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Electrodeposition of Sm-Fe Thin Film in Aqueous Solution under a High Magnetic Field

Changsheng Lou[1,*], *Ying Kou*[2], *Xiao Lyu*[1], *Weiqiang Zhang*[1]

[1] School of Materials Science and Engineering, Shenyang Ligong University, Shenyang 110159, China
[2] Shenyang Aerospace Xinguang Group Ltd., Shenyang 110861, China
[*]E-mail: chsh_lou@163.com

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The effects of a high magnetic field up to 4 T in the perpendicular or parallel to current configuration on the electrodeposition process and quality of Sm-Fe film were investigated. The behaviors of hydrogen evolution reaction and desorption from cathode surface were recorded by a digital camcorder. The microstructures, Samarium content and the phase composition of deposited Sm-Fe films were characterized by using of SEM equipped with EDS and GIXRD, respectively. The magnetic property was tested by VSM. It was found that quality of deposited films was strongly affected by the imposed high magnetic field. Moreover, magnetohydrodynamic (MHD) effect plays a predominant role in hydrogen evolution reaction rate and raising trajectory when the magnetic field is parallel to the electrode surface, thereby results in the microstructure of the deposited films. Micro-MHD effect plays a role in the electrodeposition process of Sm-Fe film when field is perpendicular to the electrode surface. The Sm-Fe film obtained at $\boldsymbol{B}$=2 T flux density with the field perpendicular to current configuration has better magnetic property compared with that of absence of high magnetic field.

Keywords: Electrodeposition, Sm-Fe Film, High Magnetic Field, Microstructure Evolution, Magnetic Property

1. INTRODUCTION

Magnetoelectrochemistry developed in recent years is concerned with a novel electrodeposition technology, which has attracted much attention to developing permanent magnets with high performances [1-8]. The electrodeposition process, microstructure and properties of planting layers are influenced remarkably by the interaction between magnetic and electric fields.

Meanwhile, there is increasing interest and industrial use of RE-TM permanent magnetic thin films due to their wide range of applications in magnetic, magnetooptical, and thermoelectric devices [9-11]. For the method of the electrodeposition of RE-TM from aqueous solutions [12-14], RE elements is very difficult to be deposited on electrodes since their reduction potentials range from −2.52V to −2.25V vs. SCE. In addition, hydrogen evolution is inevitable in the electrodeposition process, which lets the pH value shift to positive value and gives rise to the forming of the metal oxides [15, 16]. However, Schwartz proposed a mechanism for the codeposition of the alloys, in which involves hetero-nuclear glycinato coordination complexes as a result of the zwitterionic characteristics of glycine [17].

As a potential useful giant magnetostrictive material, Sm-Fe film has aroused attention due to its negative extension coefficient. The present study is focused upon preparation of Sm-Fe alloy film by elecrodeposition in aqueous solution under an external high static magnetic field, and the effects of both flux density and orientation of the high magnetic field on microstructure and properties of the deposited film. The mechanism was discussed to provide the basis for a theory to explore a new fabricating process.

2. EXPERIMENTAL PROCEDURE

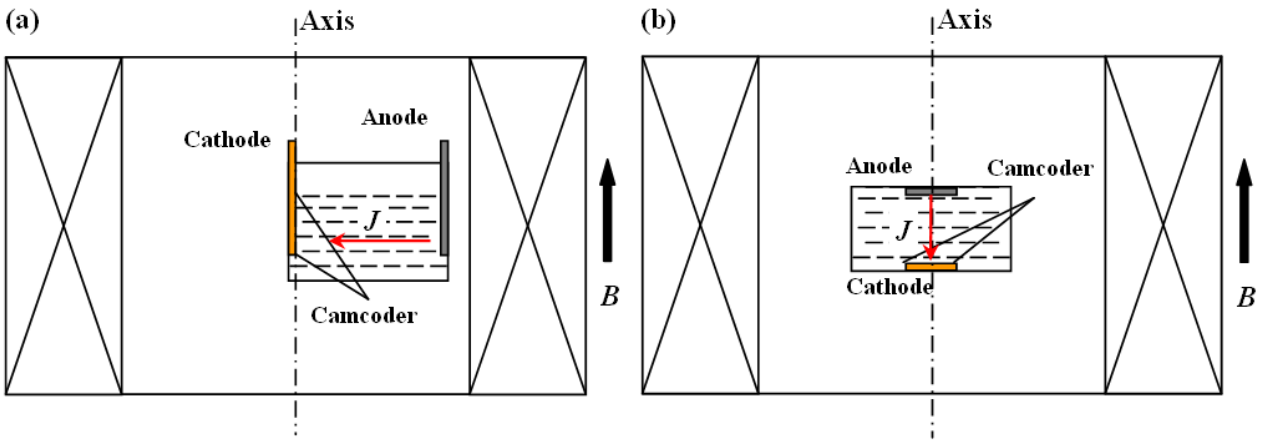

Figure 1. Schematic illustration of the electrode assembly imposed with high magnetic field, (a) $\boldsymbol{B} \perp J$ and (b) $\boldsymbol{B} // J$.

Electrochemical experiments were carried out with a double-electrode system. The experimental apparatus was, as shown in Fig. 1, consisted of a home-made electrode cell and a digital camcorder. The camcorder was connected with a personal computer for in situ observing of the bubble evolution. The magnetic density of imposed field is selected as 2 T and 4 T. During the process, the direction of magnetic field is perpendicular or parallel to the deposited current ($\boldsymbol{B} \perp J$ or $\boldsymbol{B} \parallel J$), respectively. The cathode was a sheet of copper (effective size is 15 mm x 15 mm x 0.2 mm) and the anode was a sheet of pure graphite (effective size is 15 mm x 15 mm x 2 mm). It must be pointed out that the cathode surface is settled in the centre position of imposed field whatever any situation.

An electrolyte composition was 0.60 mol l^{-1} $SmCl_3$•$6H_2O$, 0.10 mol• l^{-1} $FeCl_2$•4 H_2O, 0.40 mol• l^{-1} C_2HNO_2, 0.50 mol• l^{-1} H_3BO_3 and 0.06 mol• l^{-1} H_3NO_3S. The pH =3 of the electrolyte was adjusted by $C_6H_8O_7$ and NaOH. It was deaerated by bubbling argon gas for more than an hour. The solution temperature was maintained at 298 K. The electrodeposition was conducted galvanostatically with 270 mA•cm^{-2}. The deposited time is 10 min, and the typical pictures of deposited behaviors are captured after 30 seconds since deposition, that is the stable state of electrodeposition process.

Micrographs of scanning electron microscopy (SEM) were recorded in order to observe the morphology of the surface by Hitachi S-3400N electron microscopy. The structure of as-deposited Sm-Fe films was determined from grazing incidence X-ray diffraction (GIXRD) patterns recorded by a Rigaku Ulitima IV diffractometer using 1° incidence angle. Magnetic property was determines by Vibrating sample magnetometry (VSM, Lakeshore7407) tests.

3. RESULTS AND DISCUSSION

3.1 Observation of bubbles formation and migration

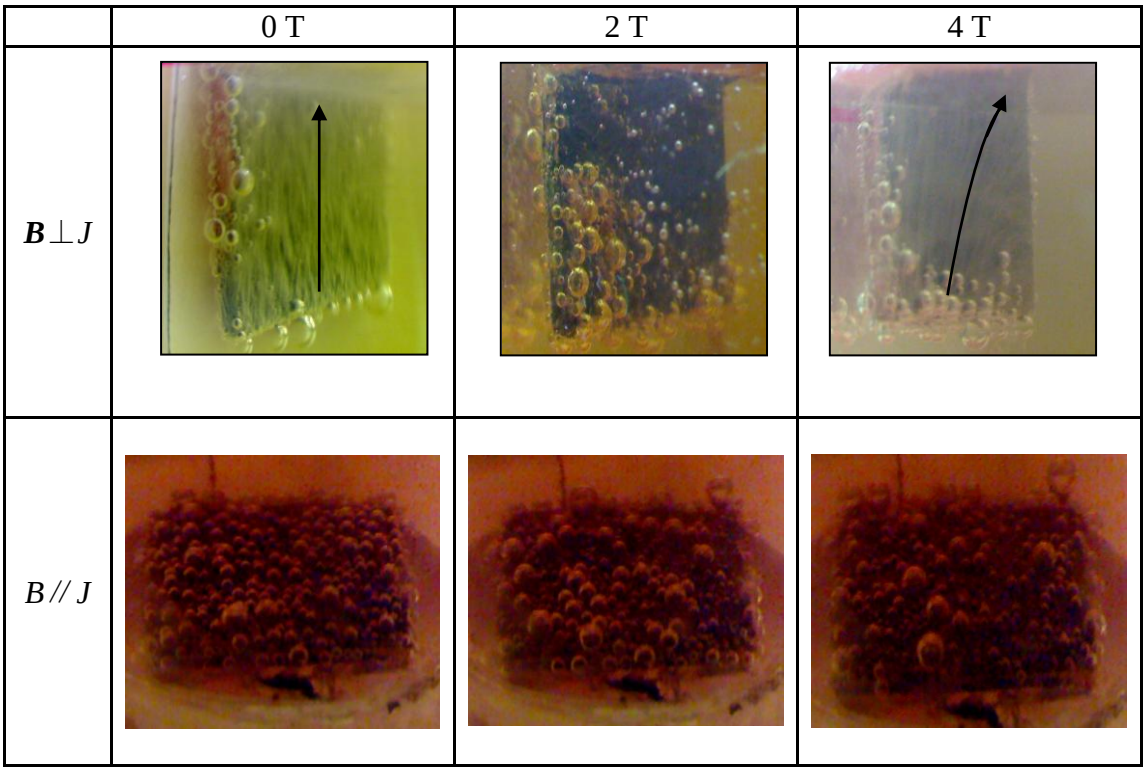

Figure 2. The bubbles occurred during hydrogen evolution of cathode with a magnetic field of ***B*** $\perp$ *J* and (b) ***B*** // *J*.

The typical photos of hydrogen bubbles under stable state are shown in Fig.2. When ***B*** $\perp$ *J*, Vast swarms of tiny and dense H_2 bubbles occurred close to the deposited surface and then rose quickly under ***B***=0 T condition. With increasing of magnetic density (2 T and 4 T), the bubbles' size

increased and they kept on the cathode surface for more time. Once the larger bubbles broke away from the surface and raised up, the migration velocity is faster than that under ***B***=0 T condition obviously. At the same time, the trajectory of ascending bubbles has shifted that is scribed to the severe turbulence, which is induced by Lorentz force when direction of imposed field is perpendicular to deposited current. All of above phenomena amounts to the hydrogen evolution reaction was aggravated by the MHD effect with a high magnetic field in the perpendicular to the current configuration [18, 19].

As with the increased desorpotion of H_2 bubbles in $\boldsymbol{B} \perp J$ condition, the hydrogen evolution reaction was improved in parallel configuration ($\boldsymbol{B} // J$), but the severe turbulence were not found with increasing of magnetic density (2 T and 4 T). Meanwhile, the time of bubbles stick to the cathode surface is decreased and aggregated to bigger and raised up drastically. It is attributed to micro-MHD effect which creates an azimuthally directed Lorentz force around the bubbles. That is consistent in agreement with observation in Jakub et al. [20].

3.2 Morphology of as-deposited films

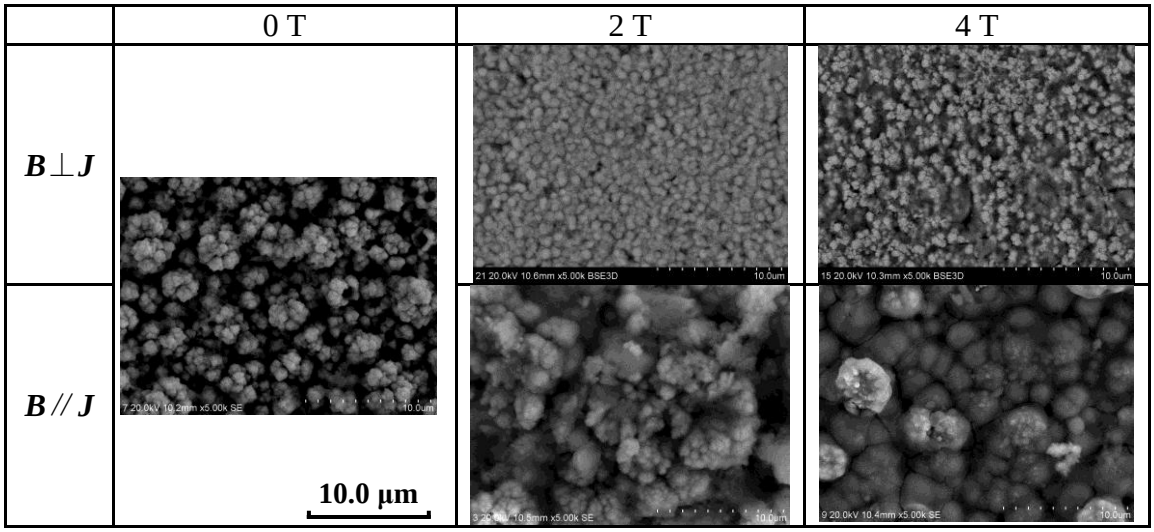

Figure 3. Top morphologies of Sm-Fe electrodeposited film with a magnetic field of $\boldsymbol{B} \perp J$ and (b) $B // J$.

The surface morphology of Sm-Fe thin films obtained in filed perpendicular and parallel to current configuration at different magnetic densities is shown in Fig.3. In $\boldsymbol{B} \perp J$ configuration condition, it is obvious that the flat films obtained at ***B***=2 T and 4 T contrast with the porous film consist of cluster structure obtained in the absence of a high magnetic field (***B***=0 T), in which the Sm-Fe film obtained at ***B***=2 T is very smooth. Whileas in the perpendicular configuration ($\boldsymbol{B} // J$), with increasing the magnetic density the rough surface have shown some improvement even then the grains still is coarse.

The morphology evolution is closely related to the interaction of an imposed high magnetic field [20], particularly the hydrogen evolution reaction on the cathode surface. In $\boldsymbol{B} \perp J$ configuration

condition, the increasing magnetic density induced MHD effect that accelerated the mass transfer process, reduced the diffusion layer beyond the cathode surface and made the film flat. The turbulence resulted from MHD effect stirred the plating solution and resulted in grains refining at ***B***=2 T. However, under ***B***=4 T, more severe turbulence aroused the metal ions concentration uneven in plating solution. The more violent hydrogen reaction changed the distribution of flow field and caused the decreased flatness compared with that of ***B***=2 T. In ***B*** // *J* configuration condition, due to absence of MHD effect, the morphologies of Sm-Fe films obtained under high magnetic field presented similar with that of ***B***=0 T, with the exception of decreased clusters.

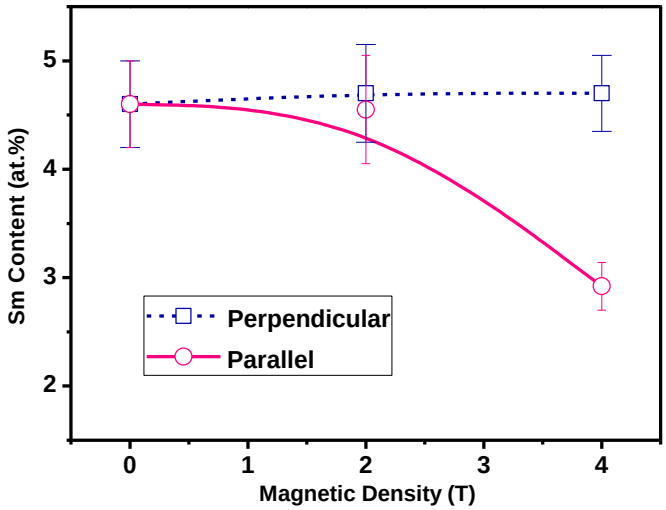

Figure 4. Samarium content of Sm-Fe thin films deposited at different magnetic field density in ***B*** ⊥ *J* and *B* // *J* configuration.

In addition, thus comprehensive effects of MHD and hydrogen reaction play an important role in the Samarium content and thickness of obtained films under imposed high magnetic field. Samarium content of Sm-Fe thin films deposited at different magnetic field density in ***B*** ⊥ *J* and *B* // *J* configuration, as shown in Fig. 4. It is clear that the Samarium content of the deposited Sm-Fe films in ***B*** ⊥ *J* are lower than that in *B* // *J* configuration. Simultaneously, the thickness of deposited films changed significantly. In ***B*** ⊥ *J* configuration condition, the obtained films thickness is ~33 μm and 19 μm at ***B***=2 T and ***B***=4 T respectively, compared with ~24 μm thick under ***B***=0 T. The stirring of solution and crushing of cluster induced by turbulence which deviating from MHD effect is benefit to the growth rate of dense film. Jakub et al. [16] studied the effect of a uniform magnetic field applied parallel to the electrode surface on the pH value close to the electrode surface during the electrodeposition of Co, Fe, CoFe alloys and concluded that the interfacial pH value is increased with the increasing of imposed magnetic field. He suggested that the hydroxyl products are removed faster from the electrode surface in the magnetic field resulting in better quality of the deposited layers. So that the Samarium content and thickness of obtained films were controlled by the imposed high magnetic field density and configuration indirectly. Whileas in ***B*** // *J* configuration condition, the

obtained films thickness is ~13 μm and 11 μm at ***B***=2 T and ***B***=4 T, respectively. It may be attributed the adsorption of hydrogen bubbles on the cathode surface too of time restrain the growth of film.

3.3 Phase composition of as-deposited films

As mentioned above, the quality of deposited Sm-Fe films under different conditions is affected by the imposed high magnetic field. There must be some changing in phase composition of obtained films. The GIXRD patterns of deposited Sm-Fe films were presented in Fig. 5. In absence of magnetic field, the Sm-Fe film is consisted of Fe phase and SmFe phase. But SmFe phase increased significantly with imposed magnetic field, even metallic oxide emerged in some conditions. In $\boldsymbol{B} \perp J$ configuration condition, when the magnetic density is increased to 4 T, the interfacial pH value has far surpasses the isoelectric point of glycine, and resulted in the formation of metallic oxide derived from OH^+ units meatllic ions near the cathode surface. For in $\boldsymbol{B} // J$ configuration condition, the influences of micro-MHD on pH value deserve further research.

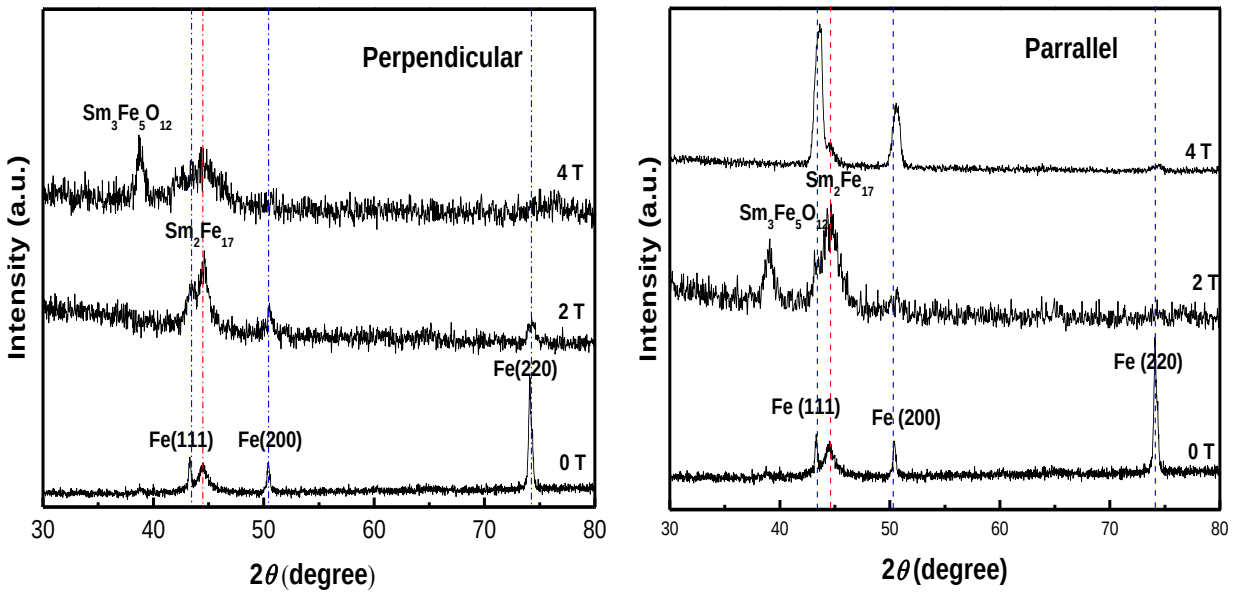

Figure 5. GIXRD patterns for the eletrodeposited Sm-Fe films: (a) $\boldsymbol{B} \perp J$ and (b) $\boldsymbol{B} // J$.

3.4 Magnetic property of as-deposited films

The hysteresis loop of deposited Sm-Fe films with different imposed magnetic field were shown in Fig. 6. The maximum remanent magnetization of Sm-Fe film was obtained under ***B***= 2 T in $\boldsymbol{B} \perp J$ configuration condition. It is consistent with morphology evolution and phase composition analysis mentioned above. In another word, the increasing content of magnetic SmFe phase improved the magnetic property of Sm-Fe film, which is resulted from the imposed high magnetic field.

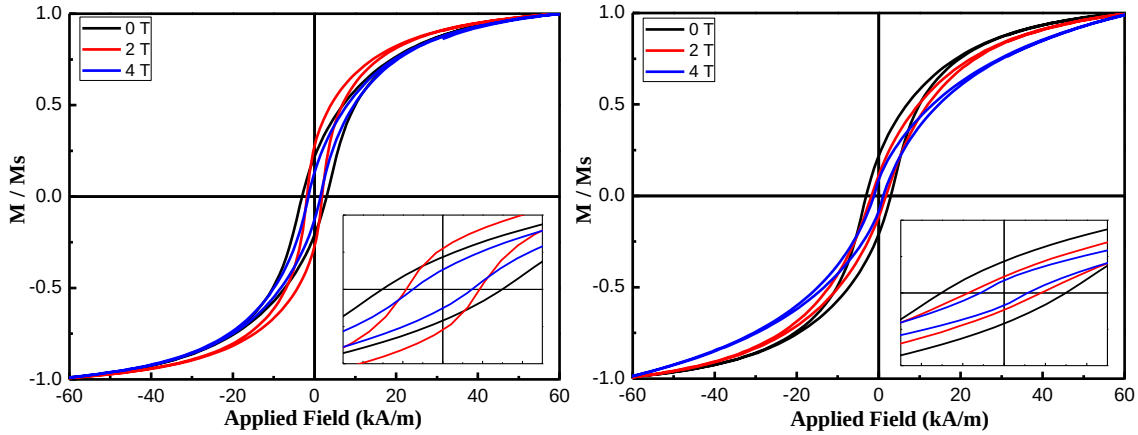

Figure 6. Hysteresis loop of deposited Sm-Fe films with a magnetic field of: (a) $\boldsymbol{B} \perp J$ and (b) $\boldsymbol{B} // J$.

4. CONCLUSIONS

The surface morphology, component, microsructure and magnetic property of as-deposited films were strongly affected by the high static magnetic field, and the magnetic flux density determines the final states of the plating layers. Moreover, magnetohydrodynamic (MHD) plays a key role when an imposed magnetic field is parallel to the electrode surface. A vertical magnetic field to current leads to a dominant effect in electrodepositon, while magnetization of a parallel field is more significantly than micro-MHD of a vertical one.

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