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Properties of iron aluminide doped with a catalytic element for the electrosynthesis of sodium chlorate

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ABSTRACT

A new family of cathodic materials for the electrosynthesis of sodium chlorate based on iron aluminide doped with a catalytic element such as ruthenium has recently been reported. Materials are prepared in a metastable nanocrystalline state by milling at high energy, mixtures of Fe_3Al and Ru powder. This paper describes the physical, chemical and electrochemical properties of these new compounds.

1. Introduction

Sodium chlorate is the most important paper bleaching agent in the world. Its production by electrolysis of brine consumes large amounts of electricity. About 5500 kWh of electrical energy is required to produce 1 ton of sodium chlorate. For more than a decade, researchers have attempted to improve the energy efficiency of the process by finding more efficient electrodes than the steel or titanium cathodes that are presently being used in the industry. Indeed, most of the energy losses in the electrochemical process is caused by the high overpotentials of steel (≅900 mV) or titanium (>1100 mV) cathodes [1–3]. In terms of voltage, steel is better than titanium but steel suffers form severe corrosion problem during shutdowns when the cathodic protection is no longer present. Titanium is much better in terms of corrosion resistance but it can suffer from decrepitation by formation of titanium hydrides during the hydrogen evolution reaction.

Recently, we have reported a new family of efficient cathodic materials for this reaction which consists of an iron aluminide (Fe_3Al) doped with a catalytic element (Ru) [4]. For instance, the overpotential of $Fe_3AlRu_{0.2}$ is about 600 mV that is 300 mV lower than steel. The material does not absorb hydrogen and iron aluminide is known for its good oxidation and corrosion resistance. In fact, iron aluminide coatings have been developed as potential replacement materials for stainless steels in some applications [5]. Therefore, this new family of compounds offers great potentials for the application under consideration.

This article discusses the structural, thermal and chemical properties of these new electrocatalytic materials.

2. Experimental

The method of preparation of the metastable nanocrystalline powders has been described in details in a previous paper [4].

The thermal properties of the materials were characterized using a DSC/TG Netzsch STA 449C apparatus and a Perkin Elmer TGA 7 instrument. The instrument was equipped with a magnet to measure Curie temperatures. The X-ray diffraction data were obtained with a Siemens D-5000 apparatus and CuKα radiation. The microstructural investigations were conducted using a Hitachi S-3500 scanning electron microscope equipped with an EDX detector.

The electrochemical procedures have been described previously [4]. The overpotentials for hydrogen evolution at −250 mA/cm^2 were calculated from the electrode potential values, after correction for the ohmic drop and the reversible potential of hydrogen (−0.5805 V versus Ag/AgCl).

3. Results and discussion

3.1. Structural and physical properties

Fig. 1 shows a schematic representation of the atomic structure of Fe_3Al. In the ordered state, the alloy has the DO_3 structure. There are two Fe sub-lattices with two distinct magnetic moments (2.14 μ_B and 1.46 μ_B). The γ sites (0 0 0) has eight Fe near-neighbours while the α sites (1/41/41/4) has four Fe and four Al neighbours. The Al occupies the (1/21/21/2) sites and is surrounded by Fe atoms. As mentioned in a previous report [4], during mechan-

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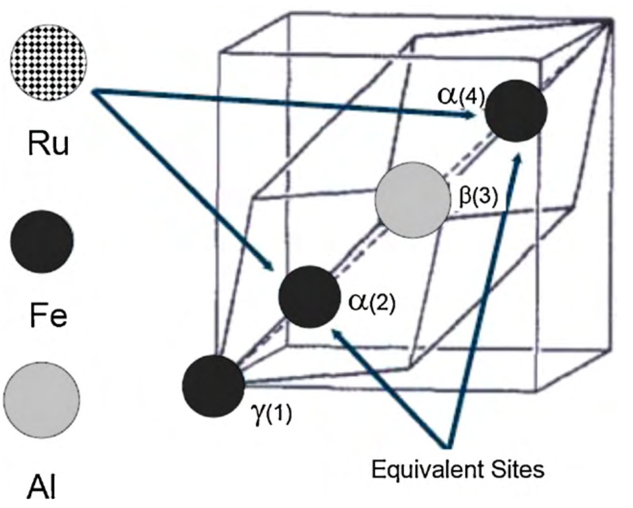

Fig. 1. Schematic representation of the atomic structure of Fe_3Al.

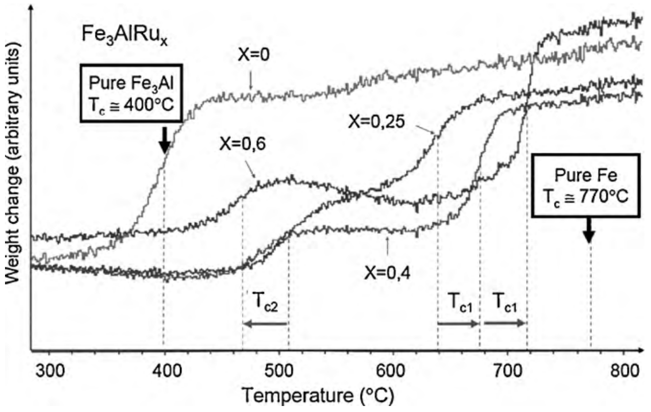

Fig. 2. Weight changes in arbitrary units as a function of temperature for Fe_3AlRu_x alloys where $x = 0$, 0.25, 0.4 and 0.6 measured on a thermo-balance equipped with a magnet.

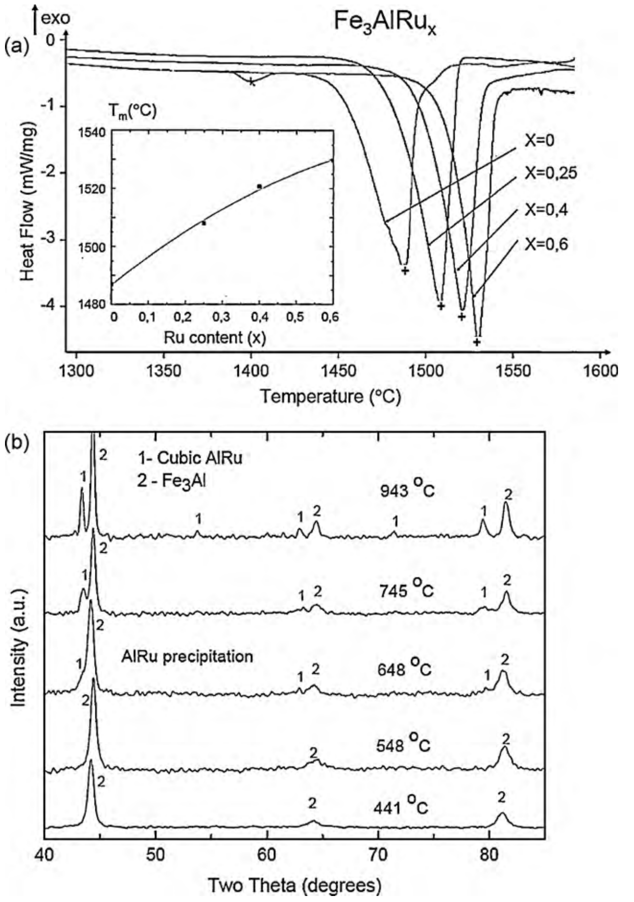

Fig. 3. (a) DTA traces showing the heat flow as a function of temperature for Fe_3AlRu_x where $x = 0$, 0.25, 0.4, and 0.6. The insert shows the melting point of the alloys as a function of the Ru content. (b) X-ray diffraction spectra of $Fe_3AlRu_{0.4}$ alloys annealed 1 h at different temperatures.

ical alloying, Ru substitutes preferentially Fe on the α sites in order to maximize Ru = Al pairs since the heat of mixing of Ru and Al is about four times the heat of mixing Ru and Fe.

When alloying occurs, the magnetic properties of the material change significantly. Fig. 2 shows the changes in the Curie temperatures (T_c) of mechanically alloyed Fe_3AlRu_x with increasing Ru content measured by mass change on a thermo-balance. Without Ru, Fe_3Al has a single T_c at about 400 °C. The Curie temperature splits in two when Ru is introduced in the lattice. For $x = 0.25$, the upper Curie temperature T_{c1} is about 640 °C while the lower Curie temperature is about 510 °C. With increasing Ru content, the upper Curie temperature moves continuously toward that of pure Fe (770 °C) while the lower Curie temperature decreases. This physical phenomenon is most likely related to a change in the chemical short range order associated with the increase number of Ru = Al pairs.

This tendency of Ru to form strong bonds with Al also affects the thermal properties of the alloys. In a first set of experiments to measure melting points, Fe_3AlRu_x alloys with different Ru content were heat treated to high temperatures at a scan rate of 20 °C/min. Fig. 3a shows the endothermic peaks associated with the melting of the compounds and the insert shows the variation of the melting points (T_m) with the Ru content. The melting point increases with increasing Ru according to the following equation:

$$T_m(x) = 1487 + 102.3x - 50.13x^2 \ (^\circ C) \tag{1}$$

In a second series of experiment to measure structural stability, mechanically alloyed $Fe_3AlRu_{0.4}$ compounds have been heat treated for 1 h at different temperatures (T_a) followed by a rapid quench to room temperature. Fig. 3b shows the X-ray diffraction spectra of the alloys after various heat treatments. At low T_a (441 °C and 548 °C), the alloy has a CsCl type B2 structure typical of disordered Fe_3Al compounds. Indeed, the high energy ball milling treatment introduces Ru into the material and chemical disorder. The structure changes from DO_3 to B2. As mentioned in a previous report [4], the introduction of large Ru atoms into the structure and the disordering process increase the lattice parameter of the compound. The lattice parameter increases by about 0.8% from 5.78 Å to 5.827 Å. At the annealing temperature of 648 °C which is close to the ordering-disordering temperature in the Fe_3Al system, atomic mobility is high enough and precipitation of the intermetallic AlRu compound is observed. At the highest annealing temperatures (745 °C and 943 °C), the cubic AlRu phase grows to a significant extent. The formation and precipitation of this AlRu intermetallic phase upon heating is consistent with the tendency of forming Al = Ru pairs during mechanical alloying as discussed previously. Detailed structural analyses of a mechanically alloyed $Fe_3AlRu_{0.4}$ compound heat treated for an hour at 1050 °C suggest that the following reaction takes place during the heat treatment:

$$\text{Metastable}Fe_3AlRu_{0.4} \rightarrow \ 0.4RuAl \ + \ 3.6Fe_{0.83}Al_{0.17} \tag{2}$$

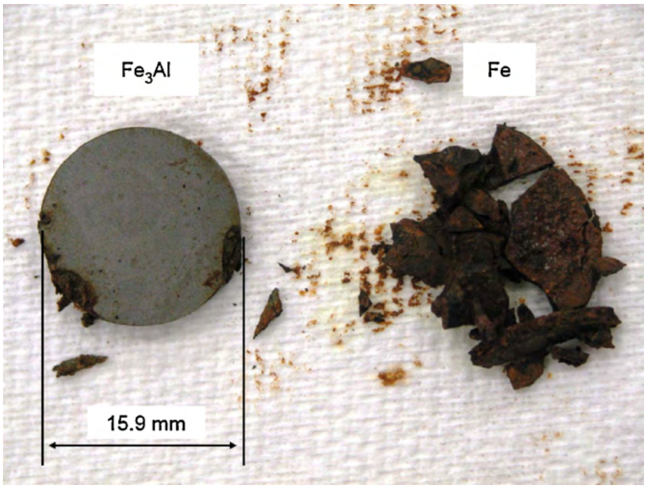

Fig. 4. Pellets made of Fe_3Al (left) and pure Fe (right) powder after 54 h of immersion at room temperature in a sodium chlorate electrolyte.

3.2. Chemical and electrochemical properties

Iron aluminide alloys are well known for their good high temperature oxidation and corrosion resistance which originates from the natural aluminum oxide layer (Al_2O_3) present on the surface of these materials [5]. A sample of Fe_3Al made in the form of a pellet by pressing powders has been immersed in a chlorate solution. Fig. 4 on the left end side, shows the appearance of the Fe_3Al pellet after 54 h of immersion in a sodium chlorate electrolyte while the right end side shows a similar pellet made of pure iron powder after the same treatment. The much better corrosion resistance of the iron aluminide pellet is obvious.

Similar samples of Fe, Fe_3Al and $Fe_3AlRu_{0.6}$ were studied in a potentiostat by scanning the current density from $-158\,mA/cm^2$ to $+158\,mA/cm^2$ and back to $-158\,mA/cm^2$ at a rate of 2 mA/s (see Fig. 5). The electrolyte was a standard chlorate electrolyte at 20 °C and a DSA was used as a counter electrode. At the starting point in the cathodic region (negative currents), H_2 evolution takes place on the surface of the sample. The (*I*–*V*) current–voltage curves for all samples cross the zero current density at about −1.0 V versus Ag/AgCl. In the anodic region, the first material to oxidize is Fe. The break point in the *I*–*V* curve of Fe at about 0.2 V is related to the formation of an iron oxide. A reddish color emerges from the surface of the electrode at that point. The *I*–*V* curve of Fe_3Al is shifted toward the anodic region by about 0.2 V compared to the *I*–*V* curve of Fe indicating that iron aluminide has a better corrosion resistance as observed in Fig. 4. However, in spite of the presence of the alumina layer which protects the surface to some extent, pitting corrosion occurs at about 0.4 V and iron oxide eventually forms as in the previous case. The fact that Fe_3Al is not that much better than Fe in the sodium chlorate electrolyte is understandable because of the aggressiveness of the electrolyte which contains high concentration of Cl^- ions. More interesting, however, is the behaviour of the $Fe_3AlRu_{0.6}$ electrode. Surprisingly, this material has much better corrosion resistance than the previous two electrodes. Anodic voltages in excess of 1 V are required before starting to observe some surface oxidation and degradation. The origin of this phenomenon is still unknown but we believe it may be related to the formation of a complex passive surface layer containing Ru which protects the surface from corrosion since all investigated Ru doped iron aluminide matrices [4] show better corrosion resistance than the Fe_3Al matrix itself.

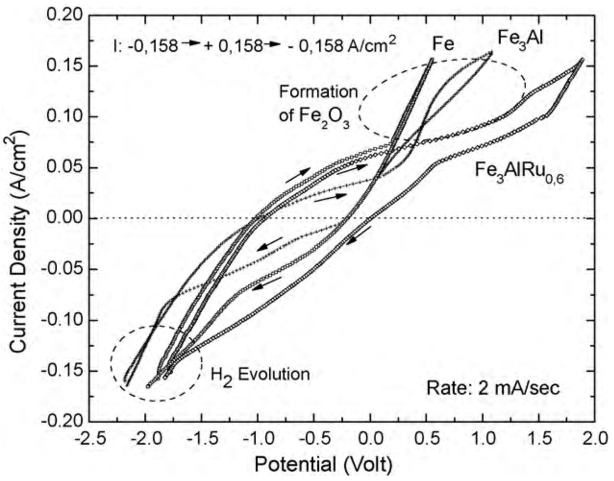

Fig. 5. Current density versus voltage traces measured at room temperature in a sodium chlorate electrolyte by varying the current at a rate of 2 mA/s for Fe, Fe_3Al and $Fe_3AlRu_{0.6}$ cathode samples. The counter electrode was a DSA anode.

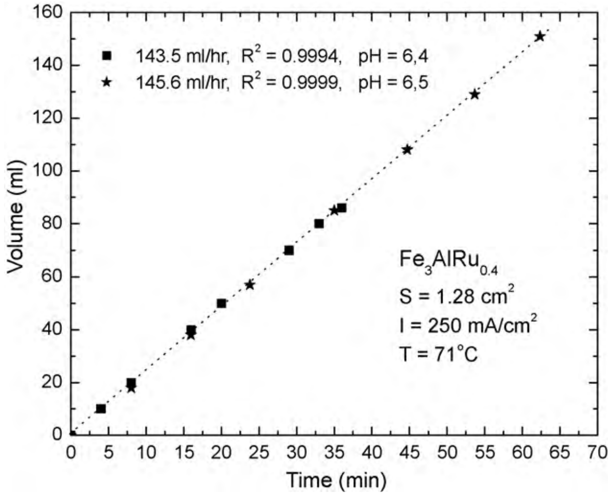

Fig. 6. Volume of hydrogen collected as a function of time from the surface of a $Fe_3AlRu_{0.4}$ cathode sample of $1.28\,cm^2$ of surface at 70 °C and polarized at $250\,mA/cm^2$.

In a previous report [4], we have shown that Fe_3Al doped with Ru can lead to substantial energy savings when used as cathode for producing sodium chlorate. After activation, a Fe_3AlRu_x with $x = 0.3$ electrode displays an overpotential of 575 mV which is at least 300 mV lower than that of an iron electrode (900 mV) and 600 mV lower than titanium. In [4] we have also shown that the structural parameters of the catalytic material such as the lattice parameter and the electrochemical properties such as the overpotential do not change much with the Ru content beyond $x = 0.3$. Therefore, in the rest of the paper, a $Fe_3AlRu_{0.4}$ alloy was chosen as being representative of the fully doped and activated materials and was further investigated in terms of current efficiency and long term stability.

Good current efficiency and long term stability are basic requirements for all industrial applications. The cathodic reaction associated with the chlorate production involves two electrons for each mole of hydrogen (H_2) produced.

$$6H_2O + 6\acute{e} \Rightarrow 6OH^- + 3H_2 \qquad (3)$$

The hydrogen gas evolving from a $Fe_3AlRu_{0.4}$ cathode sample of $1.28\,cm^2$ of surface at 71 °C and polarized at $250\,mA/cm^2$ has been collected and measured as a function of time to evaluate current efficiency. Fig. 6 shows the results. The slope of the straight line (~144 ml H_2/h) indicates a current efficiency of nearly 100%.

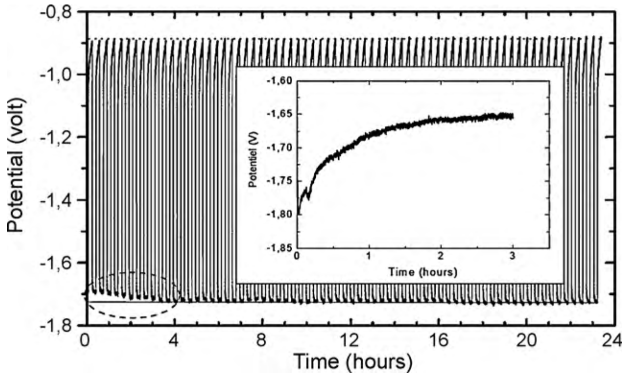

Fig. 7. Potential versus time for a $Fe_3AlRu_{0.4}$ cathode sample during 70 cycles of 10 min at 250 mA/cm^2 followed by 10 min in open circuit. The insert shows the evolution of the potential as a function of time when a constant polarization is applied after the cycling test.

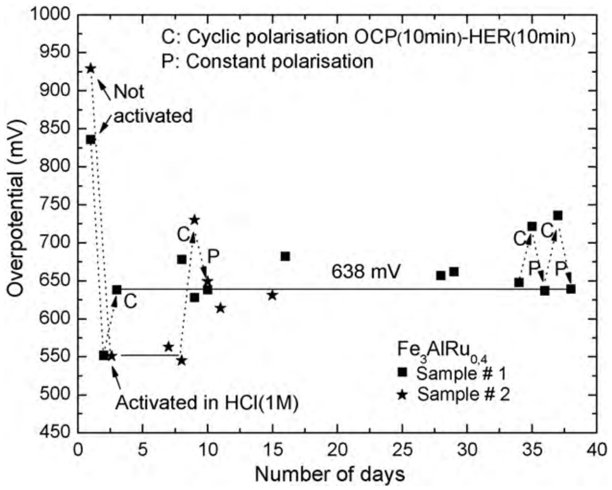

Fig. 8. Long term test showing the evolution in time of the overpotential of $Fe_3AlRu_{0.4}$ cathode samples over a period exceeding one month.

The stability of the $Fe_3AlRu_{0.4}$ electrode has also been investigated by long term continuous and cyclic polarization. Fig. 7 shows the evolution of the potential of a $Fe_3AlRu_{0.4}$ electrode during 70 cycles of polarization at 250 mA/cm^2 for 10 min (HER—hydrogen evolution reaction) followed by an open circuit for 10 min (OCP—open circuit potential). Such test, where H_2 is released during polarization and where corrosion occurs during open circuit, is usually more severe than the simple continuous polarization test [6]. As we can see in Fig. 7, the voltage stability is very good except for a small increase in potential (in absolute value) in the first 4 h of the experiment. However, this initial loss of performance, most likely associated with corrosion, is erased when the electrode is continuously polarized after the cycling test for a period exceeding 3 h (see insert of Fig. 7).

Finally, long term continuous polarization tests intermixed with cycling periods of OCP–HER have been conducted on two samples of $Fe_3AlRu_{0.4}$ for a duration exceeding one month. The results are shown on Fig. 8. We observe good stability and on average, the samples have exhibited overpotential of 638 mV which is significantly lower than the overpotential of commercial cathodes.

4. Conclusions

The insertion of Ru in the Fe_3Al matrix changes the properties of iron aluminide substantially. Two distinct Curie temperatures, a higher melting point and a tendency to form AlRu precipitates upon heating suggest important changes in the chemical short range order of the alloy. These changes are most likely associated with the formation of Ru = Al bonds in the alloy. The corrosion properties of Fe–Al–Ru in the sodium chlorate electrolyte are improved compared to Fe and Fe_3Al and the current efficiency for the hydrogen evolution reaction in the context of the production of sodium chlorate is basically 100%. The long term stability of Fe_3AlRu_x cathodes is excellent in conditions of constant and cyclic polarization.

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