Nitriding Iron at Lower Temperatures


The microstructure in the surface layer of a pure iron plate was refined at the nanometer scale by means of a surface mechanical attrition treatment that generates repetitive severe plastic deformation of the surface layer. The subsequent nitriding kinetics of the treated iron with the nanostructured surface layer were greatly enhanced, so that the nitriding temperature could be as low as 300°C, which is much lower than conventional nitriding temperatures (above 500°C). 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.

Most surface-modification techniques used for solid materials are based on various chemical reactions that produce optimized structure and properties in order to improve the global performance of the materials. However, widespread uses of these techniques are frequently hindered by the reaction kinetics involved. For example, nitriding is a chemical treatment widely used to form surface nitrides. This technique is of great industrial interest, because it forms a unique composite structure with a hard surface (a layer of Fe-nitride compounds) and a tough interior, so that the global mechanical performance and wear/corrosion resistance of alloys and steels can be greatly improved (1). However, nitriding processes are performed at high temperatures (>500°C) for a long duration (~20 to 80 hours) (1, 2) and may induce serious deterioration of the substrate in many families of materials.

A change of the surface microstructure by means of grain refinement is one option that can be used to accelerate the chemical reaction of a material surface. It is known that nanocrystalline materials possess ultrafine grains with a large number of grain boundaries that may act as fast atomic diffusion channels (3, 4). Greatly enhanced atomic diffusivities in nanocrystalline materials relative to their conventional coarse-grained counterparts have been experimentally observed (5, 6). A large number of grain boundaries with various kinds of nonequilibrium 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 to the nanometer scale and structural defects are created by the severe plastic deformation (7–9). Nitriding of iron was observed when Fe powders were processed in situ by ball-milling in a nitrogen-containing atmosphere at nominal ambient temperature (10, 11), although a considerable transient temperature rise (as high as a few hundred degrees) generally accompanies 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 a nanocrystalline structure, using the nitriding of Fe as an example. Our experimental observations show that surface nanocrystallization greatly facilitates the nitriding process, and it thus provides an alternative approach to surface modification of metallic materials.

A surface layer with nanocrystalline grains can be produced on a bulk metal by using a recently developed surface mechanical attrition treatment (SMAT) (12–14). 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 on 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. Stainless steel balls (with a mirrorlike surface and a diameter of
grains in the surface layer (which could be as much as 50 μm thick) were effectively refined into the nanometer scale.

An iron plate (7 mm by 100 mm by 100 mm in size) with a purity of 99.95 weight percent (wt %) was treated to achieve a nanostructured surface layer. Before treatment, the Fe sample was annealed at 950°C for 120 min to eliminate the effect of mechanical polishing on the surface.

Fig. 2. Cross-sectional observations of (A) an original coarse-grained Fe sample and (B) a SMAT Fe sample after nitriding at 300°C for 9 hours. [In (B), 3A indicates Fig. 3A and 3C indicates Fig. 3C.] We measured (C) nitrogen concentration (by using an electron probe) and (D) microhardness (using nanoindentation) along the depth from the top surface layer in the original Fe sample (dashed lines) and in the treated one (solid lines), respectively.

Fig. 3. (A) A dark-field TEM image and (B) the corresponding electron diffraction pattern for the compound layer indicated in Fig. 2B. (C) A TEM image for the microstructure beneath the compound layer indicated in Fig. 2B. Indicated by arrows are ε-phase particles, as confirmed by the electron diffraction pattern (inset) formed at grain boundaries and junctions of the α-Fe phase. (D) An XRD profile of the ε (102) peak for the SMAT Fe sample (solid circles) and the original sample (open circles) after nitriding at 300°C for 9 hours. The dashed line indicates the tabulated 2θ position for the ε (102) peak.
Surface layers provide a large number of defective grain boundaries (other defects) that enhance the nitrogen diffusion.

From a thermodynamic point of view, the driving force for nitride formation is also enhanced when the Fe phase is nanostructured. The Gibbs free energy change for the formation of nitrides in coarse-grained Fe at 500°C is about $-8.22 \text{ kJ mol}^{-1}$ for the $\gamma'$ phase and $-1.69 \text{ kJ mol}^{-1}$ for the $\epsilon$ phase. Yet at 300°C, both values become positive, thus implying that these nitrides cannot form at this temperature. The mechanically induced nanostructures store a large excess energy in the grain boundaries and grain interior in the form of nonequilibrium 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$^{-1}$. With this stored excess energy, one may find from calculations that the Gibbs free energy change for the formation of nitrides in the nanocrystalline $\alpha$-Fe phase at 300°C becomes negative (i.e., the formation of nitrides becomes possible).

Our experimental evidence confirmed that the mechanically 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 the diffusion of foreign atoms (such as chromium or aluminum) and are used in industry to improve the performance of engineering materials can also be enhanced by SMAT. We found a greatly enhanced diffusivity of chromium in the SMAT Fe at 350°C, which is about 300° to 400°C lower than the conventional treatment temperature.

The substantial reduction of the nitriding temperature by means of surface nanocrystallization is a marked advancement for materials processing. The reduced nitriding temperature may allow for the nitriding of materials families (such as alloys and steels) and work-pieces that cannot be treated by conventional nitriding.

References and Notes
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Figs. S1 and S2

Asynchronous Climate Changes in the North Atlantic and Japan During the Last Termination
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Pollen records from the annually laminated sediment sequence in Lake Suigetsu, Japan, suggest a sequence of climate changes during the Last Termination that resembles that of the North Atlantic region but with noticeable differences in timing. An interstadial interval commenced a few centuries earlier [15,000 years before the present (yr BP)] than the North Atlantic GI-1 (Bølling) event. Conversely, the onset of a Younger Dryas (YD)–like cold reversal (12,300 to 11,250 yr BP) postdated the North Atlantic GS-1 (YD) event by a few centuries. Climate in the Far East during the Last Termination reflected solar insolation changes as much as Atlantic influences.

One of the most pressing matters in late Quaternary paleoclimate research is to establish whether abrupt climatic events were globally synchronous, for this is pivotal to testing ideas about the mechanisms of global climate change. The main obstacle to