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Material problems in electrowinning of aluminium by the Hall–Heroult process*

S. WILKENING, G. WINKHAUS

Vereinigte Aluminium-Werke, Leichtmetall-Forschungsinstitut, Postfach 24 68, D-5300 Bonn 1, FRG

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An overview is given for the process and constructional materials used in the molten salt electrolysis of aluminium by the Hall–Héroult process. Carbon materials, which constitute the anode, the cathode and the side lining, have been and are still the universal front or hot face materials in the electrolytic cell. A comment is made on the various types of anode and on the attempts to substitute the anode carbon by non-consumable ceramic oxide artefacts. The metallic electrical conductors and their joints play an important role in the design and operation of the cells. In this context particular attention is paid to the properties and behaviour of steel as a material for passing the electrolytic current into the anode and cathode up to temperatures of about 950° C.

1. Introduction

An aluminium smelter or aluminium electrolytic reduction plant consists of long buildings, called pot rooms, which house one or two rows of electrolytic cells or pots. Depending on production capacity and cell size, 100–200 cells may be connected in series to form a so-called pot line or cell system. The size of the cell is characterized by the nominal current load usually ranging from 100 to 300 kA [1].

One type of cell is illustrated by Figs 1a–1c [2]. Figure 1a is a cross section of a 180 kA cell showing the essential constructional and process-related parts of an aluminium reduction cell. Since the subject of the conference session is focused on material problems, the various materials of this cell are depicted by different shades. Figure 1b represents a front view of the cell, where the half on the left hand side is cut open to show a longitudinal section. The half on the right hand side illustrates the casing and the exterior conductor bars of the cell. Figure 1c is a top view of the cell, where again the left part is shown uncovered to display the arrangement of the anode and cathode blocks.

Some fundamental process data of the aluminium reduction cell are compiled in the form of the scheme in Fig. 2. The physical properties of the electrolytic bath, the raw materials and products as well as the distribution and consumption of energy can be recognized in this figure.

2. Materials in aluminium electrolysis cells

Before going into detail on specific materials in aluminium reduction cells, a survey will be given of their classification.

A first essential category of materials (see Table 1) comprises the raw, intermediate, and waste materials which are used or produced in the electrolytic process. The materials as listed in Table 1, except the carbon anodes, will not be discussed further here. In Table 2 materials are outlined which surround the molten salt

Table 1. Process Materials in the Electrolytic Winning of Aluminium

Raw materials	*Reprocessed Materials*	*Waste Materials*
● Alumina	● Alumina from fluoride adsorption	● Dirty dust from dry cleaning of pot – room gases
● Petroleum coke } Carbon anodes ● Pitch }	● Butts, rest of prebaked anodes	● Dirty dust from cleaning of butts
● Bath constituents: Aluminium fluoride Cryolite Calcium fluoride Sodium carbonate Lithium carbonate	● Bath material removed from butts	● Various solutions or precipitates from wet cleaning of waste gases (baking furnaces, Soederberg cells, etc.) ● Spent potlining First cut: Cathode carbon material Second cut: Insulating material

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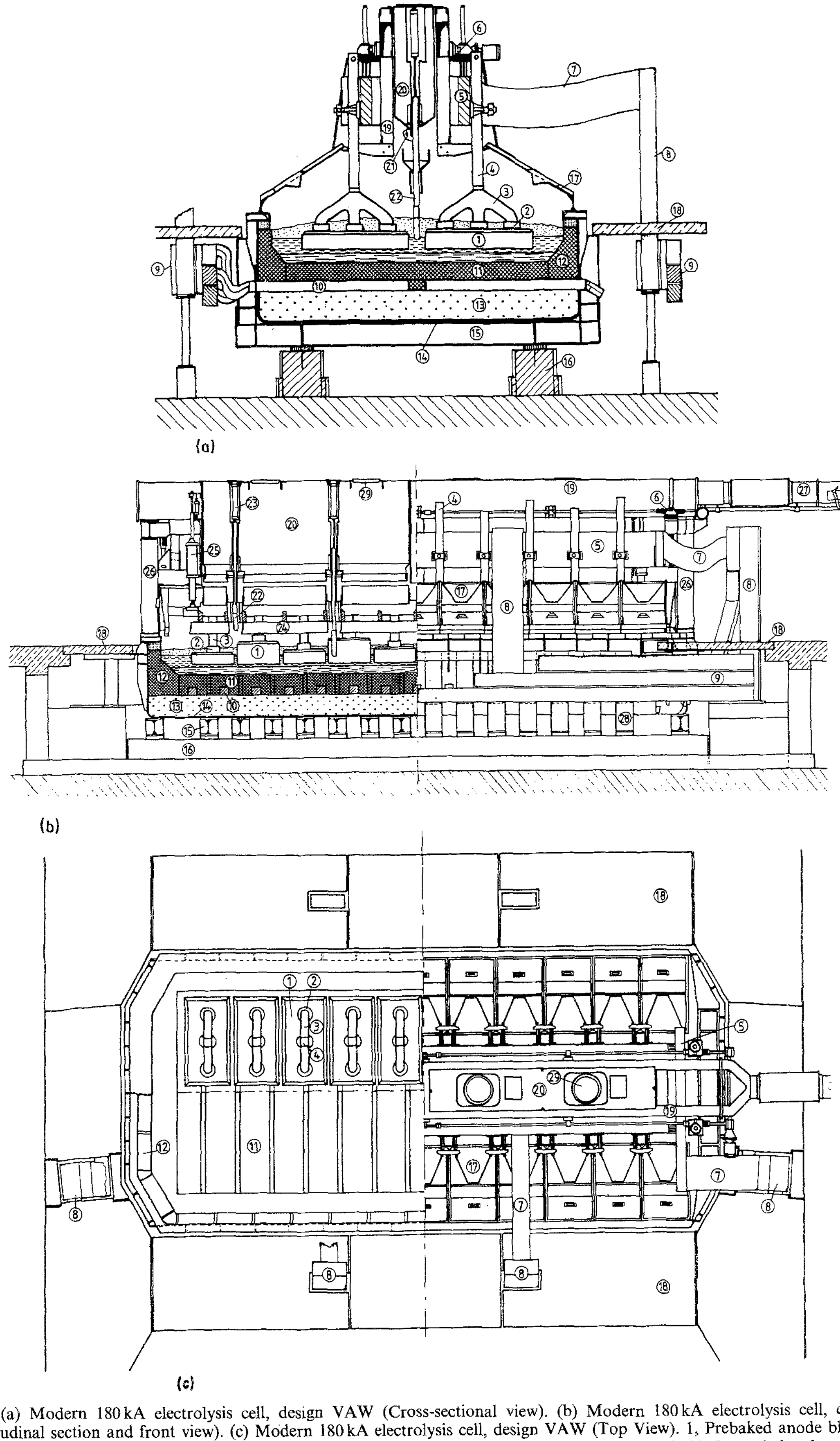

Fig. 1. (a) Modern 180 kA electrolysis cell, design VAW (Cross-sectional view). (b) Modern 180 kA electrolysis cell, design VAW (Longitudinal section and front view). (c) Modern 180 kA electrolysis cell, design VAW (Top View). 1, Prebaked anode block, carbon; 2, nipple protection, Al sleeve + Carbon paste; 3, yoke and stubs, cast steel; 4, anode hanger or rod, Al; 5, anode bus bar, Al; 6, lifting device; 7, flexible connection, Al; 8, Riser, Al; 9, Cathode bus bar, Al; 10, collector bar, mild steel; 11, prebaked cathode block, carbon; 12, side wall lining, carbon; 13, bottom insulation; 14, steel shell; 15, steel stiffening frame; 16, concrete; 17, cover sheets, Al; 18, concrete slabs; 19, gas collection chamber; 20, alumina container; 21, alumina flap; 22, rammer of point feeder; 23, compressed air cylinder of point feeder; 24, beam for crust breaking; 25, compressed air cylinder of beam; 26, pillar of superstructure; 27, waste-gas pipe; 28, supports for cathode bus bar; 29, filling holes for Al_2O_3.

Table 2. Classification of permanent materials for aluminium reduction cells

Front Materials (At the hot face)	*Back Materials (At the periphery)*	
	Electrical Conductors	*Construction Materials*
1. Carbon: Anode and Cathode	1. Aluminium	1. Mild steel
2. Frozen bath or crust	2. Copper	2. Lining materials a) For thermal insulation: Fire – clay brick, alumina, light weight insulating materials b) For cooling: Carbon, graphite, silicon carbide etc. c) Against penetration: Steel sheets, glass, tiles
3. Liquid aluminium	3. Steel	
4. (Refractory hard metals, e.g. TiB_2)	(Carbon)	

Materials in Aluminium Electrolysis Cells

bath. These may be divided into front and back materials. The carbon cathode constitutes a large and important structural section of the cell. A paper devoted to cathode problems has been presented by Sørlie and Øye [3] and for this reason, we have omitted this from our paper.

The consumable carbon anode combines two functions. On the one hand, it serves as the anodic electrode at which oxygen is liberated from the decomposition of alumina. On the other hand, it can be classified as a process material, because the electrochemically effective combustion of the anode carbon to carbon dioxide and carbon monoxide contributes significantly to the energy balance of the electrolytic process. Hence, the anode material will be briefly treated here.

At the periphery of the cell, a variety of constructional materials are used. Besides refractory lining materials in the bottom and along the sidewalls of the cell, the metal construction consists chiefly of steel and aluminium. The metallic parts of the cell can be grouped into those which carry current and those which do not. About 90 tonnes of engineering metal are needed for the construction of a 180 kA cell. The current-bearing amounts of steel and aluminium are almost equal, e.g. 55 tonnes per 1000 tonnes of annual capacity, but only minor quantities of aluminium are installed in areas where strength and low construction costs are required.

It may be mentioned that, in the early days of aluminium production, the steel shell or vessel containing the bath with little insulation was utilized as a cathodic current conductor. Nowadays the steel shell is isolated from the electric current.

3. Current-carrying elements of the cell

Aluminium, copper and steel are the metals by which the electrolytic current is conducted to and into the cell. Some properties which are significant with respect to the appliction of these three metals as electrical conductors are summarized in Table 3.

In up-to-date high amperage cells, copper elements

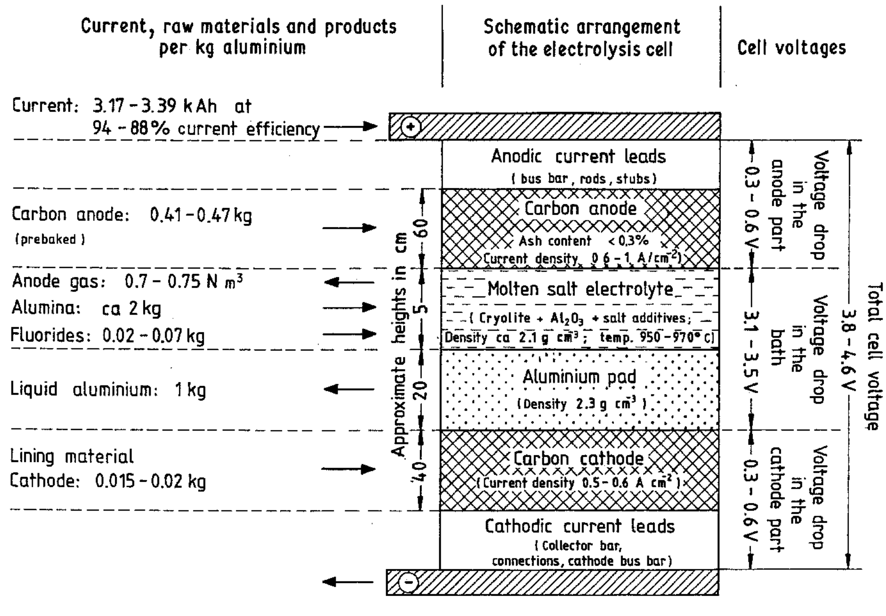

Fig. 2. Principle of aluminium electrolysis.

Table 3. Properties and load of the electrical conductors in aluminium reduction cells

Property		*Aluminium*	*Copper*	*Steel*	*Carbon*
Coefficient of thermal expansion in 1/°C (range 0–100°C)		24×10^{-6}	17×10^{-6}	12×10^{-6}	4×10^{-6}
Electrical resistivity in $\mu\Omega$m	At 20°C (RT)	0.0286 (≙ 1/35)	0.0179 (≙ 1/56)	0.14 (≙ 1/7)	60
	Temperature coefficient in 1/°C (range 0–100°C)	0.0040	0.0038	0.005	−0.0004
	At ultimate application temperature	0.0771 at 400°C	0.0464 at 400°C	1.12 at 1000°C	48 at 1000°C
	Change from RT to upper temperature	2.70	2.60	8.03	0.80
Thermal conductivity in W mK^{-1} (range 0–100°C)		220	380	50	4.5
Ratio thermal cond./electr. cond.		6.3	6.8	7.0	270
Current density in A mm^{-2}		0.2–0.6	0.4–1.0	0.15–0.20	0.005–0.01

are no longer employed for electrical conductance. Copper has been completely replaced by aluminium. For the sake of comparison, the relevant values of copper and also of carbon are included in Table 3. The temperature range of application, as indicated in the fifth line of Table 3, is absolutely uncommon for aluminium, copper and steel in electrical engineering. In aluminium reduction cells they are used to their utmost temperature limit which is set by corrosion and mechanical strength. The economical current density (see lowest line in Table 3) of the aluminium bus bars depends on the price of both electrical energy and aluminium ingot. Higher current densities lead, of course, to increased heat generation in the conductor bars, but to lower investment costs. The electrical resistivity of steel is about five times higher than that of aluminium, and one may raise the question as to why it is applied as current conductor. Presently there is no better choice for passing current into the carbon anode or cathode from room temperature up to about 1000° C. Thermal conductivity also plays an important role for the current-carrying bars. Thermal conductivity values are also given in Table 3. The ratio of thermal and electrical conductivity is similar for the metallic conductors as is known from the Wiedemann–Franz–Lorenz law. This means, if cross sections are installed by different metals with the same electrical resistance, the heat flow through these cross sections will be similar. Carbon, however, with a conductivity ratio of 270 (see last column in Table 3) or graphite, which is even worse, has to be regarded as a bad material for extended current passages. Therefore, it should be a rule to conduct the current by metallic elements as close as possible to the liquid aluminium and electrolyte bath. A heat balance of an aluminium cell is illustrated in Fig. 3 [4]. It shows that approximately 16% of the total heat losses of a cell are conducted to the outside by the anode steel stubs and the cathode steel collector bars. This is relatively little compared with the losses through the side wall and from the anode surface.

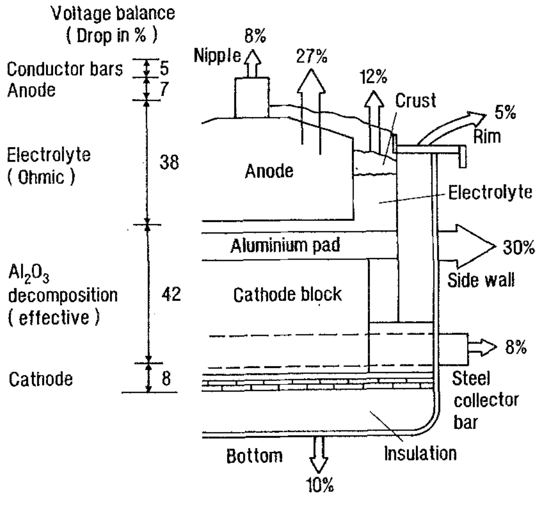

Fig. 3. Voltage balance and typical heat losses of a modern electrolytic cell with central feeding of alumina.

4. Properties of steel as an electrical conductor at higher temperatures

In an aluminium reduction cell, steel has gained a unique application as an electrical conductor. It is useful to know a few of the characteristics of steel in the temperature range up to 1000° C. The electrical resistivity of iron is increased by alloying elements, particularly carbon. Consequently, a low carbon steel is preferred.

A glance at the iron-carbon phase diagram in Fig. 4 [5] may facilitate the understanding of certain phenomena. Pure iron changes from the α to the γ modification of 911° C. At carbon concentrations above 0.02% the transition from α to γ starts at ca 730° C and is finished between 900 and 800° C, for carbon contents up to about 0.3%. In addition, it may be noted that the magnetic α iron becomes nonmagnetic at 769° C, at the Curie point.

The linear thermal expansion of technically pure iron

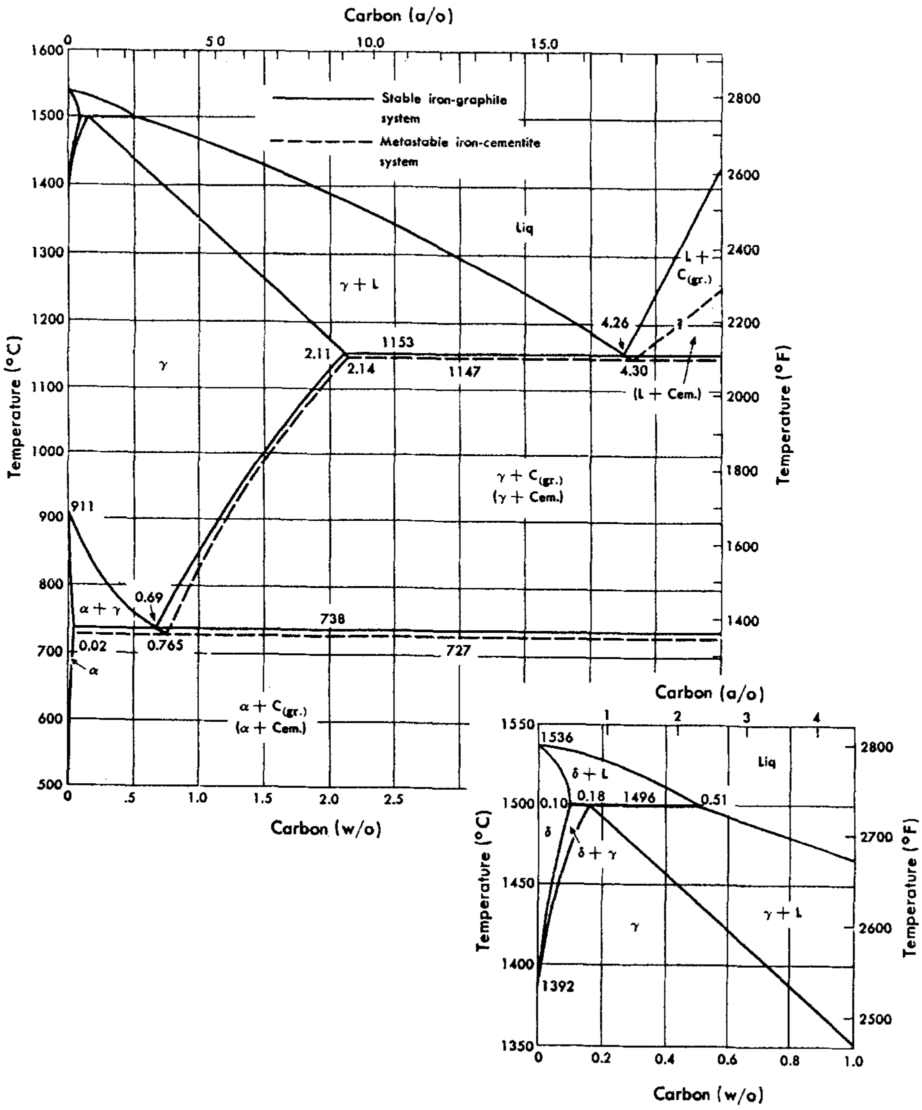

Fig. 4. Iron-Carbon phase diagram according to Benz and Elliott [11].

measured by us as a function of temperature is shown in Fig. 5. The α–γ transition is associated with a contraction and happens exactly at the defined temperatures in the phase diagram. The expansion curve of low carbon steel, i.e. of a sample from the collector bar, is also reproduced in Fig. 5. It can be noticed, as already pointed out, that the transition from α to γ begins at about 730° C and ends at about 900° C.

The dilatation of steel is approximately three times higher than that of carbon (see Table 3). This dif-

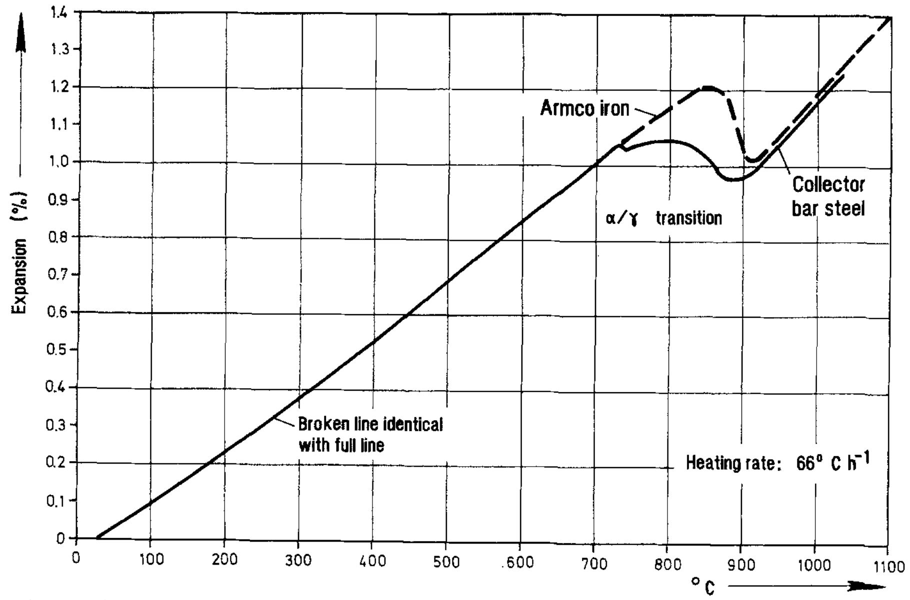

Fig. 5. Linear thermal expansion of Armco iron (technically pure iron) and of collector bar steel (Measurements by the authors in 1970 and 1975).

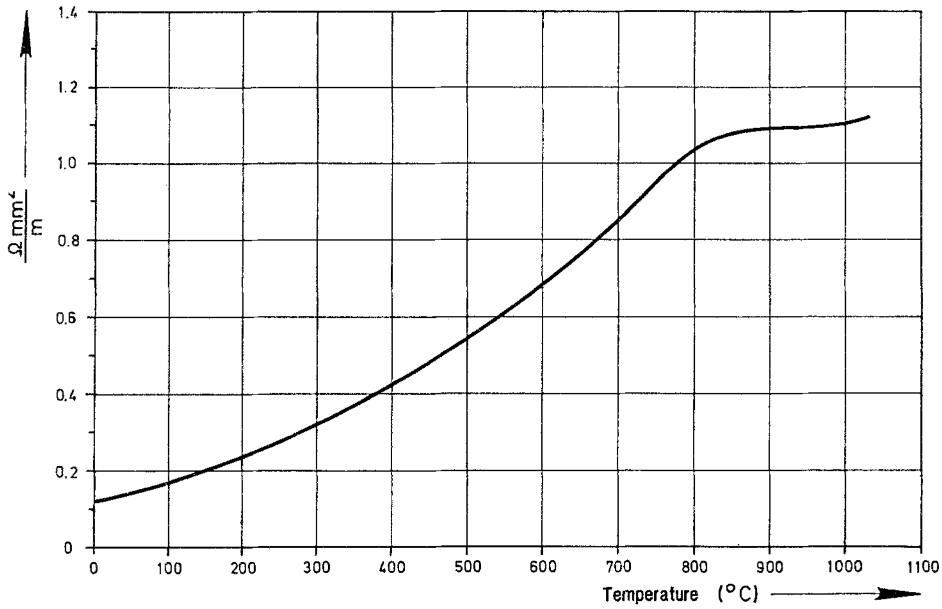

Fig. 6. Resistivity of collector bar steel (Measurement by the authors in 1975).

ference causes problems when heating up joints of steel and carbon. If the junction is tight at room temperature, carbon may be cracked or disrupted by the expansion of steel on reaching the operating temperature. The steel collector bars embedded in the carbon cathode blocks must be allowed to slide. Another example may demonstrate the significance of the expansion anomaly in the α–γ transition range. These temperatures occur in the carbon cathode. If a vertical temperature gradient of 50° C is assumed across the steel bar, i.e. perpendicular to its length, it will form a slight arch according to the 0.1% expansion difference between the top and bottom line. The steel bar may be straight between 750 and 850° C and deflect in the opposite direction around 850° C. Above 900° C the same bending situation is reached as below 700° C. To avoid steady movements of expansion and deflection, it is necessary to keep the cathode temperature as constant as possible.

The variation of electrical resistivity and thermal conductivity of steel with temperature is shown in the diagrams in Figs 6 and 7. Whilst up to 900° C the electrical resistivity changes by a factor of eight, the thermal conductivity decreases only by a factor of about two. Consequently, the ratio of thermal and electrical conductivity increases with temperature. In other words, the excessive heat generated by the higher electrical resistance is not held in place to the same extent.

Another point worth considering in this context is the mechanical strength of mild steel at elevated temperatures. It is well known that the tensile stength of steel reaches its maximum at ca 300° C and then drops steeply. Going from the α to the γ crystal an increase of strength is observed. We have carried out experiments on the creep rate of collector bar steel. The results are plotted in Fig. 8. Even at low loads of 1–5 N mm^{-2} we measured an appreciable rate of

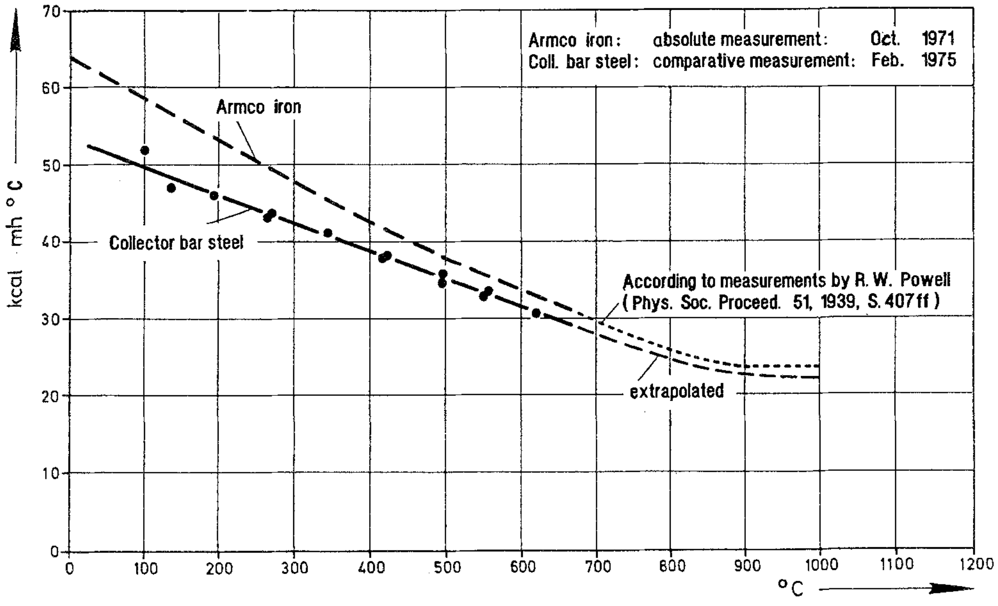

Fig. 7. Thermal conductivity of Armco iron and collector bar steel.

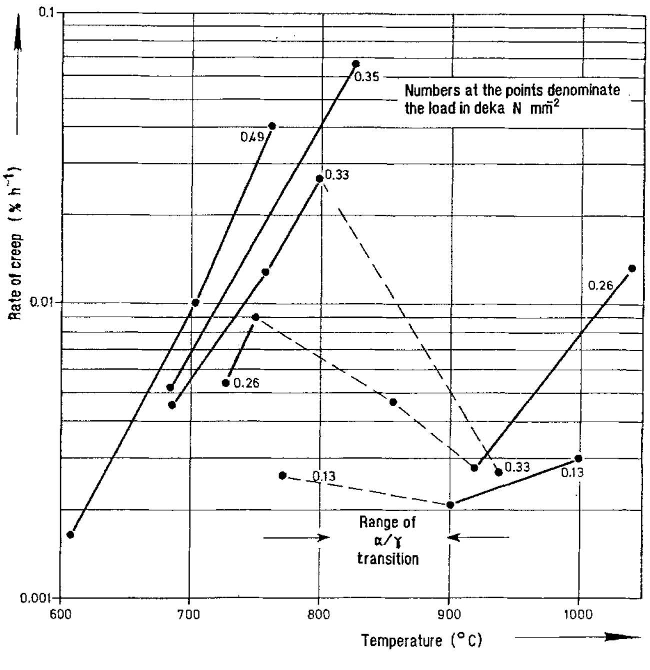

Fig. 8. Dependence of the creep rate of collector bar steel on the temperature at various pressures.

creep. We concluded that steel is slowly deformed by comparatively small forces in the cell above 700° C. When steel has been inserted in baked carbon products it may adjust its shape to thermal pressure forces at these temperatures. The increase of strength in the α–γ transition range reduces the rate of creep.

A particular property of steel for current transfer into the cell is its corrosion behaviour. In the dry and warm operating state up to 400° C mild steel is sufficiently resistant to air oxidation. At dark glowing temperatures scaling is initiated and intensified with increasing temperature. The presence of fumes from the bath enhances the oxidative corrosion significantly. Fortunately fluorides are not as harmful on corrosion rates of steel as chlorides. Under fully reducing conditions steel is not attacked by fluoride melts or fluoride vapours. Such conditions prevail, for example, when the steel surface is tightly covered with carbon, but traces of oxidizing gases may cause severe corrosion. The anode stubs are corroded just above the anode surface. A measure taken to prevent the corrosion of the steel contact pins is a sleeve of aluminium sheet filled with a kind of Soederberg paste.

Liquid aluminium, which penetrates through cracks in the carbon cathode blocks, destroys the collector bars to a large extent due to its strong dissolving and alloying power. So far no economical and stable coatings have been found which protect the current-bearing steel elements efficiently nor have other types of material been found which may replace steel.

5. Contact resistance of joints

The types of joints in an aluminium reduction cell are described in Table 4. It is a prime constructional goal to make the contact resistances of the joints as low as possible. This is best achieved by welding all permanent connections. The various aluminium conductors are connected by the MIG (metal–inert gas) welding process. Only the big detachable connections between the cells in a line have screwed joints. It is a general experience that all screwed or bolted metal joints deteriorate when they become hot, mainly due to advanced oxidation. An excellent junction between steel and aluminium is achieved by means of two-metal plates which are connected by explosive welding and then inserted by welding between the corresponding metal conductors.

Table 4. Problems of current carrying contacts in aluminium reduction cells

Connected material	*Kind of joint*
Aluminium and aluminium	1. Screwed or bolted, contact pressure about 10 N mm^{-2} 2. Argon arc welding (MIG process) by using a package of bridging aluminium strips
Aluminium and steel Copper and steel	1. Screwed or bolted 2. Argon arc welding, by using intermediate explosion plated pieces 3. Friction welding, especially for the joint anode rod–anode stub
Steel and carbon	1. Screwed connection, extensively used in former days 2. By ramming pastes, tar or resin bonded 3. By Soederberg pastes, mainly in Soederberg anodes 4. By glueing pastes, chiefly resin bonded 5. By cast iron, predominant method of today

Inert gas welding has brought about an almost perfect joining method for metal conductors. Problems still arise as to the joints between steel and carbon. Casting of pig iron into a small gap between steel and carbon is the most popular connecting technique for prebaked anodes and cathodes. At higher temperatures and under light contact pressure iron picks up carbon and creates an intimate junction. The carbon material of the anode contains sulphur or is permeated by sulphur compounds which may get to the surface of the steel stubs. The sulphur interacts with iron to form a diffusion layer of iron sulphide, causing higher contact resistances. Another drawback of the steel–carbon junction is the higher current density in the carbon material near the interface. Further away, the current spreads into the larger dimensions of the carbon block.

6. The carbon anode

The problems which affect the performance of the carbon anode may originate from any of the following three: (a) the raw materials; (b) the manufacture; (c) the type of anode. Currently, we may distinguish between three types of prebaked anodes and two types of the self-baking Soederberg anode. Perhaps a new variant may appear in the future.

Among the anode versions with prebaked carbon blocks, the oldest type features two rows of anode blocks and side working, i.e. crust breaking and alumina feeding along both sides. This is now out of data for the following reasons. It was difficult to conceive a simple anode construction to fulfil today's requirements, which comprise complete encapsulation of the cell, entire gas collection and its recovery, and full automatization of crust breaking and alumina feeding. The anode type with continuous prebaked anode blocks suffers from the same difficulties just mentioned. In addition, it has the disadvantage of a higher voltage drop in the anode. Also, it could not be implemented for high current intensities above 150 kA. During the last two decades, noticeable progress was made by the centre-worked cell type as shown in Fig. 1. The Soederberg anode with side studs or horizontal spikes was a favorite conception in the thirties. Its anode size could not be extended above 70 kA. There are still a few pot lines in operation using the side-stud Soederberg anode. High amperages or cell capacities were made possible by the vertical-stud Soederberg anode. All Soederberg anodes cause environmental problems due to the emission of fume and smoke from the coking of the Soederberg paste in the cells. It is hard to meet national standards for the PAH at the work place. New smelters are not built with Soederberg cells anymore.

The raw materials for the carbon anodes are calcined petroleum coke and electrode pitch. For the time being there is no scarcity of petroleum coke nor of electrode pitch. The spectrum of petroleum coke quality is wide and depends primarily on the oil sources. Large quantities of petroleum coke are offered with comparatively high sulphur contents, for instance in the range between 1.8 and 3.5%. In many areas and smelters, the processing of high-sulphur cokes is not allowed because of the legal limitations on SO_2 emissions. Extremely high vanadium contents, above 150 ppm up to 350 ppm, may also cause trouble by carbon burn-off and dust formation. Vanadium is the most effective catalyst for air oxidation of anode carbon at low temperatures above 350° C, particularly in conjunction with sodium. The anodes have to be shielded against access of air which is normally done by a thick layer of alumina on the anode blocks. The two foregoing examples cover but one facet out of several quality factors.

7. The non-consumable anode

Attempts have been made with enormous effort and considerable expenditure to develop an inert, non-consumable anode on the basis of electronically conductive oxides [6–10]. The oxides taken into account were selected using the criteria of low solubility in the cryolite melt and sufficient electrical conductivity. Meanwhile, thermodynamic aspects of the candidate materials such as decomposition voltage and their reactions with aluminium metal and aluminium fluoride have been added to the selection pattern. Anodes made from tin oxide, SnO_2, with different oxide additives and combinations of iron and nickel monoxide have been extensively tested in laboratory and pilot cells. The results were disappointing. The problems of anode corrosion and metal contamination could not be overcome. Presently, experiments with inert anodes aim at a lowering of the electrolyte temperature and at combination anodes containing a high-conductive body with a resistant coating. The future of the dimensionally stable anode in the molten salt electrolysis of aluminium is still open, but we have doubts that it will succeed in the near future.

8. Conclusions and outlook

Since the invention of the Hall–Héroult process (1886) for the electrolytic winning of aluminium, the materials of electrodes, metallic current leads and constructional parts of the cell have remained basically unchanged. However, the design of the cell, the installation of the current conductors as well as the quality and performance of the carbon materials have been improved substantially. Today, computer models are applied to optimize the construction, lining and operation of the cell. The magnetic and thermal fields, the arrangement of current conductors, the optimum current densities and the economical consumption of materials and energy are calculated.

There is still much scope for the introduction of new advanced materials into the cell. Attempts have been made with titanium diboride in the cathode and with stable conductive oxides for a non-consumable anode, but so far with very little or no success.

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