INDUCTION PLASMA SYNTHESIS OF Al-Ni-Mo INTERMETALLIC POWDERS AS PRECURSORS ALLOYS FOR ALKALINE WATER ELECTROLYSIS CATHODES

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Abstract

In order to optimize the powder composition used in the DC and RF plasma spray of cathodes for hot alkaline water electrolysis, there is a need to develop Al-Ni-Mo alloy powder technique which can produce low oxygen content, dense powders, which are of homogeneous composition in the range of produced grain size (-45 μm to +106 μm). The technique we have developped consists of the mechanical alloying of the powders, followed by inductively coupled plasma treatment of the resultant powder. Morphology, phase and chemical composition of the synthetized powders were studied using XRD, SEM and NAA.

1-Introduction

The objective of this work is the production of Al-Ni-Mo intermetallic powders with a minimum oxygen content, suitable for electrolysis cathode manufacture, by DC Low Pressure Plasma Spraying (LPPS) and RF Induction Plasma Spraying (IPS). Al-Ni-Mo intermetallics are energy efficient cathode materials for water electrolysis [1] with usable current density rising to values of 1 A/cm^2.

However, the intermetallics phase composition strongly influences the electrode performance. The

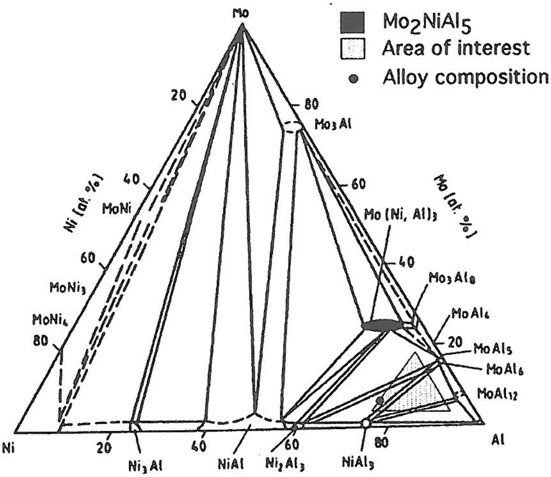

Fig. 1 Al-Ni-Mo phase diagram at 960°C [2]

Ni_2Al_3 phase provides a better Ni-Raney structure from the viewpoint of mechanical properties and electrode activity [3] and the presence of Mo enhance the electrocatalytic properties of the cathode. In order to prevent its leaching, Mo should be mainly present as the N phase, Mo_2NiAl_5. The presence of these two phases, coupled with a minimum oxide content, is a good compromise in order to achieve low overpotential values, operational chemical stability and to increase the cathode life-time, particularly where the electrolyser is in discontinuous operation.

As the composition of the Al-Ni-Mo intermetallics will be varied according to the domain of interest in Fig. 1, we developped a powder preparation technique by the mechanical alloying of the starting elements, followed by induction plasma spherodization, minimizing the powder oxydation, and elimining the pyrophoric nature of the mechanically alloyed powder. The smaller particle size fraction of this powder is to be sprayed by DC (LPPS), while the large size is to be processed by induction plasma spraying. Phase analysis, particle morphology and cross-section, as well as neutron activation chemical analysis were performed to assess powder composition homogeneity as a function of grain size.

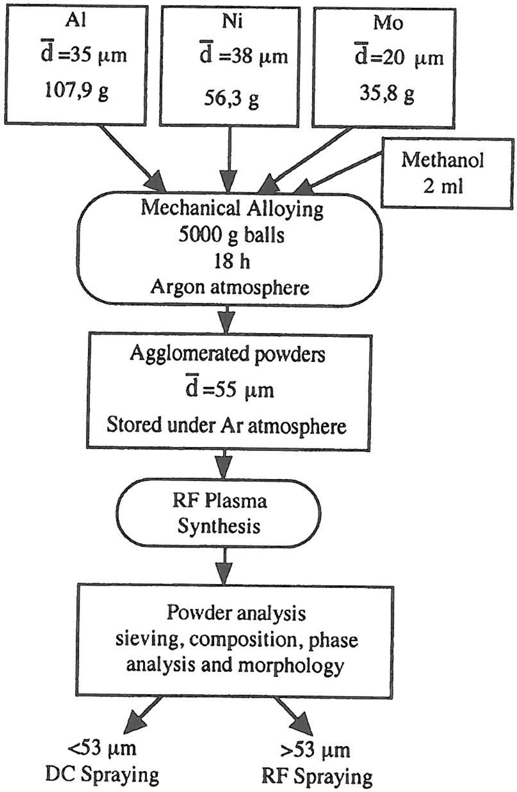

Fig. 2 Powders fabrication procedure

2-Experimental

There is a limited composition domain as shown in Fig. 1 where the N phase can be found. The first alloy prepared in this work corresponds to Kayser et al. results [1,4] which show that 53.9 wt% Al, 28.2 wt% Ni and 17.9 wt% Mo composition gave interesting electrochemical properties.

The synthesis procedure was divided into two steps, as shown in Fig. 2. These are: mechanical alloying and inductively coupled RF plasma spherodization. The plasma synthesized powder was then analyzed by XRD, SEM, NAA as a function of the individual size fraction.

a) Mechanical Alloying

The mechanical alloying process employed consisted of the mixing of Al, Ni and Mo powders in a conventional ball mill with the operating parameters as shown in

Fig. 2. The entire process was performed in an argon atmosphere to keep the powder's residual oxygen content to as low a value as possible.

A parametric study of the mechanical alloying process has been undertaken. One of the main variables used to generate powders in the desirable size fraction range (between 10 and 100 μm) is the methanol content of the alloying mixture.

After 18 hours of mechanical alloying, the powder grains are agglomerated, as a consequence of the ductility of the Al metal. No evidence of actual metallurgical alloying was found. The resultant powders were then placed into an automatic powder feeder under controlled atmosphere before induction plasma synthesis and spherodization.

b) RF Plasma Synthesis

The mechanically alloyed powders were fed at 20 g/min into a rf torch located at the top of the plasma reactor chamber as shown in Fig. 3. The injection probe was located at the center of the coil. Table 1 shows the spherodization process parameters used which minimized Al vaporization but still permitted the intermetallics to be synthesized. The exothermic synthesis reaction requires a long flight-path reactor to cool the now processed, powders. The plasma treated powders were collected at three downstream locations: at the bottom of the reactor, representing ~87 wt% of the feed material; at the bottom of the cyclone, ~3 wt%; and on the cyclone filters, ~10 wt%. Powders collected in the cyclone and on the porous metallic filters are ultrafine and contain more Al, due to its vaporization during synthesis. The densified powders, collected in the reactor, were classified and analyzed.

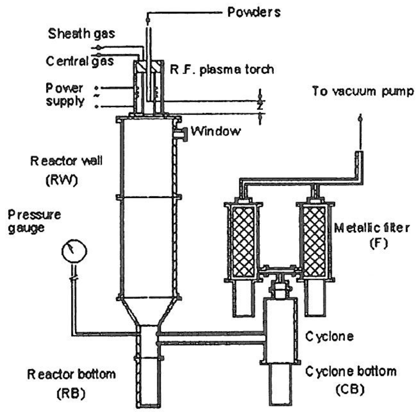

Fig. 3: Experimental apparatus

Table 1. Synthesis Parameters

Plasma gas (l/min STP)	
-Central (Ar)	47
-Sheath (Ar+H_2)	90+4
-Carrier gas (Ar)	4
Plate voltage (kV)	6,6
Plate Current (A)	4,0
Power (kW)	26,4
Pressure (kPa)	67

3-Results and Discussion

The reactor powders after extraction of the bulk sample were separated into 7 grain size powder fractions using Tyler sieves, from -45 μm to +106 μm. The bulk sample was used to perform phase and morphology analyses, whereas each of the 7 grain size fractions were analyzed using Neutron Activation Analysis (NAA).

a) Phase analysis

X-Ray Diffraction was used to determine the phase analysis. An example of the XRD patterns produced with Ni filtered Cu Kα radiation is presented in Fig. 4.

Various phases such as Ni_2Al_3, $NiAl_3$, NiAl and Mo_2NiAl_5 as well as the pure elements are identified, of these the major phase is Mo_2NiAl_5 which was also identified by Kayser et al. [1] in their gas atomized powders.

The as synthesized powder phase compositon is not entirely as predicted from the published diagram (Fig.1) The reason is that the in-flight powder grains are subjected to a post plasma quenching process, thus freezing in high temperature phases then predicted.

From that result, we expect that the Mo_2NiAl_5 phase domain is likely to extend to temperature beyond 960°C (Fig.1). The presence of unalloyed Al, Ni and Mo is a contribution of non agglomerated fine powders, and the product of preferential vaporization of Al.

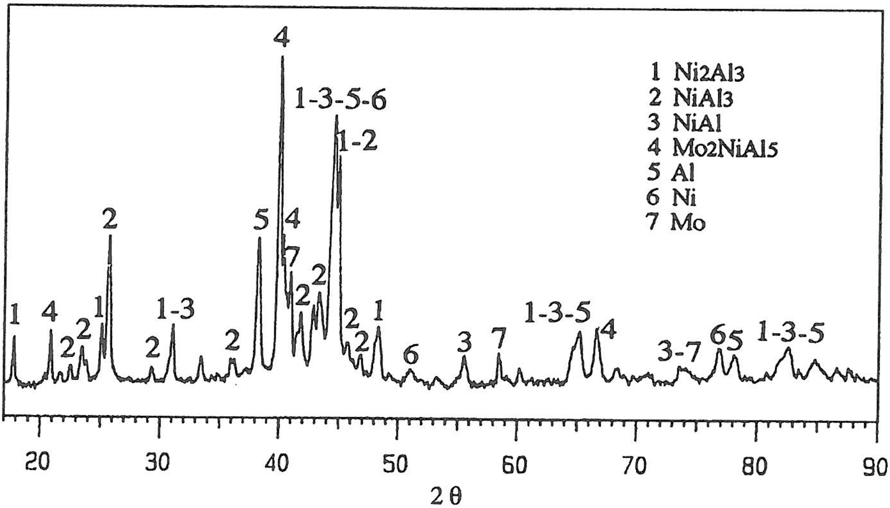

Fig. 4: XRD spectrum of synthetized powder

b) Morphology analysis

The bulk powder morphology, after plasma densification, is spherical. Back-scatterred electron (BSE) images were obtained with a scanning electron microscope on typical particle cross section (Fig. 5). Powder grains are dense, with solidified dentritic microstructure. The lighter areas correspond to high Mo content and the darker areas are the Al rich phases.

c) Quantitative elemental analysis

Each of the 7 size fractions of the plasma synthesized and densified powders were analysed by NAA. Fig. 6 shows the NAA results for Al, Ni and Mo components obtained as a mean of 3 assay samples. The typical accuracy of NAA method used is 5%, and the nominal target composition is in the error range of the measured values. These NAA analysis show that each powder class has the same composition. However the Al content in plasma synthesized powder is slightly below

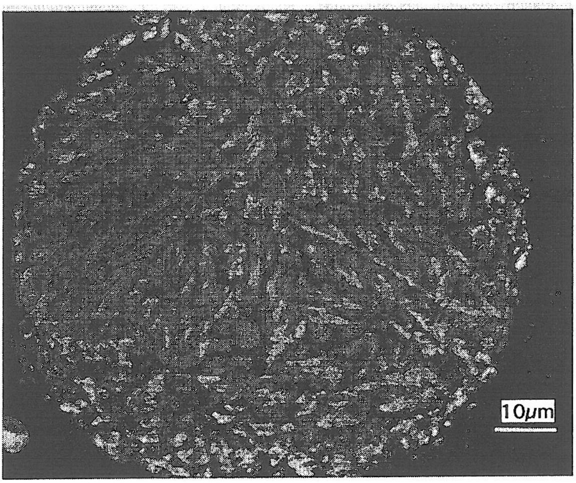

Fig. 5: BSE image of a synthesized powder particle

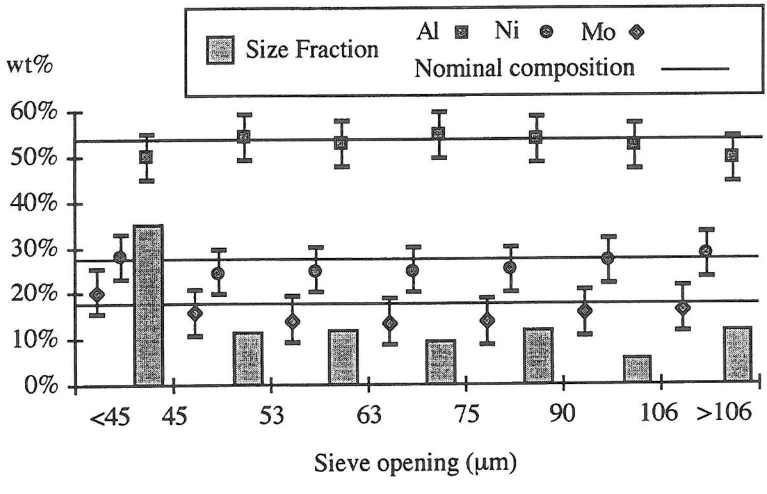

Fig.6: Neutron activation analysis and size fraction

the initial concentration for both the smallest (-45 μm) and the largest (+106 μm) fractions. The small fraction Al deficit is due to Al preferential vaporization and partially reports to the cyclone filter product, while for the large size powder, the slight Al deficit may originate from the mechanical alloying process itself.

Fig. 6 also shows that production of the -45 μm powder size fraction is the most prefered while the other powder sizes are almost uniformly distributed.

From the phase analysis, powder morphology and elemental analysis results, it appears that the mechanical alloying process, followed by RF inductively coupled plasma powder treatment, can produce powders of constant composition that may be used for the DC and RF plasma spraying of cathodes used in the hot alkaline water electrolysis. After assessment of the electrochemical properties, the nominal powder composition will be modified according to the area of interest as shown in Fig. 1., using the same powder preparation technique.

5-Conclusions

As the electrochemical properties of the intermetallics of Al-Ni-Mo are strongly dependant on their composition, there was the need to develop a simple and reproducible process to produce spray quality powder with the desired composition, so that it can be sprayed by DC and RF plasma process. The combination of the mechanical alloying technique, followed by RF inductively coupled plasma powder treatment, resulted in powders of homogenous composition, over the range of grain sizes, from 45 μm to 106 μm. The "as synthetized" powders are dense, low surface area material and can be readily handled in the air. The study of the as-synthesized phases suggest that particle quenching, as-occurs in-flight after the intermetallics exothermic formation, is mainly responsible for the final phase composition.

6-Acknowledgment

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7-References

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