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Full Length Article

Improved microstructure and properties of 12Cr2Ni4A alloy steel by vacuum carburization and Ti + N co-implantation

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ABSTRACT

The carburized 12Cr2Ni4A alloy steel was implanted by Ti + N double elements implantation. The microstructure, nano-hardness and corrosion properties were investigated by EPMA, TEM, XPS, nano-hardness and electrochemistry tests in detail. The results showed that the Ti + N co-implanted layer is composed of FCC TiN and TiC phases with BCC martensite. Compared with the un-implanted layer, the Ti + N implanted layer has higher nano-hardness and better corrosion resistance. In addition, the higher nano-hardness was presented below the surface of 1800 nm compared with un-implanted layer, which is far beyond the thickness of the implanted layer. The results also indicated that the generation of nanoscale ceramic phase and structures are not the only factor to impose the influence on the nano-hardness and corrosion resistance, but the radiation damage and lattice distortion will play an important role.

1. Introduction

The 12Cr2Ni4A low carbon alloy steel is widely used as gear or bearing material in aerospace and heavy-duty industries after carburizing because of its good surface mechanical strength and wear resistance. They are often applied in harsh environment to suffer continuous heavy load, high speed and corrosive media containing S, Cl and other elements [1,2]. Therefore, the various failures such as contact fatigue damage, wear and corrosion generally appear on the surface or in the subsurface region of gears and bearings [3,4]. In recent years, ion implantation as an effective technique has been applied to improve the surface properties of various materials by producing new metastable phase, amorphous phase and solid solutions [5,6].

A large number of researches show that ion implantation would not change the sizes and machining precision of work pieces. The friction and wear resistance, hardness, contact fatigue and corrosion resistance of metal work pieces have been proved to be selectively modified by implanting different elements [7–9]. The earlier media for implantation was mainly nonmetallic elements (like N, C and O), metal elements (Ti, Zr and Cr) and double elements (metal and nonmetal, metals, nonmetals). Fang et al. [1] found that the implantation of carbon into M50NiL aerospace bearing steel showed lower current density and corrosion rate in 3.5% NaCl aqueous solution, and the pitting potential increased. Liu et al. [5] had investigated the influence of Ti and N implantation on the surface properties of 9Cr18Mo steel. They discovered that by Ti or N implantation nano-hardness and wear resistance increased but friction coefficient reduced, especially the N ion implantation resulting in the formation of a non-homogeneous surface layer composed of Fe_xN and Cr_xN strengthening ceramic phases. Vlcak et al. [10] employed N ion implantations in Ti6Al4V alloy and discovered that the formation of higher proportion TiN phase on the surface could significantly enhance hardness of the substrate. Jin et al. [11] performed N + Zr ion co-implantation into Cr4Mo4Ni4V steel. The wear and fatigue resistance were improved and the median fatigue life was improved nearly 5 times.

Most previous studies [5–12] have focused on the hardness and mechanical properties of ion implantation layer, while for the detailed surface structures and corrosion property are relatively few, especially the double ions implantation layer with complicated ceramic phases. Thus, this work focuses on the evaluation of the surface structures, mechanical and corrosion behavior of Ti and N ions co-implanted 12Cr2Ni4A carburized samples. After ion implantation, the detailed surface analysis is investigated by using XPS, EDS, TEM and EPMA techniques. In addition, the mechanical and corrosion of implanted 12Cr2Ni4A carburized samples were evaluated by nano-hardness test and polarization test. Finally, the strengthening mechanism was discussed.

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2. Experimental

The composition (wt.%) of experimental 12Cr2Ni4A steel was 0.11C, 1.30 Cr, 3.13 Ni, 0.53 Mn, 0.12 Cu, 0.22Si, 0.11 Mo and Fe in balance. In present study, the 12Cr2Ni4A steel specimens were cut with dimensions of 14 × 14 × 14 mm^3. Considering high hardness (>60HRC) are necessary for high precision class of the 12Cr2Ni4A bearings under the actual working conditions, before ion implantation, the samples were polished with SiC emery paper up to #1000 and then treated by La implanting and vacuum carburizing. Our previous studies [13] have shown that rare earth La ion implantation can effectively improve the structure and performance of vacuum carburizing layer. In the carburizing process, the temperature was 925 °C for 4 h in vacuum (1×10^{-5} Pa) circumstance. The following MEVVA (metal vapor vacuum arc) source implanter was used to conduct the Ti and N co-implantation. The ions implantation were both at a nominal dose of 2×10^{17} using acceleration potential of 45 KV in the vacuum level of 2×10^{-3} Pa at room temperature.

After Ti and N co-implanted, the phase were analyzed by X-ray diffraction (XRD) in type of PANalytical X'Pert Pro MPD ranging from 20° to 100° with scanning speed of 3°/min, Cu Kα radiation, tube voltage of 40 kV, and tube current of 40 mA. The microstructure observations were performed on transmission electron microscopy (TEM) by JEM-2010 transmission electron microscopy equipped with an energy-dispersive X-ray spectroscopy (EDS). The foils for TEM observation were prepared by grinding and mechanical polishing followed by focused ion beam (FIB, FEI Nova 200 Nano Lab-dual beam). The elements distribution of surface were detected by electron probe microanalysis (EPMA, JEOL 8800R). The chemical states and depth of the elements were conducted by X-ray photoelectron spectroscope (XPS, ESCALAB 210) using monochromatic Al Kα radiation, and the etching was achieved by Ar+ ion gun. The XPS was employed to detect the relative amounts of chemical composition of elements (C, Ti, N, O and Fe) along depth by the following equation [14]:

$$C_x = \frac{(I_x/S_x)}{\sum_i (I_x/S_x)} \qquad (1)$$

where *I* was peak area of each element after background correction getting from the XPS spectrum and *S* was atomic sensitivity factors.

Nano-mechanical property tests were carried out using nano-indenter system (Agilent G200) in the continuous stiffness mode and the surface approach velocity of indenter was 20 nm/s with strain rate of 0.05 s^{-1}. The corrosion behavior of the co-implanted layers samples in 3.5% NaCl solution was studied by potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS, CHI660E) after 30 min of immersion at a frequency range open-circuit potential. The polarization curve was measured with the scanning speed of 1 mV/s and the scanning potential range of $-1\ V_{SCE} \sim +0.5\ V_{SCE}$. The impedance spectra were acquired between 100 kHz and 10 Hz with a perturbation of 10 mV.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of specimens treated and untreated by Ti + N ions co-implantation. It presents that the main phase of the compound layer is martensite, and the diffraction peaks of sample implanted by Ti and N shifts to right, with right-shifting angle of 0.31° for the second strongest diffraction peak compared with un-implanted sample. According to the Bragg equation, the increase of diffraction angle means the decrease of the lattice plane distance, thus it can be determined that the lattice parameter of martensite decreases due to the solution of N atoms with small atomic radius into the layer, which results in lattice distortion [15]. Compared with un-implanted sample, three new peaks can be observed, which belong to austenite peaks with face-centered cubic (FCC) structure. By calculation, the lattice parameter of austenite and martensite phase are 3.58 Å and 2.88 Å, respectively. However, in our design, the TiN or TiC phase may occur, but they could not be detected due to the penetration far beyond the thickness of implanted layer and the low sensitivity nature of the XRD analysis in the implanted region. However, in the following study, the XPS core spectra and TEM are measured to accurately clarify the phases of Ti + N ions co-implanted layer.

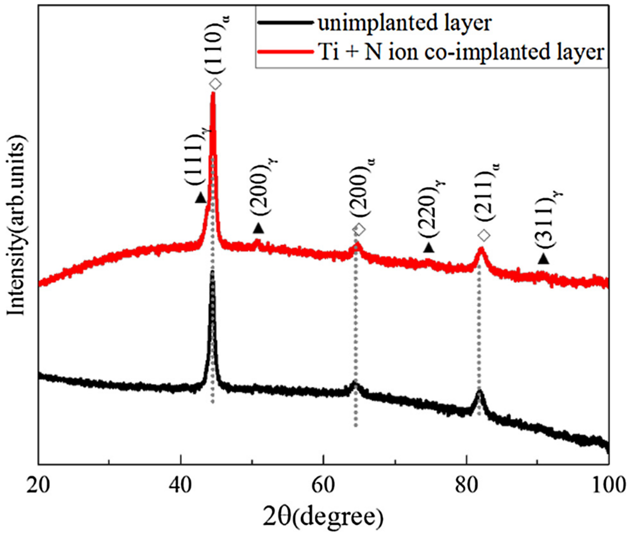

Fig. 1. XRD spectra of unimplanted and Ti + N ion co-implanted layers.

3.2. XPS analysis

The high resolution XPS spectra of C 1s, O 1s, La 3d, Fe 2p, N 1s and Ti 2p along depth in both layers have been measured as shown in Fig. 2. It can be seen that compared to the un-implanted layer, the chemical states of La and Fe basically remain unchanging after Ti + N ions co-implantation, and at different depth, they are all in the same chemical state. By further analysis, La- and Fe- oxides exist on the top surface and as the etching depth increases, the formation of elementary substance (La and Fe) are detected. For both layer, the C 1s spectrum consists of several components which can be divided into three groups as C—H—O bond at 288.8 eV, C—C bond at 285.0 eV and C—Me (metal) bonds from 282.5 to 283.9 eV [16–18]. Besides, as the depth increases, the C exists in the form of C—Me bond, at the same time the peaks of C—H—O and C—C bond disappear. The existence state and change trend of O 1s is similar to that of C 1s. The O—H and O—Me present on the surface, while the metal oxide is the only existed form below 10 nm. However, the deviation of O 1s and C 1s spectrum on surface of compound layer can be observed compared with un-implanted sample, which may result from the new oxide and carbide formed by element implanted [19]. The N 1s and Ti 2p spectra are detected, and discover that the compounds of Ti and N exist in the Ti + N ions co-implanted layer. Therefore, the XPS results indicate that except the new phase generated by Ti + N ion co-implantation, the chemical state of main element (Fe and La) of the original substrate will not be affected.

Taking oxygen and water adsorbed by the surface into consideration, XPS spectra of 10 nm below the surface is selected to analyze