Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

APPLICATION OF GREY RELATIONAL ANALYSIS FOR CORROSION RATES OF INERT ANODES IN ALUMINUM ELECTROLYSIS

Qingwei Qin[1], Yanling Xu[1], Jianhong Yang[1, 2], Xin Zheng[1]

[1]State Key Lab of Refractory Materials and Metallurgy, Wuhan University of Science and Technology,
947 Heping Avenue, Wuhan, Hubei 430081, China
[2]Zhengzhou Research Institute of Chalco. Zhengzhou, Henan 450041, China

Keywords: aluminum electrolysis, inert anode, corrosion rate, grey relational analysis

Abstract

Grey relational analysis was a data processing method used to sort out the correlation extent of effect factors in a system with uncertain information. In the paper, it was applied to evaluate the effect of operating parameters on corrosion rates of inert anodes in aluminum electrolysis. The corrosion rates of 5%Ni–$NiFe_2O_4$ cermet anodes were investigated as a function of some operating parameters. To reach a better understanding of the corrosion mechanism, the behavior of the anodes was observed under some designated conditions, such as in pure cryolite solvent, high current densities, and varying cathode surface areas. It was confirmed that low alumina concentration and high temperature were detrimental. The experiment results showed that grey relational analysis was an innovative data process method used to rank the corrosion extent of effect factors in the corrosion processes.

1. Introduction

The successful development of an inert anode would mean a technological revolution of the traditional Hall–Héroult process. The designation *inert anode* is being used to represent any oxygen–evolving anode. With such anodes the primary cell reaction, which in the Hall–Héroult process is,

$$1/2\ Al_2O_3 + 3/4\ C = Al + 3/4\ CO_2$$

is changed to,

$$1/2\ Al_2O_3 = Al + 3/4\ O_2$$

The anode material is inert in the sense that it is not consumed in the cell reaction, as the carbon anode is. However, as is demonstrated in the following, the materials in question undergo a slow corrosion, i.e. they are not completely inert; hence the designations non-consumable or oxygen–evolving may be more appropriate. At present, research on inert anodes is still being conducted on a small scale, i.e. in laboratory cells and in small pilot cells [1].

The core of inert anode technology is the corrosion and corrosion control of anode materials. The corrosion rates of inert anodes are not only related to composition and microstructure of materials, but also related to operating parameters. Aimed at the core of inert anode technology, the primary thrusts of the paper were to develop an inert anode and evaluate its corrosion behaviors systematically. In order to find out the main cause of corrosion rates of inert anodes, investigation and experimental research were made in a laboratory–scale cell.

Due to the complexity of corrosion behaviors of inert anode in aluminum electrolysis, practical and experimental data was difficult to obtain and there was too much scatter for analysis. The general methods based on classical statistics were not efficient enough to solve such complex problems and find out the main factors. The grey system initiated by Deng [2] in 1982 has been proven to be useful for dealing with poor, incomplete, and uncertain information. The grey relational analysis based on the grey system theory can be used to solve effectively the complicated interrelationships among the multiple performance characteristics. Using the grey relational analysis, a grey relational grade is obtained to evaluate the multiple performance characteristics.

The present work is focused on a study of the corrosion rates of 5%Ni–$NiFe_2O_4$ cermet anodes at varying operating conditions. Aimed at the complex coupling characteristics of operating parameters, the grey relational analysis was applied to evaluate the effect of operating parameters to corrosion failure of inert anodes and find out the main factors to control the corrosion behaviors of inert anodes.

2. Principles of grey relational analysis

The mathematics of grey relational analysis is derived from space theory [3]. The degree of influence of comparative series on the reference series, the grey relational grade, can be represented by the relative distance between them in an imaging grey space without making prior assumption about the distribution type. If the relative variation of two variables is basically consistent in developing trend, then the grey relational grade between these two variables is large. Considering the corrosion experiments were conducted under designated conditions, the present paper selected grey absolute relational grade to rank the correlation extent of operating parameters in the corrosion processes.

Let the original reference sequence and comparative sequence be represented as $X_0(\mathrm{k})$ and $Y_i(\mathrm{k})$, $k = 1, 2, \dots, n$; $i = 1, 2, \dots, m$, respectively. Data preprocessing is normally required since the range and unit in one data sequence may differ from the others. Data preprocessing is also necessary when the sequence scatter range is too large, or when the directions of the target in the sequences are different.

Data preprocessing is a process of transferring the original sequence to a comparable sequence. Depending on the characteristics of data sequence, there are various methodologies of data preprocessing available for the grey relational analysis. The reference sequence and the comparative sequences can be simply normalized by the zeroization of the first value of the sequence:

$$X_0^0 = \{x_0^0(1), x_0^0(2), x_0^0(3), \cdots, x_0^0(n)\},$$

$$Y_i^0 = \{y_i^0(1), y_i^0(2), y_i^0(3), \cdots, y_i^0(n)\}$$

where: $x_0^0(k) = x_0(k) - x_0(1)$ … $y_i^0(k) = y_i(k) - y_i(1)$

After the data preprocessing, a grey absolute grade can be calculated with the preprocessed sequences. The grey absolute relational grade is defined as follows:

$$\varepsilon_{0i} = \frac{1 + |s_0| + |s_i|}{1 + |s_0| + |s_i| + |s_i - s_0|}$$

where: $$|s_0| = \frac{1}{2}|x_0^0(2)| + \frac{1}{2}(|x_0^0(2)| + |x_0^0(3)|) + \dots + \frac{1}{2}(|x_0^0(n-1)| + |x_0^0(n)|) = \left|\sum_{k=2}^{n-1} x_0^0(k) + \frac{1}{2}x_0^0(n)\right|$$

$$|s_i| = \frac{1}{2}|y_i^0(2)| + \frac{1}{2}(|y_i^0(2)| + |y_i^0(3)|) + \dots + \frac{1}{2}(|y_i^0(n-1)| + |y_i^0(n)|) = \left|\sum_{k=2}^{n-1} y_i^0(k) + \frac{1}{2}y_i^0(n)\right|$$

$$\begin{aligned}|s_i - s_0| &= \frac{1}{2}|y_i^0(2) - x_0^0(2)| + \frac{1}{2}(|y_i^0(2) - x_0^0(2)| + |y_i^0(3) - x_0^0(3)|) \\ &\quad + \dots + \frac{1}{2}(|y_i^0(n-1) - x_0^0(n-1)| + |y_i^0(n) - x_0^0(n)|) \\ &= \sum_{k=2}^{n-1}|y_i^0(k) - x_0^0(k)| + \frac{1}{2}|y_i^0(n) - x_0^0(n)|\end{aligned}$$

Here, the grey absolute relational grade ε_{0i} represents the level of correlation between the reference sequence and the comparative sequences. The relational grades are numerical measures of the influence of factors on the objective values, and the numeric values are between 0 and 1. Therefore, if a particular comparative sequence is more important than the other comparative sequences to the reference sequence, then the grey relational grade for the comparative sequence will be higher than other grey relational grades. Grey relational analysis is actually a measurement of absolute value of data difference between sequences, and it could be used to measure approximation correlation between sequences. Once the effect factors are ranked, the corrosion control of inert anodes will be distinguished.

3. Experimental procedures and results

3.1 Anode fabrication

The nickel ferrite anodes were prepared from analytical grade chemicals. Nickel metal is added to a previously calcined nickel ferrite powder that has been ground and dried. This mixture was then milled and dried. Binder (polyvinyl butyral from alcohol) level of 0.1% was used. Green compaction of anode samples was pre–compacted in alloy moulds by biaxial die pressing at pressure of 200 MPa and then transferred to a cold isostatic press (CIP). The CIP pressure was 250 MPa. The green anodes were sintered under controlled atmosphere for 4 hours at temperature of 1400 °C. Pure argon should be avoided to keep from reducing the ferrite phase. Final sintered phase was determined using X-Ray Diffraction (Rigaku D/max 2550 VB$^+$). Anode density was determined according to ASTM Archimedes method prior to electrolysis testing. Density of approximately 96% of theoretical was obtained.

3.2 Electrolysis testing

5%Ni－$NiFe_2O_4$ cermet materials were used in the corrosion tests. The electrolyte was made up of synthesized cryolite (Na_3AlF_6), sublimed AlF_3, reagent grade CaF_2 and technical grade alumina. To compensate for the alumina consumption during electrolysis, extra alumina was fed to the bath during the tests according to a current efficiency of 85%. A sketch of the experimental cells is presented in Figure 1. The cell consisted of a graphite crucible (inner diameter 90 mm, height 120 mm, which served as the counter electrode) and a working electrode (cermet anode). The electrolyte was contained in the graphite crucible with a sintered corundum lining, but this lining was not used when the effect of the alumina concentration was investigated. The crucible, containing about 600 g of the salt mixture, was placed in a vertical laboratory furnace and heated to the required temperature (superheat is 10 °C). The electrolysis temperature was controlled by a Pt-Pt10%Rh thermocouple with cold junction was held at 0 °C in an ice bath. Aluminum was not added prior to tests.

The current and the cell voltage were recorded with a Multi–Purpose Potentiostat/Galvanostat（model 273A，Perkin – Elmer Instruments）. The current was kept constant throughout the experiments, which normally lasted 8 hours. The exposed surface area was determined from the depth of immersion of the anode. Before each experiment the size of the anode were determined. After the experiment any adhering bath was removed with the assistance of ultrasonic from the anode by washing in a 30% $AlCl_3{\cdot}6H_2O$ solution at 80 °C and subsequently in water, and size was determined again. The corrosion rates were determined from the contamination of the metal and the electrolyte.

Samples of the electrolyte were taken before immersion of the anode and every 10 min during the first hour of electrolysis. In the followed 60 min, samples were taken every 20 min. In the third hour, samples were taken every 30 min. After this initial period, samples were taken every 60 min. The samples were frozen on a Pt rod, which was quickly dipped into the bath and removed for solidification. The samples were ground in an agate mortar and analyzed with Atomic Absorption Spectrum (WFX–120, BRAIC). The produced aluminum metal was determined using Inductively Coupled Plasma – Atomic Emission Spectrometry (Thermo Jarrell Ash IRIS Advantage 1000). The analyses were carried out at the State Key Laboratory for Powder Metallurgy, CSU. Some standard samples from National Analysis Center for Iron & Steel were prepared to calibrate the analytical method.

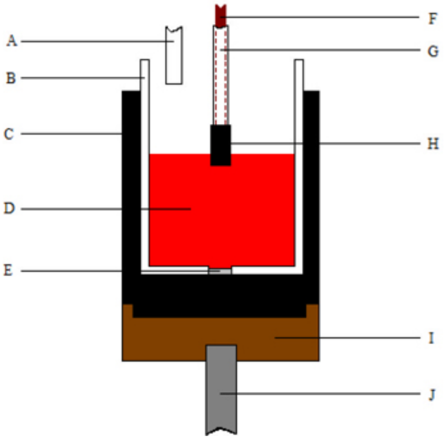

Figure 1 Schematic of experimental cell

A— tube for alumina feeding; B—alumina crucible with a hole at the bottom; C—graphite crucible; D—bath; E—molten aluminum; F—stainless steel rod; G—alumina sleeve; H—inert anode; I— graphite pad; J—stainless steel tube.

4. Results and discussion

In order to study the effect of bath ratio, temperature and electrolyte composition, a number of tests were carried with different electrolyte compositions. The performance of the anodes greatly depended on the test conditions. To avoid the anodic dissolution in the anode, the anode composition containing 5%Ni and 95%$NiFe_2O_4$ was chosen for these studies.

The bath ratio, Al_2O_3 concentration, temperature and additives, e.g., CaF_2, et al. cannot be varied independently. Table 1 shows the results of the tests. On the basis of condition of inert anodes and measuring data shown in Table 1, corrosion rate was chosen as the reference sequence, which described the behavior characteristics of cermet anodes. Other operating parameters e.g., Al_2O_3 concentration, cryolitic ratio (CR), anodic current densities, etc. were regarded as comparative sequences to affect the corrosion behaviors of inert anode in aluminum electrolysis.

Table 1 Hall cell test results

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Corr. Rate / ($mg\cdot cm^{-2}\cdot h^{-1}$)	0.9371	0.7542	0.8282	0.8713	0.9390	0.9242	28.1987	19.0254	14.5532	10.9857	9.5127	9.0199	8.6909	8.5263	1.7425	1.7874	2.3429	3.5243	4.8612	5.8933
w(Al_2O_3) / %	6.6496	7.8345	8.4698	8.8824	9.0838	9.1856	1.0000	2.0000	3.0000	4.0000	5.0000	6.0000	7.0000	8.0000	8.1820	8.1820	8.1820	8.1820	8.1820	8.1820
Current Density / ($A\cdot cm^{-2}$)	0.2708	0.2631	0.2329	0.2267	0.2297	0.2247	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	1.0	2.0	3.0	4.0	5.0
Cryolitic Ratio (CR)	2.0	2.2	2.4	2.6	2.8	3.0	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Cathode Area / Anode Area	5.5964	5.4206	4.8137	4.8374	4.8579	4.7379	16.7529	16.9502	17.8260	16.0722	13.3253	14.8338	15.3415	15.6808	0.4291	0.4246	0.4192	0.4641	0.4113	0.4268
Temperature / °C	930.9	948.2	958.5	963.7	965.4	965.0	986.5	980.4	974.9	969.9	965.4	961.1	957.2	953.4	954.1	954.1	954.1	954.1	954.1	954.1

Zeroization of the first value of the sequences was shown in table 2.

Table 2 Zeroization of the first value of the sequences

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$X_0^0(k)$	0	-0.1829	-0.1089	-0.0658	0.0019	-0.0129	27.2616	18.0883	13.6161	10.0486	8.5756	8.0828	7.7538	7.5892
$Y_1^0(k)$	0	1.1849	1.8202	2.2328	2.4342	2.536	-5.6496	-4.6496	-3.6496	-2.6496	-1.6496	-0.6496	0.3504	1.3504
$Y_2^0(k)$	0	-0.0077	-0.0379	-0.0441	-0.0411	-0.0461	0.7292	0.7292	0.7292	0.7292	0.7292	0.7292	0.7292	0.7292
$Y_3^0(k)$	0	0.2	0.4	0.6	0.8	1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
$Y_4^0(k)$	0	-0.1758	-0.7827	-0.759	-0.7385	-0.8585	11.1565	11.3538	12.2296	10.4758	7.7289	9.2374	9.7451	10.0844
$Y_5^0(k)$	0	17.3	27.6	32.8	34.5	34.1	55.6	49.5	44	39	34.5	30.2	26.3	22.5

No.	15	16	17	18	19	20
$X_0^0(k)$	0.8054	0.8503	1.4058	2.5872	3.9241	4.9562
$Y_1^0(k)$	1.5324	1.5324	1.5324	1.5324	1.5324	1.5324
$Y_2^0(k)$	0.2292	0.7292	1.7292	2.7292	3.7292	4.7292
$Y_3^0(k)$	0.3	0.3	0.3	0.3	0.3	0.3
$Y_4^0(k)$	-5.1673	-5.1718	-5.1772	-5.1323	-5.1851	-5.1696
$Y_5^0(k)$	23.2	23.2	23.2	23.2	23.2	23.2

$$\varepsilon_{01}=\frac{1+|s_0|+|s_1|}{1+|s_0|+|s_1|+|s_1-s_0|}=0.6132$$

$$\varepsilon_{02}=\frac{1+|s_0|+|s_2|}{1+|s_0|+|s_2|+|s_2-s_0|}=0.5764$$

$$\varepsilon_{03}=\frac{1+|s_0|+|s_3|}{1+|s_0|+|s_3|+|s_3-s_0|}=0.5211$$

$$\varepsilon_{04}=\frac{1+|s_0|+|s_4|}{1+|s_0|+|s_4|+|s_4-s_0|}=0.8189$$

$$\varepsilon_{05}=\frac{1+|s_0|+|s_5|}{1+|s_0|+|s_5|+|s_5-s_0|}=0.5989$$

The ranked results are as follows: ε_{04}(area ratio of cathode to anode) > ε_{01}(alumina concentration) > ε_{05}(temperature) > ε_{02}(current density) > ε_{03}(cryolitic ratio). These results were consistent with experimental results. It is seen that cell voltages decrease with increasing cathode areas. No metal was collected during the large cathode area experiments. The graphite crucible is cathodic and Al_4C_3 is formed on it which has appreciable solubility in cryolitic melts. Although it is not always recognized by people involved in aluminum smelting, the solubility of aluminum carbide in bath is a key issue in the electrowinning of aluminum. Ødegård et al [4] showed that carbon can be electrodeposited on different substrates by anodic polarization of these materials in aluminum carbide containing cryolitic melts. It was suggested that “spikes” could be a result of electrodeposition of carbon from dissolved aluminum carbide. When dissolved aluminum carbide is oxidized electrochemically, solid amorphous carbon is deposited at the anode, the overall anodic reaction for aluminum carbide oxidation can be written

$$Al_3CF_8^{3-} + F^- \rightarrow C_{(s)} + 3AlF_{3\,(diss)} + 4e$$

where $Al_3CF_8^{3-}$ is the proposed carbide species in solution. It's obvious that cermet anodes may be reduced there. by air.

Keller [5] observed that a decrease in the reduction rate of anode constituent species at the cathode is an efficient measure to increase anode life. Aside from keeping the solubility limit of anode constituents in the electrolyte as low as possible, cell design and operating parameters should be selected to keep the size of the cathode area as small and mass transfer rates as low (*i.e.* the diffusion layer as thick) as possible. Switching from a liquid pool cathode to a solid electrode covered with a thin layer of liquid aluminum may bring considerable improvement.

In the experiments, it was found that the cermet anodes were subjected to serious corrosion at low alumina concentrations. In order to investigate the extreme effect of depletion of alumina on the corrosion of inert anodes, electrolysis was carried out in pure cryolite. The duration of the experiments was shortened to 2 hours due to observed voltage increase and instability. The backscattered SEM picture after electrolysis and the appearance of an unused anode were shown in figure 2. The anodes were found corroded badly.

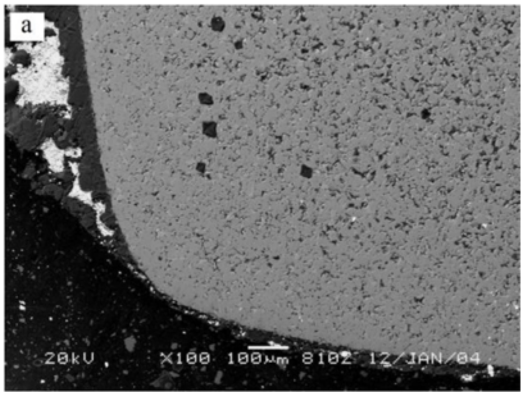

Figure 2 Samples of anodes

(a) SEM picture after electrolysis; (b) an unused anode

If the electrolyte becomes depleted with respect to alumina, the anode materials may start to decompose, supplying oxide ions to the process,

$$1/2\, M_2O_3(an) + AlF_3 = Al + 3/4\, O_2 + MF_3$$

This reaction, which has been described as "catastrophic corrosion" [6], can be avoided by maintaining an adequate supply of alumina dissolved in the electrolyte.

It is evident that the corrosion rate of inert anodes can be reduced to a significant degree by using low temperature electrolysis. It is believed that the inert anode corrosion rate will be reduced at a lower operating temperature because of reductions in solubility of metal species and cermet components. Using the Stokes-Einstein Equation as a guide for the behavior of a diffusion coefficient, $D = \frac{kT}{6\pi\eta R}$, One can see that the high temperature of the electrolyte (about 1000℃) favors higher diffusion coefficients, while the viscosity η, which is more than two times larger than water, favors lower diffusion coefficients.

The twofold characteristic of current density was observed in the experiments. During electrolysis, the anode will be surrounded by O_2. The resulting high oxygen pressure will certainly lower the dissolved metal activity. Meanwhile a high current density will lead to an increase of bath temperature and flow velocity. Low O_2 potential on the anode surface presumably exposes $NiFe_2O_4$ to Al, resulting in aluminothermic reduction of ceramic phase.

When the tests were conducted in the low temperature–low ratio electrolyte, the anode material was found to swell and degrade by the formation of Fe and Ni fluorides. One of the principal mechanisms for anode degradation appears to be the fluoridation of anode constituents and subsequent dissolution in the electrolyte. For suitable performance of inert anodes with this composition, an optimum bath composition, current density, cell configuration should be well controlled.

5. Conclusions

A cermet anode, $5\%Ni-NiFe_2O_4$ was chosen to evaluate the operating parameters on the corrosion rates. Aimed at the complex coupling characteristics of operating parameters, grey relational analysis method was proposed to determine the correlative extent of factors and corrosion behavior of inert anodes. The importance of the controllable factors for corrosion rates, in sequence, is area ratio of cathode to anode, alumina concentration, temperature, current density and cryolitic ratio.

Acknowledgement

The present work was performed under the support of the Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education (FMRU201206), China's postdoctoral Foundation (20100480885) and Hubei provincial New Century Talents Project.

References

[1]. J. Thonstad, P. Fellner, G. M. Haarberg, Aluminium electrolysis: Fundamentals of the Hall–Héroult process, third ed., Aluminium-Verlag Marketing & Kommunikation GmbH, 2001, pp. 328–339.

[2]. Deng Julong, Control problems of grey systems, Systems and Control Letters 1(1982) 288–294.

[3]. Deng Julong, Fundamentals of grey theory, Wuhan: Huazhong University of Science and Technology Press, 2002, pp. 158–162.

[4]. R. Ødegård et al., On the solubility of aluminum carbide and electrodeposition of carbon in cryolitic melts, J. Electrochem. Soc. 134(1987) 1088–1092.

[5]. R. Keller et al., Mass transport considerations for the development of oxygen-evolving anodes in aluminum electrolysis, Electrochimica Acta 42(1997) 1809–1817.

[6]. H. Xiao et al., Studies on the corrosion and the behavior of inert anodes in aluminum electrolysis, Metallurgical and Materials Transactions B 27B (1996) 185–193.