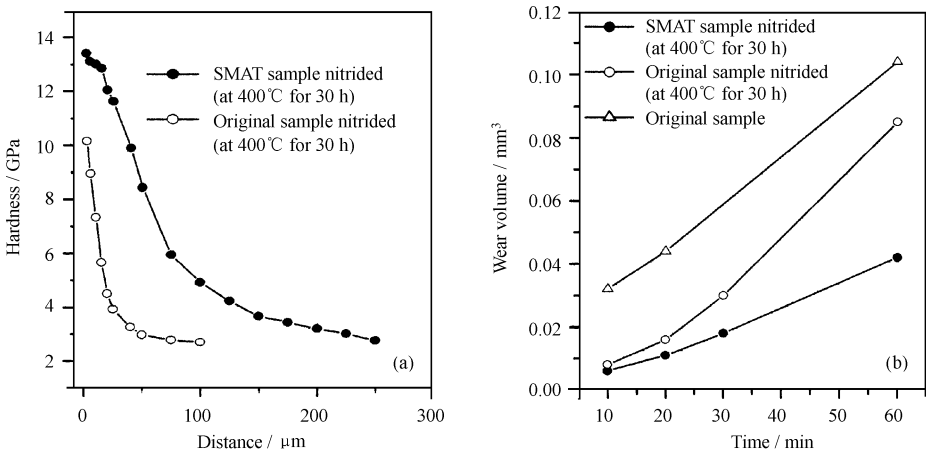
Fig. 7 (a) **Microhardness of nitrided layer along the depth from the top surface and (b)**
variations of wear volume loss with duration for different 38CrMoAl samples as indicated

38CrMoAl steel samples. For both samples nitrided, it can be seen that wear volume loss increases with increasing duration, but the wear of the SMAT sample nitrided is lower than that of the orginal sample nitrided under each sliding time, especially under the duration between 30~ 60 min. This indicates the wear resistance of the 38CrMoAl steel sample nitrided has been improved by per-SMAT processes. This improved abrasion resistance for the SMAT sample nitrided can be mainly attributed to the higher hardness and case depth, especially the higher effective case depth, because wear resistance is closely related to the hardness ratio during different sliding time for the original sample nitrided.

4　Discussion

The much depressed nitriding temperature may be attributed to enhanced nitrogen diffusion in the nanocrystalline surface layer relative to the coarse-grains. In conventional nitriding of coarse-grained iron and steels, nitrogen diffusion in the Fe lattice dominates. For the nanocrystalline materials samples, however, nitrogen mostly diffuses along Fe grain boundaries because of a much smaller activation energy (approximately a half) compared with that for the lattice diffusion. Based on the literature data[10], nitrogen diffusivity in α-Fe lattice is about 3.8×10^{-8} cm^2/s at 500 ℃, and it is about 2 orders of magnitude smaller (5.4×10^{-10} cm^2/s) at 300 ℃. Nitrogen diffusivity along grain boundaries at 300 ℃ is estimated to be about 3.3×10^{-7} cm^2/s (based on an activation energy of about 0.6 times that for the lattice diffusion), which is 3 orders of magnitude larger than the lattice diffusion at the same temperature, and is even higher than the nitrogen diffusivity in lattice at 500 ℃. Evidently, the ultrafine-grained Fe phase in the surface layer provided a large number of defective grain boundaries (and other defects) which enhance the nitrogen diffusion.

On the other hand, the formation of compound phase is a process of nucleation and growth. Grain boundaries are preferable heterogeneous nucleation sites for ε-Fe$_{3-2}$N and γ'-Fe$_4$N phase, of which the activation energy barrier is much smaller than that for homogeneous volume nucleation in the α-Fe lattice. The relative magnitudes of the heterogeneous and homogeneous volume nucleation rates can be expressed by Ref. [11]

$$\frac{N_{he}}{N_{ho}} = \left(\frac{\delta}{D}\right) \exp\left(\frac{\Delta G_{ho}^* - \Delta G_{he}^*}{kT}\right), \qquad (1)$$

where δ is the average grain boundary thickness, D is the average grain size, k is Boltzmann constant and T is temperature. ΔG_{he}^* and ΔG_{ho}^* are activation energies for heterogeneous nucleation at grain boundaries and

homogeneous nucleation, respectively. According to equation (1), the heterogeneous nucleation rate at grain boundaries may increase by an order of 10^4 when grain size reduces from 100 μm to 10 nm. The much enhanced heterogeneous nucleation of compound phase at the ne-Fe grain boundaries may correspond to the enhanced nitriding kinetics observed in the SMAT sample with respect to the coarse-grained counterpart.

From a thermodynamic point of view, the driving force for nitride formation is also enhanced when the Fe and steels are nanostructured. The Gibbs free energy change for the formation of nitrides in coarse-grained Fe at 500 ℃ is about − 8.22 kJ/mol for the γ' phase and − 1.69 kJ/mol for the ε phase. But at 300 ℃, both values become positive, implying these nitrides cannot form at this temperature. The mechanically-induced nanostructures stored a large excess energy in the grain boundaries and grain interior in the form of non-equilibrium defects (such as dislocations), which constitutes an extra driving force for the nitride formation process. The estimated stored energy in a ball-milled nanocrystalline Fe sample with 10 nm grain size is about 2.3 kJ/mol[3]. With this stored excess energy, one may find from calculations that the Gibbs free energy change for the formation of nitrides in the nanocrystalline α-Fe phase at 300 ℃ becomes negative (i.e., formation of nitrides becomes possible). Our experimental evidence 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 temperatures.

Similarly, other surface chemical treatments that are controlled by diffusion of foreign atoms (such as chromium or aluminum) and used in industry to improve the performance of engineering materials can also be enhanced by SMAT. We found a significantly enhanced diffusivity of chromium in the SMAT Fe at 350 ℃, which is about 300~400 ℃ lower than the conventional treatment temperature[12].

5   Summary

In this work, we obtained a nanostructured surface layer on a pure iron and a 38CrMoAl steel samples by means of SMAT. The subsequent gas nitriding kinetics of the SMAT samples with the nanostructured surface layer were found to be greatly enhanced. Effective nitriding can be performed at temperatures as low as 300 ℃ for iron and about 400 ℃ for 38CrMoAl steel, respectively, which are much lower than the conventional gas nitriding temperatures. The much reduced nitriding temperature for the SMAT samples can be attributed to the nano-scale grains with a large amount of grain boundaries. These defects not only provided more nucleation sites for nitrides, but also greatly enhanced atomic diffusion that facilitates the nitriding process. The remarkable depression in the nitriding temperature by means of the surface nanocrystallization demonstrates a significant advancement for materials processing. The depressed nitriding temperature may allow for the nitriding of material families (alloys and steels) and work-pieces that could not be treated by the conventional nitriding at high temperature.

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38CrMoAl

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　　　　　　　(SMAT) ,　　　　　38CrMoAl　　　　　　　　　　　　　　　,

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(> 500 ℃) ,　　　　300 ℃　400 ℃.

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