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Preparation of high entropy alloy thin film fenicobimn by electroplating deposition method

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ABSTRACT

High entropy alloy has excellent performance, such as high mechanical property, thermal stability and corrosion resistance, etc., as compared to the traditional alloys, which presents a high research value and great potential application in industry. It might be an alternative material that could be used in ultra high temperature and corrosion resistant equipments in future. This paper reports the preparation of FeNiCoBiMn high entropy alloy film by electroplating deposition method, and the test results of microscopic observation, energy dispersive spectrometer and X-ray diffraction analysis. Research results indicates that the film is amorphous, the molar content of each element in the high entropy alloy film is greater than 5%, the surface of the film is granular structure with grain size of about 1μm. It provides a new way for exploring preparation of high entropy alloy.

KEYWORDS

High entropy alloys;
Electroplating deposition;
Structure characterization;
Spectrum analysis;
Amorphous;
Film.

INTRODUCTION

With the development of energy resource industry, chemical engineering, mechanical engineering, aerospace, aviation, electronics and communication technology, the requirement for material with excellent properties becomes challengeable, traditional material couldn't meet the demands solely. Synthetic and novel materials appear as a new way to satisfy the new requirements.

Jien - Wei Yeh, et al proposed a new concept of "high entropy alloy" in 1990s[1], which is a novel breakthrough to overcome the disadvantage of the traditional material, thereafter more and more attention has been attracted to the high entropy alloy preparation and characterization.

High entropy alloy has the excellent mechanical property, thermal stability and corrosion resistance due to its characteristics of multi-principal elements instead of multi minor elements, which makes the atom easy to form solid solution phase and nano - structure, or even amorphous structure, while difficult to move, and thus results in a high disorder structure or high entropy, and therefore high mechanical property, thermal stability and corrosion resistance.Up to now, the preparation of high entropy alloy is still a basic problem for the study of this new type of alloy. Recently, the preparation of high entropy alloy has attracted more and more attention. In

Jien-Wei Yeh group, the AlCoCuFeNi high entropy alloy is prepared and studied[1]. The analysis of microstructure and properties showed that: (1) the hardness and percentage of body centered cubic volume increase with the increase of the content of Al atom, while, its frictional coefficient decreases due to the change of the wear mechanism from stratification to oxidative one; (2) the addition of Fe into AlCoCrCuNi high entropy alloy doesn't change the solid solution phase and its microscopic structure obviously, which makes the hardness of AlCoCrCuNi close to that of AlCoCrCuNiFe high entropy alloy; (3) the addition of Ag into AlCoCrCuNi high entropy alloy makes the micro-structure of the ingot of alloy laminar ones, one layer is composed of hypoeutectic composition (Ag-Cu), the other layer is mainly composed of other major elements; While, the addition of Au into AlCoCrCuNi high entropy alloy could make a good alloy, since the above five elements could bind with Au very well, so Au can be considered as a good binding intermediary. It indicates that the maximum mixing entropy between the main atom pair should not exceed 10kJ/mol so that an effective hybrid could be achieved, which is considered as the rule in the design of high entropy alloy[1].

Yu-Jui Hsu studied the corrosion behavior of FeCoNiCrCu high entropy alloy at in 3.5% concentration salt solution[2]. In 3.5% concentration salt solution, surface analysis showed that electrochemical corrosion occurs in the copper rich interdendritic and dendrite position in the alloy after 30 days immersion. While, K.G. Pradeepÿet al[3], I.Kunce, et al[4], V.Dolique, et al[5], K.B.Kim[6], and P.J.Warren, B.Cantor[7], et al, have studied other properties of high entropy alloys as well.

So far, most of the preparation of high entropy alloy, such as vacuum evaporation, arc melting and casting under vacuum, electron beam evaporation and ion sputtering, laser cladding, etc., is physical one[8]. Other approach is quite rare. Recently, Yao Chenzhong proposed an electrochemical deposition method to prepare high entropy alloys containing rare earth elements[9], which is a new approach.

In this paper, we try to employ the basic electroplating method to prepare high - entropy alloy FeNiCrCoBiMn film. The microscopic analysis of the product is conducted as well.

EXPERIMENTAL

The chemical agents used in the experiment for the preparation of high entropy alloy with electroplating method are shown in TABLE 1.

The detail of the experimental procedure is as follows.

1) Treatment of Cu electrode

A 30 mm ×50 mm ×1 mm copper slice is polished with sand papers from 200 to 1500, and degreasing is conducted in a mixture solution of NaOH 20g/L, $NaCO_3$ 30g/L, and $NaPO_4$ 40g/L at 60°C.

After that, the copper slice is washed with distilled water, and immersed in a solution of 5% *HCl* concentration for 10min, then drying. A copper wire is soldered at one end of the slice.

2) Treatment of metallic salt

The metallic salts of $Bi(NO_3)_3$, $CoCl_3$, $MnCl_2$, $FeCl_2$, $NiCl_2$, and $LiClO_4$, are dried at 80°C, 120°C, 140°C, 198°C, 150 °C, 130°C for 12h, respectively, to remove the crystallized water in the corresponding salt.

3) Preparation of electroplating solution

A mixture solvent of CH_3CN and C_3H_7NO with the ratio of 8:2 is prepared and stirred in the electrolytic bath first. The dehydrated metallic salts of $Bi(NO_3)_3$, $CoCl_3$, $MnCl_2$, $FeCl_2$, $NiCl_2$, and $LiClO_4$, are added into the mixture solvent in accordance with 0.002 mol/L, 0.01 mol/L, 0.01 mol/L, 0.01 mol/L, 0.01 mol/L and 0.1 mol/L, respectively.

4) Electroplating process

The copper electrode and graphite electrode are placed in the electrolytic bath, both the electrodes are connected to DC power supply (GWL-305-2) of the positive and negative poles, respectively. The deposition potential is controlled to be -2.5V. After 12h, the sample is removed from the electrolytic bath. The microstructure and chemical composition of the sample is analyzed by scanning electron microscopy, energy spectroscopy (SEM) and X-ray diffraction (XRD) instrumentations, respectively.

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EXPERIMENTAL RESULTS AND ANALYSIS

SEM analysis

The sample of the high entropy alloy film FeNiCoBiMn prepared by electroplating deposition method is analyzed by using a Hitachi S-2700 scanning electron microscope, the microscopic surface morphology shown in Figure1.

From Figure1, it can be seen that the alloy film is formed by the accumulation of different grains, the smaller ones exhibit spherical grain, the larger ones exhibit flat shape. In the surface of the alloy film, there are some larger irregular grains, which may be the result of surface oxidation. From SEM image of 5000 times magnification, it is seen that the film is stacked by spherical grains with different sizes, and these grains are around 1μm.

Spectrum analysis

Energy dispersive spectrometer (EDS) analysis result is shown in Figure 2, the corresponding element content is shown in TABLE 2.

In the right part of Figure2, the EDS is shown which corresponds to the microscopic region in the left of Figure2. It can be seen from TABLE 2 that the molar content of each element is greater than 5%, it is basically qualified experimental sample.

X-ray diffraction analysis

The X-ray diffraction (XRD) of this film is also conducted, the result is shown in Figure3.

Figure3 indicates that the high entropy alloy film FeNiCoBiMn as received is in amorphous state.

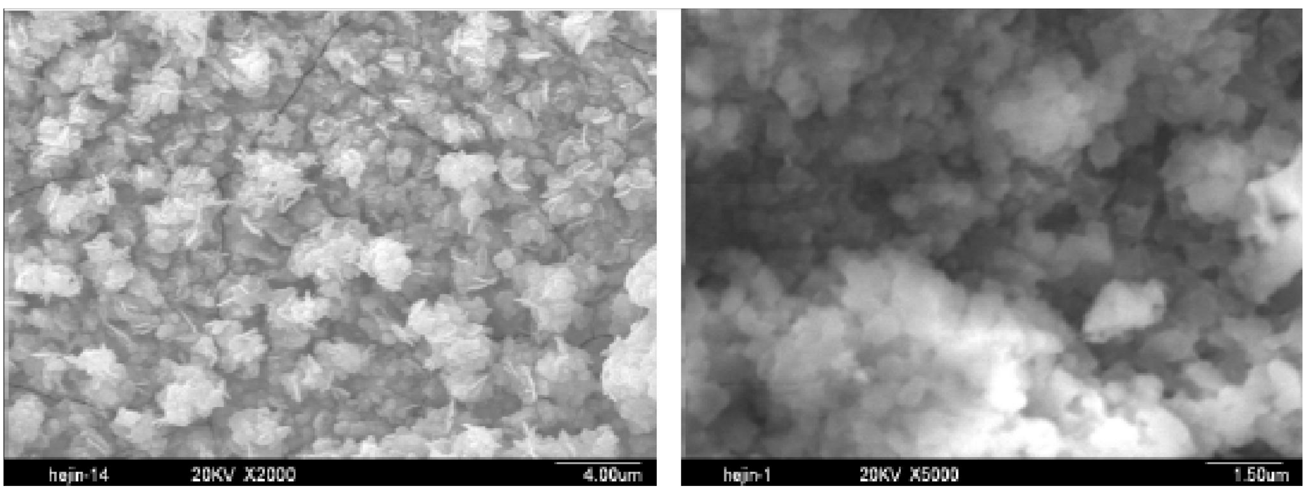

Figure 1 : SEM image of high entropy alloy film FeNiCoBiMn; (A) a magnification of 2000 times; (b) a magnification of 5000 times

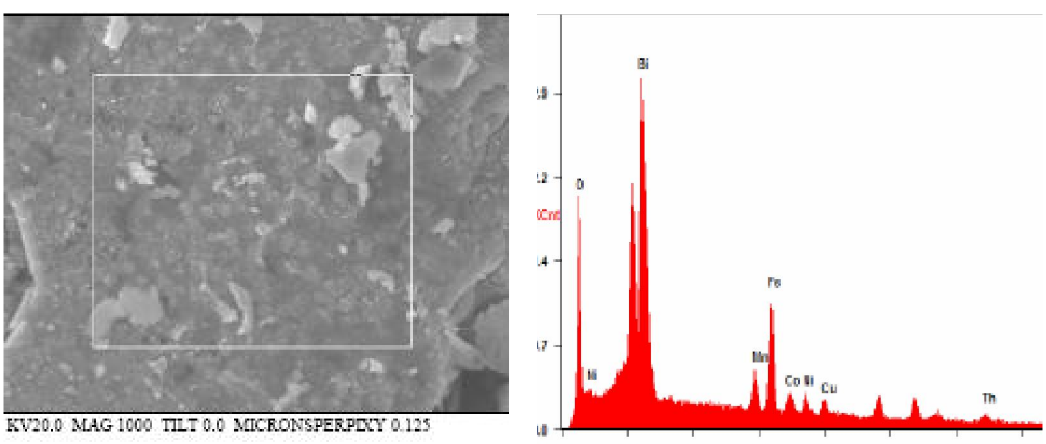

Figure 2 : Spectroscopy of high entropy alloy film FeNiCoBiMn; (a) analysis area; (b) spectrum of the sample

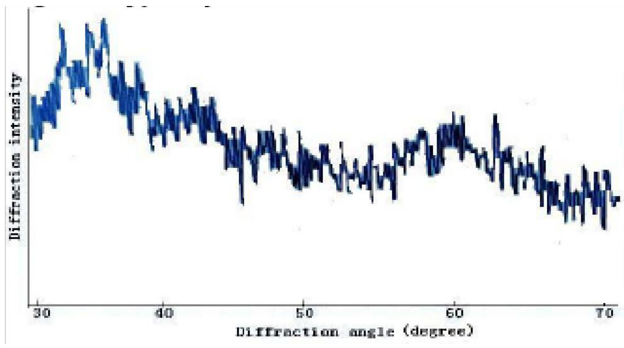

Figure 3 : XRD feature of the high entropy alloy film FeNiCoBiMn

CONCLUSION

In this paper, the electroplating deposition method is employed to prepare high entropy alloy thin film FeNiCoBiMn. The results indicate that the content of each element in the prepared high entropy alloy thin film is greater than 5%, the film is with a granular structure, and the crystal grains are about 1mm. The electroplating deposition can be a quick and easy method to prepare high entropy alloy thin film, which opens a new way to synthesize high-entropy alloy.

TABLE 1 Chemical reagents used in this experiment

Agent	Specification	Manufacturers
$NiCl_2$	AR	Tianjin Fucheng Chemical Reagent
$FeCl_2$	AR	Tianjin Fucheng Chemical Reagent
$MnCl_2$	AR	Tianjin Chemical Reagent Factory
$Bi(NO_3)_3$	AR	Tianjin Fucheng Chemical Reagent
$CoCl_3$	AR	Xi'an Chemical Reagent
$LiClO_4$	AR	Tianjin Guangfu Fine Chemical Research Institute
NaOH	AR	Tianjin Guangfu Fine Chemical Research Institute
Na_3PO4	AR	Tianjin Chemical Reagent first factory PPP
Na_2CO_3	AR	Xi'an Chemical Reagent
CH_3CN	AR	Tianjin Kermel Chemical Reagent Co., Ltd.
C_3H_7NO	AR	Tianjin Kermel Chemical Reagent Co., Ltd.
HCl	AR	Xi'an Chemical Reagent
C electrode		Wuhan Instrument Co., Ltd.
Cu electrode	99.99%	

TABLE 2 : Components of high entropy alloy film FeNiCoBiMn in the selected area

Element	Content (mass percentage)	Content (atom percentage)	Element	Content (mass percentage)	Content (atom percentage)
Ni	5.84	9.10	Co	4.31	7.29
Bi	58.41	27.67	Mn	7.95	14.32
Fe	23.49	41.62			

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