

Preparation and microstructure of CaMoO_4 ceramic films prepared through electrochemical technique

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Abstract Crystallized calcium molybdate films have been prepared on molybdenum foils by electrochemical method under galvanostatic condition. The influences of the processing parameters on the growth of the films were studied experimentally. The current density controls the dissolution of molybdenum which associated with the concentration of MoO_4^{2-} . The more Ca^{2+} exists in the alkaline solution, the easier the CaMoO_4 film is formed. The temperature of the solution affects the reaction rate. These parameters of the electrochemical reaction affect the morphologies of CaMoO_4 films markedly. Intergrowth of the crystalline grains of the film is observed in the rapid crystalline growth mode.

Keywords CaMoO_4 film · Electrochemical techniques · Crystalline growth

1 Introduction

Scheelite-type structure materials possess attractive luminescence and interesting structural properties, and are used in different applications. Scheelite-type molybdate crystals are used as laser host materials and scintillators. Calcium molybdate is a kind of scheelite-type material, and it produces green

luminescence required for the uses of electro-optical devices [1]. Recent researches show that molybdate crystals have good prospect for application in the search for rare events as cryogenic phonon-scintillation detectors [2], and some new applications of calcium molybdate were also investigated. Such as Calcium molybdate has also been paid attention as possible negative electrode materials to replace the graphite presently being used in the Li-ion batteries (LIB) [3].

A lot of methods have been used to synthesize single crystal and powders of CaMoO_4 successfully. However the preparation of the CaMoO_4 films has been less investigated. The main problem is the volatile characteristics of MoO_3 during the high temperature treatments for the film crystallization. The feature may require low temperature processing to synthesize a crystallized luminescent CaMoO_4 film. Anyway, the studies of the preparation of molybdate films are necessary for better performance and more industrial applications.

In recent years, the films of alkaline-earth metals molybdates, such as CaMoO_4 , SrMoO_4 and BaMoO_4 , were synthesized by electrochemical method at room temperature on foils [4–6]. These films were prepared under potentiostatic conditions and their luminescence properties were studied. In present paper we report the growth of CaMoO_4 films by electrochemical technology under galvanostatic conditions, particularly concentrate upon the effect of the electrochemical parameters on the growth of CaMoO_4 films.

2 Experimental

A molybdenum foil (purity more than 99.9%) with dimension of $10 \times 10 \times 0.1$ mm was used as anode (working electrode), a foil of platinum with same purity and dimension was used as the cathode (counter electrode). Prior to

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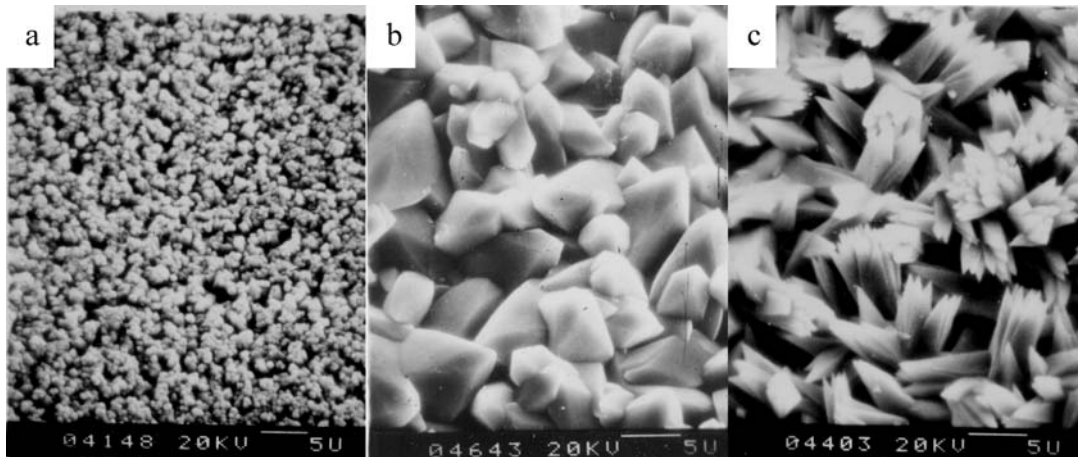


Fig. 1 SEM images of the CaMoO_4 films prepared at the conditions of (a) 0.8 mA/cm^2 , 25°C , 0.011 M ; (b) 0.5 mA/cm^2 , 60°C , 0.011 M ; and (c) 0.3 mA/cm^2 , 70°C , 0.055 M

the electrochemical deposition, the molybdenum substrate and platinum flake were degreased in acetone with ultrasonic cleaner for 10 min respectively, the molybdenum substrate was etched subsequently in mixture acid of hydrochloric acid and nitric acid for 5 min, and then washed in distilled water with ultrasonic cleaner for two times. All electrochemical depositions were performed under galvanostatic conditions by a Voltalab50 analytical potentiostat (Radiometer analytical company, France). A series of different processing parameters, such as the current density (in the range of 0.3 to 3.0 mA/cm^2), the Ca^{2+} concentration of electrolytes (in the range of 0.011 to 0.15 M), and the electrochemical deposition temperature (in the range of 10 to 70°C), were carried out to investigate the growing characteristics of molybdate ceramic films. The resultant phase of the films was analyzed by using X-ray diffraction (XRD) method, and the morphology of the films were observed by using scanning electronic microscopy (SEM).

3 Results and discussion

Figure 1 gives the SEM images of the CaMoO_4 films. It is easy to see that when the films are deposited with various processing parameters the surfaces of the films show different characteristics.

Figure 2 gives the X-ray diffraction (XRD) patterns of CaMoO_4 ceramic film deposited by electrochemical technique. The crystallization of the CaMoO_4 scheelite phases is identified. All peaks are ascribed to a tetragonal structure. A further analysis of the XRD data indicates the lattice parameters of $a = 5.2361 \pm 0.0008 \text{ \AA}$, and $c = 11.4506 \pm 0.0011 \text{ \AA}$. These values are also close to the bulk materials ($a = 5.226 \text{ \AA}$, $c = 11.434 \text{ \AA}$). It is interesting that even though the films' surfaces are different in mor-

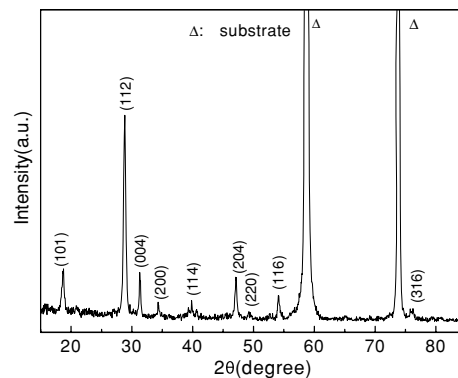


Fig. 2 XRD patterns of CaMoO_4 film prepared in 0.011 M Ca(OH)_2 aqueous solution with 0.5 mA/cm^2 at 25°C

phologies, the XRD patterns of the films show that they all have the same single tetragonal feature with scheelite type.

How the processing parameters affect the morphologies of the films is an important and interesting question. In order to solve the question further researches were carried out. Figure 3 gives the diagram of overpotential ver-

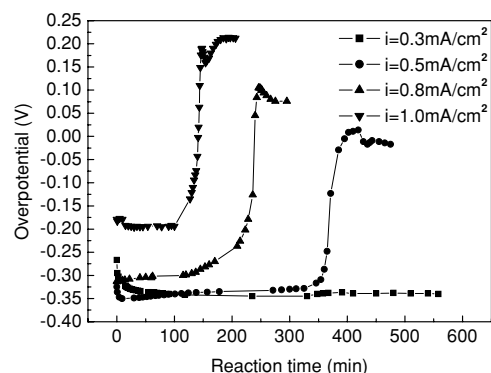


Fig. 3 Diagram of overpotential versus reaction time (Ca^{2+} concentration 0.055 M and the reaction temperature 70°C)

sus reaction time for the growth of calcium molybdate films at different current densities. The overpotential is defined as the potential difference between the work potential and the Ag/AgCl reference potential while the current density is maintained at a pre-set value. All the films were deposited on a metallic molybdenum foil in a calcium hydroxide aqueous with 0.055 M Ca^{2+} concentration at 70°C. Different current densities were used. They were 0.3, 0.5, 0.8 and 1 mA/cm² respectively. From Fig. 3, it is obvious that the current density in electrochemical reaction affects markedly the reaction time at which the overpotential reaches its maximal value. According to our experimental results, the diagrams of overpotential versus reaction time for the growth of calcium molybdate films at different Ca^{2+} concentrations in the solution and at different reaction temperature possess the same trade as demonstrated for the diagram of overpotential versus reaction time at different current densities in Fig. 3.

According to Cho et al. [5], the course of the film formation by using of electrochemical technique can be divided into two processes: a faradic process and a chemical process. It starts from the faradic process. At the early stage of the film deposition, the faradic process is the dominating reaction. The nuclei of CaMoO_4 are formed and deposited on the working electrode with the increase of the MoO_4^{2-} species. The deposition of CaMoO_4 leads to the decrease of the working electrode area. Under the galvanostatic electrochemical mode, the working electrode potential would rise to maintain the pre-set current density. And the overpotential would also increase. Once the CaMoO_4 film is formed and deposited on the whole working electrode, the overpotential would get to its maximal value. So, the time of overpotential maximal value can indicate the reaction rate indirectly. A shorter period of the overpotential maximal time reached means a faster reaction rate.

The effect of the deposition parameters on the reaction rate was investigated experimentally. Figure 4 shows the effect of the current densities on the reaction time at the temperature of 25°C and 65°C respectively. In this paper, the reaction time is defined as the time that overpotential reaches its maximal value. It is easy to see that the reaction time is sharply shortened with the increase of the current density from 0.3 to 1.0 mA/cm² at 65°C and from 0.5 to 2.0 mA/cm² at 25°C respectively. As the driving force of a faradic process [4], the current density controls the dissolution of the molybdenum that is associated with the amount of the MoO_4^{2-} . The larger the current density, the larger the amount of the MoO_4^{2-} produced in alkaline solution, and the shorter reaction time needed to deposit. According to our research, the minimum value of current density is 0.5 mA/cm² at 25°C and 0.3 mA/cm² at 65°C for the formation of CaMoO_4 films in 0.011 M Ca^{2+} solution. From Fig. 4,

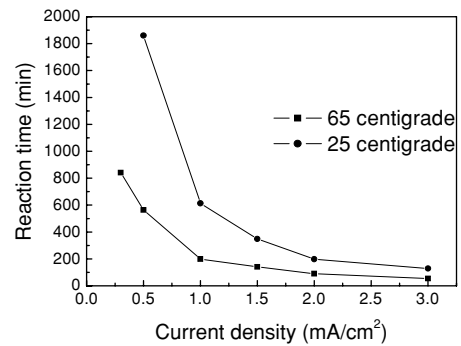


Fig. 4 Diagram of reaction time versus current density (Ca^{2+} concentration of electrolyte is 0.011M)

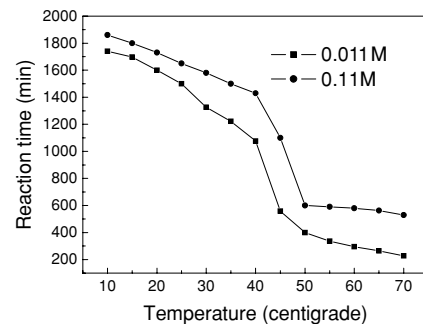


Fig. 5 Diagram of reaction time versus temperature (current density is 0.5 mA/cm²)

one can see that temperature can also affect the reaction time.

Figure 5 shows the effect of reaction temperature on reaction rate. From Fig. 5, it is easy to see that in the temperature range from 10° to 40°C it will take longer time to finish the preparation of CaMoO_4 films. By heating the solution to 40°C and above the reaction time will be shortened obviously. It is suggested that the rates of Ca^{2+} diffusion and CaMoO_4 formation are accelerated in thermal solution. As a result, it is easier for Ca^{2+} to reach to near anode resulting in reacting with MoO_4^{2-} there.

The effect of Ca^{2+} concentration of the solution on reaction rate is shown in Fig. 6. Obviously, high concentration of Ca^{2+} is helpful to shorten the reaction time. It is useful for the nucleation and the growth of CaMoO_4 ceramic grains. Nevertheless, the dissolution of molybdenum will be weakened because of the depressed PH value. The PH value can be depressed by the over-increase of the amount of Ca^{2+} . The acceptable maximal Ca^{2+} concentration is 0.14 M in our experiments.

The deposition parameters influence the morphologies of the films in the same way. Only fewer nuclei of CaMoO_4 crystalline grains can be produced on molybdenum foil in the solution of lower Ca^{2+} concentration at lower temperature

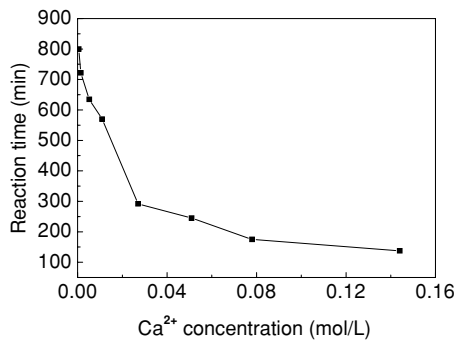


Fig. 6 Diagram of reaction time versus Ca²⁺ ions concentration

even though a larger current density is used. In such case, the rate that Ca²⁺ ions diffuse to the anode is very low. And the majority of the Ca²⁺ ions that diffuse to the anode are consumed in the nucleation of CaMoO₄. So the growth of the nucleus is so difficult that the crystalline grain of the film is small such as the morphology showed in the Fig. 1(a). If the solution is heated, the rate of the Ca²⁺ diffusing to the anode is faster. Some of the nuclei begin to grow preferentially and larger crystalline grains are observed (Fig. 1(b)). If the solution is heated and the Ca²⁺ concentration is increased at the same time, the growth of the crystalline grains increases greatly, and the grains may grow preferentially in the vertical direction of the substrate. In this case the intergrowth, that is the grains with not only twins but also triplets, quadruplets, sextuplets, etc., is observed (Fig. 1(c)). It is suggested that the intergrowth is the crystalline grain growth associated with rapid crystalline growth cases.

4 Conclusion

CaMoO₄ ceramic films were prepared by electrochemical technique in the galvanostatic mode. The minimum value of current density needed in the process is 0.5 mA/cm² at 25°C and 0.3 mA/cm² at 65°C respectively for the formation of CaMoO₄ films in 0.011 M Ca²⁺ solution. Higher temperature of the solution increases the diffusion of the Ca²⁺ and the nucleation of CaMoO₄ in the solution so that the electrochemical reaction is accelerated. Higher concentration of Ca²⁺ is helpful to the formation of CaMoO₄ and the growth of CaMoO₄ ceramic films. The acceptable maximal Ca²⁺ concentration is 0.14 M in our experiments. The morphologies of the films are affected by the reaction rate. The reaction rate is related to the values of the processing parameters. The rapid crystal growth may be responsible for the intergrowth.

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