Nickel Ferrite Cermets as inert Anodes for Aluminum Electrolysis

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Abstract

Cermet materials made of 83% nickel ferrite (51.7% NiO and 48.3% Fe_2O_3) and 17% of a metallic phase (14% Cu+3% Ag, or 17% Cu) have been previously shown to function effectively for short terms as inert anodes. The intent of this work was to confirm these results and to quantify their effectiveness under small-scale electrolysis. Three compositions were manufactured containing the same proportion of nickel ferrite, but were different in their metallic content. Composition #1 used a mixture of copper and silver powder (14%-3%); composition #2 used a silver coated copper powder containing about 18% of silver, resulting in the same proportion (14%-3%) of copper and silver in the cermet; and composition #3 contained 17% of copper (no silver). The use of a scanning electron microscope (SEM) confirmed that all compositions of cermet produced had fine, dense, and homogeneous microstructures, with uniform distribution of the metallic phase. It was observed that the nickel ferrite consisted of particles typically 5 to 10 microns and that the nickel to iron ratio in the ferrites was varying within reasonable range. It was also seen that the metallic phase regularly presented phases very high (pure) in silver. Densities of the cermets were all above 5.95 g/cm^3.

Electrochemical measurements were made on the three compositions of cermets in order to measure their open circuit potential (O.C.P.), their corrosion current right after immersing the anode in the melt, and the same corrosion current but after anodic polarization of the anode. Reproducible results were obtained, indicating that the lowest corrosion was expected from the cermet anode made by addition of silver coated copper powder (composition #2). The cermet made using the mix of copper and silver powder (composition #1) was expected to have chemical corrosion slightly higher than the one with silver coated copper powder, while the cermet containing only copper powder was expected to be the most affected by corrosion. All three compositions showed ability to auto-protect themselves to some extent, by comparing the evolution of their corrosion current values before and after potentiostatic anodic polarization.

Short term aluminum electrolysis (8 hours) at various current densities (0.5 to 0.8 A/cm^2) allowed the comparison of the behavior of each composition when used as an anode in hot (970-980°C) cryolitic molten salts. In general, the composition #1 (copper and silver powder mix) showed the best performance, followed by the composition #2 (silver coated copper powder). The composition #3 (copper powder only) showed more tendencies towards degradation. The first sign of degradation is the loss of the metallic phase at the perimeter of the anode. This may progress a significant distance within the volume of the anode. The next phase of degradation involve de-cohesion of the nickel ferrite matrix. The composition #1 operated at 0.5 A/cm^2 shows very little degradation after 8 hours.

Introduction

There are three main materials for inert anodes: semi-conducting ceramics, cermets, and alloys. Each material has advantages and disadvantages – usually around mechanical, electrical, and chemical properties. The focus of this work is on cermets and our independent manufacturing and assessment of compositions described[1] as having potential as inert anodes. With this work, we have started developing cermet anode materials with optimized properties compared with those which were achieved earlier by various researchers.

Cermet anode manufacturing

The cermet anode manufacturing protocol was developed and performed at the Queen's University *Centre for Manufacturing of Advanced Ceramics* under the direct supervision of Dr. Vladimir Krstic. Review of the literature showed that nickel ferrite compositions had been developed and tested, and that this has been the subject of a number of patents[1,2,3,4,5]. Review of the patents and literature gave general guidelines for the cermet fabrication, but many protocol details were missing. The preparation of the powder (pre-milling, microstrucutre control, sizing. etc.) and the control of the perovskite structure of adequate composition appeared as key parameters. Heating rates and precise sintering temperature control also proved to be very sensitive parameters. Finally, the control of the atmosphere combined with optimization of the binder addition was found to be essential in achieving high sintered density. After significant development work, good reproducibility was shown for the production of pellet disc samples, with no metal bleeding, no micro cracks and even distribution of metal and ceramic phases in the bulk material. Other properties criteria included high density (>5.95 g/cc), high mechanical strength (>100 MPa) and high electrical conductivity (>100 $(\Omega cm)^{-1}$ at 960°C).

<u>Synthesis of Nickel-Ferrite ($NiFe_2O_4$)</u>

Commercially available nickel-oxide green powder purchased from Fisher Scientific and iron-oxide powder (metallic based 99.5%) purchased from Alfa Aesar were used as the raw materials for the fabrication of nickel-ferrite.

All cermet to be manufactured were to contain 83% of oxides (made of 51.7% NiO and 48.3% Fe_2O_3) and 17% metal. The nature of the metallic portion of the cermet is an important parameter and defines the three different families of cermet fabricated and tested, as described below.

The first step in the fabrication process was to prepare a nickel ferrite powder mix. This was done by mixing 51.7 % of NiO and 48.3 % of Fe_2O_3 and ball milling the mixture for 16 hours using stainless steel as milling media. The ball to powder ratio was kept at 5 to 1 and alcohol was used as a vehicle to create suspension.

After drying the ball milled powder mix at 90°C for 8 hours, the dry powder mixture was calcined at 1000°C for 2 hours. The objective of the calcination step is to promote the formation of a perowskite structure in the oxide phase of the cermet.

Technological parameters used for anode manufacturing

The synthesized $NiFe_2O_4$ powder was then mixed with the required metallic powders in order to meet the target compositions: composition #1 used a mixture of copper and silver powder (14%-3%); composition #2 used a silver coated copper powder containing about 18% of silver, resulting in the same proportion (14%-3%) of copper and silver in the cermet; and composition #3 contained 17% of copper (no silver).

Previously calcined $NiFe_2O_4$ powder was ball milled with the metallic powders for 16 hours using stainless steel media and alcohol (methanol) as the vehicle. Polyvinyl alcohol (PVA) in the amount of 3 wt% was added to the powder mixture. As for the initial ferrite powder preparation, the ball to powder ratio used was 5:1.

After mixing and ball milling the ferrite powder with the metallic powders, all compositions were dried in the oven at 90°C for 2.5 hours, followed by the sieving of the powder mixtures. At least 10 samples of each composition were pressed by cold isostatic pressing at a pressure of 220 MPa. The dimensions of the green samples were typically 14.0 mm x 13.5 mm x 108.1 mm.

Sintering was done in an electric resistant furnace (Sentro Tech SST-1700) under a constant flow of argon doped with different concentrations of oxygen. The sintering temperature ranged from 1100°C to 1400°C and sintering time was varied from 1 to 4 hours. After sintering, the density of the samples was measured (water displacement method), as a primary mode of quality control of the cermet produced. Samples with a density above 5.95 g/cc were used for further measurement of other physical properties or for the electrochemical testing.

Physical properties of the samples - Methods and measured values

Electrical Conductivity

Electrical conductivity of the sintered cermet samples was measured using the conventional four-point method, measuring the imposed potential across the sample. The results of the high temperature electrical conductivity measurements for the first composition are shown in Figure 1. The other compositions showed similar trends, with composition #2 ranging from 60-170 S/cm and #3 from 5 to 45 S/cm over the same temperature range as for #1. This can be compared to other researchers[6] that found the electrical conductivity of similar samples to range from 10 to 47 S/cm up to 960°C. Other work[7] saw the electrical conductivity range from 20-30 S/cm with a spike at 650°C to 275 S/cm that has not been duplicated by others.
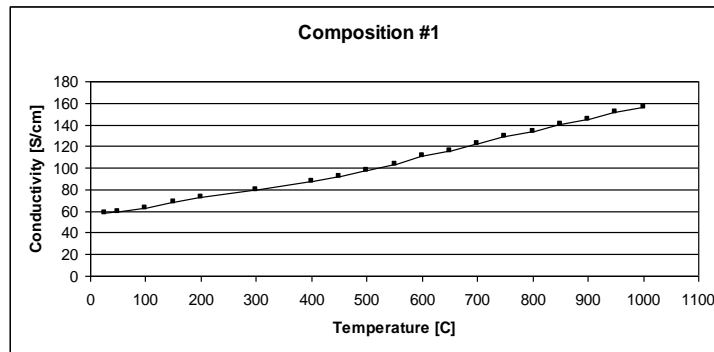

Figure 1: Change of electrical conductivity with temperature for Composition #1

Mechanical Strength

At least 5 samples of composition 1, 2 and 3 were machined into rectangular bars with dimensions 3mm x 4mm x 35mm and used to measure flexural strength of the sintered samples using the MOR 4 pt. method. The jig used to measure strength had the inner span of 14 mm and the outer span of 30 mm. The samples were broken under the conventional four-point bending configuration.
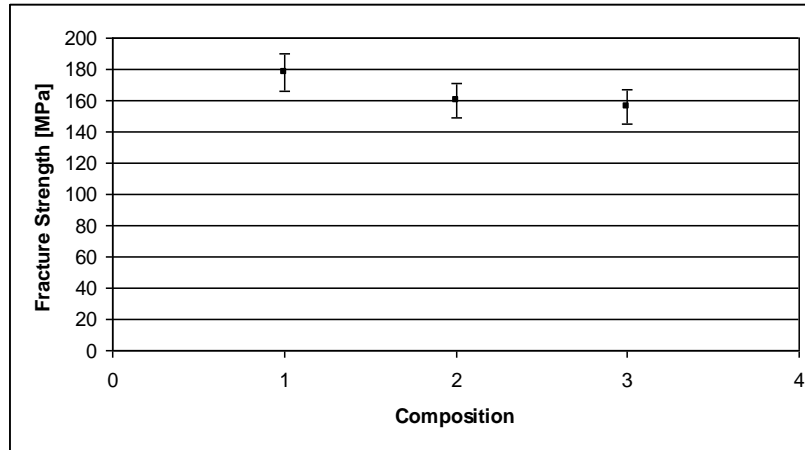

Figure 2: The average bending/flexural strength of the three different cermet compositions.

No significant difference in strength was measured for the three compositions. All compositions had flexural strength in the range of 140-180 MPa. This compares very well with other researchers[8] using similar cermets whose fracture strengths were found to be also between 140-180 MPa with a maximum at 5% metal of 176.4 MPa.

Microstructural characterization of nickel ferrite cermet samples

Each composition of cermet samples produced was observed under scanning electron microscope (SEM) in order to characterize their microstructure. The ferrite grain size, the metal component size and distribution, the homogeneity of the microstructure, the presence of porosity and micro-cracks, or other defects, were among the observations of interest. These are shown in Figure 3, Figure 4, and Figure 5 below.

In general, all the cermet samples observed show fine and homogenous microstructure. Some present open porosity, but in general the structure is fully dense. Typical grain size is in the range of 5 to 10 microns. The nickel ferrites have a variable composition, which is reflected by different intensity of gray on the back-scattered image (the darker is richer in Fe).

The metal phase size and shape seems to present more variability. The composition #2 using Ag coated copper flakes seems to produce coarser metal phase and generate more linear alignments. Taking into account the limited number of samples observed, this composition is the only one where cracks and linear defects have been observed. This might be detrimental to the stability of the cermet samples during electrolysis.
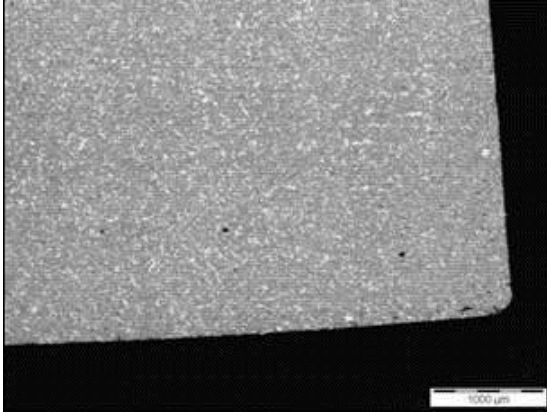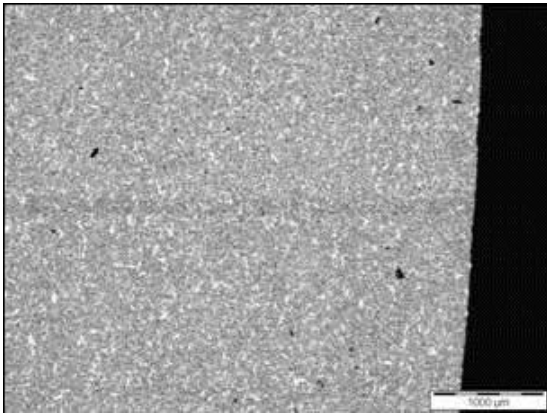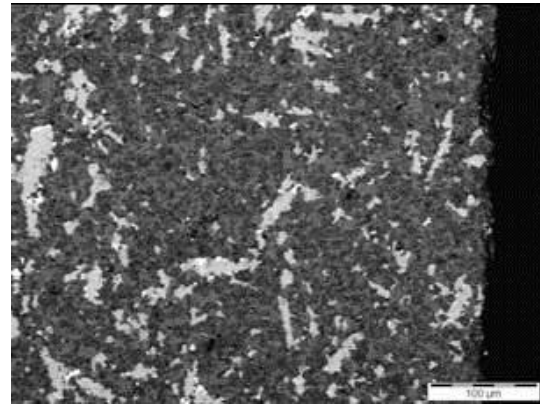
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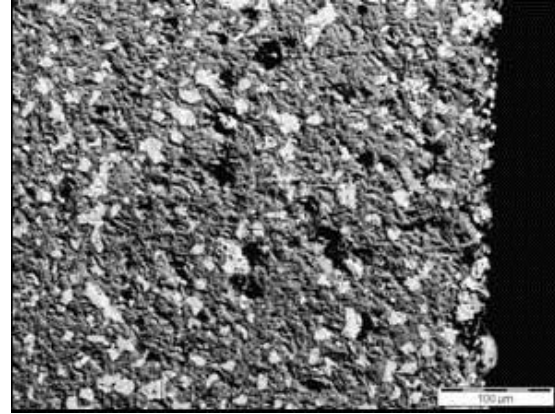
081020-1 S1 (500x)

Figure 3: SEM micrographs of the cermet, composition #1 (Ag + Cu)
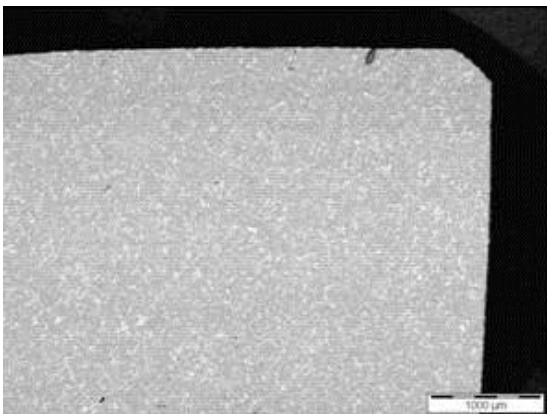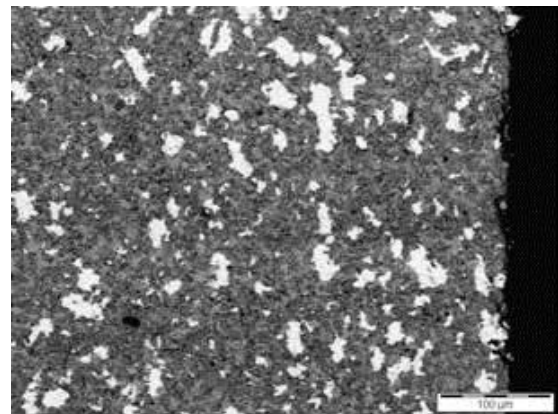

081112-1 S2 (50x)

081106-1 S1 (500x)

Figure 4: SEM micrographs of the cermet, composition #2 (Ag coated Cu)

081118-1 S2 (50x)

081114-1 S1 (500x)

Figure 5: SEM micrographs of the cermet, composition #3 (Cu)

Electrochemical measurements of cermet anodes properties

The objective of the electrochemical measurements was to determine the corrosion parameters of the three composition of nickel ferrite cermet to be used as anode for molten salts aluminum electrolysis. Open circuit potentials and corrosion currents were calculated from the electrochemical tests. The corrosion currents values were determined at different scan rates, after initial immersion of the cermet anodes in the electrolyte and after an anodic polarization. The three compositions of anodes were tested in duplicate.

Experimental

The 1 x 1 x 10 cm cermet sticks were cut at 4 cm lengths. A graphite holder was used in order to hold the 1 x 1 x 4 cm cermet anode. The aluminum reference electrode and a 1 mm Mo wire cathode were used in the cell for electrochemical characterisation of anode samples.

The alumina saturated electrolyte with a weight ratio of 1.13 was prepared by mixing 285.3g of Na_3AlF_6, 36.7 g of AlF_3 and 28 g of α-Al_2O_3. (8 wt%). A crucible made of 99.8% alumina was used for melting the salts mixture. The crucible was put inside a stainless steel well. The reactor was enclosed by a stainless steel lid where the electrodes were attached. This reactor was sealed and had argon cover. Tests were done at 960ºC - 970ºC.

Definition of the corrosion parameters

The corrosion resistance of the cermet anode is characterized by three parameters:

- ➢ The open circuit potential (O.C.P.), defined as the potential where there is no current
- ➢ The corrosion current after immersing the anode in the melt
- ➢ The corrosion current after anodic polarization of the anode

The corrosion current (A cm^{-2}) is defined as the anodic current density occurring at the thermodynamic oxygen evolution potential.

The corrosion of the cermet anode takes place in a potential zone between the OCP value and the potential of the thermodynamic oxygen evolution. A large OCP value will decrease the potential zone where the corrosion takes place.

The difference between the corrosion current value after immersing the cermet anode in the melt and after anodic polarization of the anode will characterize the ability of the anode to develop an anodic passive film that will decrease its corrosion.

In order to determine the corrosion parameters, the following electrochemical measurements were performed in sequence:
- ➢ Determination of the ohmic drop using impedance spectroscopy
- ➢ Linear sweep voltammetry at 5, 10, 20, 30, 40 and 50 mV s^{-1} right after immersion
- ➢ Determination of the ohmic drop
- ➢ Galvanostatic (anodic) polarization at +0.5 A cm^{-2} during 2 hours
- ➢ Determination of the ohmic drop
- ➢ Linear sweep voltammetry at 5, 10, 20, 30, 40, 50 mV s^{-1} right after anodic polarization

Linear sweep voltammograms were corrected for the ohmic drop before determining the corrosion current.

Results of electrochemical measurements

Figure 6 shows the linear sweep voltammogram (corrected for the ohmic drop) between 1.2 and 2.8 V, at 5 mVs^{-1} obtained after immersing the anode in the melt for sample of composition #1, which was the copper/silver mixture alloy. Figure 7 shows the same voltammogram in Tafel format. The OCP value was 1.433 V. For comparison, S. Pietrzyk[9] found an OCP value of 1.441 V for a cermet anode with a density of 4.59 g cm^{-3}, made of 42.9% NiO, 40.1% of Fe$_2$O$_3$ and 17% of Cu. The thermodynamic oxygen evolution potential occurred at 2.28 V. The corrosion current measured at the thermodynamic oxygen evolution potential was 0.072 A cm^{-2}. Between the OCP value and the thermodynamic oxygen evolution potential, we can see an anodic peak which was probably attributed to copper or silver oxidation.
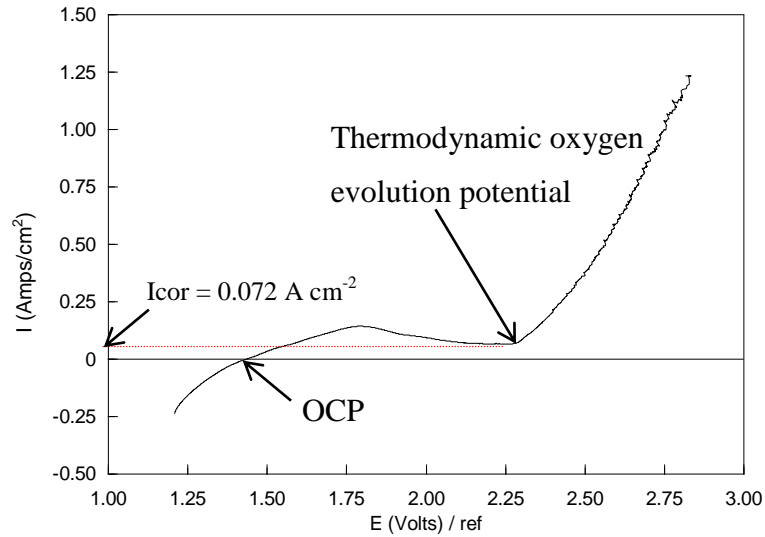

Figure 6. Linear sweep voltammogram obtained at 5 mVs^{-1}, composition #1
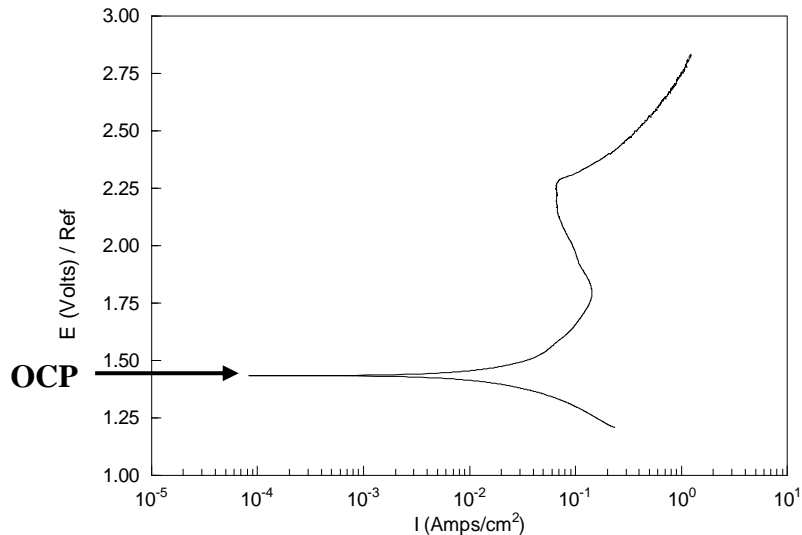

Figure 7: Linear sweep voltammogram plotted in Tafel format at 5 mVs^{-1}, composition #1

Error! Reference source not found. gives a compilation of all the OCP values and Table 2 shows the associated corrosion currents. It can be concluded that the cermet anode that gave the lowest corrosion current values was the one that was made by the addition of silver coated copper powder (anodes #2a and #2b). The highest corrosion currents values were obtained with the anode prepared with only copper powder. The composition using the mix of copper and silver powder show good performance, but did not reach the lowest corrosion obtained with the addition of silver coated copper powder. The difference in values of OCP between the types of anodes was very close, but the best (higher) OCP value was obtained with the cermet prepared with the silver coated copper powder as well. Finally, all of the types of cermet anodes were able to decrease their corrosion by forming a passive layer during an anodic polarization. The best protection was established by the anode with addition of the mixture of copper and silver powders (20%), followed by the anode prepared with addition of silver coated copper powder (15%) and by the anode prepared with addition of copper powder (12%). After protection, the cermet anode prepared with addition of silver coated copper powder remained the one with the lowest corrosion.

Table 1. OCP values of the cermet anodes tested

	OCP / V
Anode #1a	1.433
Anode #1b	1.431
Anode #2a	1.448
Anode #2b	1.449
Anode #3b	1.426

Table 2. Corrosion currents values in A cm^{-2} at different scan rates (mV s^{-1}) after immersion and after anodic polarization of the cermet anodes tested

	Icor / A cm^{-2} at 5 mV s^{-1}	Icor / A cm^{-2} at 10 mV s^{-1}	Icor / A cm^{-2} at 20 mV s^{-1}	Icor / A cm^{-2} at 30 mV s^{-1}	Icor / A cm^{-2} at 40 mV s^{-1}	Icor / A cm^{-2} at 50 mV s^{-1}
Anode #1a After immersion	0.072	0.086	0.11	0.126	0.139	0.153
Anode #1b After immersion	0.069	0.085	0.111	0.126	0.137	0.153
Anode #1a After polarization	0.063	0.071	0.088	0.098	0.111	0.12
Anode #1b After polarization	0.065	0.069	0.087	0.1	0.109	0.12
Anode #2a After immersion	0.056	0.066	0.086	0.107	0.121	0.133
Anode #2b After immersion	0.054	0.064	0.085	0.106	0.12	0.132
Anode #2a After polarization	0.05	0.059	0.073	0.087	0.094	0.108
Anode #2b After polarization	0.051	0.06	0.073	0.088	0.095	0.109
Anode #3b After immersion	0.109	0.123	0.157	0.182	0.202	0.216
Anode #3b After polarization	0.098	0.11	0.141	0.159	0.177	0.184

Short term electrolysis

The cermet samples manufactured were tested by using them in the performance of laboratory scale aluminum electrolysis. The 1 cm x 1 cm x 10 cm cermets were tested using a molten aluminum electrolysis cell. All three compositions were tested in duplicate during an 8 hour electrolysis with a current of 5A. The cermets' immersion depth was adjusted for having about 10 cm^2 working area of cermet anode, resulting in a target current density of about 0.5A/cm^2.

Electrolysis Set-up

The liquid aluminum cathode electrolysis cell consisted of a graphite crucible, alumina liner, and a small alumina crucible (Figure 8). At the bottom of the graphite container deep cavity was machined out in order to position the small alumina crucible inserted for control of the active cathode area.   The internal alumina liner was placed inside the graphite crucible to electrically insulate the walls of the crucible. The entire cell was enclosed by using a stainless steel (SS) well, collar, silicone o-ring, and a water cooled lid. About 6 g of Al shot (4-8mm) was weighed and placed between the liner and the central alumina crucible. According to ICP-OES analysis Al shots had the following composition: 470 ppm Fe, 184 ppm Ni, 103 ppm Cu, and 0.7 ppm Ag. Subsequently, 275 grams of cryolite mixture with a NaF/AlF$_3$ ratio of 1.13, supplemented with 8wt% Al$_2$O$_3$ alumina was charged into the crucible.
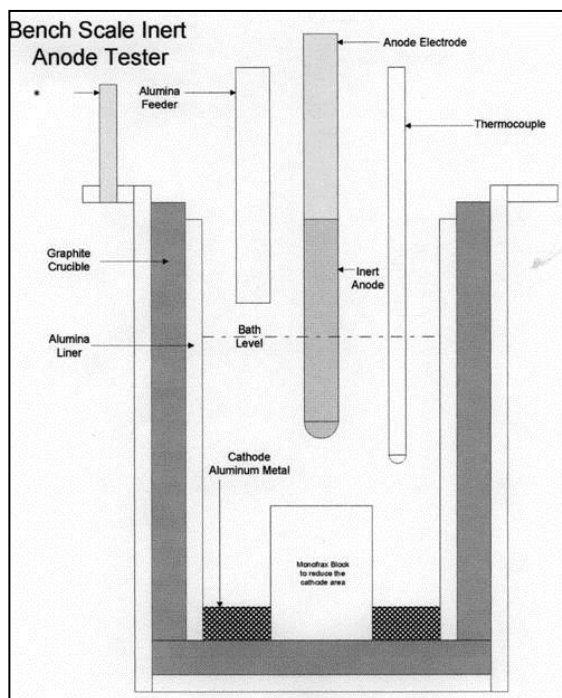

Figure 8: Electrolysis Cell Schematic

Neutron activation analysis of the initial bath composition showed that it was contaminated with 132 ppm Fe, 10.3 ppm Ni, <175 ppm Cu, and 2.73 ppm Ag. A 200ml/min flow of argon through the gas-in port was used during heat up to create an inert gas atmosphere inside the cell. Scanning electron microscopy (SEM) was performed on a slice of the cermet cut from one end of the sample tested, before the electrolysis, and on one slice of the working area after the electrolysis.
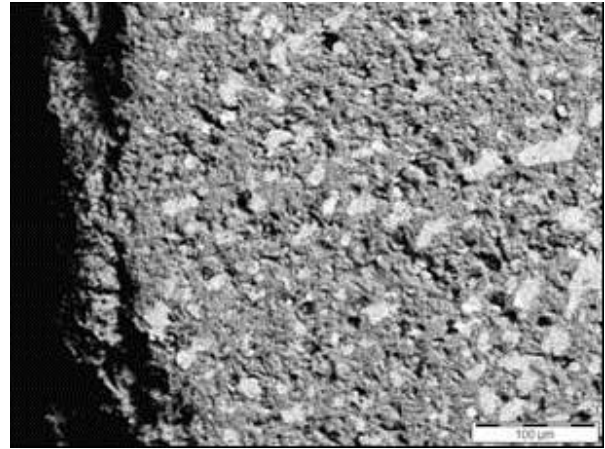
<u>Electrolysis Runs at 0.5A/cm^2 – Results</u>

Run #1 – Ag/Cu Powder Mix

The SEM micrographs (Figure 9, at 500x magnification) show that the fine, dense and homogeneous microstructure is preserved after 8 hours of electrolysis at 0.5 a/cm^2. After the test, a thin layer of about 25 microns at the surface of the sample seems to have lost its metallic fraction.
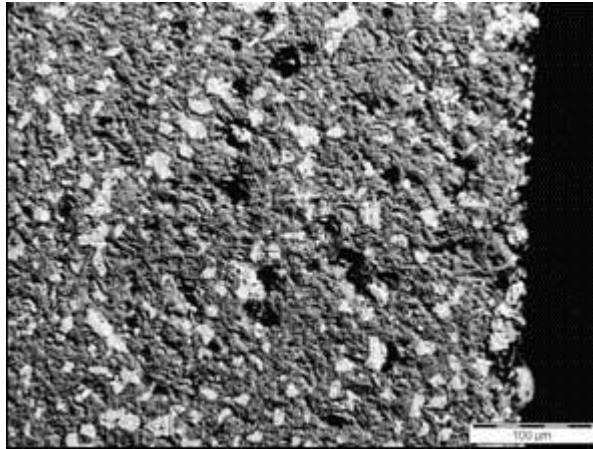
081020-1 S1 (500x)   081020-2 S1 (500x)

Figure 9: SEM micrographs of the cermet before (left) and after (right) the electrolysis run #1

Run #3 – Ag Coated Cu Powder

The SEM micrographs (Figure 10) show that the fine, dense and homogeneous microstructure is generally preserved after 8 hours of electrolysis at 0.5 a/cm^2. The bottom left micrograph (081106-1 S3 se400x) highlights a rare area showing a porosity defect before electrolysis (visible on the 50x picture at the top left). After the test, a layer of about 200 microns shows a loss of the metallic fraction all around the working anode area and the development of porosity in that area.
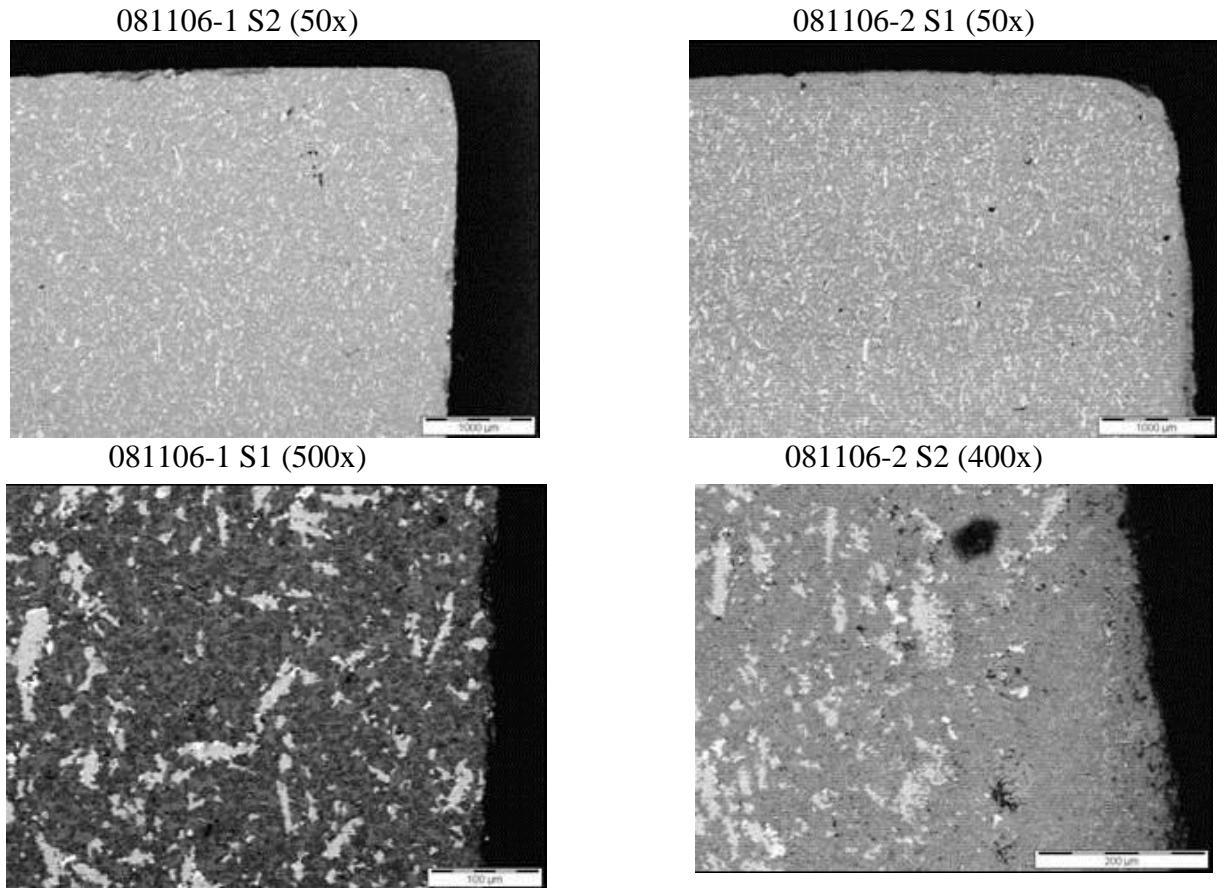
081106-1 S2 (50x)

081106-2 S1 (50x)

081106-1 S1 (500x)

081106-2 S2 (400x)

Figure 10: SEM micrographs of the cermet before (left) and after (right) the electrolysis run #3

Run #6 – Cu Powder

The SEM micrographs Figure 11 show that the fine, dense and homogeneous microstructure is preserved after 8 hours of electrolysis at 0.5 a/cm^2, except for a 200 to 300 micron layer where the metallics are gone. In that transition zone, the nickel ferrite seems to have loss cohesion (lower right picture). The metallic layer at the interface of the degraded cermet and the crust, was analyzed at multiple location and showed to be made of Cu, with traces of Ni.
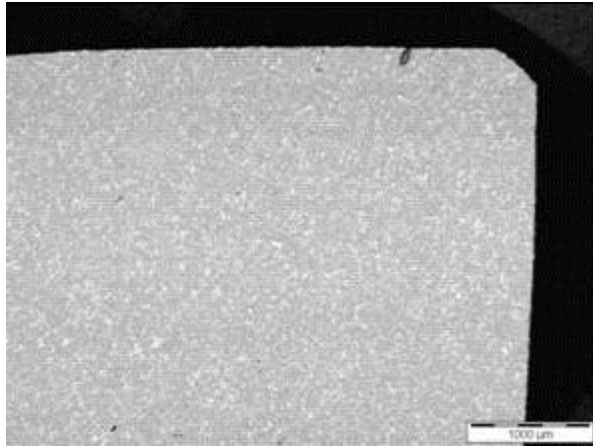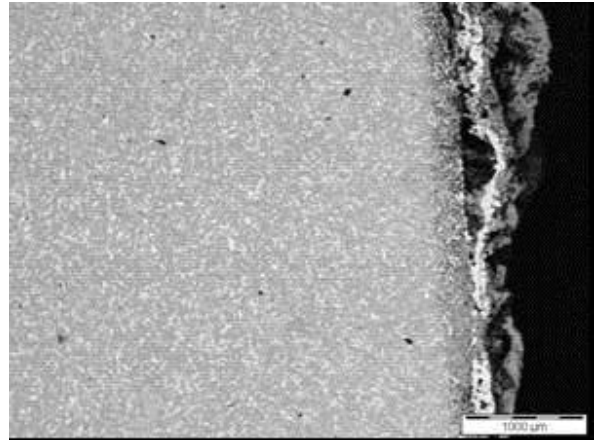
081118-1 S2 (50x)   081118-2 S2 (50x)

Figure 11: SEM micrographs of the cermet before (left) and after (right) the electrolysis run #6

Electrolysis at higher current density

The both Ag contained cermet compositions that showed the best performance in the 0.5A/cm^2 short term electrolysis trials and the electrochemical behavior study were then tested at two greater current densities: 0.65 and 0.8 A/cm^2.

The SEM micrographs (Figure 12) show a sample of *Ag/Cu Powder Mix* cermet with more pronounced porosity than after electrolysis at 0.5 a/cm^2 for the same composition. We can see a sharp transition between the dense part of the used sample and the layer with metal loss and the crust. The 150x picture shows the transition in the crust area. The 500x picture shows nickel ferrites particles, with variation in the gray intensity. The group of lighter grains is a high (Ni) nickel ferrite, which is rimmed by essentially pure Cu. The zone with complete metallic loss is about 150 to 200 micron thick on the sides and within 100 microns all along the bottom of the cermet anode.
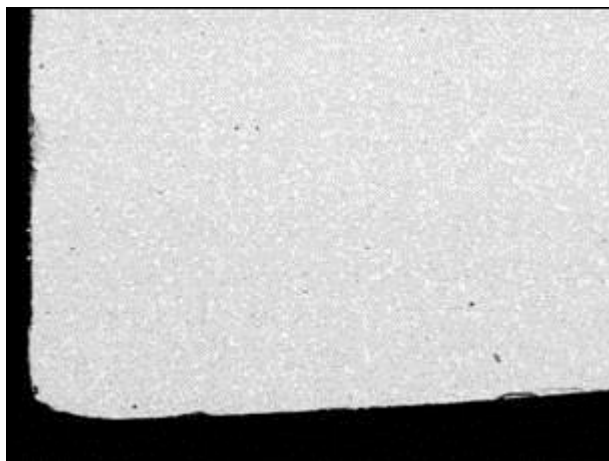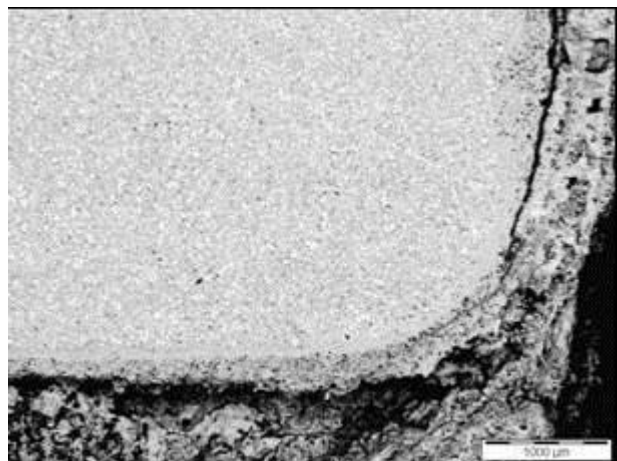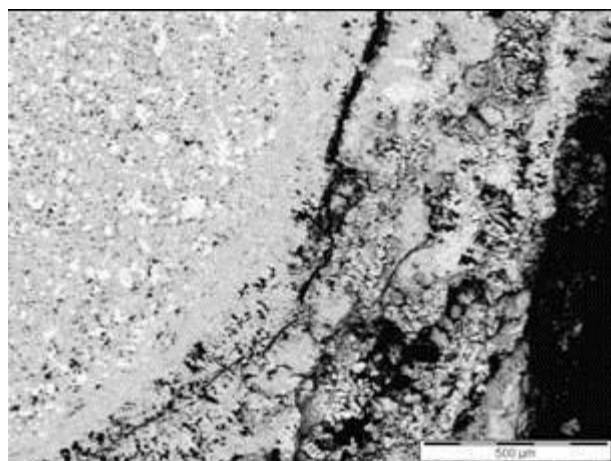

081203-1 S1 (50x)   081203-2 S2 (50x)
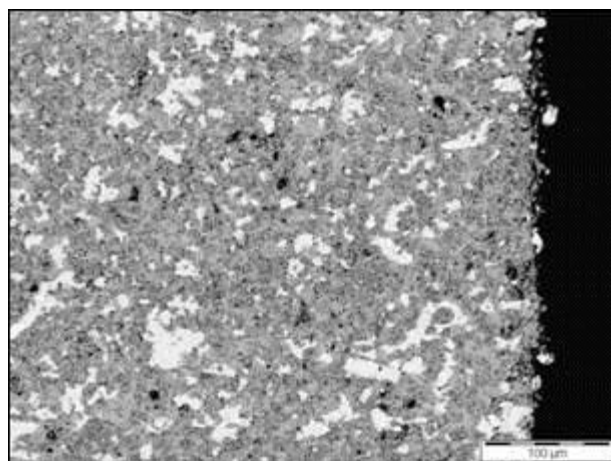
081203-1 S3 (500x)   081203-2 S4 (150x)

Figure 12: SEM micrographs of the cermet before (left) and after (right) the electrolysis run #10

Electrolysis results summary

Results for the electrolysis tests are shown in Table 3. It should be noted that, according to the measures taken, all three compositions showed the ability to protect themselves from catastrophic corrosion, following measurements before and after a 2 hour potentiostatic anodic polarization. In addition to the physical degradation, an important criterion for judging the performance of the nickel ferrite cermets is the composition of the aluminum produced. Short term electrolysis is certainly not sufficient for definitive judgment on the purity of the aluminum to be produced. In one way, impurities are diluted by the aluminum used as initial charge. As well, it is expected that the cermet degradation will be worst in the initial period of operation. As such, the micrographs are considered the best evidence of survivability of the anodes during electrolysis.

The loss of metal from the nickel ferrite matrix in the periphery of the sample, followed by de-cohesion of the matrix appears as the main degradation mechanism. The composition #3 (copper powder) is clearly the most sensitive to that mechanism. The nickel ferrite matrix loses its cohesion more easily. Surprisingly, after measuring the electrochemical performance indicating that the silver coated copper powder gives better resistance to corrosion, this composition seems to have a higher tendency for loss of its metallic fraction. However the nickel ferrite matrix stays fairly cohesive, potentially allowing the sample to stabilize. The best stability clearly goes to the cermet fabricated from the copper and silver powder.

The copper and silver powders have smaller average diameter than the silver coated copper powder but, more importantly, they have a much higher effective surface area (based on microscopic observations). This likely allows for a better small scale interaction with the nickel ferrite particles and a better distribution. The flaky and dense nature of the silver coated copper powder seems to promote linear defects and channeling of the metallics out of the nickel ferrite matrix.

Table 3: Results of short term electrolysis tests

Run #	Cermet Type	Cermet Density (g/cm³)	Current Density (A/cm²)	Al° Produced (g)	Fe (ppm) in salt	Ni (ppm) in salt	Cu (ppm) in salt	Ag (ppm) in salt	Fe (ppm) in Al°	Ni (ppm) in Al°	Cu (ppm) in Al°	Ag (ppm) in Al°
1	Ag/Cu	5.97	0.50	5.2	362	330	378	140	1499	1115	1701	273
2	Ag/Cu	6.10	0.50	4.5	94	49.9	200	20.0	2113	561	719	150
3	Ag Coated	6.08	0.50	4.9	128	64.9	<280	19.9	3102	2504	4070	680
4	Ag Coated	6.07	0.50	4.0	289	85.5	555	90.5	6221	244	2675	818
5	Cu	6.01	0.50	5.1	171	10.7	<150	0.42	9808	588	497	49
6	Cu	6.03	0.50	5.2	193	29.5	227	0.73	4163	442	2385	19
7	Ag Coated	6.00	0.80	10.9	719	1004	1965	470	5170	243	3295	1450
8	Ag Coated	6.08	0.65	9.2	269	122	302	39.1	2674	225	2847	959
9	Ag/Cu	6.08	0.65	6.9	112	59.0	<200	11.7	4293	471	3376	440
10	Ag/Cu	6.06	0.80	11.3	227	138	361	120	3491	454	2784	943

Conclusions

Cermet anode manufacturing procedure were developed which allowed to produce sample meeting properties criteria:

➢ Density of not less than 5.95 g/cm³ - *the best value achieved was 6.08 g/cm³ for Ag coated Cu and Ag/Cu mixed metal phase.*

➢ Electrical conductivity (at 960°C) of not less than 100 ohm⁻¹cm⁻¹ - *the samples of both compositions containing Ag met that criteria, with high temperature conductivity of over 150 ohm⁻¹cm⁻.*

➢ Mechanical strength not less than 100 Mpa - *all compositions had strength of 140 Mpa or more.*

➢ Absence of bleed out of the metal phase - *the samples produced did not show metal phase bleed out.*

➢ Absence of micro cracks - *the vast majority of the samples produced were free of microcracks.*

➢ Even distribution of metal and ceramic phases in the bulk material - *all micrographs showed homogeneous distribution of the phases.*

The electrochemical measurements performed allowed for quantification of the ability of each cermet composition to resist the chemical corrosion during high temperature aluminum electrolysis in a bath of molten cryolite. The cermet using the silver coated copper powder (Composition #2) showed the best performance, followed by the cermet made using the mixture

of copper and silver powder (Composition #1), while the cermet using only copper powder (Composition #3) showed the worst performance.

All compositions performed adequately during the 8-hour electrolysis. The increase in current density from 0.5 to 0.65 and 0.80 A/cm^2 had a drastic impact on the ability of the cermets to resist degradation. At 0.5 A/cm^2, the degradation was limited to a very thin layer and cermets may be able to withstand a much longer electrolysis run. The loss of metal from the nickel ferrite matrix in the periphery of the sample, followed by de-cohesion of the matrix appears as the main degradation mechanism. Based on micrographic observations, the best cermet composition seems to be the one using the copper and silver mix, followed by the one using the silver coated copper powder. Again the composition using only copper powder showed much more degradation at all current densities.

As an initial interpretation of these results, we believe that the morphology of the metallic powder used has a very important role to play in anode stability.

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