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The low-temperature ion sulfurizing technology and its applications

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Abstract

A solid lubrication film mainly consists of FeS, which has excellent tribology properties, can be formed on the sulfurized iron or steel surface. The sulfurizing technology has aroused intense attention from the day it appeared. However, the widespread industrial application of sulfurizing technology was promoted by the low-temperature ion sulfurizing (LTIS) process. This paper summarized the phylogeny and sorts of sulfurizing technology firstly; then, the process flow of LTIS technology, the forming mechanism, microstructure and tribological properties of ion sulfurized layer were introduced detailedly; and then, the technological, economic and environmental merits of LTIS technology were generalized; finally, the industrial applications of LTIS technology in various typical rolling, sliding and heavy duty parts were reviewed briefly. LTIS technology, with the advantages of high sulfurizing speed, good performance of sulfurized layer and without sideeffect, has played an important role in the tribology modification of ferrous parts, and the LTIS process will become more green, simple and efficient in the future.

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Key words: ferrous metal; low-temperature ion sulfurizing; technological advantages; industrial applications.

1. Introduction

According According to incomplete statistics, about the 1/3~1/2 of the primary energy sources were consumed by friction, and about the 70% of failure and damage accidents of equipments resulted from wear (Sun, 1992). Therefore, how to improve the lubrication state of machinery and equipments, and thus reducing the material loss, energy consumption and safety incidents caused by friction and wear, is of great significance.

Chemical heat treatment is an effective method to optimize the surface properties of common material at low cost. Sulfurizing is a chemical heat treatment process with purpose to form ferric sulfide by infiltrating sulphur element into the surface layer of steel or iron parts (Wang et al., 2002). A solid lubrication film mainly consists of FeS,

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which has excellent tribology properties, can be formed on the sulfurized iron or steel surface. The crystal structure of FeS is similar to that of graphite and molybdenum disulfide, namely close-packed hexagonal lattice. So it has low resistance to shearing force and easily slips along the plane of ｛0001｝, and thus showing good tribological properties.. Sulfurizing technology has attracted great attention and has been widely used at the instant when it appeared. Various sulfurizing processes have been developed by researchers, but it failed to achieve large-scale industrial applications because economical or environmental reasons. In the late 1970s, France scientists successfully developed low temperature electrolysis sulfurizing technology, and then it became the main sulfurizing technique at that time. But this method has many environmental protection problems, such as salt bath ageing, absorption deliquescence, decomposition volatilization and stench producing etc.

With the development of vacuum and plasma technologies, in the 1980s, according to ion nitriding technology, Chinese scientists invented a new sulfurizing technique, low temperature ion sulfurizing (LTIS) (Zhang, 2000). This new technique without the similar flaws of electrolysis sulfurizing technology, and has been widely used in metallurgy, automobile, machinery and other industries (Wang et al., 2011). This paper will review the basic mechanisms, technical characteristics and application examples of LTIS technology, with the purpose to provide a reference for the research and application of LTIS technology.

2. Low temperature ion sulfurizing (LTIS)

2.1. Technological process of LTIS (Wang et al., 2003)

The basic mechanism of LTIS, also known as glow ion sulfurizing, is similar to that of ion nitriding. The technological process of LTIS can be summarized as follows. Solid sulfur is selected as the sulfur source. First, connect the workpieces and furnace wall to the cathode and anode, respectively. Then, introduce ammonia into the furnace (about 0.3L/min) when the vacuum degree fall to about 10 Pa. And then, apply a direct current about 600V between the anode and the cathode. In the electrical field, ammonia gas containing sulfur is ionized into plasma. The plasma beam moves toward the cathode and generates grey-white glow. Ammonia ions will be accelerated by the cathode drop and bombard the surface of iron-steel workpiece. The bombardment increases the surface temperature and surface activity of workpiece. The bombardment stops at the temperature range of 190～200 ℃. At this temperature, the solid sulfur will be gasified, and the sulfur gas permeates the entire furnace and occurs glow discharge. Then, sulfur atoms (ions) diffuse into the surface layer of workpiece along the grain boundary and surface crystal defects to form sulfides. Finally, a FeS film with certain thickness will be obtained after thermal retardation for some time. The typical schematic diagram of sulfurizing equipments is shown in Fig. 1 (Wang et al., 2003).

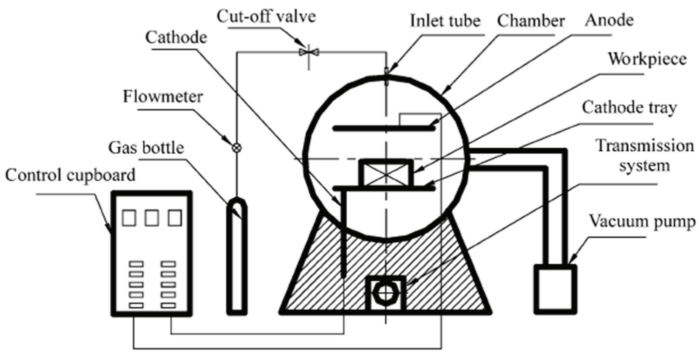

Fig. 1. The schematic diagram of equipments of LTIS (Wang et al., 2003)

2.2. The formation mechanism of sulfide layer prepared by LTIS

Under the bombardments of ammonia and sulfur ions, various crystal defects, such as distortion of lattice and dislocation density increase in the surface layer of the workpiece, even some pits also appear on the surface. So, the surface of the pending workpieces is activated and easy to react with the active S atoms (ions). Moreover, the atomic radius of sulfur (r_S=1.02 Å) is much bigger than that of nitrogen (r_N=0.75 Å) and carbon (r_C=0.77 Å), and so sulfur atoms is difficult to dissolve in the ferrum matrix. Referring to the configuration of extra-nuclear electron of sulfur, sulfur atom has many outer-shell electrons(6) and shows strong chemical activity. In addition, the crystal structure of sulfur is significantly different from that of iron. So, the solid solubility of sulfur atoms in ferrous metal is very limit, and it is inclined to form sulphide (Zhang, 2000).

According to the Fe-S binary phases diagram, the solubility of S in Fe is very small, which is only 0.02% at 930 ℃, and nearly 0 at 700℃, while the treat temperature of LTIS is about 220℃. So, the S and Fe elements have no choice but to form compound during LTIS process (Ma et al., 2010). The microstructure of sulfurized layer and the variation of its composition with the sulfurizing time show that, the initially formed sulfide nucleate at the location of surface defects with high energy, then grow up as "islet". The "islets" continue to grow around and meet each other when they reach a certain size, which will lead to the appearance of cavities at the junctions (Ma et al., 2004). During the formation process of sulfurizing layers, sulfide formed in the protruding parts of the surface preferentially, while its growth speed at the cupped parts is slower, which can also lead to the formation of cavities. With the increase of sulfurizing time, sulfides become expanded and thickened gradually. Finally, the sulfurizing layer with small and loose holes shows a honeycomb-like appearance. At the same time, the active S atoms diffuse into the subsurface layer and react with iron. With the increase in thickness of the sulfide layer, the diffusion velocity and reaction speed of sulphur atoms becomes weakened. And the continuous bombardment and sputtering may induce decomposition of sulfides. So the thickness of sulfide layer tends to be stable after some time's treatment (Zhuang et al.,1999).

2.3. The microstructure of ion sulfurizing layer

2.3.1 Surface morphology and composition of sulfurizing layer

Fig. 2 shows the AFM surface morphology of FeS film on sulfurized 1045 steel. The FeS film is stacked randomly with "cotton ball"-shaped particles, and the granularity of most grains is less than 100nm (about 30～80 nm). The FeS film is loose and porous in macroscopy (Wang et al., 2011).

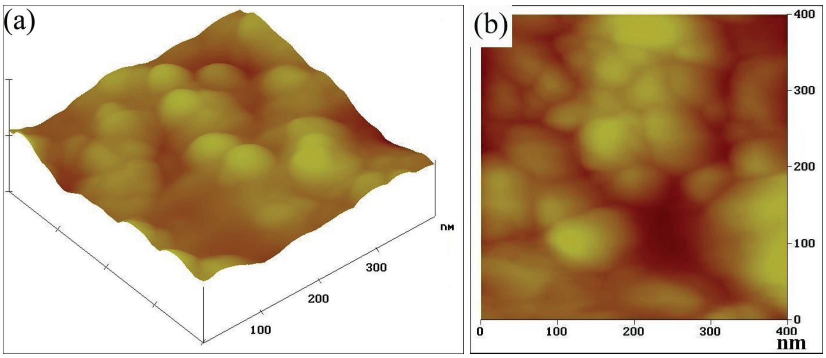

Fig. 2. AFM surface morphologies of FeS film (Wang et al., 2011). (a) Three-dimentional morphology; (b)Two-dimentional morphology

Fig. 3 (a) shows the SEM morphology of sulfide film on 1Cr18Ni9Ti stainless steel prepared by LTIS (Ma et al., 2010). The sulfide film is correspondingly compact and homogeneous. It can be seen from the different contrast of the black and white film that there is also convex peaks and valley on the film surface. The sulfurizing layer is heaped randomly by lots of small particles, and the particle size is about 50 to 100 nm. There are also some coarse grains about 500 nm agglomerated with small particles. EDS analysis shows that, a sulfur-rich layer formed in the workpiece surface, the content of S in the surface layer is high (Ma et al., 2010).

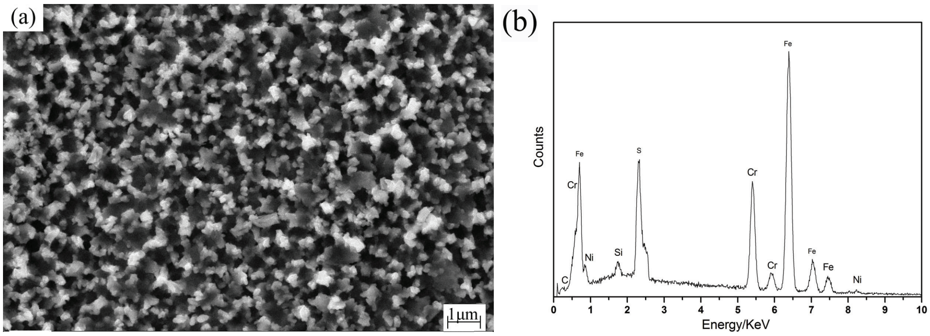

Fig. 3. The surface morphology and EDS analysis of sulfurizing layer on 1Cr18Ni9Ti stainless steel: (a) SEM morphology; (b) EDS analysis result (Ma et al., 2010)

2.3.2 The cross-sectional morphology and elemental depth profiles

Fig. 4 shows the cross-sectional morphology and element distribution profiles of the sulfide layer on 1Cr18Ni9Ti stainless steel (Ma et al., 2010).

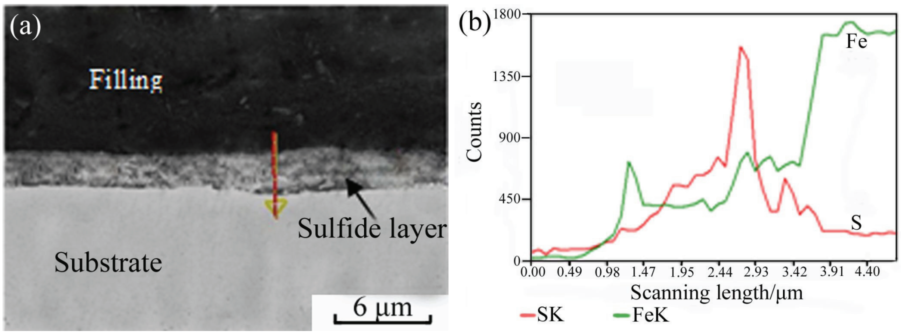

Fig. 4. Cross-sectional morphology(a) and element distribution profiles(b) of sulfurizing layer (Ma et al., 2010)

It can be seen that, sulfide layer is a continuous gray and black zonal layer, the sulfide layer bonds with the substrate tightly and there is no obvious transition layer, the thickness of the sulfide layer is about 3~4 μm. From the line scanning results of the distribution of Fe and S elements along the direction of surface to substrate, the content of S element increased gradually and reach a peak point at about 2.65 μm, and then decreased undulately, finally, it tended to be stable at about 3.8 μm. At the same time, the content of Fe element increased continually.

2.3.3 Phase constituents of sulfurizing layer

As is shown in Fig. 5 (a), the main phase constituents of typical sulfurizing layer consists of matrix Fe, solid lubricant FeS, and a small amount of FeS_2 (Qiao et al., 2009). Fig. 5 (b) shows the comparison of phase constituents of sulfurizing layers with different thickness (Wang et al., 2011). With the increase in thickness of the sulfurizing layer, the diffraction peaks corresponding to FeS_2 appeared and increased gradually. Previous research has shown that, with the increase in thickness of sulfide layer, the diffusion velocity of sulfur reduced gradually, and the S element enriched in the surface layer. It's easy to form FeS_2 without lubricating ability when the active sulfur is oversaturated (Wang et al., 2003).

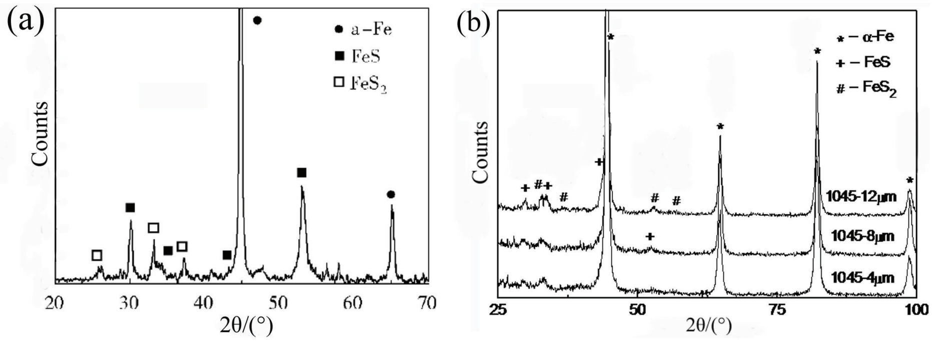

Fig. 5. Phase constitution of the sulfide layers on (a)52100 steel and (b)1045 steel (Wang et al., 2011)

2.4. Tribological properties of sulfurized layers

Many researchers' studies about the tribological properties of sulfurized layers have shown that, the anti-scuffing and wear-resistance properties of ferrous metal materials can be enhanced notably after sulfurizing, and the sulfide layer has very low friction coefficient. As is shown in Fig. 3(a), Zhang Ning studied the sulfide layer on 1045 steel and showed that, at the initial stage, μ_b of the sulfurized surface was only about 30% of that of the plain surface, the ultimate μ_t was also slightly lower than that. The sulfurized layer possessed a remarkable friction reduction effect. Fig. 3(b) shows that, the anti-scuffing load of the sulfurized sample is obviously higher than that of the original material (Zhang et al., 2000).

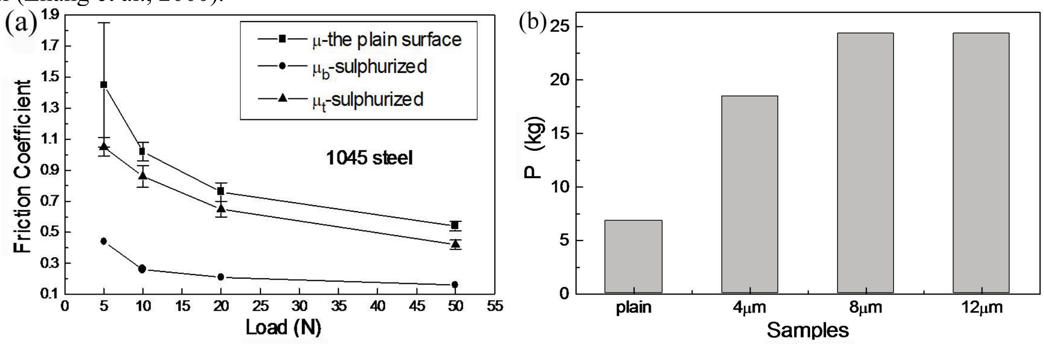

Fig. 6. Variation of the friction coefficients with load(a) and the anti-scuffing properties(b) of sulfurized 1045 steel (Zhang et al., 2000)

Our group has researched the tribological properties of the original and surface nanocrystallization assisted sulfurizing 1Cr18Ni9Ti steel, as is shown in Fig. 7 (Wang et al., 2011). After the combining treatment of surface nanocrystallization and LTIS, the friction coefficients of the sulfurized samples were low and stable both in air and in vacuum and remained around 0.3 during the steady-period. Initially, the friction coefficient curves under various atmospheric pressures are similar. After running to 400s, the increase of friction coefficients in air become quicker, while the friction coefficients in vacuum still varied quite slowly with time. The wear losses of the treated samples are roughly equal and much less than those of the original samples. And the wear loss in high-vacuum down to the 1/4 of that of the corresponding original substrate sample. So, the sulfide layer formed by the combining treatments can enhance the wear-resistance and reduce the friction coefficient of 1Cr18Ni9Ti steel effectively.

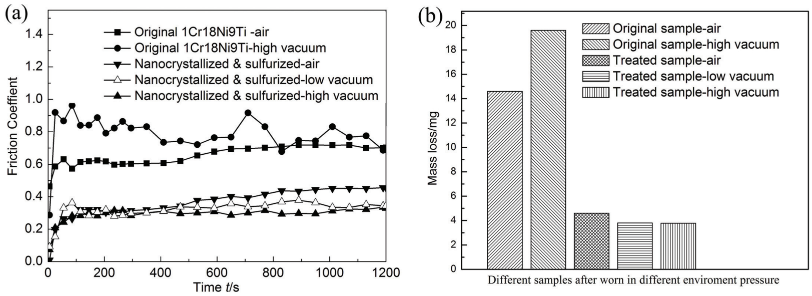

Fig. 7. Comparison of tribological properties of the original and treated 1Cr18Ni9Ti steel: (a)The variation of friction coefficients with sliding time; (b)Comparison of wear loss (Wang et al., 2011)

3. The unique advantages of LTIS technology

3.1. Technical advantages

The LTIS technology can enhance the surface properties of ferrous metal materials easily without any change in the substrate structure and its basic performance. The LTIS process operated at a temperature of about 200 ℃, which can avoid thermal deformation or phase transformation of the workpiece. The change in hardness and geometry of the workpiece can be ignored. So, LTIS is especially suitable for the final treatment of low-temperature tempered steel. The process of LTIS is operated in vacuum environment. There is not excess oxidation and inclusion, and is no need to clean the workpiece after LTIS treatment. The process of LTIS is relatively simple and stable. The thickness and composition of sulfide layers can be controlled easily by adjusting the process parameters, and it's easy to achieve automated production and industrial applications.

3.2. Economical advantages

The production efficiency of LTIS technology is very high, a sulfurized layer about 6-10μm thick can be formed on common ferrous materials after sulfurizing for 2h at about 200℃. The consumption of energy and time is little (Wang et al., 2002). In addition, the raw materials of LTIS process only contain a small quantity of ammonia and solid sulphur. Therefore, the labor intensity and cost of LTIS technology is very low.

3.3. Environmental advantages

On the whole, LTIS technology is very green and safe. It is unlike the cyanide salt bath sulfurizing, it don't use or release any toxic liquids; it can eliminate the risk of explosion of gas sulfurizing; it can also avoid the flaws of salt bath ageing, stench producing and instability of electrolytic sulfurizing process.

4. Applications of LTIS

LTIS technology has been widely used in the typical friction parts of metallurgy, automobile, machinery and other industries, these parts can be roughly divided into three sorts:

4.1. Application examples in rolling parts

Rolling bearing is a kind of key parts in machinery and equipments, most of its failure is resulted from the wear and fatigue caused by friction between the balls, roller conveyer and cage. Zhang Ning et al. using LTIS technology treated the supporting bearings of rolling mills which run in heavy-duty, high humidity and dust conditions. The results showed that, the service life of the sulfurized bearing increased more than 3 times than that of the original bearing. And their reliability and stability were also improved notably (Zhang, 2000). Wang Jinsong et al. treated the surfaces of brimful roller bearings using LTIS and found that, the shape, dimension and mechanical properties of the treated bearing didn't changed, while the surface roughness and friction coefficient reduced obviously, and the fatigue endurance increased more than 10 times (Wang et al., 2012).

4.2. Application examples in sliding parts

In There is a kind of parts often work in high temperature, high pressure, high speed and poor lubrication conditions, such as cylinder-piston ring of engine, cutting tools and drill rod joints etc. The main failure cause of such parts is the excessive wear and adhesion resulted from friction and frictional heating effect.

The cylinder of certain type diesel engine was sulfurized by Zheng et al using LTIS process. After sulfurizing, the scratch-resistance and wear-resistance of the cylinder surface improved observably, and the running-in time and fuel consumption reduced effectively, while the discharge of waste heat and smoke can be reduced notably. So, the sulfurizing process showed significant economic and social environmental benefits (Zheng et al., 2005).

The machining tool is one of the largest consumption of tools in machinery manufacturing industry. The leading failure reasons of tools are the adhesion of chips and excessive wear during cutting. The sulfurizing treatment not only can reduce the wear, but also averts the adhesion phenomenon. Using sulfurized tools, the machining quality can be improved significantly, and the tool life also increased 2-5 times (Zhang, 2000).

The joints of drill rod bear great stress, and need to be installed and disassembled frequently. In poor lubrication condition, the threaded joints are easy to break and induce the failure of entire drill. Che Yangang et al. treated the joint material of drill rod 35CrMo using sulfonitriding process and tested its dry friction properties. Compared to nitriding treatment, the sulfonitriding process can improve the tribological properties of the drill rod joint significantly, and it is expected to become an effective process to extend the service life of drill rod joints (Che et al., 2009).

4.3. Application examples in heavy-duty parts

There is a kind of parts with the function of passing load and movement in machinery and equipments, such as gear, camshaft, die and roller. These parts work under heavy stress and load. They are easy to be damaged for wear and fatigue, and so seriously affect the reliability and lifetime of devices.

Zhao Junjun et al. (Zhao et al., 2003) treated the driving gears of the gearbox and side decelerator of a certain tank using LTIS, and tested their properties in real vehicle. The results showed that, after sulfurizing treatment, the wear resistance of the two gears increased by 180% and 80%, respectively. Kong Da et al. (Kong et al., 2006)sulfurized the punching die for roller and the formed punch for bearing ring and showed that the sulfurizing treatment not only improved the formation quality of workpieces, but increased the life of the dies more than 2.5 times. Roller and collar are the key parts of rolling mills. Their usual working temperature is about 800℃~1000℃, and the rolling load is very great. Zhang Yifei et al. (Zhang and Zhang, 2004)treated the rollers made of chilled (alloy) cast and increased their service life about 1 time.

5. Conclusions

A solid lubrication film mainly consists of FeS, which has excellent tribology properties, can be formed on the sulfurized iron or steel surface. Various sulfurizing processes have been developed by researchers. All of them can improve the tribological properties of ferrous metal more or less, but also have respective shortages, such as high labor-consumption, low production efficiency and environment pollution. The basic mechanism of LTIS is similar to that of ion nitriding. In vacuum, at a temperature of about 200℃, under the combining effects of glow discharge, ion sputtering and diffusion, a sulfide film of about several microns thick can be quickly generated on the workpiece surface. Compared to the traditional sulfurizing technologies, LTIS technology has unique advantages of high efficiency, good effect and pollution-free. It has been widely used in the surface modification of typical friction parts, such as bearing, gear and machining tools. In the future, the LTIS technology with so many technical, economic and environmental advantages will continue to play an important role in the modification of tribological properties of friction parts.

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