Preparation of master alloy of aluminium with strontium by electrolysis of molten chlorides

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Current efficiency of the electrolysis of molten mixtures of alkali metal chlorides with strontium chloride was investigated. In the case that the melts are of low density in comparison with aluminium-based cathode, the current efficiency depends on content of strontium in the alloy and on cathodic current density. If the cathodic current density is higher than 5 A dm^{-2} current efficiency rapidly falls down.

Изучен выход по току электролиза расплавов хлоридов щелочных металлов, содержащих хлористый стронций. Было найдено, что при использовании расплавов, плотность которых ниже, чем плотность катода образуемого сплавом алюминия, зависит выход электролиза по току от содержания стронция в сплаве и от плотности тока на катоде. Если последняя выше, чем 5 А дм$^{-2}$ выход по току резко падает.

The most important commercial aluminium casting alloys used today contain 5—12 mass % of silicon which improves significantly the casting characteristics of pure aluminium. However, if these alloys are used without "modification" coarse, plate-like primary crystals of silicon are formed through cooling. These particles are brittle and owing to that the alloy loses its strength and ductility. Modification process involves an undercooling of the alloy and selective inhibition of silicon nucleation and growth of crystals [1]. The process results in formation of finely dispersed Al—Si eutectic surrounding primary aluminium. Due to desired structure marked improvement of mechanical properties of the alloy is evident. In the past mainly metallic sodium in amount of 0.01—0.02 mass % had been added to achieve the modification of aluminium—silicon alloys. Disadvantage of this method of modification is that sodium burns violently during the addition and it volatilizes through subsequent holding at molten metal temperature and therefore the modification effect is only short lived. The problem cannot be solved by an excessive addition of sodium because it leads to "overmodification" caused by the formation of coarse Al—Si—Na compounds.

An alternative modification process uses strontium instead of sodium. The modification ability of strontium is similar to that of sodium but its oxidation is

much slower and the alloy modified by strontium keeps approximalety five times longer its desirable properties.

This paper deals with the preparation of master alloy of aluminium with strontium by the electrolysis of molten salts. Also the electrolysis of molten electrolyte is discussed which allows to deposit strontium directly into aluminium—silicon alloy. The modification process is then more intensive if compared with methods based on simple chemical reactions between aluminium—silicon alloy and strontium salts [2, 3].

Experimental

The electrolytic deposition of strontium was carried out in graphite or sinter-corundum crucibles of diameter 30 mm, height 50 mm. The crucibles were placed in a shaft furnace heated by a resistor heating element. An inert atmosphere was assured and temperature which was measured by PtRh10—Pt thermocouple was kept constant with precision 1 K. In the begining phase of each experiment the cathode was formed by pure aluminium or by aluminium—silicon alloy (containing 12 mass % of Si). For anode a graphite rod of diameter 4 mm was used. In the case of sinter-corundum crucibles current supply to the cathode was given by tantalum wire insulated by sinter-corundum capillary. Potentiostat (Ple-60, VPZ SVÚOM, Czechoslovakia) working in a galvanostatic regime as a power supply was used. The analysis of strontium was carried out by the method of atomic absorption spectroscopy (Perkin—Elmer 305 A). The metallographic observations were carried out by the metallographic microscope Epityp 2 (GDR).

Chemicals used were of anal. grade and they were dried at 650°C.

Results and discussion

Having the data on Gibbs energy of formation of NaCl, KCl, and ṠrCl$_2$ [4, 5] it is possible to calculate the following values of standard decomposition potentials of these compounds at 1000 K: E^0(NaCl) = 3.286 V, E^0(KCl) = 3.529 V, E^0(SrCl$_2$) = 3.493 V. So the standard decomposition potential of strontium chloride is about 0.2 V higher than the standard decomposition potential of sodium chloride. Therefore, should strontium be the primary cathodic product of the electrolysis of melt of the system NaCl—KCl—SrCl$_2$, the cathodic process has to include a depolarization effect of about 0.2 V. It was confirmed by experiment that at low content of strontium in cathodic alloy (lower than 3 mass % Sr) and at low current density (less than 5 A dm^{-2}) it is really strontium which is primarily deposited on the cathode. The remarkable depolarization in the process of electrodeposition of strontium into aluminium cathode can be explained by the existence of compound Al$_4$Sr [6]. In the phase diagram of the system Al—Si—Sr [6] three compounds can be seen: Al$_4$Sr, SrSi$_2$, and SrSi. If only the binary system

Al—Sr is considered then the depolarization of 0.2 V corresponds to Gibbs energy of formation of Al_4Sr equal to -38.6 kJ mol^{-1}. (The relation $\Delta G^0 = nFE^0$ was used; n means the charge number of the reaction, which equals 2 for strontium ions and F is the Faraday constant.) Calculation of the phase diagram Al—Sr [7] confirmed that this value of Gibbs energy is consistent with the experimental phase diagram.

All experiments were carried out at temperature of 1000 K. Composition of the melt was determined by two aspects, both phase diagram of the system $NaCl$—KCl—$SrCl_2$ [8] and density of melts of this system [9] were taken into account.

The first series of experiments were done with electrolyte of the binary system KCl—$SrCl_2$ (50 mole % KCl + 50 mole % $SrCl_2$). However, the obtained results were unsatisfactory. The aluminium cathode contained only *ca.* 0.015 mass % of strontium regardless of current passing through the cell. This result can be explained by a small difference in density of metal and the melt (0.09 g cm^{-3}) which resulted in bad contact between graphite cathode and aluminium. Probably happened that simultaneously with strontium also potassium was deposited. Mechanism of electrode processes is apparently similar to that in the case of production of strontium by the electrolysis of the melt KCl—$SrCl_2$ [10].

In further experiments melt having composition 35 mole % $NaCl$ + 35 mole % KCl + 30 mole % $SrCl_2$ was used. Density of the melt at 1000 K is 1.98 g cm^{-3}, which is about 0.3 g cm^{-3} lower value than for aluminium. Results of electrolyses carried out at different current densities and duration of electrolysis are summarized in Table 1. Repetition of experiments at the same conditions allowed to evaluate relative dispersion of current efficiency $\pm 5\%$. From the obtained results it follows that a high current efficiency of the electrolysis can be achieved if both content of strontium in alloy and cathodic current density are low.

Table 1

Dependence of current efficiency (η) on current density (j) and duration of electrolysis (t)
Composition of electrolyte: 35 mole % $NaCl$ + 35 mole % KCl + 30 mole % $SrCl_2$
Temperature 1000 K, aluminium cathode

j/A dm^{-2}	t/min	mass % Sr in Al	η/%
1	30	0.49	90.4
4	30	2.16	102.3
4	60	3.49	84.2
4	120	5.06	61.4
4	240	4.95	30.0
8	30	1.96	30.0
16	30	0.0025	0.02
16	60	0.0025	0.01

If the cathodic current density exceeds 5 A dm^{-2}, current efficiency of electrodeposition of strontium sharply decreases. This phenomenon can be explained by slow transport of strontium from the surface of cathode into the bulk of metal. From the phase diagram of the system Al—Sr can be seen that at 1000 K the solid compound Al$_4$Sr coexists with melt containing 5 mole % of strontium (14.6 mass %). It allows to explain why the increasing content of strontium in alloy and/or the increasing current density influences unfavourably current efficiency of electrodeposition of strontium. If the activity of strontium in surface layer of the cathode increases the depolarization effect is diminished and primary product of cathodic reaction appears to be sodium the solubility of which in aluminium is low.

Recently, papers on the electrode processes in the system Zn (resp. Zn—Sb)—melt NaCl—KCl—SrCl$_2$ [11, 12] have been published. Concerning current efficiency and electrode potentials the authors observed some phenomena which are qualitatively similar to those reported here. The authors explain their observations by the existence of Sr^{2+} and Sr$^+$ ions in the melt. The existence of Sr$^+$ ions in this system seems to be unprobable. We suggest that the data published in [11, 12] can be explained in a similar way as in this paper, namely by the depolarization caused by the formation of intermetallic compounds in the system Zn—Sr [13].

The results obtained with cathode formed by aluminium—silicon alloy were principally the same as those obtained with aluminium cathode. It is obvious that this result can be utilized for the preparation of Al—Si—Sr master alloy or for direct modification of Al—Si alloy if a small desired amout of strontium is electrodeposited. In comparison with simple treatment of Al—Si alloys with strontium salts the electrolytic process is substantially faster [14]. In the former case the concentration of 0.01 mass % Sr was achieved in 4 h but the electrolytic process allows to accomplish modification in several minutes. Besides, the content of strontium can be higher than in the case of currentless process.

References

1. Píšek, F., Jeníček, L., and Ryš, P., *Nauka o materiálu I/3.* (Material Science.) Academia, Prague, 1973.
2. Martin, L. L. and Rodriquez, S. F., *Fonderie 26*, 353 (1977).
3. Leandro, L. M. and Serafin, R. F., *Span. 466422* (Cl.C22C) (1978).
4. *JANAF Thermochemical Tables*, 2nd Edition. U.S. Dept. of Commerce, NSRDS-NBS 37, Washington, 1971.
5. *JANAF Thermochemical Tables, 1975 Supplement, J. Phys. Chem. Ref. Data 4*, No. 1 (1975).
6. Vakhobov, A. V., Dzhuvaev, T. D., and Ganiev, S. N., *Zavod. Lab. 43*, 73 (1977).
7. Fellner, P., unpublished results.
8. Levin, E. M., Robbins, C. R., and Murdie, H. F., *Phase Diagrams for Ceramists, 1969 Supplement*. The American Ceramic Society, Columbus, Ohio, 1969.

9. Fellner, P. and Chrenková-Paučírová, M., *Chem. Zvesti 35,* 321 (1981).
10. Baimakov, Yu. V. and Vetyukov, M. M., *Elektroliz rasplavlennykh solei.* Izd. Metallurgia, Moscow, 1966.
11. Zhuravlev, V. I., Lebedev, V. A., Volkovich, A. V., Nichkov, I. F., and Vink, A. V., *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.* No. 6, 11 (1970).
12. Zhuravlev, V. I., Lebedev, V. A., Volkovich, A. V., and Nichkov, I. F., *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.* No. 6, 16 (1979).
13. Pascal, P. *et al., Nouveau traité de chimie minérale,* T. *XX, Alliages Metalliques,* p. 1727. Masson et Cie, Paris, 1963.
14. Fellner, P. and Lubyová, Ž., *Czech. Appl.* 7341/80.

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