PREPARATION OF Al-Sc ALLOY IN CHLORIDE SYSTEM WITH MOLTEN SALT ELECTROLYSIS[①]

Tian Yanwen, Sun Benliang and Zhai Yuchun
School of Materials & Metallurgy, Northeastern University, Shenyang 110006, P. R. China

ABSTRACT NaCl-KCl(equimolar)-$ScCl_3$ system was chosen as the electrolyte, 3-factor quadratic common rotation combination orthogonal design was employed to investigate the effects of temperature, t, current density, J, and the content of $ScCl_3$ in the molten salt, $w(ScCl_3)$, on the content of Sc in the Al-Sc alloys, $w(Sc)$, and the current efficiency, η, in the preparation of Al-Sc alloy with molten salt electrolysis. The regression functions of the relationships of $w(Sc)$ and η with t, J and $w(ScCl_3)$ were set up. Under the conditions chosen in the experiments, $w(Sc)$ and η can reach about 8% and 85% respectively.

Key words Al-Sc Alloy NaCl-KCl(equimolar)-$ScCl_3$ system molten salt electrolysis

1 INTRODUCTION

Scandium possesses excellent physicochemical properties. When a little of Sc is added into Al alloy, the strength and hardness of Al alloy can be increased remarkably, the synthetic mechanical properties can be improved largely[1-4]. Especially, Al-Sc alloy has excellent superplastical property, the elongation of Al alloy with about 0.5% Sc can reach up to 1100% by means of superplastic forming[5]. In addition, because there is only a little difference in the density of Al and Sc, Al-Sc alloy with high special strength (the ratio of strength to mass) can be prepared. This kind of Al-Sc alloy has a good prospect to become new generation structural materials used in aerospace industry. Therefore, investigations on preparation and development of Al-Sc alloy are being paid more and more attention and have become a new focus of research in the world[6-10].

Up to date, all Al-Sc alloys were prepared by adding the required amount of Sc into Al liquid. This process has many disadvantages. It is not easy to prepare homogeneous Al-Sc alloys in both the composition and the structure because of the remarkable difference of the melting points of Al(660 ℃) and Sc(1439 ℃). Furthermore, Sc is fired out seriously in this process. As we know, metallic Sc is very expensive, obviously this process is not reasonable in economic. Contrastly, the process of preparing Al-Sc alloys with molten salt electrolysis is possible, it is not only easy in operations but also reasonable in economic. In the present paper, NaCl-KCl(equimolar)-$ScCl_3$ system was selected as the electrolytes, the 3-factor quadratic common rotation combination orthogonal design was employed to investigate the effects of temperature (t), current density (J) and $ScCl_3$ content in the electrolytes $w(ScCl_3)$ on the contents of Sc in the Al-Sc alloys ($w(Sc)$) and the current efficiency (η) in preparing Al-Sc alloys with molten salt electrolysis.

2 EXPERIMENTAL

2.1 Materials

NaCl, KCl were analytically pure reagents, before use all of them were heated to 400 ℃ for 2 h respectively, then exactly measured according to the stoichemistry and mixed with the ap-

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propriate amount of analytically pure ammonium chloride and fully ground to powder in a mortar, and then heated to 400 ℃ for 2 h in order to remove a little of water existed in the chemicals.

$ScCl_3$ was prepared by reacting 99.5% pure Sc_2O_3 with heavy hydrochloric acid. The process of the preparation was as follows: firstly solved Sc_2O_3 with hydrochloric acid and filtered the solution to remove a little of insoluble impurities, then added an appreciate amount of ammonium chloride and heated to evaporate to dry, finally heated to 300 ℃ for 4 h and $ScCl_3$ was obtained.

2.2 Apparatus

A high purity graphite crucible with the size of 80 mm in height, 50 mm in outer diameter, 40 mm in inner diameter, was used as both a container and a cathode. In it there was an alumina crucible with the size of 50 mm in height, 40 mm in outer diameter and 38 mm in inter diameter in order to insulate the anode and the cathode. In the middle of the bottom of the alumina crucible, there was a hole with the diameter of 10mm as a passway of two electrodes. The molten salt electrolytes were put in the alumina crucible, which has a cathode chamber of the volume of 1 cm^3 in the middle of the bottom of the graphite crucible to contain Al liquid.

3-electrode cell was employed in the experiments: the graphite crucible was used as the working electrode (cathode), a 6 mm diameter spectroscopically pure graphite rod as the auxiliary electrode (counter electrode), and an Ag/AgCl(1%) + NaCl-KCl(equimolar) electrode as the reference electrode. NiCr alloy wire was used as the electrode connection. Model 173 Potentiostat/Galvostat made by Princedon Applied Research Co., U.S.A., was employed as an electrochemical measurement apparatus.

Experimental apparatus consisted of an oven, a temperature controller, a temperature measurement system and a gas purifying system. The oven was an electric resistance oven in which there was a SiC double spiral tube as heating element, a 55 mm inner diameter alumina tube as the oven's tube which was tightened with a high pressure-resistant rubber cushion at the bottom and a rubber stopper at the top. On the stopper there were 3 holes for the electrodes and 1 hole for the gas passway. A water cooling apparatus was put at two sides of the tube. All the experiments were conducted under the condition of Ar gas protection. Ar gas was led into the tube from the bottom after being purified through a Cu deoxidization oven at 600 ℃. The temperature was controlled by DWK702 precise temperature controller whose precision was 0.5 ℃. The temperature of the working zone was monitored by PtRh-Pt thermocouple connected to UJ31 electrometer.

2.3 Experimental method

Before experiments, 2.12 g Al (99.99%) was put in the cathode chamber at the bottom of the graphite crucible, and the alumina crucible was put in the graphite crucible and 40 g molten salt electrolyte was charged into the alumina crucible. Then the graphite crucible was put into the constant temperature zone of the oven, and heated to 120 ℃ for 1 h, 400 ℃ for 3 h under the condition of vacuum, and finally heated to the set temperature for the experiment under the protection of Ar gas. Al-Sc alloy ingot was taken out, Sc content in the Al-Sc alloy was analyzed. The current efficiency was calculated according to the following Eqn.:

$$\eta = W/(c \cdot I \cdot t) \times 100\% \quad (1)$$

where W is the content of Sc in the sample (g), c is the electrochemical equivalent (0.5591 g/Ah), I is the current of electrolysis (A) and t is the duration of electrolysis (s).

3-factor quadratic common rotation combination orthogonal design was employed to design the experiments. This kind of experimental design possesses the following advantages: the sampling is even, the results are uniform and comparable, and the mathematics model with high precision can be obtained by fewer experiments.

NaCl-KCl(equimolar) system with the different amount of $ScCl_3$ was chosen as the electrolytes. Temperature (Z_1), current density (Z_2), and the content of $ScCl_3$ in the molten salt electrolytes(Z_3) were chosen as 3 variable factors. The values of the factors were coded according to the coding formula[11]. Table 1 is the coding of the experimental design. The effects of temperature (Z_1), current density (Z_2), and the content of $ScCl_3$ in the molten salt electrolytes(Z_3) on the content of Sc in the alloys, w(Sc), and the current efficiency, η, were investigated. The results of the experiments are shown in Table 2. Through the calculation for the results of the experiments according to the formula[11], the quadratic regression functions of the relationships of w(Sc) and η with every factor, t, J, and $w(ScCl_3)$, can be obtained. In order to affirm the precision of the regression functions, the tests of significance to the regression functions were done according to the theory of statistics. The optimal conditions of the electrolysis can be set up according to the results of the tests of significance.

Table 1 3-factor quadratic regression test coding

X_j	Factors		
	Z_1 t/ ℃	Z_2 J/(A·cm^{-2})	Z_3 $w(ScCl_3)$/%
+ γ	900	1.000	40
+ 1	870	0.920	36
0	825	0.800	30
− 1	780	0.680	24
− γ	750	0.600	20
Z_{0j}	825	0.800	30
Δ_j	45	0.120	6

3 RESULTS AND DISCUSSION

Through mathematical treatment to the results in Table 2 according to Eqn. (1)[11], the regression functions of the relationship of w(Sc) with X_1, X_2, and X_3 is obtained as follows:

$$w(\mathrm{Sc}) = 7.8399 - 0.40606X_1 + 0.51779X_2 - 0.1088X_3 - 0.0275X_1X_2 - 0.0425X_1X_3 +$$

Table 2 Design and results of 3-factor quadratic common rotation combination orthogonal experiment

No.	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	w(Sc)/%	η/%
1	1	1	1	1	1	1	1	1	1	1	7.45	72.5
2	1	1	1	− 1	1	− 1	− 1	1	1	1	7.53	80.2
3	1	1	− 1	1	− 1	1	− 1	1	1	1	6.21	70.1
4	1	1	− 1	− 1	− 1	− 1	1	1	1	1	6.90	73.2
5	1	− 1	1	1	− 1	− 1	1	1	1	1	8.09	80.3
6	1	− 1	1	− 1	− 1	1	− 1	1	1	1	8.36	85.6
7	1	− 1	− 1	1	1	− 1	− 1	1	1	1	7.10	78.7
8	1	− 1	− 1	− 1	1	1	1	1	1	1	7.26	80.9
9	1	− 1.682	0	0	0	0	0	2.828	0	0	7.80	85.7
10	1	1.682	0	0	0	0	0	2.828	0	0	6.12	78.5
11	1	0	− 1.682	0	0	0	0	0	2.828	0	6.35	75.7
12	1	0	1.682	0	0	0	0	0	2.828	0	8.20	78.2
13	1	0	0	− 1.682	0	0	0	0	0	2.828	7.82	85.3
14	1	0	0	1.682	0	0	0	0	0	2.828	7.65	80.2
15	1	0	0	0	0	0	0	0	0	0	7.90	85.9
16	1	0	0	0	0	0	0	0	0	0	7.92	86.2
17	1	0	0	0	0	0	0	0	0	0	7.80	86.5
18	1	0	0	0	0	0	0	0	0	0	7.83	86.7
19	1	0	0	0	0	0	0	0	0	0	7.76	85.8
20	1	0	0	0	0	0	0	0	0	0	7.85	86.6

$$0.0625X_2X_3 - 0.29626X_1^2 - 0.18487X_2^2 - 0.02219X_3^2 \quad (2)$$

It is known from the test of significance that the regression function is highly remarkable at the level of $\alpha = 0.01$, that is, the reliability of the regression function is 99%. It is clearly seen from the tests of significance to the regression coefficients that all the coefficients are remarkable at various levels except b_{12}, b_{33}. So, the regression function can be rewritten as follows:

$$w(\mathrm{Sc}) = 7.84 - 0.406X_1 + 0.518X_2 - 0.109X_3 - 0.0425X_1X_3 + 0.0625X_2X_3 - 0.296X_1^2 - 0.185X_2^2 \quad (3)$$

Similarly, the regression function of the relationship of η_I with X_1, X_2, and X_3 is obtained as

$$\eta_I = 86.3535 - 3.0467X_1 + 1.4574X_2 - 1.968X_3 + 0.3875X_1X_2 - 0.4125X_1X_3 - 0.9625X_2X_3 - 2.008X_1^2 - 3.8294X_2^2 - 1.7783X_3^2 \quad (4)$$

And finally after the tests of significance to the regression coefficients, Eqn. (4) can be rewritten as

$$\eta_I = 86.3535 - 3.0467X_1 + 1.4574X_2 - 1.968X_3 - 2.008X_1^2 - 3.8294X_2^2 - 1.7783X_3^2 \quad (5)$$

3.1 Effects of temperature on contents of Sc in Al-Sc alloys and current efficiency

Taking the place of the standardized factor, X_1, with the real variable, Z_1, in the Eqns. (3) and (5), and let Z_2 and Z_3 equal to zero, the functions of the relationships of $w(\mathrm{Sc})$ and η_I with t can be expressed as follows:

$$w(\mathrm{Sc}) = -84.156 + 0.232t - 0.000146t^2 \quad (6)$$

$$\eta_I = -532.692 + 1.568t - 0.000992t^2 \quad (7)$$

According to Eqns. (6) and (7), the relationships of $w(\mathrm{Sc})$ to t and η_I to t are drawn in Fig. 1 and Fig. 2.

It is clearly seen from Fig. 1 and Fig. 2 that both $w(\mathrm{Sc})$ and η_I reach higher values at ~ 800 ℃, Because as we know, when the electrolysis is carried out at lower temperatures, the viscosity of electrolyte is high, as a result the flow of electrolyte will become bad and the electrolysis can not proceed normally; in addition, the movement of the particles with charges will be affected under the act of the force of electric field, it will result in bad effects to the electrolysis; furthermore, Al-Sc alloys with homogeneous composition will be prepared only when Sc ions deposit on the surface of liquid Al cathode and the deposited Sc diffuse fully into the internal part of liquid Al cathode. So that when the electrolysis proceeds at a lower temperature, the deposited Sc atoms diffuse at a lower speed, it is unfavorable for both the improvement of current efficiency and the preparation of Al-Sc alloys with homogeneous composition. On the contrary, when the electrolysis is carried out at a higher temperature, the diffusion speed of the deposited Sc atoms is fast and the viscosity of electrolyte is small, it is favorable for the improvement of current efficiency; but, the molten salt electrolyte evaporates seriously at high temperatures, it is also unfavorable for the smooth

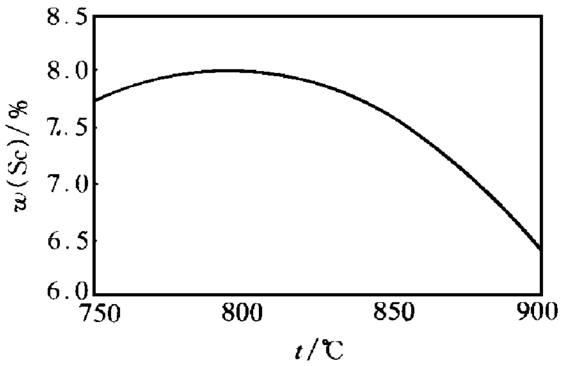

Fig. 1 Relationship between $w(\mathrm{Sc})$ and t

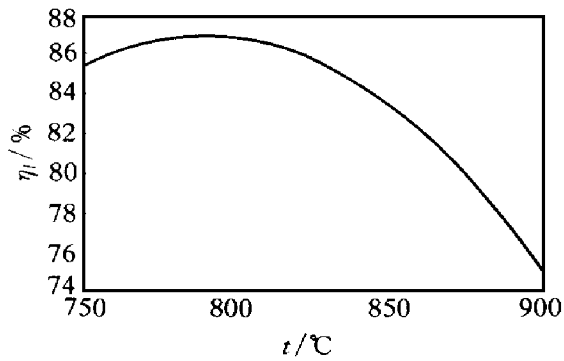

Fig. 2 Relationship between η_I and t

electrolysis and the improvement of current efficiency. Therefore the optimun temperature for preparing Al-Sc alloys is 800 ℃, when the electrolysis proceeds at 800 ℃ the current efficiency will reach 87% and the content of Sc in Al-Sc alloys will be more than 8%.

3.2 Effects of current density on contents of Sc in the alloy and current efficiency

Taking the place of the standardized factor, X_2, with the real variable, Z_2, in the Eqns. (3) and (5), and let Z_1 and Z_3 equal to zero, the functions of the relationships of w(Sc) and η_i with t can be expressed as follows:

$$w(\mathrm{Sc}) = -3.835 + 24.873J - 12.847J^2 \quad (8)$$

$$\eta_i = -93.537 + 437.586J - 265.903J^2 \quad (9)$$

According to Eqns. (8) and (9), the relationships of w(Sc) to J and η_i to J are drawn in Fig. 3 and Fig. 4.

The electrochemical deposition speed of

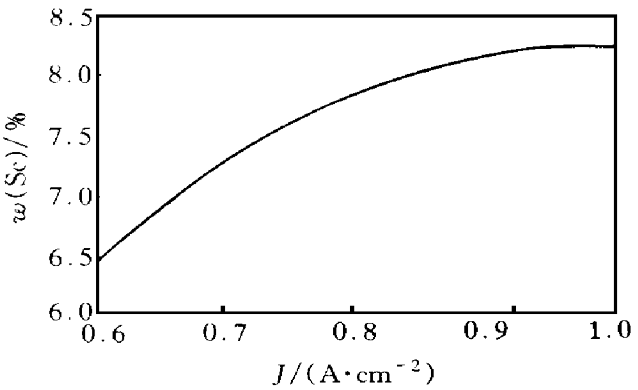

Fig. 3 Relationship between w(Sc) and J

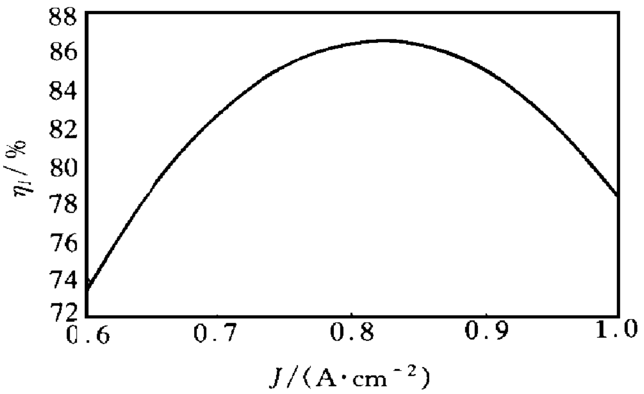

Fig. 4 Relationship between η_i and J

metallic ions and the alloying process of Al-Sc alloy depend on the current density of cathode. Sc atoms deposit on the surface of Al liquid, at the same time, Sc atoms diffuse into the internal part of Al cathode. The match of these two dynamics processes is important for the improvement of current efficiency and the uniformity of alloy. When the electrolysis proceeds at a higher current density, the potential of cathode will be more negative, metallic Sc will deposit at a higher speed. But Sc atoms diffuse slowly in Al liquid, a part of the deposited Sc atoms on the surface of cathode can not diffuse into the internal part of Al liquid, and these Sc atoms will resolve into the molten salt, so it will result in the decrease of current efficiency. In addition, when electrolysis proceeds under the condition of too high current density, the potential of cathode will be so negative that it is possible to reach the deposition potential of basic metals, as a result, the basic metals, such as Na^+, K^+, will deposit on the cathode of liquid Al. It results in the decrease of current efficiency. In contrast, when the electrolysis proceeds under the condition of too low current density, the potential of cathode will be so positive that the deposition speed of Sc ions decrease, the amount of the deposited metallic Sc will decreases. It will be also unfavorable for the increase of current efficiency. It is known from Fig. 3 and Fig. 4 that both the contents of Sc in Al-Sc alloy and the current efficiency reach higher values as the electrolysis proceeds at the current density of about 0.82 A/cm^2, the current efficiency reaches more than 85%, and the content of Sc in Al-Sc alloy reaches more than 7.9%.

3.3 Effects of content of $ScCl_3$ in the molten salts on contents of Sc in the alloy and current efficiency

Taking the place of the standardized factor X_3, with the real variable Z_3 in the Eqns. (3) and (5), and let Z_1 and Z_2 equal to zero, the functions of the relationships of w(Sc) and η_i with t can be expressed as follows:

$$w(\mathrm{Sc}) = 8.385 - 0.0182w(\mathrm{ScCl_3}) \quad (10)$$

$$\eta_i = 51.744 + 2.635w(\mathrm{ScCl_3}) -$$

$$0.0494 w(ScCl_3)^2 \tag{11}$$

According to Eqns. (10) and (11), the relationships of w(Sc) to w($ScCl_3$) and η_i to w($ScCl_3$) are drawn in Fig. 5 and Fig. 6.

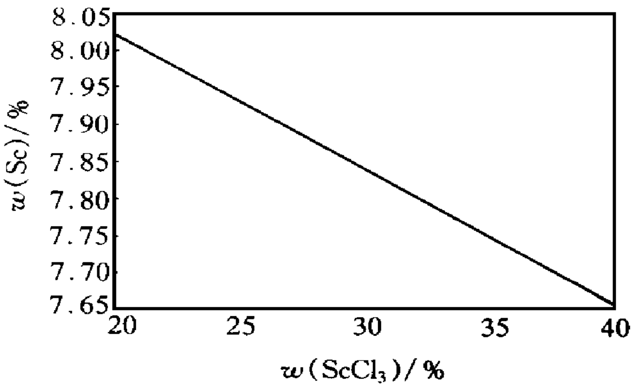

Fig. 5 Relationship between w(Sc) and w($ScCl_3$)

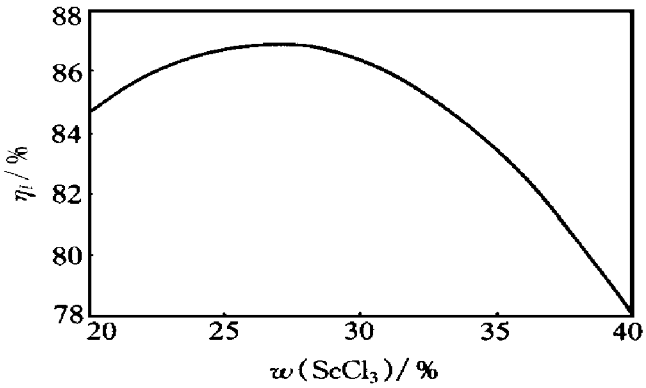

Fig. 6 Relationship between η_i and w($ScCl_3$)

For the compositions of the molten salt electrolytes, the content of $ScCl_3$ is one of the most important factors that affect the current efficiency and the contents of Sc in Al-Sc alloys. When the content of $ScCl_3$ is too low, the basic metallic ions will co-electrodeposit with Sc ions. It will result in the decrease of the current efficiency and the purity of Al-Sc alloys. In contrast, when the contents of $ScCl_3$ is too high, the viscosity of molten salt electrolytes will increase, besides serious evaporation of $ScCl_3$, the electric resistance of the molten salt electrolytes will increase. All of them will decrease the current efficiency. It is known from Fig. 5 that when the content of $ScCl_3$ stands in the range of 20% ~ 40%, the content of Sc will decrease in straight line, that is, the content of Sc in Al-Sc alloys will reach the highest value when the electrolysis proceeds with 20% $ScCl_3$. But, it is seen from Fig. 6 that when the electrolysis proceeds with the content of 27% $ScCl_3$, the current efficiency will reach 87%. In order to obtain the highest current efficiency, the electrolysis should proceed with the content of 27% $ScCl_3$. Under such a condition, the content of Sc in Al-Sc alloy can reach more than 7.9%.

4 CONCLUSIONS

NaCl-KCl(equimolar)-$ScCl_3$ was chosen as the molten salt electrolytes, the electrolysis proceeded under the conditions of the temperature of 750~ 900 ℃, the current density of 0.6~ 1.0 A/cm^2, and the contents of 20% ~ 40% $ScCl_3$, Al-Sc alloys with the contents of 8% Sc was obtained, the current efficiency reached more than 85%.

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