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Low Temperature Reactivity of Aluminum Nanopowders with Liquid Water

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Abstract

In this paper, we present an experimental study of the isothermal reaction of aluminum nanoparticles with liquid water in the temperature range [45 – 95°C]. Gas phase chromatography and X-ray diffraction analyses have revealed that the reaction $\text{Al} + \text{H}_2\text{O}$ yields to a solid aluminum oxyhydroxide (AlOOH) and to hydrogen (H_2). Hence, in order to describe the macrokinetics of the oxyhydroxidation of aluminum, the H_2 gas release was measured as a function of time and temperature. Furthermore, the effect of salt water (3% NaCl or KCl in mass) compared to pure water was investigated. It is shown that the hydrogen release is preceded by an induction period corresponding to the destruction of the oxide film initially covering the Al particles. The induction and the maximal hydrogen flow rate follow an Arrhenius law. Activation energies are calculated. In opposition to the works about the corrosion of salt water, the kinetics of reactions are slowed down by the addition of chloride ions.

Introduction

According to scientists hydrocarbon energies will soon be short supply. In the present context it is primordial to try to develop alternative energies as renewable energies for medium and long term applications. The hydrogen production may partially meet consummation need. The hydrogen is an abundant element on earth but it is found in hydrogenated compounds (water, hydrocarbons...). Today most of the hydrogen is produced from oil and others fossil fuels. This paper presents an alternative method for hydrogen production from aluminum nanoparticles reacting with water.

Experimental

Aluminum Nanopowder

Aluminum is known to be among the most stable metals in terms of resistance to oxidation. This physicochemical property has thus promoted its use, pure or alloyed, in numerous industrial applications (transportation, construction, packaging...). However, the corrosion of aluminum and its alloys by water has been widely investigated [1]. Even if the corrosion of aluminum by water is remarkably slow or absent in normal conditions, it can be favored by increasing temperatures, the pH, or the salinity of the aqueous solution. Furthermore, it has been shown that nano-sized aluminum particles were particularly reactive with water [2,3]. Ultrafine aluminum powders (UFP) are produced since some decades yet. There are several methods, but the exploding wire method is the most wide-spread. By this process a strong electric current is sent through an aluminum wire which explodes; the vaporization/condensation so yields to nanoscaled spherical Al powders. The Al particles obtained is called *Alex* (Aluminum Explosive, commercial name) and have a set of unusual properties in comparison with the usual metal [4,5]. It was found that oxidation of *Alex* particles occurs at a lower temperature with a higher

rate of conversion. This is believed to be mainly due to the higher reactivity associated with greater surface area of the *Alex* particles. For this reason, Al nanopowders can be found covered with different sort of materials to prevent risks of self-ignition. Al nanoparticles used in our experiments are Russian commercial powders with a gaussian particles diameter distribution. The mean diameter is 100 nm and the full width at half maximum (FWHM) is 50 nm (Figure 1). This powder is passivated in air with a thin natural alumina coating (Al mass fraction=0.92, i.e. Al_2O_3 thickness= 1 ± 0.5 nm).

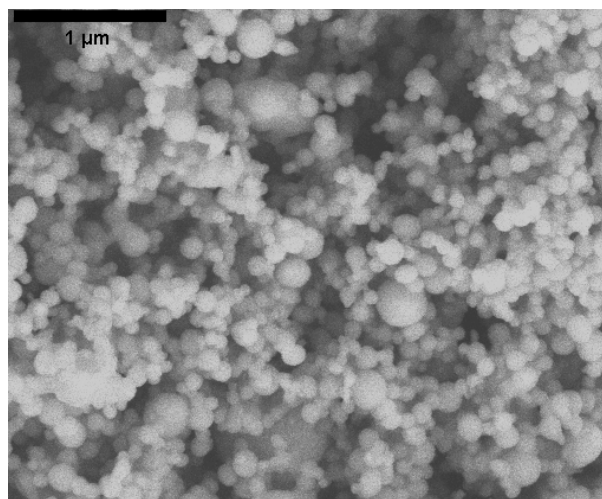


Fig. 1: Image of the Alex powder by scanning electron microscopy.

Experimental set-up

The aim of our experiments is to study the reaction $\text{Al} + \text{H}_2\text{O}$ with variations of two parameters: the temperature and the salinity of the solution.

The experiments were carried out in the temperature range [45 – 90°C]. Indeed, for temperatures higher than 45°C the reaction occurs significantly. On the contrary,

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above 90°C the reaction was too intense to measure precisely the gas release.

During the investigations, distilled water was used in a wide excess in order to limit the effect of the heat released by the reaction. Isothermal processes are required to determine the influence of the temperature on the gas release. The following mixture was chosen: 60 g of distilled water and 0.1 g of *Alex* powder (0.17% weight of Al).

Our saline solutions have been obtained by dissolution of KCl(s) and NaCl(s) crystalline powders. The molar concentration is 0.95 %, i.e. near the sea salt concentration.

Figure 2 illustrates the experimental installation. The evolution of gas was measured with a graduated test-tube (precision 1 ml) authorizing the measurement of volume according to time. The mixture temperature was also followed by a type K thermocouple connected to a thermograph. The procedure first consists to heat the 60 g of water in a closed system with a hot plate stirrer. The reactor is immersed in an oil bath. Two magnets allow the temperature homogeneity in the reactor and in the oil bath. When the temperature reached the required temperature, a mixture with 100 mg of *Alex* powder and 1 or 2 ml of water is prepared and then is introduced with a syringe in the reactor through a little orifice. According to Ivanov *et al.* [2] the 100 mg of powder should product about 120 cm³ of hydrogen. After each experiment the hydrogen gas volume is plotted as a function of time, and the maximal hydrogen flow rate is deduced by derivation of the curve. This parameter will characterize the kinetics of reaction.

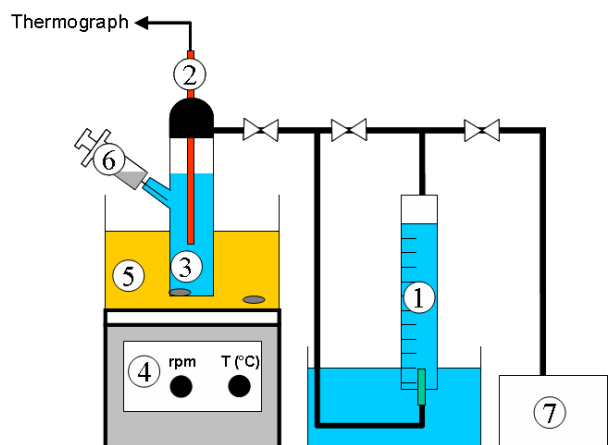


Fig. 2: Experimental set-up. (1) Graduated test-tube. (2) Type K thermocouple. (3) Reactor with 60 g of water. (4) Hot plate stirrer. (5) Oil bath. (6) Syringe with the mixture Al+H₂O. (7) Vacuum pump.

Results and discussion

The reaction between water and *Alex* powder at low temperature

The reaction between water and *Alex* powder in the temperature range [45-90 °C] involves the production of a gas and a white solid powder. The gas-phase chromatography revealed that the gas was dihydrogen

(H₂). The solid phases characterized by X-ray diffraction are aluminum oxyhydroxide AlOOH also called boehmite with small amounts of unreacted aluminum (Figure 3). The broadening of the peaks of AlOOH shows that the crystallites size is very small and are around 5-10 nm.

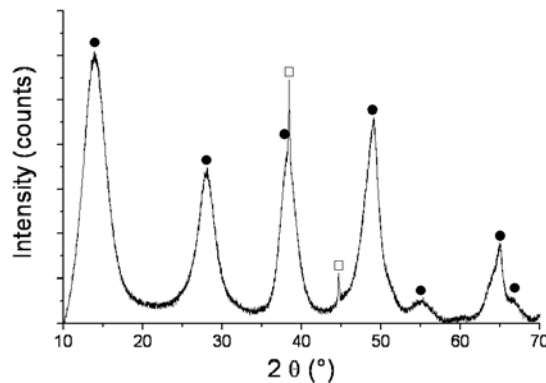


Fig. 3: Diffraction diagram of the Al+H₂O reaction residues. ●: AlOOH (JCPDS 00-049-0133); □: Al (JCPDS 01-085-1327)

Furthermore, observations with TEM of the aluminum oxyhydroxide phase show that the product is in the form of “thin layers” (Figure 4).

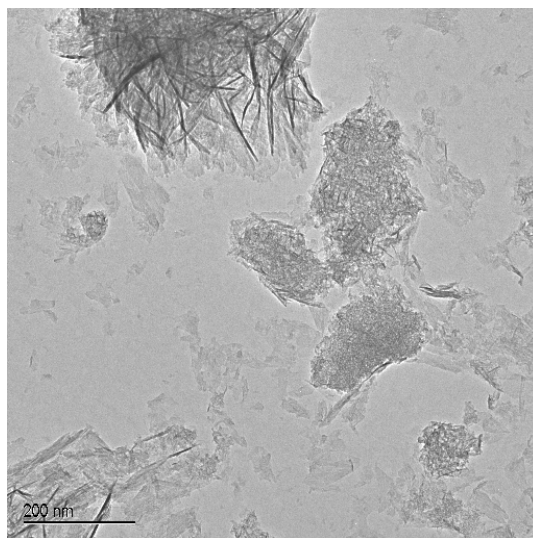


Fig. 4: Image of the solid product by transmission electron microscopy.

These analyses suggest that the aluminum powder conversion process in water for the temperature range [45-90 °C] is such as:



In theory a mass of one gram of aluminum should lead to a release of 1350 cm³ of H₂ at 20°C. A stoichiometric mixture has a composition of 57 % of water and 43 % of aluminum in mass proportion.

A significant number of experiments (85) have been performed and gathered in series corresponding to the study of the influence of the temperature on two kinds of solution: pure water and saline solution. Figure 5 illustrates the gas evolution process for different temperatures in pure water.

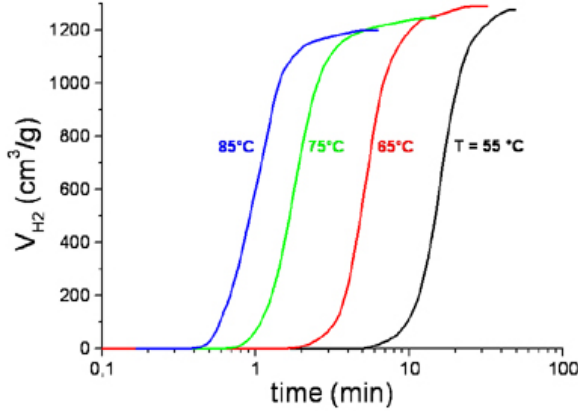


Fig. 5: Gas evolution process in water for different temperatures.

First it is observed that the reaction occurs after a period called induction period (t_{ind}) during which no gas release is observed [2,6]. Rat'ko *et al.* [6] suggest that this period corresponds to the hydration of the oxide film initially covering the aluminum particle surface. The oxide Al_2O_3 is hydrated which leads to the formation of the complex $Al_2O_3(H_2O)_x$ (where x is equal to 2 or 3). This compound is a porous oxide-metal composite material, so the hydration of the oxide film affects its homogeneity and continuously promoting the access of water to the metal surface and the occurrence of chemical reactions. The hydrated complex is then dissolved and finally precipitates in boehmite [8]. For each experiment the induction period was measured. Then the hydrogen degassing really starts with a "S shaped" gas evolution. It can be observed that the value of the volume theoretically released is not reached ($1350 \text{ cm}^3 \text{ H}_2/\text{g Al}$). Many reasons can be considered. The oxyhydroxidation of the powder may be incomplete; the presence of Al traces is revealed by the X-ray diffraction diagram (Figure 3). Furthermore, small amounts of Al powder stick on the walls of the syringe during injection and are estimated as 3% of total weight. Here the conversion rate is defined by the ratio of gas volume released during the reaction to the volume that should have been released in theory for the same mass of aluminum. However above 75°C the conversion rate tends to the unity. The conversion rate increases like the increase of the temperature.

As the gas release is measured as a function of time, its temporal derivative represents the hydrogen flow rate. The maximal gas flow rate has been considered. Our results are compared to those of Ivanov *et al.* [2] and Lur'e *et al.* [7] who worked on nanoparticles of aluminum. However precise characteristics of their powders are not given in their papers.

Induction period

The induction period is measured experimentally as the period between the injection of the powder in the reactor and the appearance of the first gas bubble. Figure 6 illustrates the variation of t_{ind} as a function of the temperature for pure and salt water. It is observed that the induction period follows an Arrhenius law for both of our solutions such as:

$$t_{ind} = t_{ind}^{\infty} \cdot \exp\left(\frac{-Ea}{RT}\right)$$

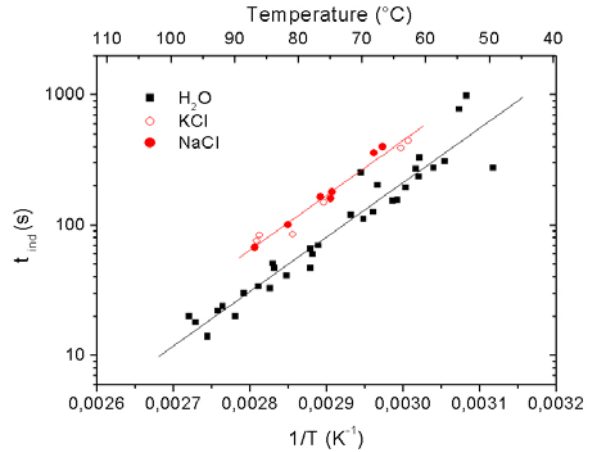


Fig. 6: Induction period as a function of the temperature for pure and salt water.

The characteristics (t_{ind}^{∞} , Ea) are summarized in Table I:

Solution	t_{ind}^{∞} (s)	Ea (kJ/mol)
H_2O	$6.41 \cdot 10^{-11}$	-79.9 ± 4.1
NaCl, KCl solutions	$1.12 \cdot 10^{-10}$	-80.4 ± 4.3

Table I: Arrhenius law parameters for the induction period.

Gas evolution

To characterize the reaction kinetics, the maximal hydrogen flow rate is considered. Figure 7 illustrates the variation of W_{max} as a function of the temperature for both solutions. Results from Ivanov *et al.* [2] and Lur'e *et al.* [7] also plotted even if our knowledge on their aluminum powder is very tight. According to Ivanov *et al.* [2], the maximal flow rate is expected to follow an Arrhenius law, similar to the induction period:

$$W_{max} = W_{max}^{\infty} \cdot \exp\left(\frac{-Ea}{RT}\right)$$

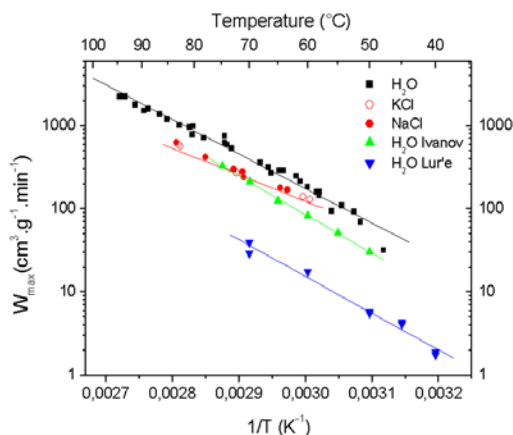


Fig. 7: Maximal hydrogen flow rate as a function of the temperature and for pure and salt water.

As for the induction period, the parameters of the Arrhenius law are summarized in Table II.

Solution	W_{\max}^{∞} ($\text{cm}^3/\text{g}/\text{min}$)	Ea (kJ/mol)
H ₂ O, present work	$1.90 \cdot 10^{14}$	77 ± 1.5
H ₂ O, Ivanov <i>et al.</i> [2]	$7.93 \cdot 10^{15}$	89 ± 1.5
H ₂ O, Lur'e <i>et al.</i> [7]*	$3.02 \cdot 10^{14}$	85 ± 4.3
NaCl, KCl solutions, present work	$7.70 \cdot 10^{11}$	62 ± 3.5

Table II: Arrhenius law parameters for the maximal hydrogen flow rate.

* for micrometric powders (3-4 μm)

Discussion

First it can be stated that the replacement of KCl instead of NaCl in saline solutions do not modify the reaction process. Indeed the kinetic parameters (t_{ind} and W_{max}) belong to the same curves, so it appears that K^+ and Na^+ ions played similar roles.

The remarkable point concerns the comparison between pure and salt water. It is clearly observed that the induction period and the maximal hydrogen flow rate in both solutions are different. t_{ind} in salt water is longer than in pure water, and W_{max} is lower in salt water than in pure water. Such results seem to suggest that saline solutions tend to slow down the reactivity of the oxyhydroxidation of Al nanoparticles. This observation is really surprising because it has been shown that salt water promotes the corrosion of pure or alloyed aluminum [1]. Indeed, aluminum corrosion is particularly sensitive to chloride solutions in the field of pitting corrosion [9,10]. In this kind of corrosion, chloride ions attack the defects of the oxide film and allow to the water to access directly the aluminum surface. The contradiction of our results with the whole community of aluminum corrosion is questionable and

no explanation can be reasonably given here. However, it has to be noticed that nanoparticles were used in this study, and it has been already observed that aluminum particles have unusual properties in comparison to micrometric particles or an aluminum bulk.

Concerning the influence of the temperature on the reactivity of aluminum nanopowders with pure and salt water, it is clearly shown that the induction period and the maximal hydrogen flow rate follow an Arrhenius law. It has also to be remarked that the *Alex* powder exhibits the most efficiency (lower t_{ind} and higher W_{max}) compared to previous works [2,3,7].

The activation energies for the induction period are the same for pure and salt water (80 kJ/mol). This value is close to the activation energy for the surface hydrolysis of amorphous oxide (71 kJ/mol). Vedder and Vermilyea [8] noticed that this value was also close to the activation energy of the proton diffusion in many oxides, and suggested that the proton diffusion may be an important step of the hydrolysis mechanism.

The activation energy for the maximal hydrogen flow rate is higher for pure water than for salt water (+20%). These results are in good agreement with [2,3,7]. However, the maximal hydrogen flow rate does not describe completely the kinetics of oxyhydroxidation of aluminum. As Ivanov *et al.* [2] suggest, the value of W_{max} corresponds to the main stage of hydroxidation that is without the decelerating phase ('S-shaped'). In this case, the kinetic process is similar to a zero-order reaction.

Conclusion

The temperature dependence and the influence of the salinity have been investigated for the reactivity of aluminum nanoparticles with water. It has been shown that the production of hydrogen is preceded by an induction period corresponding to the hydration-dissolution-precipitation of the oxide film initially covering the particles. This induction period is thermally activated ($E_a=80$ kJ/mol). The hydrogen released by the reaction (oxyhydroxidation) and characterized by W_{max} is also thermally activated with similar values of E_a found in the literature. Contrary to the literature on the corrosion of aluminum in salt water, the oxyhydroxidation of the nanopowder is slowed down in the presence of chloride ions.

Further work will be led to complete the investigation. Saline solutions with different concentrations will be tested to study the influence of the salinity on the kinetic parameters (t_{ind} , W_{max}). Al nanopowders with different particle sizing and/or coating will be also examined. Indeed, as the specific surface increases with the reduction of the diameter of particles, one expects to observe higher maximal flow rates for smaller aluminium particles. In conclusion, the influence of the pH also could be studied.

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