Evaluation of surface-modified 20CrMo by plasma nitriding coupled with ion sputtering and SMAT


A R T I C L E   I N F O

Article history:
Received 26 June 2012
Accepted in revised form 22 October 2012
Available online 29 October 2012

Keywords:
Nitriding
Surface mechanical attrition treatment
Toughness
Hardness
Wear resistance

A B S T R A C T

Plasma nitriding treatment is a well-established method of improving the wear and corrosion properties of steel materials by the formation of a unique composite structure with a hard surface layer and a tough interior. However, the toughness of the nitrided layer that arises from the nitriding treatment is substantially lower than the underlying substrate. This paper describes the combined treatment of ion sputtering and SMAT on a nitrided steel sample which leads to the decomposition of the compound layer and the formation of a nanostructured diffusion layer. Optical microscopy, transmission electron microscopy, X-ray diffraction and microhardness testing were used to investigate the structure and mechanical properties of the modified surface layer in comparison with those of the nitrided sample. The result indicates that a nanostructured diffusion surface layer with satisfactory hardness and wear properties was formed on the treated sample relative to that of the conventional nitrided sample. Especially, the toughness of surface layer was greatly improved by this combined treatment. This method demonstrates the technological significance of SMAT in improving traditional processing techniques. It also provides a new approach for preparation of a nitrided surface layer with high strength and high toughness.

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1. Introduction

Plasma nitriding is one of the most widely used surface modification techniques to improve surface hardness, anti-corrosion property and wear resistance of ferrous materials by the formation of a unique composite structure with a hard surface (a layer of ε-Fe₂₃N₃ and γ′-Fe₄N compounds) and a tough diffusion layer [1–3]. However, the compound layer formed in the nitriding process is usually accompanied by substantially lower surface toughness in comparison with that of the diffusion layer and the underlying substrate. This will affect the performance of components subjected to severe service environments involving high shear, compressive and/or impact loading conditions [4–7]. For this reason, some measures were developed such as optimizing the nitriding process parameters (nitrogen concentration, gas pressure, nitriding duration) to obtain a single γ′-Fe₄N phase or to form a thinner compound layer with relatively low toughness [8]. This is because the single γ′-Fe₄N phase is much tougher than the dual phase (ε-Fe₂₃N₃ and γ′-Fe₄N) based on the previous study [9]. Additionally, the decomposition of the compound layer by ion sputtering after nitriding was widely used to form a nitrided layer without compound layer in order to eliminate brittleness [10,11]. Based on this treatment, brittleness of the surface nitrided layer could be eliminated because the diffusion layer is much tougher than the compound layer. However, these measures will induce serious deterioration of surface hardness and wear properties of nitrided steel [8]. Therefore, the fabrication of a surface nitrided layer with high hardness and excellent toughness presents a major challenge to engineers and researchers.

Nanocrystalline materials which are structurally characterized by nanometer-sized grain with a large number of grain boundaries have been found to exhibit many novel properties relative to their coarse-grained counterparts. For example, most nanocrystalline metals and alloys possess high strength and hardness, as well as excellent tribological properties [12–15]. Recently, a new technique has been developed to obtain a surface layer with nanocrystalline structure in metallic materials by means of surface mechanical attrition treatment (SMAT) [16–18]. The SMAT-ed materials exhibited much enhanced hardness and wear property relative to their coarse-grained counterparts. At present, the SMAT technology as pretreatment technique seems to be appropriate for lowering nitriding temperature and for shortening the duration efficiently [19–23]. Previous investigation shows that the gas-eous nitriding on a pure iron plate was achieved at 300 °C with nanostructured surface layer prepared by the SMAT technique [19]. It is noted that this lower temperature nitriding technology does not improve the brittleness of nitrided layer, but it offers a new thinking to us to prepare a nitrided layer with high hardness and high toughness by means of SMAT. In this study, in order to reduce the brittleness of the nitrided layer, the ion sputtering treatment was performed prior...
to SMAT to decompose the compound layer. SMAT was utilized to induce compressive residual stress and to improve hardness and wear properties. Therefore, it is reasonable to expect that surface toughness of the nitrided steel is supposed to be improved and excellent wear property of the surface layer can be maintained via ion sputtering and subsequent SMAT. The purpose of this work is to study the effect of the combined treatment of ion sputtering and SMAT on microstructure and surface properties of the nitried steel.

2. Experimental

A 20CrMo steel plate (4 × 100 × 100 mm in size) with chemical composition of (in wt.%): 0.2 C, 0.17 Si, 0.25 Mo, 0.5 Mn, 1.10 Cr, 0.035 P (max), 0.035 S (max) and balance Fe, was used in the present study. The sample was annealed in vacuum at 950 °C for 1 h to eliminate the effect of mechanical deformation and to obtain homogeneous coarse grains with average grain size of about 50 μm. Plasma nitriding and sputtering treatment were carried out in a DC-pulsed type LOCMT-15A plasma nitriding furnace, with applied voltage in the range 0–1000 V and the pulse frequency of 20 kHz. The sample was sputtered and heated by ion bombardment in argon atmosphere until the preset temperature. Subsequently, NH3 with 500 Pa pressure was in-migrated into the vacuum furnace for plasma nitriding. The nitriding was carried out at 500 °C for 4 h. After nitriding for the required amount of time, the sample was ion sputtered in argon atmosphere for 6 h to decompose the compound layer. The temperature and pressure of the sputtering treatment were selected to be 600 °C and 500 Pa, respectively. After sputtering for a certain period, the sample was cooled to room temperature under vacuum condition.

The SMAT was performed in an apparatus which has been described previously [16–18]. In brief, a large number of hardened steel balls were placed at the bottom of a cylinder-shaped chamber which was vibrated by a generator at a high frequency of 50 Hz. Based on the high vibration frequency of the system, the sample surface was impacted repetitively by a large number of balls within a short period of time. As a consequence, the repeated multidirectional impacts at high strain rates onto the sample surface resulted in severe plastic deformation and grain refinement. In this paper, GCr15 steel balls with diameter of 4 mm were used and the samples were SMA-Treated for 180 min in vacuum at room temperature. To facilitate discussion, the samples were numbered for different treatments in this study, as shown in Table 1.

Microstructure of the surface layer was characterized by a Leica DMR optical microscope (OM) and a Jeol-4000FX transmission electron microscope (TEM) with an operating voltage of 200 kV. The sample for TEM observation was prepared by grinding and mechanical polishing followed by ion-thinning at lower temperature. Additionally, microhardness and surface toughness were measured by a model Vickers microhardness tester. The phases in the surface layer were identified by means of PW3040/60 X’Pert Pro X-ray diffraction (XRD) using Cu Kα radiation (40 kV, 200 mA). Residual stress was determined using X-ray diffraction with the classical sin²θ method [24]. The in-depth residual stress distributions in the treated surface were determined by repeating this X-ray measurement and electrolytical polishing, alternately. A ball-on-disk SRV Optimol tribometer with an oscillating ball was used to test the unlubricated wear resistance at room temperature. Tests were carried out against a WC ball (10 mm in diameter) under loads of 15, 20, 30, 40 and 50 N, respectively, with sliding duration of 30 min.

3. Results and discussion

3.1. Microstructure characterization of the surface layer

Fig. 1(a) shows the cross-sectional microstructure of the sample after nitriding treatment (noted as sample A). Evidence of a white layer of 13–17 μm thick and some needle-like nitrides can be identified in the near surface region based on the optical microscope observation. The XRD diffraction pattern reveals that the surface layer of sample A is composed of α-Fe,N and oxide phase, as shown in Fig. 1(c). A few oxide phases can also be detected, which suggests that slight oxidation occurs on the sample surface during the nitriding process. The XRD diffraction pattern indicated in Fig. 1(d) shows that the surface layer of sample A after ion sputtering treatment (noted as sample B) is composed of α-Fe,N phase only which is consistent with the OM observation, as shown in Fig. 1(b). This confirms that the compound layer can be decomposed by the ion sputtering treatment [8]. In the present study, the decomposition speed of the compound layer is significantly faster than the data found in the literature [8]. This may be due to the difference in the experiment condition including temperature, pressure and voltage. After SMAT to the sample B (noted as sample C), the severe plastic deformation layer of about 50 μm thick can be found between the surface layer and the substrate, as shown in Fig. 2(a). The obvious diffraction peak broadening is noticed relative to sample B which is attributed to the grain refinement and/or an increase in the atomic-laver lattice strain, as shown in Fig. 2(b). Furthermore, a few Fe4N phase is detected which is due to the nucleation of nitried induced by high temperature in SMAT procedure. Combined transmission electron microscope (TEM) observation shows that the top surface layer is characterized by ultrafine equiaxed grains α-(Fe,N) with random crystallographic orientations, which was indicated by the selected area electron diffraction pattern (SAED), and the average grain size is in the range 20–30 nm, as shown in Fig. 2(c) and (d). All the diffraction rings in the SAED pattern of the top surface layer are identified as α-Fe. No Fe4N phase is detected by TEM which is inconsistent with XRD result. This might be partially attributed to the fact that the XRD shows the structure information of the surface layer of about 10 μm thick, while the TEM indicates the information of surface layer about 1 μm thick, while the TEM result information of about 1 μm. We speculated that the observation thickness of TEM is too thin resulted in this phenomenon. As a consequence of severe plastic deformation, the subsurface layer consisted of subgrains with a high density of dislocations. The average size of the subgrains is about 200 nm. These results demonstrate that the diffusion layer on the nitried 20CrMo steel has been nanocrystallized after SMAT.

3.2. Hardness, wear and residual stress properties

Hardness measurements on cross section of the sample show that hardness of the top surface layer is 1305 HV for the sample C, which is much higher than that of the sample B (765 HV) and slightly higher than that of the sample A (1189 HV). Variation of hardness along the depth for the three samples, as shown in Fig. 3, indicated that sample B drops to the ground value (of about 200 HV) within the surface layer of about 230 μm thick. A much thicker hardened surface layer can be found for sample C; the hardness value exceeds 800 HV within the depth of 110 μm, and the hardened layer extends to about 300 μm deep when the hardness tends to a saturated ground value. For the 20CrMo steel sample, the increased hardness may be attributed to the
grains refinement in the surface layer and the work hardening. To distinguish the effects of work hardening and grain refinement, the relationship between the hardness and $d^{-1/2}$ ($d$ is the grain size) was examined, and the result is shown in Fig. 4. It is noted that hardness increases almost linearly with the $d^{-1/2}$. This linear increment of hardness with the $d^{-1/2}$ fulfills the classical Hall–Petch relationship.

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Fig. 1. Cross-sectional optical micrographic observations of (a) sample A, and (b) sample B and the X-ray diffraction patterns of (c) sample A, and (d) sample B.

Fig. 2. Cross-sectional optical micrographic (a) and the XRD diffraction pattern (b) of sample C. A bright-field TEM image (c) and its corresponding SAED pattern (d) of the top surface layer in sample C.
According to this relationship, the hardness of a material, $H_v$, is related to grain size, $d$, through the following relationship:

$$H_v = H_0 + k \cdot d^{-1/2}$$

where, $H_0$ and $k$ are appropriate constants. The grain size in the surface layer of sample C is about 20 nm. The average grain size in the sample B is in micron scale. Therefore, it is reasonably suggested that the strengthening of the sample B after SMAT treatment can be primarily attributed to grain refinement. Measurements of volume losses of wear scars at various loads ranging from 15 to 50 N were performed in the three treated samples, respectively, as shown in Fig. 5. It is noted that the volume losses of wear increases when the applied load increases. Thus, the volume loss of sample C is significantly smaller than that for the sample B. For example, the wear loss of the sample C is less than one half of that of the sample B under the load of 50 N, which indicates that wear resistance of the sample C has been improved by the SMAT process. Additionally, wear loss of the sample C is similar to that of the sample A, indicating that excellent wear resistance can be obtained in sample C.

The in-depth residual stress distributions of the treated samples are shown in Fig. 6, which indicates a very low level of compressive residual stress in the surface of the untreated sample. However, such compressive residual stress cannot be observed in the surface of the plasma nitriding sample, because stress is released by thermal exposure in the surface layer [27]. On the contrary, the compressive residual stress introduced by SMAT reaches about 800 MPa which is very high in comparison with the value obtained from other conventional surface treatments such as, shot peening or deep rolling [28]. In particular, the maximum compressive residual stress is not at the impacted surface, but at the sub-surface, which is attributed to the existence of a lot of defects existing in region near the surface. Additionally, the depth of peak point from surface of the sample C is slightly deeper than that of the sample A and the untreated sample, the compressive stresses caused by SMAT almost disappears at a depth greater than approximately 400 μm. These results clearly illustrate that a high value compressive residual stress is induced by the SMAT treatment. According to the previous research, high value compressive residual stress is recognized to hinder the crack initiation and propagation [29,30]. Therefore, it is reasonable to believe that fatigue lifetime can be improved on the sample C in comparison to the sample A.

### 3.3. Toughness of the surface layer

In order to investigate the toughness of the surface layer in each sample, a method of indentation measurement using Vickers hardness tester was utilized, since the conventional means of fracture toughness test is not suitable for the relatively thin surface compound layer. The use of indentation test for the toughness determination of thin and hard layer has some advantages, such as relatively inexpensive and unsophisticated test equipment. Additionally, it can be used on a wide range of sample size [31,32]. Prior to measure, the surface of the treated samples were slightly polished using 1 μm diamond paste to obtain a mirror finish while ensuring minimal loss of surface layer thickness. The polished surfaces were then subjected to Vickers hardness test.
using load of 10 kg and 30 kg. After the test, apparently different indentation morphology can be found for the sample A and the sample C, as shown in Fig. 7. Obvious radial-median cracks around indentation can be noted in the sample A, whereas no cracks can be found in SMATed sample at the same load of 10 kg. Furthermore, the concentric rings can be clearly seen at a load of 30 kg in the sample A and this becomes more significant with the increasing load, as shown in Fig. 7(c). Generally, there are two basic crack modes possible from Vickers indentations of the brittle materials: radial-median and Palmqvist cracking modes. In this paper, the predominant mode of cracking in the sample A is radial-median mode cracks initiate along the edges of the pyramidal indentation and extend deep into the material in a semi-circular manner perpendicular to the surface. When the test load increase to 30 kg, still no crack can be observed in the sample C, Strictly speaking, the method of indentation offers the possibility of a relatively simple method which just estimate the fracture toughness of nitrided surface layer. It is clear that more work is required to properly define the accuracy and limitation of the method. In the present paper, it is noticed that no obvious cracks can be observed in the sample C under the load of 30 kg, which indicates that a satisfactory toughness property is obtained in the sample C by the combined treatment in comparison with conventional nitrided sample.

4. Conclusions

The surface compound layer of about 13–17 μm in thickness with high hardness and excellent wear resistance is formed by the nitriding procedure. Surface hardening is primarily attributed to nitrogen dissolved in the α-Fe matrix. The subsequent ion-sputtering treatment decomposes the compound layer, which effectively eliminate the surface brittleness. By means of SMAT, a nanostructured diffusion layer of about 50 μm thick is formed in which the top surface layer contains nanocrystallines with random crystallographic orientations, and the average grain size is about 20–30 nm. The surface hardness of the combined SMAT and ion-sputtered sample is about 1305 HV and continuously decreases to the matrix value with deeper depth in comparison with conventional nitrided sample. The greatly enhanced hardness as well as the gradient distributions of the structure contributes to satisfactory wear resistance in the combined SMAT and ion-sputtered sample. Additionally, the compressive residual stress was induced by the SMAT in the combined SMAT and ion sputtered sample which could improve its fatigue lifetime. More importantly, the surface toughness of the combined SMAT and ion-sputtered sample was greatly enhanced relative to the conventional nitrided sample.

In conclusion, the formation of a nanostructured diffusion layer by using the SMAT and ion sputtering technique not only provides an effective approach to improve toughness of the nitrided steel but also enhances the surface hardness and wear resistance of the nitrided layer to some extent.

Acknowledgments

This research was supported by Project of Science and Technology Plan of Shenyang City (F12-027-2-00), the Fundamental Research Funds for the Central Universities (N110809001 and N090109001), National High Technology Research and Development Program 863 (2012AA03A508), and the 111 Project (B07015).

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