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MINIMUM TiB_2 CONTENT IN A COMPOSITE CATHODE WETTED WITH ALUMINUM

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The minimum content of functional component (titanium borideTiB$_2$) in cathodic refractory material that provides wetting with molten aluminum is substantiated. It is established that total cathode wetting with aluminum is observed with some minimum content of TiB_2 in a powder composite (16 – 18 vol.%), when according to occurrence theory there is formation of an "infinite cluster", i.e., a bonded percolation network of titanium boride particles. The volume of wetted composite containing a fixed amount (for example, 1 kg) of TiB_2 does not depend on its phase composition and porosity, but is determined by the diboride volume content. A TiB_2 content in the range 18 – 20 vol.% should be considered the optimum that creates reliable continuous wetting of a composite surface.

Keywords: aluminum electrolysis, wetted cathode material (WCM), composite material, titanium diboride, "infinite cluster" (IC), percolation.

INTRODUCTION

A fundamental problem in the field of aluminum electrolysis is creating a refractory material for a cathode wetted with aluminum. This cathode is used in operating electrolyzers in order to increase their service life and improve economic indices, and it is required in prospective energy saving technology using draining baths or a bath with vertical electrodes [1, 2]. The idea of a wettable cathode started in the 1980s, numerous engineering solutions were patented, but so far results of research and pilot plant work performed by leading scientific laboratories and companies in this field, i.e., aluminum producers, has not been translated into life seriously. This is due both to the complexity of the problem of creating stable material, retaining functional properties for a long time, and economic reasons, i.e., the material appears to be very expensive. The basis of resolving the task is a requirement for creating physicochemical bases for predicting its composition, properties and technology. Wettable cathode material (WCM) should have properties corresponding to its use, be economically expedient in a multi-tonnage industrial application, be adaptable, and consist of available components.

It is generally accepted that as a functional component providing WCM wetting TiB_2 is most suitable, combining good adhesion and wettability with a boundary angle below 90°, and also good chemical stability under action of overheated aluminum melts and fluoride electrolyte, and an oxidizing gas atmosphere. Use of TiB_2 in the form of a dense ceramic is limited by the high cost of starting powder and energy content of the technology for preparing monolithic objects. Dense ceramic exhibits serious disadvantages in this application, i.e., low resistance to thermal shock.

The task of reducing the diboride content due to introducing into the composition cheaper fillers, simplification of their manufacturing technology, and an increase in thermal shock resistance are conceptual for WCM materials science. Research is carried out mainly in the area of developing heterophase unsintered powder composites prepare by energy saving technology of binding phase components in "artificial stone" at relatively low temperature, of the order of the cathode working temperature, due to introduction of binder. Carbon and Al_2O_3 are normally considered as suitable fillers from the point of view of chemical resistance to molten aluminum, and low cost, which under certain condi-

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tions participate in processes of forming a strong monolithic body as a binder substance [3 – 9]. Binders harden at low temperature providing workpiece strength as a low-temperature binder-adhesive, and at the same time act as a high-temperature cement.

It is apparent that the quantitative content of each phase component in a WCM of the general composition $TiB_2/Al_2O_3/C$, and also their neutral ratio affects wettability by molten aluminum, electrical conductivity, strength, chemical resistance, and wear rate. The overall value of a specific property for this material is determined by a collection of the corresponding properties of the individual phases and depends on numerous factors: phase and dispersion compositions, quantitative ratio of components, nature of interphase reaction and structural units, etc. due to the complex action of numerous factors composite material properties are difficult to predict. Composite wettability is one such weakly substantiated property.

WCM WETTING

On the whole the problem of wetting composite porous surfaces has not been entirely resolved, although there is a considerable number of publications concerning wetting of porous rough chemically inhomogeneous surfaces, including a theoretical plan in model systems and biological objects. The dimensions of inhomogeneity in bio-objects lies as a rule in the nanosize region, and therefore these results are difficult to use for practical problem of wetting micro-non-uniform surfaces. In studies for an inert cathode this information, and also clear and substantiated assessment for the question of wetting, is lacking. Therefore solution of this problem is of fundamental interest from the point of view wetting composite hard surfaces and at the same time its practical importance for selecting the optimum content of expensive TiB_2 in WCM, i.e., substantiated saving, and a reduction in cathode material cost.

Our experience of laboratory electrochemical tests of WCM specimens indicates that reliable continuous wetting of a cathode surface by aluminum settling on it is observed with some minimum content of TiB_2 powder in the material, i.e., normally from 30 to 40 wt.% with overall composite porosity of the order of 25 – 35%. These figures have also been provided by other authors (for example with respect to TiB_2/C composites) [4, 10]: the preferred minimum TiB_2 content is 35 wt.%, although wetting may be achieved with somewhat lower values.

We analyze some actual WCM compositions of phase components TiB_2, Al_2O_3, and C in order to match the volume fraction of diboride. Rough values of the volumetric percentage of the content of TiB_2 powder in WCM for some values of overall material porosity θ (2, 20, and 35%) are given in Table 1. In the calculations theoretical density d_t of a pore-free composite of prescribed composition is calculated assuming additivity of the contribution of phase components according to the well-known relationship

$$d_t = \frac{100}{a_1/d_1 + a_2/d_2 + a_3/d_3}, \qquad (1)$$

where d_i is true density of individual phase components. g/cm^3; a_i is content of these components in material, wt.%. In calculations values of true density were adopted of 4.9, 3.9, and 2.2 g/cm^2 correspondingly for TiB_2, Al_2O_3, and C.

Specimens of cathodes made from materials of compositions Nos. 1, 3, and 4 with porosity of about 35% were tested in a laboratory electrolyzer, demonstrating satisfactory (No. 1) and good, continuous (Nos. 3 and 4) surface wetting with aluminum. With a TiB_2 content in similar composites less than 30 wt.% in the best case incomplete “island” wetting of a cathode surface was observed.

As experience and data provided in Table 1 show, the content of TiB_2 powder in all compositions developing functional conformity lies somewhat below 15 vol.%. This value is connected with a value of the threshold for occurrence in percolation theory and leads to the idea of a connection between an existing percolation cluster and solid composite surface wettability, within which the capacity for wetting on contact with a liquid is only exhibited by one phase component. In this case titanium diboride.

A composite of the overall composition $TiB_2/Al_2O_3/C$ consists of phase components differing considerably with respect to properties. Description of the generalized (or effective) conductivity of this type of composite is a spatial-inhomogeneous medium with randomly distributed strong inhomogeneous phase components, based on process theory [11, 12]: with some critical threshold value of volume faction X_c of the conducting component its separate inclusions are in contact, a conducting “infinite cluster” (IC) arise,

TABLE 1. Volume Content of TiB_2 Phase and Composite Specific Volume

Composition number	WCM composition, wt.%	θ, %	TiB_2 content, vol.%	WCM volume for 1 kg TiB_2, dm^3
1	$30TiB_2–50Al_2O_3–20C$	35	15.4	1.45
2	$35TiB_2–50Al_2O_3–15C$	35	19.0	1.17
3	$40TiB_2–50Al_2O_3–10C$	35	22.0	1.00
4	$40TiB_2–60C$	35	16.0	1.39
5	$45TiB_2–55C$	35	18.6	1.20
6	$40TiB_2–50Al_2O_3–10C$	20	27.4	0.81
7	$35TiB_2–50Al_2O_3–15C$	20	23.0	0.97
8	$30TiB_2–50Al_2O_3–20C$	20	18.9	1.18
9	$40TiB_2–50Al_2O_3–10C$	5	32.5	0.68
10	$40TiB_2–60C$	5	23.3	0.95
11	$35TiB_2–65C$	5	19.8	1.12

and conductivity of the system increases jumpwise. In the vicinity of a transit a system experiences a sharp change similar to the change in characteristics for substances during phase transitions. A critical concentration of conducting phase exists (occurrence of a threshold) below which there is no "infinite cluster" and conducting inclusions, partly combined in into an "infinite cluster", are separated by layers of poorly conducting phase. In this region an increase in conducting phase content has a weak effect on material conductivity, increasing it somewhat. With a content of X of conducting phase above the threshold for occurrence $X_c < X < 0.5$ and low conductivity of the second component the effective material conductivity $\tilde{\omega}$ also increases insignificantly in accordance with an expression

$$\tilde{\omega}/\tilde{\omega}_o = \alpha(X - X_c)^\kappa \qquad (2)$$

where $\tilde{\omega}_o$ is highly conducting phase conductivity; α and κ are constants. Theory also gives the magnitude of the volume fraction critical value $X_c = 0.15 \pm 0.03$, or (15 ± 3) vol.%, and $\kappa = 1.8 \pm 0.2$. Comparison of experimental results for different systems [13] gave the most probable values: $X_c = 0.16 \pm 0.01$, $\kappa = 1.6$, $\alpha = 1 - 1.6$. The value of volume faction $X_c = 0.16 \pm 0.01$ observed by experiment is a standard value for the three-dimensional problem of process theory [14].

There are similar problems in the region of conducting composites based on polymer matrices [15] Although the approach to resolving the problem of conductivity in these systems is somewhat different and prediction of a threshold volume of the proportion of conducting component is based on resolving model distributions of its particles, the calculated value of X_c coincides with that provided above: $X_c = 0.146 - 0.167$. Therefore, the content of phase component providing of an IC in a pore-free composite is in the range 15 – 17 vol.%. In this case porosity in calculations of volume fractions should be considered as a separate phase.

On the basis of this it is possible to expect that the content of more than 15 vol.% of TiB_2 powder in WCM leads to formation of IC of diboride particles in material. In view of this there is quite an evident correlation of the phenomenon of wetting a composite surface and its total coating with aluminum with presence of bonded percolation network of particles of functional component TiB_2 within the volume. It is seen from Table 1 that with a normal level of porosity θ of the order of 35% reliable formation of IC of TiB_2 particles proceeds with a TiB_2 content in the range 35 – 45% (or 16 – 18 vol.%) depending on phase composition. A reduction in material porosity (for example by additional impregnation with resin or pitch followed by firing) makes it possible to reduce the content diboride in WCM maintaining in this case the required level of its volume content.

Attention should be drawn to the conditional nature of the application of the terms "total", "continuous" wetting of a chemically inhomogeneous composite surface. In a two-phase composite the surface consists of areas of wettable phase 1 (with quite good adhesion to liquid), unwettable phase 2 (with low adhesion), and some proportion s_p of pores emerging at the surface. Wetting of sections of phase 2 apparently does not occur, but with some certain proportion of s_1 of phase 1 overlapping of unwettable surface (their proportion s_2) by liquid with fulfilment of the overall requirement of a reduction in free energy of the system in this process:

$$s_1\sigma_{13} + s_2\sigma_{23} < s_1\sigma_{13} + s_2\sigma_2,$$

where σ_{13}, σ_{23}, and σ_2 are correspondingly the interphase energy of phase 1 (liquid), phase 2 (liquid), and surface energy of phase 2. In this notation we assume that $s_1 + s_2 + s_p = 1$, and the area occupied by pores remains free, and energy $s_p\sigma_2$ is identical in both sections of the inequality.

It is noted above that $X_c = 0.16$ is the standard value for a three-dimensional process theory problem. For a two-dimensional problem the threshold for occurrence is significantly greater $X_c = 0.5$, which signifies the unbonded nature of inclusions of conducting phase in a section of a percolation cluster. As an explanation of the correlation of surface wettability with formation of volumetric IC with $X_c = 0.16$ it is apparently possible to have the following expression: the actual working surface of a composite cathode has a very rough surface markedly exceeding the size of phase inclusions, and therefore should be considered as a three-dimensional phenomenon. In addition, the problem of wetting here is similar to some extent of the problem of grain boundary wetting in polycrystalline materials (see for example [16]), so that molten aluminum penetrates into the volume through the IC structure.

WCM SPECIFIC VOLUME

Apparently a very informative index, including as a useful economic characteristic, is the volume of wetted cathode composite containing fixed amount (for example 1 kg) of TiB_2, i.e., the specific volume W. calculated values of specific volume are given in Table 1 that as is seen do not depend either on the phase composition or porosity, but are regularly connected with the volume content of diboride X. data in Table 1 are shown in Fig. 1 in the form of a curve for the dependence of specific volume of WCM on TiB_2 volume content.

Comparison of expressions for specific volume of a composite as whole W and volume content of key phase component X having density d, shows that the values of W and X are connected by a simple relationship

$$W = \frac{100}{d} \cdot \frac{1}{X}, \qquad (3)$$

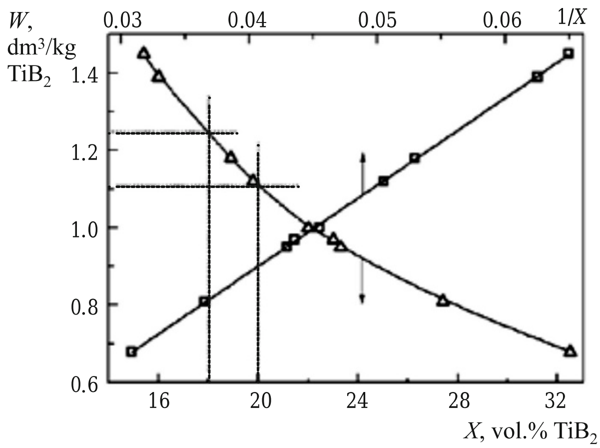

Fig. 1. Dependence of WCM specific volume W on volume content X of TiB_2.

or for a composite with titanium diboride ($s_{TiB_2} = 4.5$ g/cm^3)

$$W = 22.2 \cdot \frac{1}{X}, \quad (4)$$

which also confirms the linear nature of the $W - X$ curve rebuilt on coordinates $W - 1/X$ (see Fig. 1).

Pore-free ceramic TiB_2 ($X = 100\%$), as is seen, has a specific volume $W = 0.222$ dm^3/kg. If the optimum TiB_2 content is considered in the range 18 – 20 vol.%, which provides both formation of a n infinite diboride cluster and also reliable continuous wetting of a cathode surface, then 1 kg of TiB_2 powder makes it possible to prepare 1.1 – 1.2 dm^3 of WCM independent of the overall porosity of a finished composite and type of filler. These ranges are separated in Fig. 1 by broken lines. The curve makes it possible to calculate the weight content of TiB_2 and to evaluate directly a requirement for TiB_2 knowing input data for the phase composition of a specific composite, its porosity, and required wetted coating thickness.

The data provided for wetting were obtained for materials with TiB_2 powder with fineness less than 44 μm. It is fundamentally possible to reduce the diboride content in WCM with retention of wettability and conductivity for IC by using significantly finer TiB_2 powder. In this case it is possible to expect and achieve a value of $X_c \cong 0.08 - 0.1$ [15, 17, 18] that correspondingly reduces the minimum required weight content of TiB_2 in the system and significantly increases specific volume. With a content of fine TiB_2 powder of 9 vol.% Eq.(4) leads to a specific volume of about 2.5 dm^3/kg of TiB_2. In this case it is necessary to use sub-micron powder that however exhibits a high tendency towards oxidation and some chemical degradation.

Generally with a change in particle size but also in shape and size distribution the percolation threshold may take a value from $X_c \cong 0.01$ [19]. However, preparing these powders on an industrial scale is hardly economically expedient.

CONCLUSION

Cathode powder composite materials TiB_2/C, TiB_2/Al_2O_3/C wettable with aluminum, including functional composite TiB_2 and cheaper filler (aluminum oxide and/or carbon), are phase components participating also in bonding processes, and have the possibility to wet, starting from some minimum TiB_2 content. Continuous cathode wetting is observed with a TiB_2 powder content of 16 – 18 vol.% providing in terms of theory for occurrence of forming an “infinite cluster” a bonded percolation network of diboride particles.

A useful index for economic characteristics of WCM is the volume of wetted material containing some fixed amount (for example 1 kg) of TiB_2, which does not depend on the phase composition, porosity, and is mainly determined by the TiB_2 volume content. With the optimum TiB_2 content of 18 – 20 vol.%, which provides reliable continuous cathode wetting, 1 kg of TiB_2 powder makes it possible to prepare 1.1 – 1.2 dm^3 of WCM independent of the overall finished composite porosity and type of inert fillers.

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