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The coating layer structure of commercial chrome plates

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ABSTRACT

The surface and cross-sectional morphologies of the commercial chrome plate coating layer with the thickness of dozens of nanometers have been observed. To investigate the detailed structure of the coating layer, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) combined with the low energy Ar^+ sputtering technique have been employed. Through careful analysis of experimental data, it can be obtained that the coating layer of commercial chrome plates is composed of four layers from top to bottom with different compositions.

1. Introduction

Tinplate is widely used for packaging foodstuffs, beverages, oils, grease, paints, powdered, polishes, waxes, chemicals and many other products nowadays [1]. With the continuous growth of tin production, tin resource will eventually be faced with depletion [2]. Thus, different kinds of tin free steels (TFS) have been developed to substitute for tinplates. As the most successful TFS today, chrome plated steel sheets attract more and more attention recently with increasing annual output. Cr plating uses electrolysis to bind a thin Cr layer onto a cold rolling steel plate. The concentration of CrO_3 solution used for electroplating is about 150 g/L. The electroplating is usually carried out at the temperature of 40 °C. Because chrome plates have a number of advantages over tinplates such as lower coating weight, better organic coating adhesion and better high temperature tolerance, they have been widely used gradually in recent years.

Considering the spot welding performance, commercial chrome plates usually have very thin coating layers with Cr coating mass less than 100 mg/m^2. Because the coating layer thickness of the chrome plate is very thin, which is usually no more than 30 nm, it is difficult to obtain normal direct evaluation and characterization of it. The results obtained by electrochemical methods before indicate that the coating layer of the commercial chrome plate may comprise of an outer hydrated Cr oxide layer and an inner metallic Cr layer [3], but the detailed analysis of the chrome plate coating layer structure is seldom found [4]. As generally known, the structure and composition of the coating layer play an important role in the performance of the chrome plate. For example, the deep drawing property of the chrome plate will be seriously influenced if the oxide layer in the coating is too thick. So it is important to find out a proper method to characterize the structure of the chrome plate coating layer.

Analyzing and researching a very thin coating layer by the traditional grinding and polishing method require highly developed skills in preparing a smooth cross-sectional sample with clear characteristics. If the coating layer is easily corrosive or brittle, the traditional method usually leads to the coating layer damage. A focused ion beam (FIB) system makes accelerated ions focused on the specific location of the sample to remove material from it, and can be employed to easily prepare a cross-sectional sample with high quality. So it is a good choice in the research of chrome plate coating layer. Considering the information depth at nanoscale sizes in solids, Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) combined with the low energy Ar^+ sputtering technique have great advantages in the analysis of very thin coating layers [5,6]. AES is often used to realize surface analysis of micro-regions, while XPS can be used to investigate the chemical states of elements easily. It is suitable to investigate the thin chrome plate coating layer with Cr in different chemical states at different regions by combining these two methods.

2. Experimental

The surface and cross sectional observations on the commercial chrome plates (the substrate grade of MR T-4CA) made by

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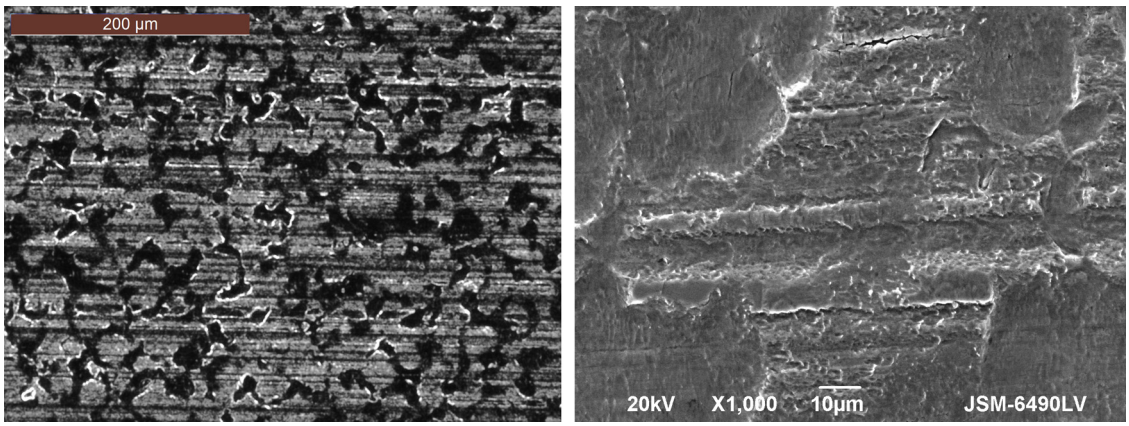

Fig. 1. The optical microscope (left) and SEM (right) images of the chrome plate coating surface.

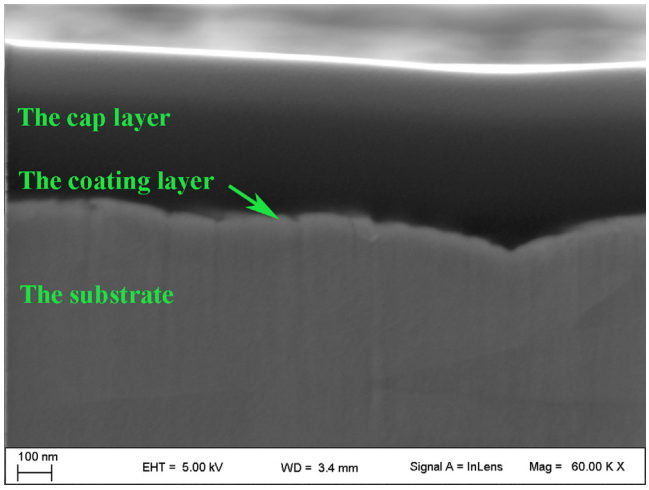

Fig. 2. The cross-sectional SEM image of the chrome plate coating.

Baosteel have been obtained by optical microscope and scanning electron microscope (SEM). There is no other element which can be detected by electron spectroscopy in the substrate except Fe. The cross sectional sample was prepared by SMI3050 FIB system made by SEIKO corporation with an ion source of liquid metallic Ga and an acceleration voltage of 30 kV. The AES and XPS depth profiling experiments of the coating layer have been carried out by PHI700 system and Quantera SXM^{TM} system made by ULVAC-PHI corporation, respectively. The acceleration voltage used in AES experiment was 3 kV. The X-ray source used in XPS system was monochromatic Al $K\alpha$ (1486.6 eV) radiation. And the instrumental binding energy scales were calibrated using standard samples of pure Cu, Ag and Au according to ISO15472. The Ar^+ with the acceleration voltage of 2 kV was used for either AES or XPS depth profiling. The XPS analysis area was about 300 μm × 300 μm.

3. Results and discussion

Firstly, the surface morphology of the chrome plate coating layer has been observed by optical microscope and SEM, respectively. It can be seen that the surface with large roughness shaped by previous cold rolling process remains its original morphology after electroplating. The coating layer does not change the surface morphology, and seems continuous and intact without any crack, as shown in Fig. 1. Through the qualitative analysis by AES, it can be obtained that there are only C, O and Cr detected on the surface of coating layer.

The cross sectional sample of the chrome plate coating prepared by FIB system has been observed by SEM. From the SEM photo revealed in Fig. 2, it can be seen that the surface of chrome plate substrate is very rough, and the coating layer is very thin. Due to the limit of focused electron beam size, it is difficult to get ideal component analysis result from the cross sectional sample by the method of energy disperse spectroscopy (EDS) or AES.

As the analysis of the cross sectional sample has not given a clear coating layer structure, the depth profiling method by electron spectroscopy (AES and XPS) with ion sputtering was employed. AES depth profiling on large area (1 mm × 1 mm) indicates that there are only O, Fe and Cr detected in the coating layer except

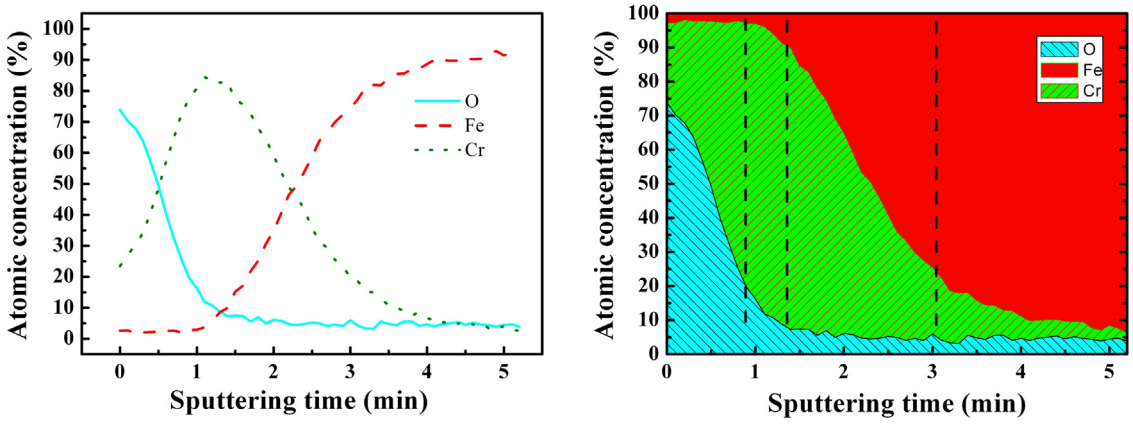

Fig. 3. The depth profiling results of the chrome plate coating.