Low-temperature nitriding of 38CrMoAl steel with a nanostructured surface layer induced by surface mechanical attrition treatment

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A nanocrystalline surface layer was fabricated on a 38CrMoAl steel plate by means of a surface mechanical attrition treatment (SMAT). The average grain size in the top surface layer (10 μm thick) is about 10 nm, and the grain size stability can be maintained up to 450 °C. The effect of the surface nanocrystalline layer on the gas nitriding process at a lower temperature was investigated by using structural analysis and wear property measurements. The surface nanocrystallization evidently enhances nitriding kinetics and promotes the formation of an ultrathin polycrystalline compound layer. The results of the investigation showed that this new gas nitriding technique can effectively increase the hardness and wear resistance of the resulting surface layer in comparison with conventional nitriding, demonstrating a significant advancement for materials processing.
The raw material used in the present investigation was a 38CrMoAl typical nitriding steel plate of 7 mm × 100 mm × 100 mm, with chemical compositions (wt.%) 0.37 C, 0.32 Mn, 1.80 Cr, 0.20 Mo, 0.98 Al and bal. Fe. The sample was subjected to SMAT processing in order to achieve a nanostructured surface layer. Prior to treatment, the 38CrMoAl steel sample was hardened (oil quenched from 940 °C) and tempered (550 °C for 2 h) to produce the desired mechanical properties (with a hardness of 290 Hv). The SMAT procedure was performed on an apparatus in which steel shots (8 mm in diameter) vibrated by a generator with a frequency of 50 Hz were peening onto the sample. The experimental set-up and the details of the SMAT procedure were previously described in the literature [16,17]. The sample surface was protected by a high-purity argon atmosphere during SMAT processing to avoid oxidation. Repeated attritions induced severe plastic deformation in the surface layer and eventually resulted in the development of nc grains. The nanocrystallization mechanism in the top surface layer is analogous to that during severe plastic deformation of bulk materials where the microstructure can also be refined into nanometer size [20,21]. After the SMAT treatment for 60 min, the surface roughness is comparable to that of the original sample.

Both untreated and treated samples were cut to 7 mm × 10 mm × 10 mm plates, washed carefully using acetone and absolute alcohol, then immediately subjected to gaseous nitriding in a home-made device. Nitriding was performed in a flowing high-purity ammonia gas (NH₃, 99.95%). Further nitriding parameters were as follows: nitrogen pressure 1 atm, temperature 400 °C, treatment duration 30 h. Both specimens were placed perpendicular to the work table of the machine using special holders to ensure uniform nitriding.

2.2. Microstructural characterization

X-ray diffraction (XRD) analysis was used to characterize the average crystallite size and the mean microstrain of the surface layer of the SMAT sample and to identify phases formed during nitriding treatments. The XRD analysis was carried out on a Rigaku D/max 2400 X-ray diffractometer (12 kW), with Cu Kα radiation. Small angular steps of 2θ = 0.02° were taken to measure the intensity of each Bragg diffraction peak. The counting time of 20 s was used to exactly measure the width of the diffraction peak in the step-scanning mode. The average grain size and mean microstrain were calculated from the line broadening of bcc Fe (110), (200), (211), (220), (310) and (222) Bragg diffraction peaks using the Scherrer and Wilson method [22].

Cross-sectional observations of the treated 38CrMoAl steel sample were performed on a JSM-6301F scanning electron microscope (SEM). Microstructural features in the surface layer were characterized by using a Philip EM-420 transmission electron microscope (TEM), operating at a voltage of 120 kV. Thin foil samples for TEM observations were prepared by cutting, grinding and dimpling with a final ion thinning at low temperatures.

The microhardness was measured using a MVK-H300 microhardness testing machine with a load of 50 g and a time of 10 s. Microhardness values were obtained by means of the dependence of the residual penetration depth of the indenter (calculated from the geometry of the Vickers pyramid import) on the applied load. Wear tests were evaluated using a SRV reciprocating sliding machine (Optimal, Germany) under dry pure slide conditions. The tests were performed at room temperature and atmospheric pressure using a WC balling of 10 mm diameter at a sliding speed 0.1 m/s under a normal load of 50 N.

3. Results and discussion

3.1. Microstructure of the SMAT sample

Fig. 1 shows a cross-sectional SEM observation of the SMAT 38CrMoAl sample. Evidence of severe plastic deformation (of about 60–70 μm thick) is present in the treated surface layer, where microstructural morphology differs from that in the matrix. Fig. 2 shows a typical TEM observation of the top surface layer (about 1 μm deep) in the SMAT 38CrMoAl steel sample. The microstructure is characterized by ultrathin equiaxed grains (bcc Fe) with random crystallographic orientations, as indicated by the selected area electron diffraction (SAED) pattern. The mean grain size in the surface layer is approximately 10 nm.

By removal of the surface layer-by-layer, structure evolution along the depth can be determined. The measured average grain size as a function of depth in the SMAT sample using different analysis techniques (XRD and TEM) is summarized in Fig. 3. At a depth of about 30–60 μm from the treated surface, the average size of the equiaxed grains is about 100–600 nm. These grains possessed random crystallographic orientations and were separated by sharp
occurs in the surface layer, as shown in Fig. 4, where grain sizes of 20 μm.

After isothermal annealing at 450 °C for 30 h, a slight grain growth of the SMAT samples to 450 °C, at a heating rate of 10 K/min and holding at this temperature for 30 h before rapidly cooling to room temperature. The isothermal annealing procedure is accomplished by heating the sample, the thermal stability of the nanostructured surface layer against grain growth was investigated. An isothermal annealing treatment of the SMAT samples was carried out in an Ar atmosphere. Detailed microstructural characterization of the surface layer in the as-treated 38CrMoAl steel sample, together with an underlying nanocrystallization mechanism during the SMAT treatment in terms of the severe plastic deformation mode of bulk materials, is analogous to that in [17].

In order to determine the experimental conditions (temperature and time) for gas nitriding in the nanocrystalline 38CrMoAl steel sample, the thermal stability of the nanostructured surface layer against grain growth was investigated. An isothermal annealing treatment of the SMAT samples was carried out in an Ar atmosphere. The isothermal annealing procedure is accomplished by heating the SMAT samples to 450 °C, at a heating rate of 10 K/min and holding at this temperature for 30 h before rapidly cooling to room temperature. After isothermal annealing at 450 °C for 30 h, a slight grain growth occurs in the surface layer, as shown in Fig. 4, where grain sizes of 20–40 nm are detected. The XRD analysis indicated that the average grain size of the annealed sample is approximately 40 nm.

### 3.2. Microstructure of nitrided layer

After nitriding, the cross-sections of the microstructures for both untreated and treated samples were observed by SEM. The nitrided layers produced at 400 °C were characterized by two different morphologies (see Fig. 5). These morphologies include a gray compound layer (upper part) and a diffusion zone (lower part) induced by the precipitation of nitrides. The observations for both samples after nitriding show that SMAT processes had a significant influence on the kinetics of the compound layer formation. The original 38CrMoAl steel sample (A) after nitriding has no continuous compound layer, and only a partial nitride layer can be observed. However, for the SMAT sample (B) under the same conditions, a continuous gray surface compound layer of about 20–30 μm thick was observed, showing that the formation of nitrides in the surface layer is faster than that in the coarse-grained sample. It also should be noted that the thickness of the compound layer in the SMAT sample is not uniform, indicating preferential diffusion of nitrogen into the material along grain boundaries and dislocations.

The X-ray diffraction analysis in Fig. 6 provides information on about 5 μm thick phase composition from the nitrided surface layer. The surface layer in the original 38CrMoAl nitrided sample contains strong diffraction peaks for the α-Fe phase, as well as weak diffraction peaks of ε-Fe2–3N and γ′-FeN compounds, whereas that of the SMAT sample nitrided under the same conditions consists of strong ε-Fe2–3N and γ′-FeN. The diffraction peaks of the ε-Fe2–3N and γ′-FeN phases obviously increase and those of the α-Fe phase disappear, indicating a substantial enhancement of the volume fraction of nitrides in the surface layer. XRD analysis simultaneously confirmed the presence of Cr2N in the SMAT sample after nitriding, which differs from the original Fe sample where no Cr2N was detected.

TEM observations combined with electron diffraction analyses show that the compound layer for the nitrided SMAT sample is composed of ultrafine polycrystalline iron nitrides and alloy nitrides (see Fig. 7). Those nitrides include ε-Fe2–3N and γ′-FeN phases, as well as a small amount of Cr2N, which are in agreement with the XRD analysis results. Compared to the conventional nitriding of 38CrMoAl steel, some nitrides were not formed due to the low mobility of nitrogen and alloy elements in the material at 400 °C. The compound layer can produce a much more complex structure with various nitride

![Fig. 3. Variations in the grain size and the mean microstrain with the depth from the treated surface of the SMAT sample determined by means of XRD analysis, TEM and SEM observations.](image-url)

![Fig. 4. A dark-field TEM image and the corresponding electron diffraction patterns (inset) of the top surface layer for the SMAT sample annealed at 450 °C for 30 h.](image-url)

![Fig. 5. Cross-sectional observations of an original coarse-grained sample (A) and the SMAT 38CrMoAl sample (B) after nitriding at 400 °C for 30 h.](image-url)
phases only by increasing the nitriding temperature to 500 °C and higher [23]. The temperature for Cr₂N formation reaches even higher than 550 °C. A detailed description of the nitrided structure for the original 38CrMoAl steel sample in this temperature range has been given in the literature [24]. Therefore, the constitution of this compound layer for the SMAT sample nitrided at 400 °C is similar to that formed during conventional nitriding at high temperatures (about 550 °C). The formation of Cr₂N for the nitrided SMAT sample was observed in the electron diffraction pattern and XRD analysis, suggesting that the diffusion ability of Cr at 400 °C in the grain-refined material is sufficient for Cr₂N formation. No Aluminium nitride particles were detected in the nitrided SMAT sample. This is because that the chemical composition of Al was smaller than that of Cr, and it is known that AlN with a more complex crystal structure can only nucleate under a high driving force [25]. Probably, the driving force of nitriding at 400 °C was not enough for AlN forming.

The diffusion zone of the nitrided SMAT sample (Fig. 8) was investigated by TEM. Underneath the compound layer, a large amount of rod-like and particle-like nitrides (about 100–300 nm) were precipitated. The electron diffraction pattern from these nitrides was found to correspond to the γ'-Fe₄N (cubic) phase. Clearly, these nitrides (γ'-Fe₄N) formed largely at grain boundaries (or junctions) of the ultrafine-grained α-Fe phase, dislocations and other defects, and the lower nitriding temperature limits the growth of precipitates [18,19,26]. In recent works it has already been demonstrated that the nitrogen activity of nitriding atmosphere, surface roughness as well as crystalline structure of the substrate influence the nitriding kinetics. Nanocrystalline nature [27], high surface roughness [28] before nitriding and nitrogen potential [29,30] (the combination of hydrogen and ammonia) are very effective in improving the growth of nitriding layer. As the surface roughness of SMAT sample was comparable to that of the original sample, and both samples were nitried under the same atmosphere condition, the present study therefore supports the conclusion that the surface nanocrystallization of SMAT sample accelerated the nitriding process.

The growth of the nitriding layer is a diffusion-controlled process of nitrogen. The nitrided layer thickness of 38CrMoAl steel can be described by [5]

\[ \frac{\delta^2}{\rho} = \frac{2[N]}{D t} \]

which is derived from diffusion theories accompanied by a phase change which has been applied to internal oxidation, where, [N] is the surface nitrogen concentration, [X] is the original alloy element in the nitride phase, \( r \) is the ratio of nitrogen to alloy element in the nitride phase, \( D \) is diffusivity of nitrogen, \( t \) is nitriding time.

Clearly, in the nitriding of conventional coarse-grained Fe, nitrogen diffusion in the lattice dominates, where the kinetics is related to temperature. For the nc 38CrMoAl steel sample, however, nitrogen may preferably diffuse at low temperatures along numerous grain boundaries with a larger enhanced diffusivity compared with lattice diffusion because there is smaller activation energy at grain boundaries (approximately half that of the lattice diffusion) [18]. Therefore, the nc structure of 38CrMoAl steel in the SMAT sample provides a large number of fast diffusion channels (grain boundaries) for nitrogen at low temperatures which may significantly enhance the nitriding kinetics.

The microstructural characterization of the SMAT 38CrMoAl steel samples indicated a high concentration of the non-equilibrium defects (dislocations and subgrain boundaries) in the sub-surface layer that are induced by plastic deformation. These defects may decrease the activation energy of diffusion and act as fast atomic transfer channels as well [31]. Similar kinetics enhancement can be accomplished for the diffusion zones obtained in the nitriding process.

Furthermore, the formation of nitrides is a process of nucleation and growth. Grain boundaries are preferable heterogeneous nucleation sites for the ε-Fe₂₋₃N and γ'-Fe₄N phases, for which the activation energy barrier is much smaller than that for homogeneous volume
nucleation in the α-phase lattice [32,33]. According to References [34,35], for nc materials with large amounts of grain boundaries, nucleation site densities will evidently increase, i.e., measurably high nucleation rates can be obtained with very small driving forces. For example, the heterogeneous nucleation rate at grain boundaries may increase by an order of $10^4$ when the grain size is reduced from 100 μm to 10 nm. Therefore, the enhanced formation ability of a compound layer in the SMAT sample can be attributed to a larger increase in the heterogeneous nucleation rate at numerous grain boundaries.

A very high heterogeneous nucleation rate was the primary reason why the compound layer for the SMAT sample consists of nanostructured nitrides. A continuous compound layer formed by abundant heterogeneous nucleation will not provide a diffusion barrier for nitrogen due to a special ultrafine polycrystalline structure, which helps to increase the thickness of the diffusion zone.

3.3. Hardness and wear resistance

The absolute hardnesses of the surface layer in the nitrided SMAT sample have been determined in this work. In the case of the SMAT sample nitrided for 30 h, there is a peak hardness of 1340 Hv at the surface (Fig. 9). The diffusion zone depth (defined by the distance from the surface to the point where the microhardness was 50 Hv higher than that in the matrix) was 200 μm. For the original 38CrMoAl steel sample nitrided under the same conditions, the hardness of about 1000 Hv, which is the yield strength of 38CrMoAl steel after conventional industrial nitriding at a high temperature, was of about micron magnitude and normally formed a pillar structure [39]. Therefore, the nanosized compound layer has a much higher hardness than that of conventional 38CrMoAl steel.

On the other hand, the greatly improved hardness of the nitrided SMAT sample can be attributed to the appearance of fine alloy nitride Cr2N. Precipitate formation is inconsistent with the diffusivity of Cr atoms in Fe. Hence, there was no sign of Cr2N formation at 400 °C for the conventional industrial nitriding of 38CrMoAl steel because the diffusivity of Cr atoms was too low at this temperature. For the nitrided SMAT sample, however, the fine Cr2N precipitates are already present due to the fast diffusion of the Cr atoms in the nanostructured crystalline layer. The formation of Cr nitride precipitates at grain boundaries has been reported in the literature [40,41]. The segregation of Cr at grain boundaries will be enhanced in the nc material due to a larger grain boundary area and the shorter distance a Cr atom has to travel to diffuse to a grain boundary, even though diffusion of Cr is occurring at 400 °C. So Cr2N precipitation could be determined by fast grain boundary diffusion. The size of individual precipitates will be very small due to an increased grain boundary area and a limited volume fraction of Cr2N which has to be distributed over the grain boundaries. Compared with 38CrMoAl steel after conventional industrial nitriding (at 550 °C), the particle sizes of Cr nitrides were normally larger or formed a lamellar structure due to the enhanced diffusion of Cr atoms at a high temperature [24]. Cr2N has very hard particles, so the appearance of this phase in the compound layer can lead to increased hardness. The fine dispersive precipitate of Cr2N (or other alloy nitrides) in a low temperature treatment is responsible for the increased hardening response in the nitrided SMAT sample.

High hardness was obtained in the first 100 μm of the diffusion zone for the nitrided SMAT sample. This phenomenon can be explained by the precipitation of nitrides at grain boundaries, dislocations and other defects in the α phase. The low nitriding temperature limits the growth of precipitates, resulting in fine dispersions of the γ-Fe4N phase in the diffusion zone. Together with ultrafine crystallites and the high defect density in the subsurface layer, the precipitation produces a greater hardness in the diffusion zone.

Sliding wear test results showed that gas nitriding in the investigated temperature range can significantly increase the wear resistance of the materials. Fig. 10 summarizes the results for various...
38CrMoAl steel samples. For both nitrided samples, wear volume loss increases with a longer duration, but the wear of the nitrided SMAT sample is lower than that of the original nitrided sample during each sliding time, especially between 30–60 min, indicating the wear resistance of the nitrided 38CrMoAl steel sample has been improved by SMAT nitriding processes.

The morphology of the worn surface is shown in Fig. 11. When sliding time was less than 20 min, both nitrided samples shared a similar wear mechanism. The wear loss results mainly from plowing and micro-cutting under the action of abrasive particles such as the tip of the WC ball and oxides derived from the sample surface [42–44]. From the morphology of the wear scar under these conditions, there are many parallel grooves formed by the plowing action and micro-cutting. But the worn surface of the original nitrided sample was very rough with deep, broad grooves as well as spalling (Fig. 11C), whereas the worn surface of the nitrided SMAT sample was relatively smooth with some narrow grooves (Fig. 11A). When the sliding time is increased (30–60 min), for the original nitrided sample, the WC ball indents more deeply into the surface, resulting in a wearing through of the hardened surface layer (compound layer). Thus the repetitive work-hardening in the new surface layer will be more severe under a repetitive sliding action. Eventually, propagating and growing cracks induced spalling of the material in the new surface layer. The dominant wear mechanism causes plastic removal and surface fatigue fracture of the deformed layer [45,46]. Fig. 11D shows cracks and pits after the surface spalled off (marked by arrow). This wear mechanism is similar to that of the original annealed 38CrMoAl steel sample. The apparent variation in the wear rate for the original sample nitrided under a sliding time of about 30 min (in Fig. 10) might result from such a change in the wear mechanism. Compared with the nitrided SMAT sample (Fig. 11B), the wear mechanism tends to a steady state during all test processes due to a very thick hardened surface layer (compound layer).

This improved abrasion resistance for the nitrided SMAT sample can be attributed mainly to the higher hardness and case depth (especially the higher effective case depth) because wear resistance is generally related to the hardness ratio. An ultrafine polycrystalline compound layer (grain size of about 30–60 nm) which formed during the gas nitriding process is also believed to contribute to the higher abrasive resistance, since wear resistance is associated with the grain size of the material surface layer.

4. Summary

In this paper it is shown that a nanostructured surface layer on a 38CrMoAl steel sample can be obtained by a surface mechanical attrition treatment (SMAT). The subsequent gas nitriding kinetics of the SMAT sample with the nanostructured surface layer was found to be greatly enhanced. Effective nitriding can be performed at temperatures as low as 400 °C, which is much lower than conventional nitriding temperatures. The nitrided layer in the SMAT sample is composed of nanostructured nitrides, resulting in relatively higher hardness and wear resistance as compared to those of the nitrided coarse-grained sample. The greatly reduced nitriding temperature for SMAT samples can be attributed to nano-scale-sized grains with a large amount of defects such as grain boundaries. These defects not only provided more nitride nucleation sites, but also greatly enhanced the atomic diffusion which facilitates the nitriding process.

The remarkable depression in the nitriding temperature by means of the surface nanocrystallization demonstrates a significant advancement for materials processing and provides a new approach for selective surface reactions in solids.

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