

## Development and Application of Metal Surface Analysis Methods

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**Abstract.** In recent years, metal surface analysis is becoming a hot topic, especially for the new composite materials used in high speed trains and aircraft. Metal surface analysis techniques are used to reveal the material surface morphology, structure, composition or state. This paper presents typical instruments and their application in various types of analytical methods, which includes microscopic surface topography analysis, surface structure analysis, composition analysis of the material surface and depth distribution analysis from surface to matrix. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Scanning Tunneling Microscopy (STM), X-Ray Photoelectron Spectroscopy (XPS), Glow Discharge Spectrometer (GD-OES) and analysis images of metal surface are discussed.

### Introduction

China has become the largest automobile manufacturing country, and the development of the automotive industry occupies an important position in the national economy. People have high hopes in the area of new automotive steel materials development. In recent years, the application of high-speed trains, new composite materials for aircraft has become a hot topic of surface science. Because of the close relationship between the metal material surface study and basic theory and engineering technology of the special nature on the problem, it makes the metal surface topics extremely active in recent years. Metal surface analysis technique involves many fields of physics, chemistry, weak signal detection technology and materials science. It is considered to be developed very quickly and a cutting-edge science which has a very close relationship with engineering technology.

Metal surface analysis technique is mainly on metal surface and surface-related macroscopic and microscopic structure. It helps us to understand and interpret chemical composition, material surface atomic composition, geometry, motion, electronic states and the contact with surface of macroscopic properties from atomic level. It generally uses a beam of particles (such as electrons, ions, photons, etc.) as a probe to detect the sample surface. According to the analysis emitted electrons, ions, photons, etc of the solid surface, variety of information of metal sample surface can be obtained. [1, 2]

Microscopic surface topography analysis refers to the "macro" analysis of the surface. Surface structure analysis of the material includes surface atomic arrangement lattice structure analysis, crystal structure analysis. Surface composition analysis of the material includes point elemental analysis, line elemental analysis, surface analysis and distribution of constituencies' elemental analysis and determination of the composition of the metal surface. Depth profile analysis of the material includes elemental content or the chemical state of the depth distribution analysis, which includes both lossy and lossless methods. Different methods vary in working principles, and they have their own range of applications, they can help people to understand the different aspects of detection information of various types of the metal surface [2].

### Metal surface microscopic morphology analysis

Electron microscope and ion microscopy are mainly used in surface topography analysis. Using general optical microscope, we can only get the grain morphology in more macro scale. In addition to the commonly used Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM),

now the High Resolution Electron Microscopy (HRTEM), Scanning Tunneling microscopy (STM), Atomic Force Microscopy (AFM) and Field Ion Microscope (FIM), have also reached atomic resolution capability, and the arrangement of surface atoms can be directly observed under a microscope [3].

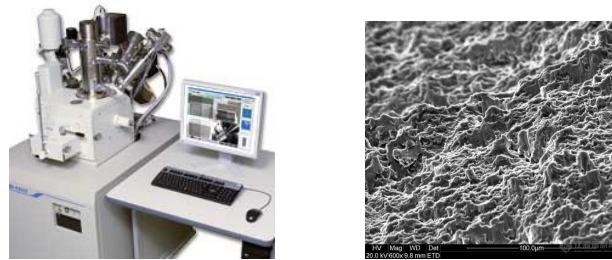


Figure 1 SEM system and titanium fracture SEM analysis image

For example, using Scanning Electron Microscopy (SEM), we can make SEM microstructure morphology analysis on titanium alloy fracture. The photo of the SEM system and analysis result is shown in Figure 1.

### Metal surface structure analysis

Surface structure analysis can be used to analyze the characteristics of how the surface atoms arrange, and discover surface atomic arrangement of the crystal, the unit cell size and atomic positions in the unit cell of the surface structure analysis and other crystal structure information. Surface structure analysis mainly uses a variety of methods of diffraction analysis. These analysis methods are based on the phenomenon of diffraction, including the X-Ray Diffraction (XRD), Electron Diffraction (ED) and Neutron Diffraction (ND) and other analytical methods.

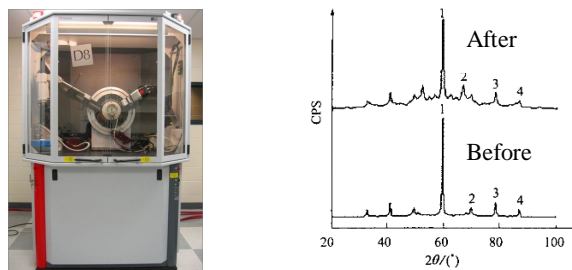


Figure 2 X-Ray Diffraction (XRD) and analysis image of a comparison of surface grain size analysis before and after the high energy shot peening of 45 steel

Take XRD as an example, there is a certain internal relation existing between surface crystal structure and X-ray diffraction pattern, by analyzing the diffraction pattern, the crystal structure can be measured, and then the grain size of the crystal could be determined. For instance, using X-ray diffraction we can analyze the surface crystal scales of peening steel. Knowing that the grain size decreases would cause X-ray diffraction peak broadening, by broadening the diffraction peaks, we could analyze and calculate the grain size. Figure 2 is a comparison of surface grain size analysis before and after the high energy shot peening of 45 steel using X-Ray Diffraction.[4]

With the development of microtechnique, high-molecular-resolution electron microscopy, Field Ion Microscope (FIM) and Scanning Tunneling Microscopy (STM) and other analytical techniques have reached atomic resolution capability [5], and situ atom arrangement can be directly observed. They become surface analysis techniques that could be made directly on real lattice measurement.

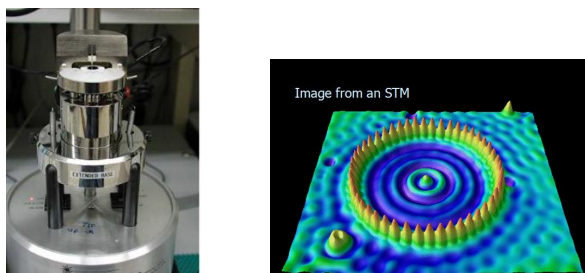


Figure 3 Scanning Tunneling Microscopy (STM) and analysis image

For instance, the Scanning Tunneling Microscope (STM) has atomic level high-resolution. The resolution of STM is up to 0.1 nm and 0.01 nm on the sample surface in a direction parallel, on which, individual atoms can be distinguished. Figure 3 shows iron atoms on copper surface detected by STM. Moreover, Ion Scattering Spectroscopy (ISS), Rutherford Backscattering Spectrometry (RBS), Surface-Enhanced Raman Spectroscopy (SERS), also could be used to indirect surface structure analysis.

### Metal surface elemental composition analysis

Metal surface elemental composition analysis includes the determination of the composition of the metal surface, and the elements chemical state of the surface element in the surface area of each distribution. But the surface microscopic measurement techniques typically only provide morphology, structure or other information, but it can not determine the chemical composition of the sample. Analytical laboratory in traditional conventional physical and chemical methods can determine the chemical composition of the material, but the analysis results often fall in a macroscopic average. The development of the modern surface composition technology makes up the shortcomings of the above two methods. It can analyze elemental chemical composition and chemical state of the uneven surface of the sample microstructure or a metallic material features micro area. Nowadays, the metal surface elemental composition analysis methods commonly includes X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Glow Discharge Optical Emission Spectroscopy (GD-OES), Glow Discharge Mass Spectrometry (GD-MS), Secondary Ion Mass Spectrometry (SIMS) X-Ray Fluorescence Spectrometry (XRF), etc. [6].

For example, in the ultra-high vacuum environment, using of X-ray irradiation on the surface of a metal sample, the photoelectrons generated by the photoelectric effect are excited and released into a vacuum. By observing the photoelectron kinetic energy, we can get element composition of the sample surface and chemical state information. In, As, C, O and other elements analyzed by XPS is shown in Figure 4.

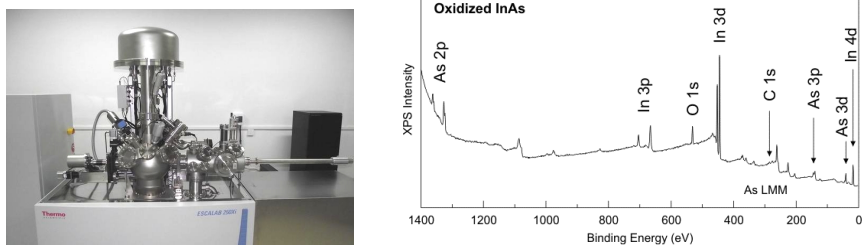


Figure 4 X-Ray Photoelectron Spectroscopy (XPS) and XPS survey spectrum of an oxidized InAs surface

Glow Discharge Optical Emission Spectroscopy (GD-OES) is a recent modern analytical instrument for chemical composition of the material surface detection. Typical GD-OES instrumentation photograph and GD-OES analysis for the surface coating of the hard disk are shown in Figure 5. Hard disk surface image on the left side is measured by optical microscope, and the right side

of the figure shows the surface of the hard disk coating thickness distribution in P, Ni, Al, Mg elements. [7]

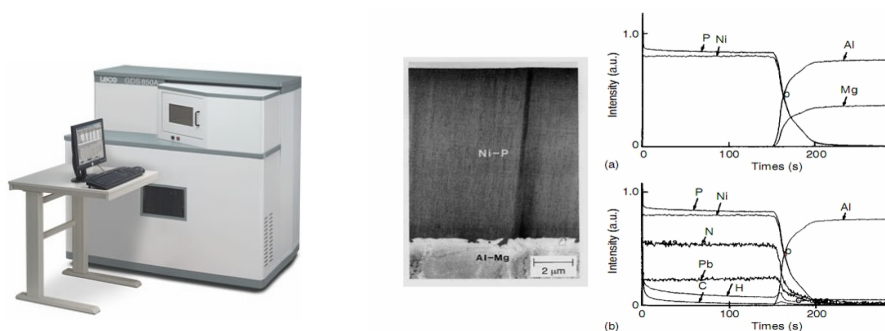


Figure 5 Glow discharge optical emission Spectroscopy (GD-OES) and Hard disk surface coating analysis by RF GD-OES

When we chose the method of metal surface composition analysis, we need to consider the scope of the elements required spectrum, the detection sensitivity, the ability to determine the chemical state of the element, whether quantitative analysis, peak resolution, the destructive of the detection for the sample surface and other factors.

### Depth distribution analysis from the surface to the matrix of metal

Regarding coating materials analysis, in addition to conventional methods for homogeneous material analysis, more depth analysis techniques are used for variety of surface. With the progress of modern industry, coating technology is used on steel material surface to improve the steel performance to meet user needs. Surface information is acquired by the interaction with the surface of microscopic particles using surface analysis techniques. The depth analysis methods which could be applied from the metal surface to the matrix are the following: Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS), Glow Discharge Optical Emission Spectroscopy (GD-OES), Glow Discharge Mass Spectrometry (GD-MS), etc. To obtain the depth distribution of matrix elements ingredient, the sample material is ion sputtering layer by layer peeling from the surface.

These methods have their application advantages, the most significant feature of XPS is that it can get a lot of chemical information with least damage on the sample surface, and its micro quantitative analysis is better. AES and SIMS have high lateral resolution. The most prominent feature of SIMS is that its detection sensitivity is very high, and it could be used on analysis of H and He and its isotopes. SIMS could also be used on micro-area analysis and organic chemistry. The most significant feature of AES is that its spatial resolution is very good, and its micro-analysis capability is high, and it can get an element distributed image of the sample surface. The sputtering speed of SIMS, AES, and XPS is slower. It is more suitable for the analysis of nanoscale coatings. The GD-OES and GD-MS have a faster sputtering rate and a higher vertical resolution, and it can be used for coating thickness of 100-200 μm to get the accurate qualitative and quantitative elemental chemical composition with depth profile analysis. In the practical application, the research process of sample may take two or more analytical tools. [8]

Taking Glow Discharge Emission Spectroscopy as an example, GD-OES could be used for analysis of the solid bulk samples directly, and also for in-depth analysis layer by layer on the surface of the sample. In recent years, Glow Discharge Optical Emission Spectroscopy technique has been widely used in metal coating, film and other sample for fast depth coating distribution analysis. Compared to Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS), it has advantages on analysis speed, quantitative convenient in surface and depth profile analysis. Figure 7 is Al-Zn-Si coated steel sheet sample spectra of GD depth analysis [9-10]. Figure 7-a) is an element qualitative

analysis, showing the relationship between the spectral intensity of the signal and the sputtering time. Figure 6-b) is a quantitative analysis, showing the relationship between the elemental concentration and the sputtering depth.

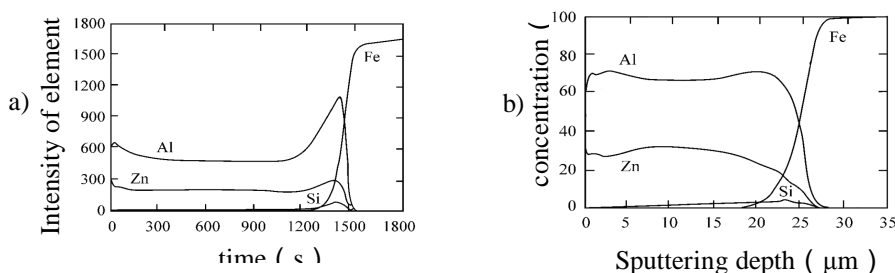


Figure 6 Depth analysis of Al-Zn-Si coated steel sheet sample  
a) Qualitative Analysis b) Quantitative Analysis

## Conclusion

This paper describes the classification, progress and typical application of modern metal surface analysis methods. It describes microscopic surface topography analysis, surface structure analysis, surface composition analysis of the material and from surface to base distribution depth analysis instruments and its application progress distributions. When we choose the analysis method, we need to consider the property of sample and the application scope of the equipment. To get the information on the different microscopic and macroscopic levels, one or more analytical methods may be applied.

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