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Dependence of electron work function of Al-Mg alloys on surface structures and relative humidity

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In many fields the determination of electronic structures of a solid material is a prerequisite in order to investigate its physical/chemical properties as well as related applications. The effect of surface structures and ambient environment on the electronic behavior is of both fundamental and practical significance. In this study, the electron work function (EWF) of Al–Mg alloys is investigated using a scanning Kelvin probe. The results show that the EWF decreases with the increase of surface smoothness, whereas surface oxidation layers would result in the increase of the EWF. Furthermore EWF is strongly dependent on the relative humidity, especially when the relative humidity is higher than 70%, implying that considerable care should be takenon such dependence in order to gain a meaningful parameter for the characterization of surface behavior.

1. Introduction

Recently, Al–Mg alloys as a structural material have received considerable interest for civil and military applications due to their low specific weight, high strength/weight ratio and excellent welding quality. The use of Al–Mg alloys in industrial applications is, however, mainly limited by their unsatisfactory surface properties and poor corrosion resistance [1,2]. To improve the corrosion resistance of Al–Mg alloys some successful and significant studies, including adjusting the contents of doped elements, analyzing the effect of intermetallic phases and raising the surface coatings have been done [3,4]. However, with respect to corrosion control and surface finishing, the heterogeneous nature of alloy surfaces is faced with many challenges. The surface characteristic of an alloy plays an important role in determining its physical, chemical and mechanical properties. For example, a rough surface brings a serious effect on the wetting behavior, hydrophobicity/hydrophilicity, nanoadhesion and wear/friction between two adjacent objects [5,6]. Therefore some important parameters associated strongly with the surface structures, such as electron work function (EWF), should be well understood.

In the theoretical solid-state physics, EWF is usually defined as the minimum energy required for extracting an electron from within the sample to a position just outside the sample (far enough to eliminate contributions from image forces). Practically, it is composed of two parts: the chemical work and the part that take into account the electrostatic work to transport the charged electron through the dipole layer of the surface, as shown in Fig. 1. For a chosen material, the former is an inherent property of the bulk material, whereas the latter depends strongly on the distribution of surface charges associated with the microscopic morphology and chemical compounds at the surface. Therefore EWF is very sensitive to the surface condition, and any change in the structural or chemical character of the sample surface (e.g., adsorption of atoms, molecules or ions) will alter EWF [7,8]. Therefore, EWF plays an important role in many aspects of physical and chemical fields related to the contact potentials, electronic kinetics and various surface properties. For metal/alloy materials, EWF is a very useful parameter to characterize the behaviors associated with the surface properties such as surface corrosion, strain and joint strength. For example, the variations in EWF of Al, Cu, Fe and Mg alloys with respect to tensile strain were experimentally investigated, and the changes of EWF of an elastically strained single crystal were calculated using the density functional methods [8,9]. These results indicated a decrease of EWF with tensile strain/strain rate. In contrast, Loskuto and Pravda [10] indicated that the EWF of Al increased with strain owing to the crystal relaxation based on a self-consistent calculation of surface energy.

For the experimental measurement of EWF the ultraviolet photoelectron spectroscopy (UPS) working under ultrahigh vacuum gives the lowest work function of the sample surface, which does not consider the effect of ambient environment [11,12]. It is to be emphasized that, with the development of scanning probe

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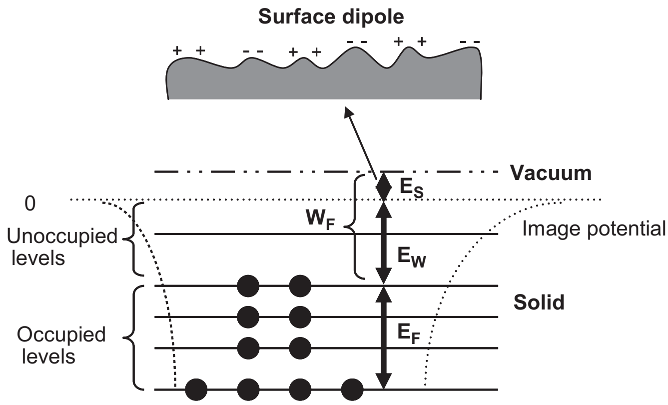

Fig. 1. Schematic diagram of EWF. Here the Fermi Level E_F is defined as the highest energy level that is occupied by electrons, and the actual work function W_F measured by SKP considers the effect of both surface microstructures and material itself.

microscopy techniques the electronic structures of the surfaces, especially the characterization of EWF, are widely measured by scanning kelvin probe (SKP) technique together with Field-emission scanning electron microscopy(SEM) [13]. The SKP technique is based on the vibrating capacitor method, which measures the volta potential difference between the sample and the reference-probe across a dielectric medium. This is to say, the principle of SKP method is: to form capacitors, to allow electronic conduction, and to detect the charge transfer. It is extremely sensitive to the changes occurring at the several outermost monolayers of the surface. Considering the comprehensive factors from the materials and ambient environment, SKP measures the average work function difference under the probe. Thus the EWF obtained by SKP is often higher than that measured by UPS, which is thought to be close to the practical case.

As a noninvasive and nondestructive examination technique, SKP has a high sensitivity to the changes in surface potential (<10 meV) and a high spatial resolution (tens of nanometers) being a powerful tool for noncontact measurement of the EWF. Especially, SKP has been employed to investigate the surface structures and properties, such as conversion coatings, synthetic metal coatings, friction of single–crystal silicon and adhesion of nano/microdevices by monitoring the changes of the EWF [13,14]. For instance the coating delamination is investigated by means of SKP, and it is found that there is a clear potential transition line separating intact from disbonded areas [15]. The changes of EWF with absorbed layers, stress and atmospheric corrosion have been investigated by SKP [2,16,17]. Recently, the effect of surface roughness on work function has also been experimentally reported on the Mg–Ti thin films [18]. In spite of these interesting results [13–19] the mechanism on the effect of ambient environment and surface structures on EWF is not very clear, and the quantitative relation between them and the physical/chemical nature is still lacking. It is well known that the electronic structures including EWF in an atmospheric environment are obviously different from those in theoretical calculations [20]. A better understanding of the effect of atmospheric conditions on EWF is therefore needed.

In the present study, the SKP technique has been used to obtain an understanding on the influence of the surface structures and atmospheric conditions on the electronic structures of Al–Mg alloys. The changes of EWF with the surface roughness and relative humidity were investigated.

2. Experimental details

The commercially available Al–Mg alloy (5083, Mg contents: 4.0–4.9 wt.%) was chosen as the sample material. All the samples had a size of $12 \times 12 \times 3$ mm^3. In order to obtain different rough surfaces, the working face of the samples was polished step by step using #320, #400, #600 and #2000 sand papers (abrasive silicon carbide). The mechanically treated surface was cleaned using an ultrasonic cleaner with purified water (18 M Ω cm) for 10 min, reagent grade acetones for 10 mins and reagent alcohol for 5 min. To reduce the surface oxidation of as-treated samples, they were always invaded into the reagent alcohol unless they were drawn out (dried under ambient conditions) for the SKP and other measurements. It should be indicated that the surface oxidation and adsorptions caused during the sample preparations or experimental measurements might not be completely eliminated. However, these factors should have a negligible effect on the present comparative study since all the samples were polished, conserved measured under the same conditions.

The accessorial measurements of the sample compositions have been characterized by X-ray diffraction (XRD, SMART APEX II) using Cu K_α radiation, and the surface morphologies have been monitored by scanning electron microscopy (SEM, Quanta 200) with an accelerating voltage of 20 kV. The measurements of EWF of these specimens were done using a commercial scanning Kelvin probe system provided by KP Technology Ltd. (Caithness, UK). The system consisted of three sub-systems (digital oscillator, data acquisition and sample translation), which were controlled by a host computer. A three-dimensional micro-stepper positioner permitted high resolution sample positioning (400 nm/step), and the spacing between the probe tip and the tested surface could be controlled within 40 nm. The SKP system allowed point-scanning for a selected position and face-scanning of topographies in a range of 0.02 mm to 20 mm on a side. The suspension system readily produced amplitudes of oscillation of 1–2 mm, permitting a stand-off distance, that could be regulated in the region of 0.1–1.0 mm and ensuring that the tip-to-sample contact did not occur. The relative humidity of the sample surface (ranging from 10% to 100%) could be accurately monitored using a seal cavity and an automatic control system that can adjust and measure the relative humidity. Owing to the accurate control of relative humidity and temperature (ranging from room temperature to 90 °C), the measured EWF had a relatively high resolution in the meV range during topographical analysis. However, it did not directly provide the absolute EWF, which would permit an easy comparison with literature data for clean surfaces. In order to determine the absolute EWF values of the samples, we have implemented a tip calibration procedure. For a rapid but less rigorous check of the EWF of the tip, the EWF difference relative to two reference samples (gold and aluminum) was measured. If the EWF difference of Al and Au is in the range we anticipate, the EWF of a tip can be obtained so that the absolute EWF of the samples could be determined. We monitored the EWFs of the tip before and after a scan procedure to ensure that no changes in EWF of the tip occur. In this case the EWF of the gold tip should be 5.1 ± 0.1 eV. In the present study, a gold tip (2 mm diameter) was used and the scanning area was 1×2 mm^2 (including 10×20 points). The oscillation frequency of the SKP tip was set to 84 Hz. All the measurements were performed at about 20 °C.

3. Results and discussion

3.1. Surface structures of Al–Mg alloys

The surface microstructures of the Al–Mg alloy after polishing with #2000 sand papers are shown in Fig. 2. One can see that the surface is relatively smooth and there is no obvious nick, defects or holes. Based on the images, for the measurements of the EWF by SKP one can select a region at the surface of the samples at random. In fact, the experimental data of the EWF also indicate