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Electrodeposition of high purity manganese from low temperature (~ - 16° C) chloride electrolyte

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Electrolytic manganese (99·98% purity and sulphur) is commercially produced by using sulphate electrolyte at 35° C with the addition of sulphur compounds at current efficiencies of about 60–65%. In the present investigations, adherent, compact and higher purity manganese was obtained by electrolysis in manganese chloride solutions at lower temperature (~ −16° C) without any additives such as sulphur or selenium compounds. A basic study was made to determine the current efficiency of deposition from low temperature chloride electrolytes. Factors affecting the process were: bath temperature, current density, ammonium salt concentration, pH and time of deposition. It was concluded that the electrodeposition of high purity manganese from low temperature chloride electrolyte was feasible. From a comparison between the $MnCl_2$–$NH_4SO_3NH_2$ and $MnCl_2$–NH_4Cl systems adopted, it was shown that the former had the advantage over the latter in its higher current efficiency (87% against 84%) below −8° C, while the latter was superior to the former with regard to its wider range of optimum current density (1–4 A dm^{-2}). The process may be used with advantage when high purity and ductile manganese free of impurities such as sulphur is required and when cooling of the bath is not an important and economic consideration.

1. Introduction

The electrodeposition of manganese is of scientific interest since the metal is a borderline metal which can be deposited from aqueous electrolytes under extremely critical conditions; the electrowinning of manganese metal is done commercially by the electrolysis of sulphate solutions at rather low current efficiency (60–64%). The main impurities in the commercially available metal (99·98% purity) are sulphur compounds such as SO_2 which are essential additives in the catholyte. On the other hand, the electrolytic production of manganese from chloride solutions, containing large quantities of ammonium salt as buffer, has been investigated for several decades without notable success [1–6]. But the current efficiency and purity so far reported were not much higher than those of the sulphate system. It seems reasonable to assume that the consumption of some part of the current for hydrogen evolution and the dissolution of deposited manganese tends to decrease the current efficiency. It proved to be possible to minimize such losses by the low temperature electrolysis without any additives, and accordingly, higher purity manganese can be electrodeposited. Also, in our laboratory, smooth and bright deposits of silver and zinc had been electrodeposited from aqueous silver nitrate and alkaline zincate solutions respectively at low temperature (about −30° C) [7, 8].

2. Experimental

2.1. *Composition of electrolytic solutions*

The composition of the manganese chloride electrolyte used was
Catholyte: Manganese(II) Chloride ($MnCl_2 \cdot 4H_2O$) 298 g dm^{-3} (82·8 g as Mn); NH_4Cl or $NH_4SO_3NH_2$ 1–4 mol dm^{-3}
Anolyte: Manganese(II) Chloride ($MnCl_2 \cdot 4H_2O$) 298 g dm^{-3} (82·8 g as Mn); NH_4Cl 2 mol dm^{-3}.
which were found preferable after several trials. To

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prepare solutions, all the chemicals used were reagent-grade and were dissolved in deionized water. Saturated KOH solution was used to adjust the pH of the catholyte. On the basis of the preliminary experiments, a comparison was made between the $MnCl_2$–NH_4Cl and $MnCl_2$–$NH_4SO_3NH_2$ systems.

2.2. *Apparatus*

An electronic cryostat functioning at a temperature as low as −30° C was used for the experiments. The laboratory cell for the electrodeposition of manganese is illustrated in Fig. 1; it consists of two compartments separated by a No. 84 filter paper or a polyvinylidene chloride (trade name 'vinyon' of Japan) canvas disk. The volumes of catholyte and anolyte were 300 and 100 ml respectively. Cooling was attained by circulating coolant which was a 50–50 vol % mixture of methanol and water. A rotating cathode was used to facilitate the diffusion of manganese ion and to remove the cathodically evolved gas. The anode was a rod of spectrograde graphite, and as cathode, brass sheets (10 x 10 x 0·2 mm) were used.

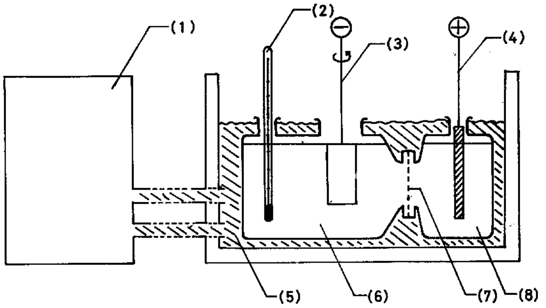

Fig. 1. Schematic diagram of experimental arrangement. 1–Electronic cryostat; 2–thermometer; 3–rotating cathode; 4–anode; 5–coolant; 6–catholyte; 7–diaphragm; 8–anolyte.

3. Results

3.1. *Measurement of specific conductivity and viscosity*

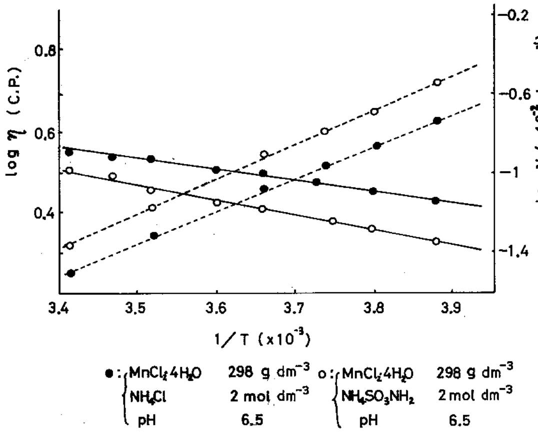

Fig. 2. Arrhenius plots of viscosity and specific conductivity.

As these solutions contained appreciable amounts of manganese chloride and ammonium salts, their freezing points were about −18° C, and the resulting cell voltage at −16° C (cathode current density: 1 A dm^{-2}) was about 3 V. The Arrhenius plots of specific conductivity and viscosity of each solution at various temperatures are shown in Fig. 2. It can be seen that the lowering of temperature from 20 to −16° C enhanced the viscosity by a factor of 2, and lowered the specific conductivity by a half. Thus, it was found that each system obeyed the Stokes' and Walden's laws quite closely over the entire range of temperature of the present study.

3.2. *Effect of bath temperature*

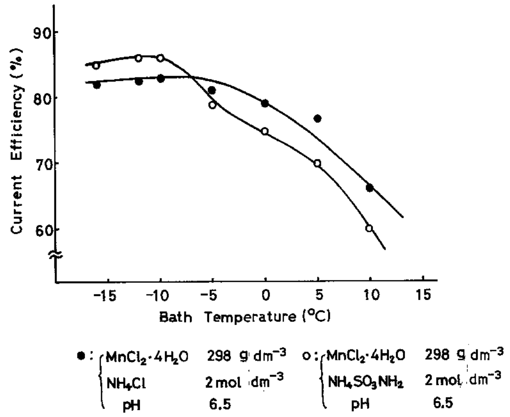

Fig. 3. Effect of bath temperature. Electrolysis time: 2 h.

Fig. 3 shows the effect of bath temperature on current efficiency. The current efficiency increased gradually with the lowering of bath temperature. Both curves reached nearly constant values below −10° C. For $MnCl_2$–$NH_4SO_3NH_2$ and $MnCl_2$–NH_4Cl systems the limiting values were 87 and 84% respectively, which were definitely higher than

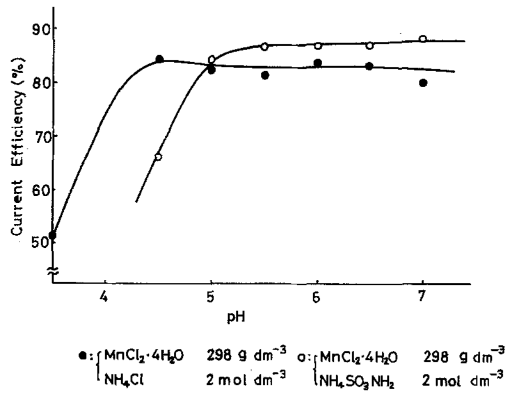

Fig. 4. Effect of pH. Electrolysis time: 2 h; bath temperature -12° C.

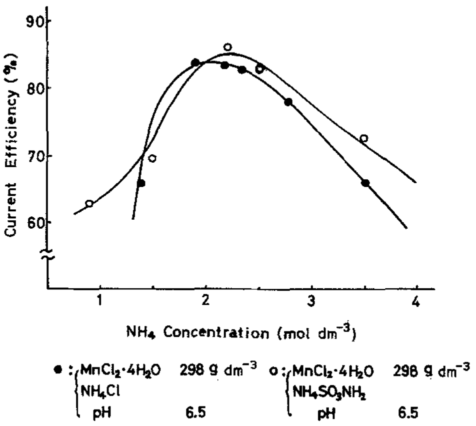

Fig. 5. Effect of ammonium salt concentration. Electrolysis time: 2 h; bath temperature: -12° C.

those attained with the conventional sulphate system (60–65%). Though the $MnCl_2$–NH_4Cl system gave a higher current efficiency than the $MnCl_2$–$NH_4SO_3NH_2$ system above -8° C, the tendency was reversed below this temperature. This phenomenon was closely related to the dissolution (corrosion) of deposited metal, further details of which will be discussed later. Thus, as far as the current efficiency is concerned, it is preferable to keep the bath temperature below -10° C.

3.3. *Effect of pH*

The effect of varying the pH of the catholyte on current efficiency was plotted in Fig. 4. The bath temperature was kept constant at -12° C. Nearly constant current efficiency was obtained by raising the pH in both solutions. It was about 84% in the $MnCl_2$–NH_4Cl system between pH 4, 5 and 7, and about 86% in the $MnCl_2$–$NH_4SO_3NH_2$ system between pH 5 and 7. As manganese hydroxide or oxide was precipitated from the solution, it was difficult to keep the catholyte composition in the pH range 7 or above. It seems reasonable that the low current efficiency below th pH 5 region can be ascribed to an increased corrosion of the deposited metal and to an increased quantity of hydrogen evolution. The appearance of the manganese metal that was deposited over the investigated pH region (3·5–7·5) was bright and finely pyramidal. Thus, it is preferable to keep the pH of the catholyte in the range of 5–6·5.

3.4. *Effect of ammonium salt*

Usually ammonium sulphate is added to the commercial sulphate bath to act as buffer and to prevent the hydrolysis of the electrolyte. The effects of varying the concentrations of the ammonium salts in the catholyte were plotted in Fig. 5. The bath temperature was kept constant at -12° C. Both curves had their maximums around 2 mol dm^{-3}. It seems that significant quantities of ammonium salts act as buffers, and have a strong influence on the current efficiencies and that corrosion of the deposited manganese by the anions (Cl^-, $SO_3NH_2^-$) is significantly dependent on their concentrations. Maximum current efficiencies in the $MnCl_2$–NH_4Cl and $MnCl_2$–$NH_4SO_3NH_2$ systems were 86 and 84% respectively. The optimum ammonium sulphate concentration in the sulphate system is 1·44 mol dm^{-3}, while the optimum in low temperature chloride system was about 2 mol dm^{-3}. The difference in optimum concentration of ammonium salt between the two systems may be attributable to the higher concentration of manganese chloride (5 times higher than in the sulphate system) and to the low reaction temperature.

3.5. *Effect of current density*

Fig. 6 shows the effect of varying current density on current efficiency. High current efficiencies were observed in a wider current density region in

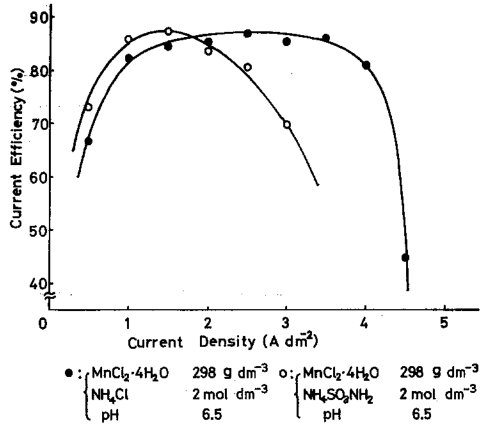

Fig. 6. Effect of current density. Electrolysis time: 2 h; bath temperature: $-12°$ C.

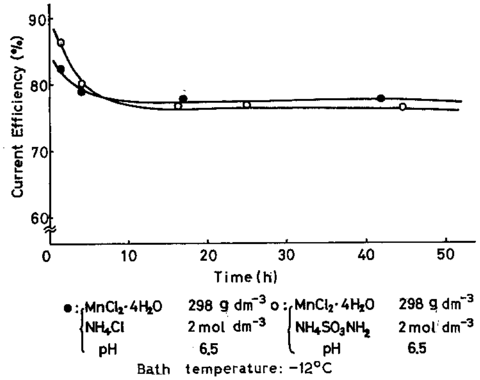

Fig. 7. Effect of exposition time. Bath temperature: $-12°$ C.

the $MnCl_2$–NH_4Cl system (1–4 A dm^{-2}). On the other hand, a peak was obtained in the $MnCl_2$–$NH_4SO_3NH_2$ system at 1·5 A dm^{-2} Since it seemed that the cathode current density below 1 A Dm^{-2} was not sufficient for cathodically preventing the dissolution of deposited manganese in both solutions, the current efficiencies decreased with decreasing current density. At higher current densities (above 4 A dm^{-2} in the $MnCl_2$–NH_4Cl system, above 2 A dm^{-2} in the $MnCl_2$–$NH_4SO_3NH_2$ system), the evolution of hydrogen increased on the cathode, and the efficiencies of manganese deposition fell accordingly. Thus, the optimum current density regions in the $MnCl_2$–NH_4Cl and $MnCl_2$–$NH_4SO_3NH_2$ systems were between 1–4 and 1–2 A dm^2, respectively.

3.6. *Effect of electrolysis time*

Fig. 7 shows the effect of electrolysis time on current efficiency. Though the initial high efficiencies dropped gradually, they reached nearly constant values after 5 h and remained at these values for over 40 h. In the $MnCl_2$–NH_4Cl and $MnCl_2$–$NH_4SO_3NH_2$ solutions they were about 80 and 78%, respectively. Thus these solutions were suitable for prolonged electrodepositions of manganese metal. Since the manganese concentration was rather high in these solutions (82·8 g dm^{-3} as Mn), the influence of concentration change on electrodeposition efficiency appeared to be negligible. As observed microscopically, the growth of pyramidal manganese metal proceeded on the cathode, and the real current density must have changed from its initial value. It is likely that such a current density variation was one of the causes of the difference between the initial and final current efficiencies; that is, dissolution of deposited manganese increased in the low current density region while the proton discharge increased in the high current density region.

3.7. *Determination of the dissolution loss of manganese metal*

Manganese ($Eo(Mn^{++}/Mn) = -1{\cdot}18V$) dissolves spontaneously in these chloride solutions accompanied by hydrogen evolution. High purity manganese metal chip (99·98% purity) which was covered with epoxy resin except for 1 cm^2 of its surface was dipped in the electrolytic solution for 2·5 h. After that, the weight loss of the chip was measured and the dissolution losses at various temperatures were determined. Similar tests were also

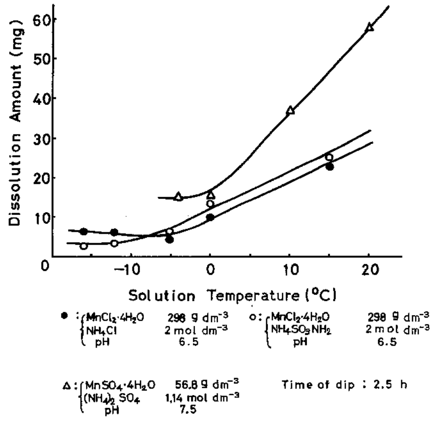

Fig. 8. Dissolution amount of manganese.

done in sulphate solution for reference. These results are illustrated in Fig. 8. Those curves which were obtained in $MnCl_2$–NH_4Cl and $MnCl_2$–$NH_4SO_3NH_2$ solutions intersected each other at −8° C. This relationship was coincident with the one described in the section 3.2. In addition, the dissolution loss in each solution reached a nearly constant value below −10° C and corresponded to the nearly constant efficiency observed in the same temperature range. As the amount of deposited manganese dissolved decreased gradually from normal temperature downwards, the current efficiency appeared to increase. The relation between weight loss and bath temperature in sulphate solutions was similar to those in chloride solutions. However, the amount dissolved in sulphate solutions around the freezing point (−5° C) was twice as much as those in chloride solutions. The commercial sulphate bath for the electrowinning of manganese which contains various additives is usually operated at 35–40° C, and its current efficiency is 60–65%. The dissolution of deposited manganese metal appeared to be one of the causes of the low current efficiency of electrodeposition in commercial sulphate systems at such temperatures. Thus, it is effective to keep the bath temperature of these chloride solutions below −10° C.

3.8. *Analysis of electrodeposited manganese metal*

Elemental analysis of the electrodeposited manganese metal which was obtained under various electrolytic conditions was carried out employing X-ray microanalyser, X-ray fluorescence and atomic absorption analysers. As these analysers detected no other elements than manganese, it was confirmed that the deposited manganese was of much higher purity than the presently available commercial electrolytic manganese, and in addition the metal was very ductile. This fact is attributable to the composition of these chloride solutions in which there were no additives such as sulphur compounds and to the fact that no manganese oxides or hydroxides were co-deposited.

3.9. *Analysis of evolved gas*

The gases evolved at the cathode were collected and analysed employing gas chromatography. Only hydrogen gas was detected under various electrolytic conditions in $MnCl_2$–NH_4Cl and $MnCl_2$–$NH_4SO_3NH_2$ solutions. It was found that the total electric current was nearly equal to the sum of the two different electric quantities used for hydrogen gas evolution, and for the electrodeposition of manganese metal. The proportion of hydrogen gas evolution decreased with lowering of the bath temperature, while the current efficiency of manganese deposition increased. As described previously, manganese metal dissolved when dipped in these chloride solutions with hydrogen evolution by the local cell action. Consequently, the loss of deposited manganese decreased and the hydrogen evolution appeared to decrease, with lowering of temperature. On the other hand, the composition of the gas evolved at the graphite anode was mostly nitrogen and a small amount of chlorine. The reaction mechanism at the anode had been proposed by J. H. Jacobs *et al.* [2] as follows:

$$6Cl^- = 3Cl_2 + 6e \qquad (1)$$

$$2NH_4Cl + 3Cl_2 = N_2 + 8HCl. \qquad (2)$$

3.10. *Photographs of sample surface*

The optical microscope photographs of the surface of electrodeposited manganese are shown in Fig. 9. The distinct and fine pyramids grew gradually on the surface during the electrolysis. Fig. 10 shows the SEM photographs of a typical surface of electrodeposited manganese. It was found that the numerous fine crystals appeared at the early stage, followed by crystal growth into large and well-defined pyramids.

4. Summary and conclusions

The results of experiments on the electrodeposition of manganese from low temperature chloride solutions have been presented and, it is concluded that the continuous electrodeposition of high purity manganese is possible without any additives in the electrolyte. The optimum conditions for manganese electrodeposition, based on the data presented, are shown in Table 1.

In assessing the conventional sulphate process and the present low temperature chloride electrolysis, the following advantages of the latter process are apparent:

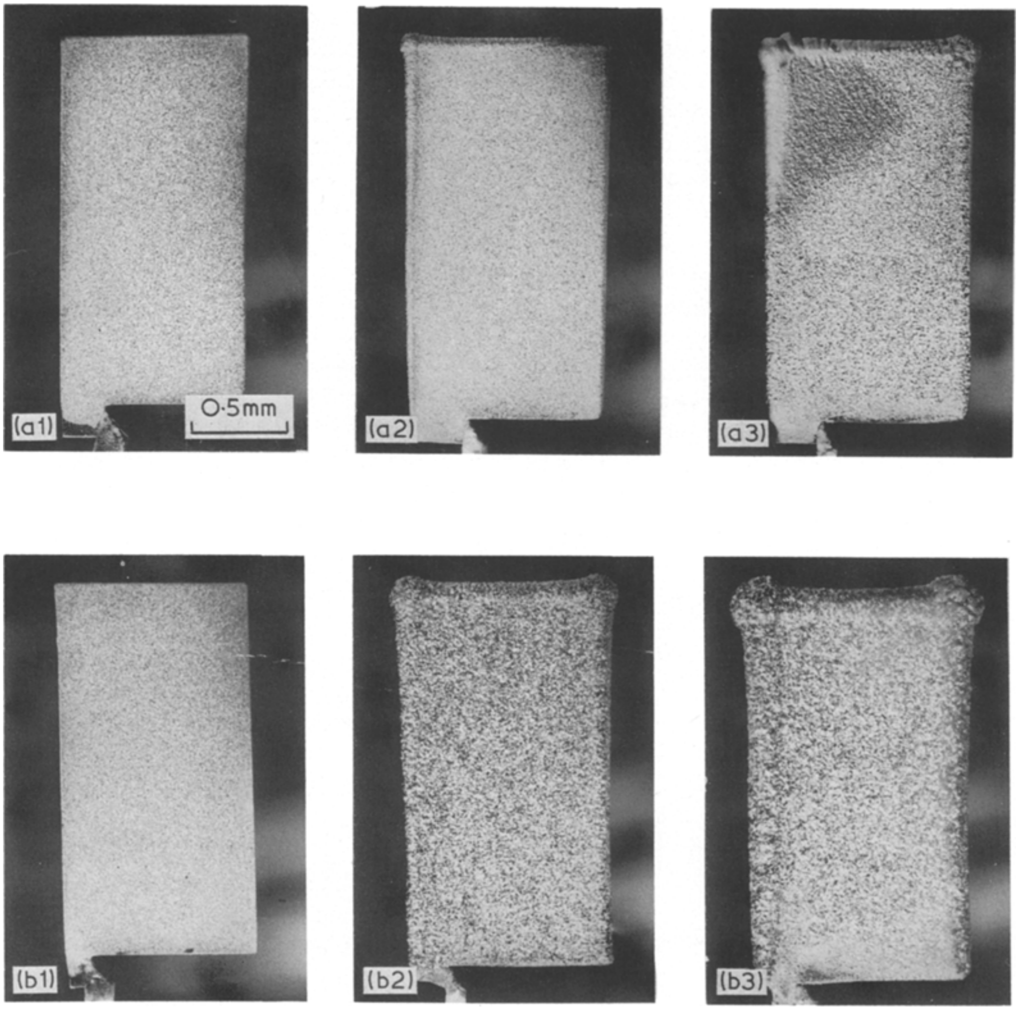

Fig. 9. Deposits of manganese on brass coupons. All photos are of the same magnification.
$MnCl_2 \cdot 4H_2O$ 298 g dm^{-3};
1 A dm^{-2}, pH 6.5
−12° C

$NH_4SO_3NH_2$ 2 mol dm^{-3}
(a_1) 2 h
(a_2) 18·5 h
(a_3) 42 h

NH_4Cl 2 mol dm^{-3}
(b_1) 2 h
(b_2) 47 h
(b_3) 94 h

Table 1. Optimum conditions for manganese electrodeposition

	$MnCl_2$–NH_4Cl	*$MnCl_2$–$NH_4SO_3NH_2$*
Anode	Graphite	Graphite
Cathode	Brass	Brass
NH_4^+ concentration	2 mol dm^{-3}	2 mol dm^{-3}
Catholyte $MnCl_2 \cdot 4H_2O$	298 g dm^{-3} (82·8 g as Mn)	298 g dm^{-3} (82·8 g as Mn)
Diaphragm	No. 84 filter paper or vinylidene chloride (trade name 'vinyon' of Japan) canvas	No. 84 filter paper or vinylidene chloride (trade name 'vinyon' of Japan) canvas
Time of deposition	40 h	40 h
Current density	1–4 A dm^{-2}	1–2 A dm^{-2}
Bath temperature	Below −10° C	Below −10° C
pH	4·5–7·0	5·0–7·0
Current efficiency	80%	78%

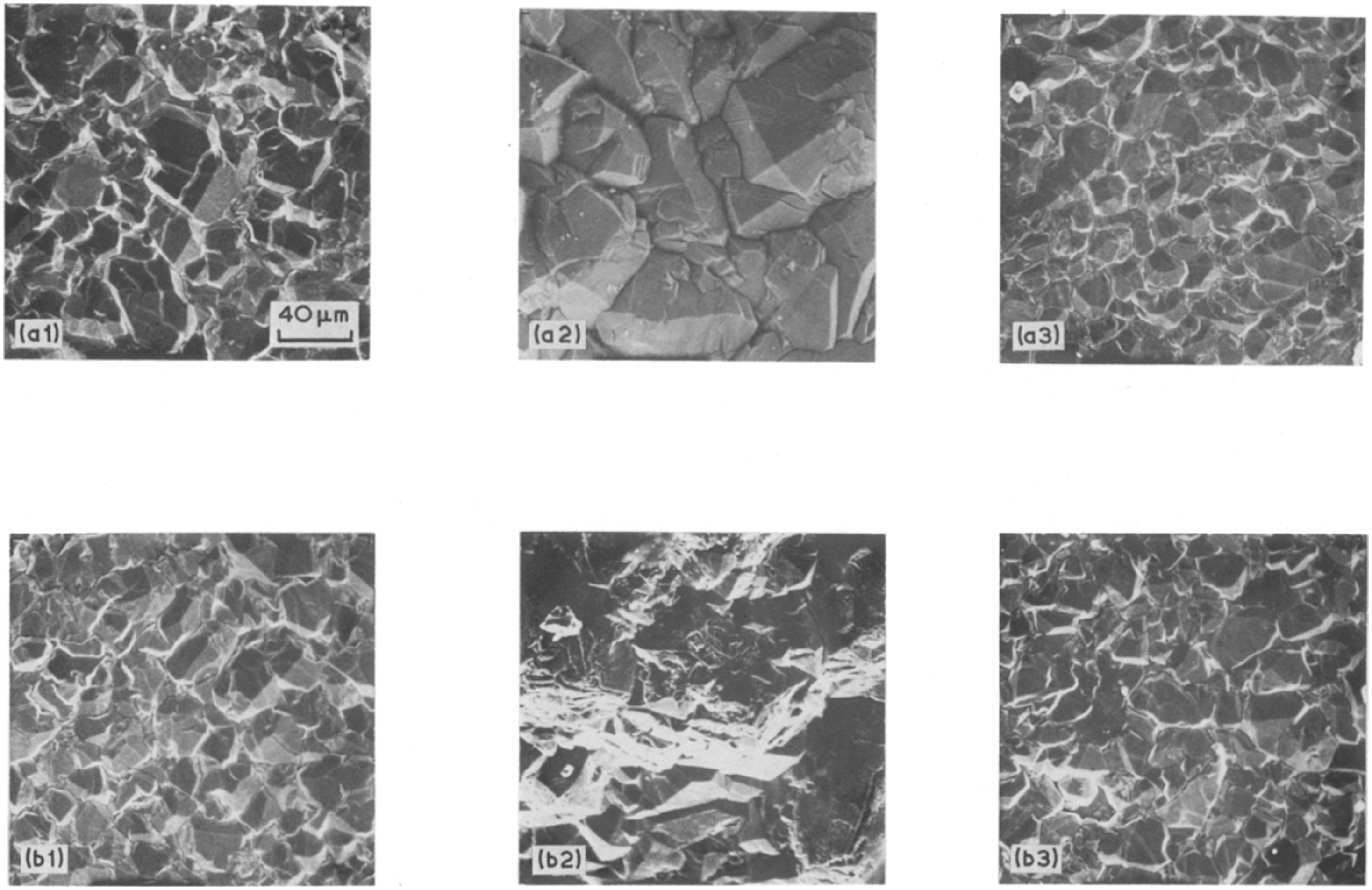

Fig. 10. SEM pictures of electrodeposited manganese. All figures are of the same magnification

$MnCl_2 \cdot 4H_2O$ 298 g dm^{-3}
1 A dm^{-2}
−12° C

NH_4Cl 2 mol dm^{-3}
(a_1) pH 4·5 2 h
(a_2) pH 6·5 2 h
(a_3) pH 6·5 40 h

$NH_4SO_3NH_2$ 2 mol dm^{-3}
(b_1) pH 4·5 2 h
(b_2) pH 6·5 2 h
(b_3) pH 6·5 44·5 h

(1) The higher current efficiency, higher electrical conductivity of the electrolytes and resulting lower cell voltage reduce the electric power consumption.
(2) The higher purity and ductile manganese metal available promises various new possibilities of application.

However, the low temperature chloride process has the disadvantage that excess energy is needed to cool the solution below −10° C. This may offset the advantage arising from the high quality of the metal.

Acknowledgements

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