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Erosion of sintered TiB_2-cathodes during cathodic aluminium deposition from $LiCl/AlCl_3$ melts

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Using an aluminium dissolution/deposition electrolysis cell, TiB_2, TiB_2/TiC and TiC sintered specimens of different porosity were tested for erosion resistance on exposure to liquid electrodeposited aluminium at 700° C to determine whether cathodes coated with such materials can be applied in aluminium chloride electrolysis cells. Although not wetted by liquid aluminium, the TiC and the TiB_2/TiC composites were extensively eroded. The densest TiB_2 specimens showed the highest resistance against liquid aluminium. The erosion rate of TiB_2 specimens of different density after exposure to the test environment for over 200 h was almost identical and reached a value of $0.16\,cm\,y^{-1}$. The observed wear rates exceed the values predicted on the basis of published solubility data by a factor of approximately 10.

1. Introduction

The use of titanium diboride as a cathode material in aluminium electrowinning cells was proposed by Ransley in 1962 [1]. A large number of publications exist devoted to studies of wettable cathodes for aluminium smelting cells, but to date none of the large aluminium producers has reported commercial implementation of refractory hard metal as a cathode. Erosion rates of TiB_2 were measured in pilot and laboratory scale tests using Hall–Heroult cells [2–6]. The reported wear of TiB_2 was higher than that expected on the basis of the assumption that uniform dissolution, limited by the saturation, is the controlling factor. Thus, Becker and Blanks [4] observed a loss of 0.01 cm thickness in a 100 h test, which is above the solubility limit by a factor of 50. The available solubility data were extensively discussed in the publications of Jones [7, 8].

The operation of the cathode in aluminium chloride electrolysis cells, for instance in the cell patented by Pechiney Aluminium [9], would occur at conditions substantially different from those of a conventional cell, in particular at 700° C rather than 900° C – with possible effects on the cathode material erosion.

This paper describes experimental work to investigate wettable cathode materials for the aluminium chloride electrolysis cell and is devoted to the determination of erosion rates in such cells. As a basis for the discussion in this work, the solubility data calculated by Jones [8] was taken. A second paper, dealing with the preparation of TiB_2-coatings on a carbon substrate by electrochemical deposition, will be published shortly.

2. Experimental details

The TiB_2 and TiB_2/TiC 1 : 1 specimens were sintered from carbothermally produced powder by Elektroschmelzwerk Kempten GmbH (Munich, FRG). The specimens were cylinders of 10 mm diameter and 5 mm thick; their characteristics as specified by the manufacturer are given in Table 1. The specimens were sintered from TiB_2 powder with a grain size smaller than 6 μm. The TiC sample with 53% of the theoretical density was supplied by VAW (Bonn, FRG). The salts, LiCl (pro analisi, Merck) and $AlCl_3$ (puriss., Fluka) were prepared as described in [10]. The pure aluminium rod (vac. dep. grade, Cerac) was cut in pieces of approximately 16 g weight. The essential elements of the experimental cell are shown in Fig. 1.

The cell consists of an outer quartz cylinder (1) purged with argon, in which an alumina crucible (2) containing the molten aluminium (4) anode was placed. The electrical connectors (8) made of alumina tube isolated stainless steel leads terminated with graphite rods (3 and 6). The anode connector was immersed in liquid aluminium, whereas the examined specimen (5) was inserted into the graphite cathode support. Forces resulting from the difference between the thermal expansion coefficients of the specimen and

Table 1. Characteristics of refractory hard metal specimens

*Sample**	*Density as % of theoretical value***	*Main impurities*
TiB_2 76	76	C max. 0.7%; O max. 1.0%
TiB_2 90	90	C max. 0.7%; O max. 1.0%
TiB_2 96	96	C max. 0.7%; O max. 1.0%
TiB_2 98	98	C max. 0.5%; O max. 0.6%
TiB_2/TiC 94	94	O max. 1.0%; N max. 1.0%;
TiC 53	53	

* The TiB_2 samples as well as the TiB_2/TiC sample were supplied by Elektroschmelzwerk Kempten GmbH; The TiC 53 sample was contributed by VAW AG.
** The theoretical density of TiB_2 from the manufacturer's data was $4.51\,g\,cm^{-3}$.

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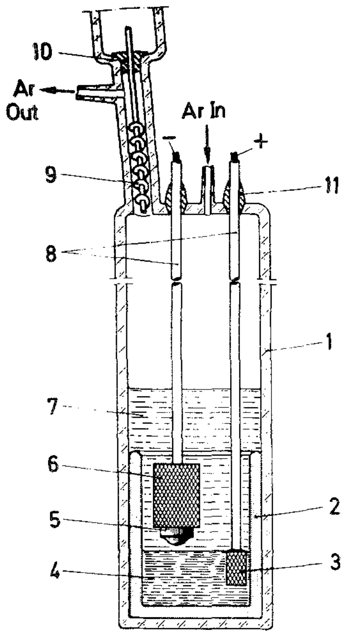

Fig. 1. Schematic of the experimental apparatus: 1 quartz vessel; 2 alumina crucible; 3 carbon rod inserted in, 4, liquid aluminium pool; 5 TiB_2 specimen, inserted into, 6 carbon rod; 7 LiCl (3 mol % $AlCl_3$) melt; 8 anode and cathode lead to steel protected by alumina tube; 9 screw feeder for $AlCl_3$ supply; 10 and 11 Teflon seals.

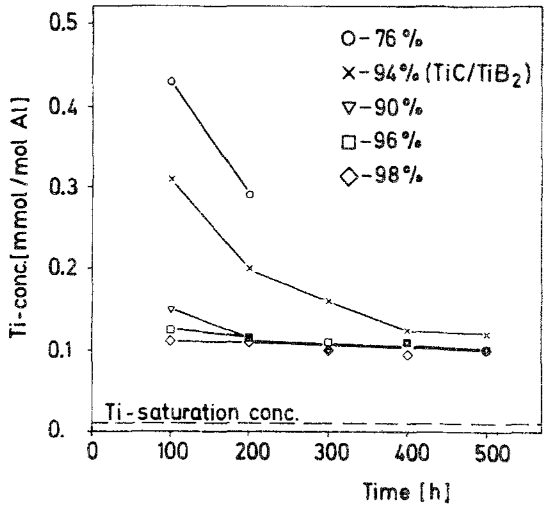

Fig. 2. Titanium concentration in continuously deposited aluminium averaged over 100 h and calculated from Ti-content of the anode pool which is exchanged after every 100 h.

the graphite substrate keep the insert in place. The distance between the specimen and the liquid aluminium surface was kept to 10 mm. The molten salt electrolyte consisted of LiCl containing 3 mol % $AlCl_3$. To prevent an excessive $AlCl_3$ loss, the system was provided with a screw feeder (9) which recycled the condensed solids (mainly $AlCl_3$), while allowing the argon gas to escape the vessel. The electrical connectors, as well as the feeder shaft, were sealed with Teflon (10 and 11) at their cool ends.

For the test, the aluminium metal piece was placed into the alumina crucible and the vessel was filled with the salt mixture – both under an inert atmosphere of dry argon. The quartz vessel was placed in a tubular furnace and heated to 700° C and kept at that temperature for 100 h. After the salt had been melted the electrodes were positioned. The electrolysis was run galvanostatically with a current density of 1 A cm^{-2} (based on the cylindric cross-section of the sample). The aluminium which collected on the TiB_2 cathode dropped continuously into the anode pool from which the aluminium content of the melt was replenished by anodic dissolution. The cell temperature was controlled within 5° C tolerance, and argon purging of the cell was maintained throughout the test. The electrolysis was interrupted every 100 h. The cathode and pool anode were removed from the vessel after cooling and again approximately 16 g of pure aluminium was supplied as fresh anode pool before resuming the next 100 h experiment. This procedure was repeated five times and each test was terminated after depositing liquid aluminium on the TiB_2 samples for 500 h.

After every 100 h of the electrolysis test, the titanium content in the withdrawn aluminium pool was determined by means of a spectroscopic method described in the literature [11]. The mean titanium concentration in the drop deposited on the specimen, averaged over 100 h, was calculated from the pool analysis. Scanning electron microscopy of the TiB_2 specimens was carried out before and after the 500 h tests using a Stereoscan 600 device (Cambridge Instruments) and a JSMT-300A (JEOL).

3. Results

The surface of all the TiB_2 specimens facing the aluminium pool was covered completely by an aluminium sessile drop; the solidified drop was attached to the specimen and was observed after the removal of the cathode from the experimental vessel. The TiC and TiC/TiB_2 samples were not covered with aluminium, i.e. they were not wetted at the test temperature. The TiC sample produced a high titanium concentration in the pool, more than 16 mmol Ti/mol of deposited Al during the first 100 h. This, together with the lack of wettability by the liquid aluminium, suggests that this material is not suitable for wettable aluminium electrodes and was, therefore, not examined any further. The extent of material erosion, expressed in terms of titanium concentration in the deposited aluminium drops, plotted against the electrolysis time, are shown in Fig. 2.

The experiment with the 76% density TiB_2 specimen was interrupted after 200 h, since the sample cracked, probably as result of liquid aluminium attack and thermal stress.

Studies of the weight changes of specimens [12] showed that the aluminium uptake became steady within 50 to 100 h, depending on the sample porosity and wettability. The specimen free volume decreased to about 40% of its initial value, obviously because the aluminium filled the greater part of the void. The erosion rate observed after 350 h may, therefore, be considered to be a value which represents the steady state of TiB_2 leaching by the deposited aluminium. After 500 h the erosion experiments were interrupted, the adhering aluminium was dissolved with dilute

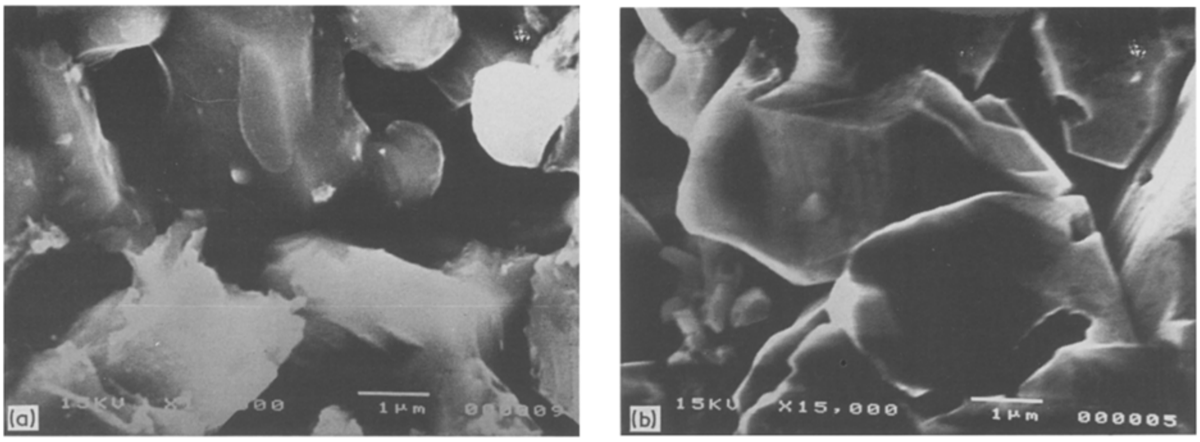

Fig. 3. SEM micrograph of 90% dense TiB_2 sample before (a) and (b) after Al-deposition for 500 h at 1 A cm^{-2}.

hydrochloric acid, which does not attack TiB_2 and the surfaces were investigated by scanning electron microscopy.

The comparison between the scanning electron micrographs of the specimens before and after the 500 h test (Fig. 3a and b) shows that, in particular, the 'glue', that is, the material of relatively low melting point which covers the TiB_2 particles providing their adherence, is leached away. The extent to which this occurs is obviously not much influenced by the density/porosity of the material. The remaining TiB_2 material is composed of more or less well developed TiB_2 crystals. The size of these crystals is particularly large for the densest materials as the crystals measure more than 15 μm for the leached material of 98% density. The authors cannot exclude the possibility that a fraction or all of these crystals have been formed by recrystallization and crystal growth owing to dissolution/redeposition of TiB_2 in liquid aluminium, although there are several reasons for the assumption that the crystals are not formed by recrystallization but have already been formed during the sintering process used for their production.

4. Discussion

The excessive titanium levels in the liquid, desposited aluminium recorded in the initial period of the tests, especially with less dense samples, may be related to titanium containing impurity segregation at the grain boundaries reported by Zdaniewski [13] and is attributed to the dissolution of lower melting material which covers the grains.

The steady-state concentration of titanium in the aluminium drop leaving the specimen is higher than the maximum solubility predicted by Jones [8]. It is conceivable that the erosion mechanism includes both refractory hard metal dissolution and grain shedding leading to higher 'apparent' solubilities of TiB_2, provided that this is not accounted for by incorrect solubility data. This is also in accord with the morphological surface changes readily observable on the SEM micrographs (Figs 3b and 4b). An important observation to be made from our tests is that all specimens with densities of 90% of the theoretical and higher show almost the same wear rate. On the other hand, the low density specimen (76%) was quickly pentrated by liquid aluminium [12] and subsequently promptly disintegrated.

The specimens with a density higher than 90% after being exposed to the test environment for over 200 h, reached an approximately constant wear rate of 7.6 mg TiB_2 per cm^2 in 100 h at the current density of 1 A cm^{-2} which amounts to a TiB_2 concentration of approximately 0.1 mg g^{-1} of Al. This wear rate corresponds to 0.16 cm y^{-1}, which is slower by a factor of

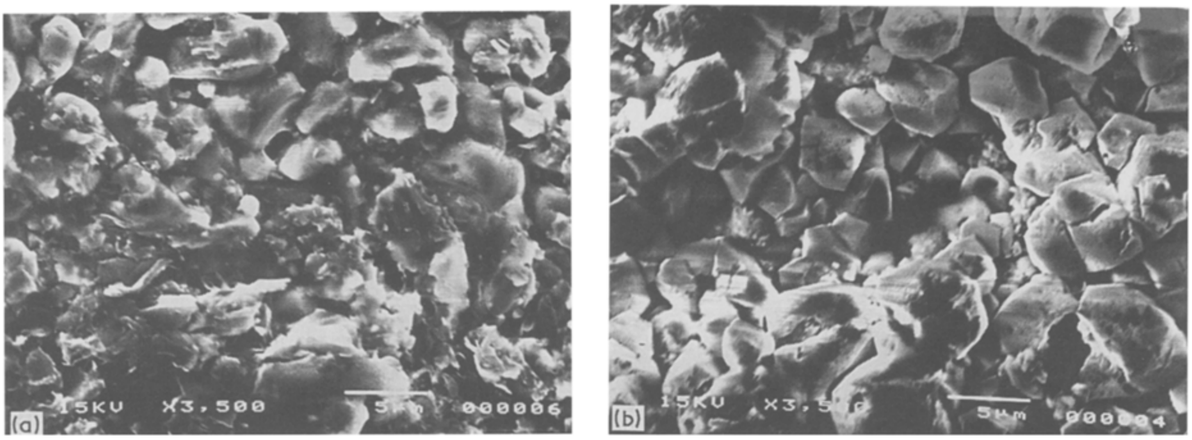

Fig. 4. SEM micrograph of 96% dense TiB_2 sample before (a) and (b) after Al-deposition for 500 h at 1 A cm^{-2}.

10 than that reported by Becker and Blanks [4]. The lower erosion rate of TiB_2 in an aluminium chloride electrolysis cell undoubtedly results from the lower operating temperature. However, one cannot exclude the possibility that there are additional factors controlling the erosion phenomenon. Thus, Mazza *et al.* [5] found that in Hall–Heroult cells sodium penetrated the refractory hard metal coating and was deposited on the grain boundaries. It must be emphasized that the observed wear rate is higher than that calculated from the solubility data given by Jones by a factor of 10.

In the technical cell, the wear rate will probably be lower than that derived from our experiments. This is primarily due to the fact that, in order to take samples to determine the titanium concentration, the whole assembly had to be cooled down until it solidifed. This resulted in additional thermal stress in the TiB_2 specimens by repeatedly cooling and remelting the assembly. Furthermore, in our experiment the specimens were continuously in contact with freshly deposited aluminium which did not contain titanium from previous erosion, while in a typical commercial cell the deposition occurs from electrolytes which contain traces of titanium, so that codeposition of the noble titanium assures an effective decrease of TiB_2 solubilities in deposited aluminium by a factor of approximately 5.

Although the TiC/TiB_2 sample was not wetted, the wear of this material is relatively high. The thermodynamic data published by Jones [7] shows that titanium carbide should be less stable in liquid aluminium than titanium boride. The enhanced erosion of the composite probably results from the excessive dissolution of TiC by liquid aluminium, thus promoting the disintegration of the specimen.

It may be anticipated that the purity of the refractory metal is crucial for its wear rate under continuous deposition of liquid aluminium, since cathodically deposited TiB_2 which is of higher purity than sintered TiB_2 seems to be significantly more resistant to erosion [14].

After we finished this experimental work, an article claiming similar conclusions concerning the applicability of TiC or TiC–composite materials as cathodes for aluminium smelting cells appeared in the literature [15].

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