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Technical Review

State-of-the-art in Surface Technologies

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Abstract

It is generally recognized that surface properties is one of the key factors which influence on the steel material performance, such as corrosion and tribology. In this article we present the recent development of the surface technology such as preventing corrosion in an extremely severe condition, improving wear and seizure resistance, as the progress with the development of surface analytical technique.

1. Introduction

Surface technologies are technologies that control material surfaces and bestow required functions to enhance the value of the material. Even if the subject material is limited to steel alone, it may be unnecessary to refer to the corrosion resistance, wear resistance, and design property such as glossiness, all of which are directly linked to the performance of steel products. Nippon Steel & Sumitomo Metal Corporation has investigated the sophistication of functions of various products and processes.

Since the atoms on the surface are in a state of coordinative-unsaturation, they have very strong reactivity, develop chemical bonding with gaseous molecules easily, and rarely undergo chemical reactions such as disconnection of a bond and or recombination. Therefore, it is not easy to control the reaction process on the surface and obtain the most appropriate surface function, the difficulty of which is briefly referred to in a section by Pauli.[1] Accordingly, understanding how to grasp the state of a surface correctly is critically important for creating new surface functions.

Since the surface is very susceptive to changes in the outer environment, in situ observation of the process of how the surface changes in accordance with the change in the outer environment is important for ensuring that the surface exerts its surface function effectively. Therefore, the extraction of material factors that control the change and the evolution to compositions and microstructures for the most suitable steel material design are strongly sought. To this end, the recent development of nanometer scale analysis technologies is realizing the observation of minute defects, impurities, and even the arrangements of atoms on a surface.[2] This article introduces the efforts being made on the sophistication of the surface function and development of observation techniques, and discusses the future prospect of surface technologies.

2. Tribology

Half a century has passed since Peter Jost coined the word “tribology” to describe the study of friction, wear, and lubrication. Since the prevention measures of wear and seizure represent a technology crucial to the life of machinery, surface hardening technologies such as nitridization and carburization have mainly been applied until now. However, for the elimination of such surface treatment processes, the application of untreated steel to machinery parts subject to various types of sliding action is also expected.

A pearlite structure having lamellar structure where ferrite (α-Fe: α) and cementite (Fe_3C: θ) overlap each other in a stratifying manner is applied for various uses as the basic structure of steel materials. For instance, the high strength steel wire used in the Akashi-Kaikyo Ohashi Bridge is a pearlite structure and the higher strength 2 000 MPa class was realized by making the lamellar structure finner in the production process.[3] Even when the pearlite lamellar structure is used for the sliding parts of crank shafts and or railroad vehicle wheels, the subsurface lamellar structure is refined and work-hardened by machining such as grinding or distortion in sliding action.

Figure 1[4] shows the sectional view of the structure of pearlite steel after an abrasion test. The lamellar is deformed in the direction of the sliding and the lamellar space in the region of about 200 nanometers of the subsurface is refined. **Figure 2** shows an example of subsurface nanohardness (*Hn* hardness) of the test sample measured directly by the indentation method applied to the sliding surface. The smaller the depth of penetration of the diamond probe used for indentation, or in other words, the closer the measured depth approaches the sliding surface, the more greatly the subsurface is work-hardened. The work hardening is in good agreement with the refinement of the lamellae of the subsurface of the sliding surface, as shown in Fig. 1. Wear is developed by hard particles and

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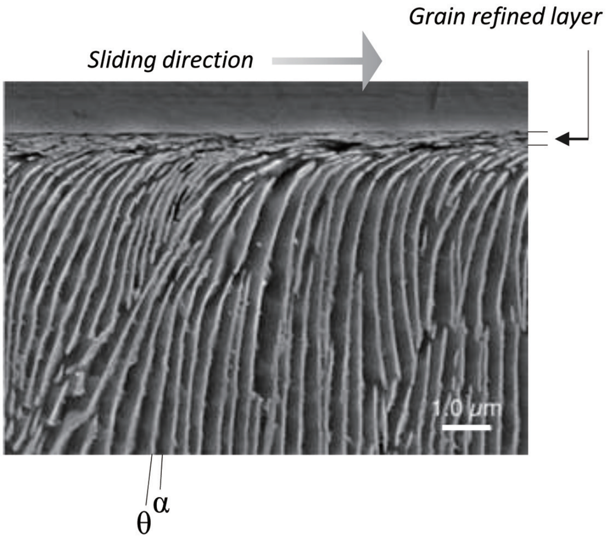

Fig. 1 SEM image of wear subsurface of the Fe-0.72C-0.19Mn wt% steel [4)]

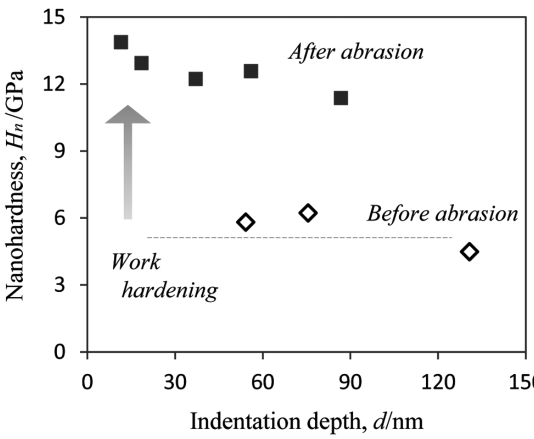

Fig. 2 Subsurface nanohardness (*Hn*) of the Fe-0.72C-0.19Mn wt% steel before and after abrasion test

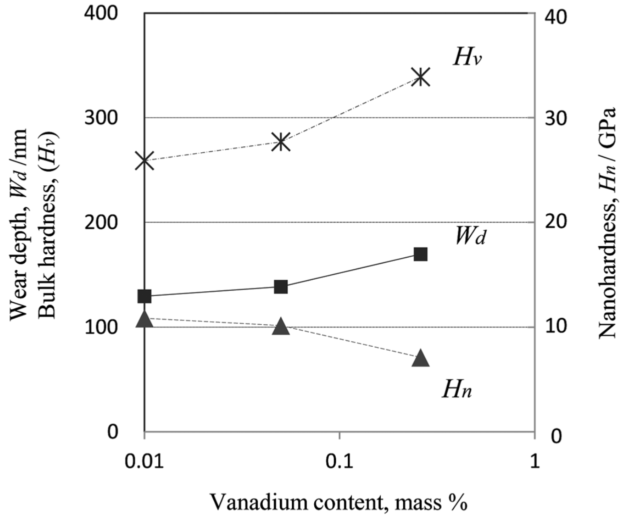

Fig. 3 Wear depth of steels for the crankshaft vs. bulk hardness and surface nanohardness

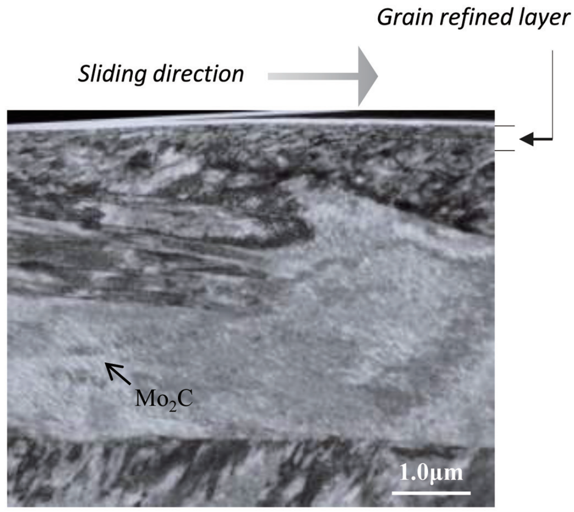

Fig. 4 Transmission electron micrographs of the wear on the subsurface layer of molybdenum addition steel

protrusions that grind off the surface and, in many cases, the governing factor is the hardness of the sliding surface. Accordingly, optimization of the subsurface structural change accompanied by sliding action is important for enhancing the tribology properties such as wear and seizure.

The material factor that governs the refinement of the lamellar structure accompanied by sliding action is complicatedly influenced by such factors as the volume fraction of pro-eutectoid ferrite, which varies depending on the carbon content and the addition of strengthening elements like V (vanadium), titanium (Ti), etc. **Figure 3** shows an example of the change in wear resistance of pearlite steel (0.4%C) with respect to the change in the amount of vanadium added, evaluated from the wear depth obtained by a rotating load testing machine simulating actual engines. As the amount of vanadium is increased, the bulk hardness (*Hv* hardness) increases, which indicates the precipitation hardening of vanadium carbide. Noteworthy is that the increase in the hardness *Hv* does not contribute to the improvement in wear resistance, but the wear depth decreases with increasing *Hn* hardness after testing. This result indicates that the addition of vanadium, which is a conventionally employed method to strengthen pearlite steel, effectively enhances the strength of the steel material, but acts as a hindrance to the formation of the refined layer in the subsurface of the sliding surface and, consequently shows that it exerts an adverse effect on the enhancement of wear resistance. [4)]

The previous section introduced the deformability of pearlite steel, or in other words, the material factors on refining of the lamellar structure, where frictional heat generated by sliding action exerts a great influence on the tribology properties. **Figure 4** shows a section image of the transmission electron micrographs (TEM) of the wear of the subsurface layer of the slide surface of martensite steel (0.4% carbon steel) added with molybdenum of 1.9wt%. Precipitation of acicular molybdenum carbide has been clarified as below the grain refined layer. This fact suggests that the temperature of the sliding surface of the test sample rose to the precipitating temperature of Mo_2C (about 550°C) by the frictional heat and the Mo atoms, which had solid-soluted to steel material precipitated as refined carbide. Depending on the carbon content, martensite steel softens when annealed under 400–500°C or above. Material designs with the addition of elements such as Mo, Cr, and V are expected to take advantage of their secondary hardening effects through the generated frictional heat. [5)]

Under a more pragmatic sliding condition, a lubricant such as lubricating oil is often used, wherein the reaction product formed between the steel material and the lubricating oil on the sliding surface (tribofilm) greatly influences the properties of tribology. Since tribofilm changes constantly depending on frictional heat and contact pressure in sliding action, in situ analysis in the field of friction is required. However, in many cases, the conventional evaluation method was limited to analysis after the sliding test. Therefore, the true nature of the tribofilm developed during sliding action could not be appropriately captured. In order to resolve the problem, Nippon Steel & Sumitomo Metal developed a sliding test machine capable of observing the friction surface directly and, by combining it with the Raman scattering spectral analysis method that does not require a high degree vacuum, further developed a method of in situ analysis of tribofilm formed on a sliding surface. This is expected to be a powerful tool for investigating the reactivity between steel composition elements and the lubricant components, and the correlation between the reaction product and the tribology properties such as wear and or seizure. [6)]

"Being trapped in mud of wear" is a phrase often used in the industry. This means that material factors other than bulk hardness have been scarcely considered even though many other factors play a role in tribology phenomena such as wear and seizure. By using the new analysis method and precisely capturing the dynamic transition taking place in the subsurface layer, the understanding of the emergence mechanism of new tribology properties is expected to be further promoted and measures for improving performance based on material factors such as steel material compositions and structures will be shown.

3. Corrosion Developed in Aqueous Solution (Wet Corrosion)

Corrosion in aqueous solution is developed on the interface where a steel material contacts an aqueous solution. Steel products and equipment react to the chemical compositions contained in the environmental aqueous solution and the part exposed to the reaction is metal-ionized or oxidized and then dissolves and dissipates into the aqueous solution. Since the development of the corrosion in an aqueous solution and loss of metallic substance through the reaction to environmental compositions increase the deterioration of functions of products and equipment and the danger of fracture, research on enhancing corrosion resistance has developed several solutions. However, since many of the materials supplied to chemical plants as structural materials are applied to harsh and special environments such as higher temperatures and pressure than ever before, the development of corrosion under more adverse conditions is required.

To understand corrosion phenomena, test samples are often taken out of a corrosive atmosphere after a corrosion test, and then evaluated and analyzed in the open air or under a vacuum. However, since the surface state of the test sample changes due to oxidization and other effects of being exposed to a different environment, such methods have made it difficult to obtain a proper understanding of the corrosion phenomena. To solve the problem, Nippon Steel & Sumitomo Metal developed an electrochemical cell that enables the direct observation of the interface between a steel material and an aqueous solution under harsh environments (i.e. room temperature–300°C and atmospheric pressure–350 atm) that exceed the environmental conditions (i.e. –90°C and atmospheric pressure) of conventional glass cells. [7)]

By using the cell, in situ observation of the corrosion in a high temperature and high pressure corrosive aqueous solution has been realized. As shown in **Fig. 5**, observation of the corrosion behavior of a low alloy steel in the aqueous solution containing carbon acid gas under the conditions of 100–200°C and 30 atm has been made possible, and the corrosion product developed under a harsh corrosive environment simulating actual plants can be identified. [8)] Since the corrosion of a steel material in an aqueous solution progresses through an electrochemical mechanism, the characteristics of the film of the corrosion product formed on the steel material surface greatly influence the corrosion behavior. By using the in situ observation technique for harsh environments, the creation of novel corrosion-resistant materials is expected based on the metallurgy such as optimization of the elements to be added for suppressing corrosion based on rules and principles.

4. Oxidization under High Temperature (Dry Corrosion)

Under an oxidizing and high temperature gaseous environment, an oxidized scale is formed on the surfaces of steel and metallic materials by the oxygen in the environment. The oxidized scale of various structures is formed depending on the compositions of the material, temperature, and atmosphere, and subsequently exhibits different characteristics. Accordingly, for the processability of steel products wherein most of the production processes are hot-processing and for the structural materials used under a high temperature environment, it is necessary to design material compositions and structures by grasping the scale and the physical and chemical characteristics of the scale at the interface between the oxidized scale and the base metal. Furthermore, for this purpose, analysis under high temperature oxidizing conditions is essential and details of the in situ observation of the spalling behavior of the oxidized scale is considered in this special issue. [9)] This section shows an example of the analysis of a scale/base metal structure in a nondestructive technique and the action mechanism of added elements.

By exposing the piping materials used in the synthetic gas production equipment of a plant that produces liquefied fuel from natural gas to an environment of high temperature with high carbon potential with low oxygen partial pressure, the corrosion of a carburizing nature termed Metal Dusting (MD) [10)] progresses. As the MD corrosion reduces the wall thickness, deteriorates the material life, and influences the operating efficiency, a technology that suppresses MD has been long sought.

To solve the problem, the effectiveness of copper is recognized as an element suppressing the corrosion by MD, however the action mechanism has not been clarified. Therefore, there has been a need for a nondestructive analysis of the interfacial structure between the scale and the base ferrous material. Although the subsurface with a depth of 2–3 nanometers was the limit of analysis with the conventional X-ray photo electron spectroscopy method, using the hard X-ray in Spring-8, a large synchrotron radiation facility, has made it possible to perform a nondestructive evaluation of the state of chemical bonding to a depth of 60 nanometers. [11)] As shown in **Fig. 6**, copper segregation developed on the scale/base material interface at 10 and several nanometers below the top surface was confirmed for the first time. This analysis also showed that the formation of the oxidized scale containing protective Cr and Si and the suppression

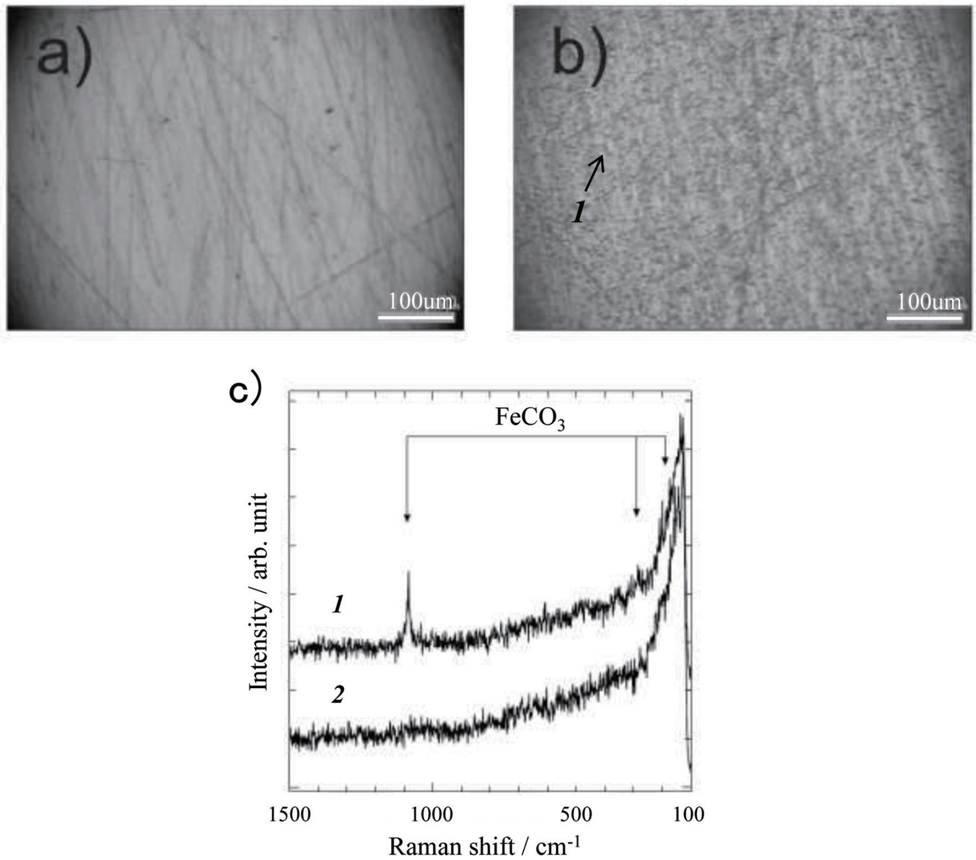

Fig. 5 Corrosion surface of a steel immersed in 5 mass% NaCl solution containing CO_2 and in situ Raman spectra from corrosion products
(a) At room temperature, (b) At around 185°C during heating to 200°C and (c) Raman spectra on the black spot (specrtrum 1) and the region where the black spot were not formed (spectrum 2)

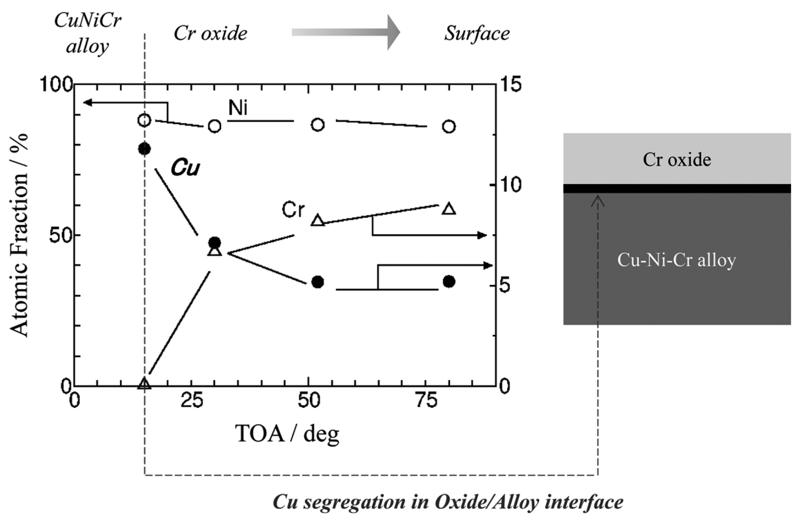

Fig. 6 Atomic fraction of Cu, Ni and the Cr-metallic dependent on take-off angle (TOA)

of CO molecule divergence and absorption by the copper segregation work to enhance the resistance to MD. The Ni alloy steel (NSSMCTM696) developed using this mechanism is beginning to be used widely in the MD-corrosive environment in synthetic gas production facilities.

By using the powerful synchrotron radiation X-ray, which is 10^{11} times stronger than the conventional X-ray, it will become possible to clearly capture the change on the interface between oxidized scale and base material under a high temperature environment, which has been unclear until now. Hereafter, using the big science represented by the synchrotron radiation facility should lead to the creation of novel materials aimed at exerting excellent performance under pragmatic service environments.

5. Conclusion

This paper has presented an outline of several endeavors by Nippon Steel & Sumitomo Metal to enhance surface function. Surface functions are becoming increasingly important, particularly in the automotive and energy fields. Using state-of-the-art nanometer-level analysis technologies to pursue the true nature of the reactions occurring on the surface under pragmatic service environments will create an evolution of the conventional surface technologies on the order of micrometers to the "surface metallurgy" of creating novel materials such as steel material compositions and structures in the subsurface region of 100 nanometers subsurface. The computational scientific method taken up in this special issue is also an important analysis method of the sophistication of surface function. By combining the analysis of fundamental reaction processes by the first principle computation and state-of-the-art experimental technologies, further evolution of surface technologies is expected. Hereafter, we are determined to promote further sophistication of surface functions such as corrosion prevention technologies and tribology in addition to the basic performance of steel materials such as strength and elongation to meet broad and high level customer requirements.

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