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EXPERIMENTAL AND ECONOMIC STUDY OF ALUMINIUM-GALLIUM ALLOYS AS A FUEL/CATALYST FOR HYDROGEN PROPULSION

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ABSTRACT

An investigation was carried out into the feasibility of using Al-Ga alloys as a renewable agent to produce hydrogen from water, following positive claims from a research group in the USA. The hypothesis was that pellets of Al-Ga would oxidise in water, resulting in hydrogen evolution which could be directly used in a fuel cell to power a vehicle. This paper reports on new experiments on the reaction of a range of compositions of binary Al-Ga pellets in contact with water. It was found that the reaction does not go to completion, resulting in only a fraction of theoretical hydrogen evolution, and that – contrary to research findings of others – gallium is not a passive catalyst and is also partially oxidised in water. A new proposal on the reaction mechanism is presented. Even if theoretical H_2 output was achieved, we show that the aluminium cycle is uneconomic and impractical, and that total CO₂ emissions per km travelled are significantly higher than those from an equivalent petrol engine. Guidelines for improved alloy design and optimum microstructure for renewable hydrogen production from water are suggested.

KEYWORDS: Carbon, Climate, Energy, Renewable

1. INTRODUCTION

With much uncertainty surrounding the world's reserves of cheaply available oil, there is currently great interest in alternatives to fossil fuel propulsion. The search is intensified by the need to combat climate change. Alternatives to oil should be carefully evaluated for their true potential to remedy the world's oil addiction and lower the world's carbon footprint.

Aluminium has been proposed as an energy storage method both for stationary and propulsive applications [1-8]. This is because of its very high specific energy density of 29.2MJ/kg [3]. It is also an attractive option because aluminium is already produced cheaply on a large scale, limiting the need for infrastructure.

The two methods of releasing the energy stored in aluminium are by the generation of hydrogen or by generating electricity from an aluminium battery. Both methods are, in theory, capable of powering a vehicle however only the use of aluminium to generate hydrogen was investigated in this paper. The generation of hydrogen *in situ* for propulsion purposes merits investigation because it obviates the need for hydrogen generation, transport and storage infrastructure. It is also safer.

Aluminium reacts readily with water at room temperature to produce hydrogen but the reaction stops due to the formation of a coherent oxide layer. The continual removal and or disruption of this adherent oxide layer is necessary for the reaction to proceed [8]. There are two main methods of generating hydrogen at room temperature. The first and most widely used method is to place aluminium in an alkaline environment [4,7,8]. A solution of sufficient pH will dissolve the oxide layer, facilitating hydrogen evolution.

The second method involves alloying aluminium with additives which disrupt the formation of an oxide layer [1,4,8-11]. These additives allow hydrogen to be evolved in neutral water at room temperature. This is appealing for hydrogen propulsion because there is not a requirement for toxic chemicals. Woodall [1,13] experimented with a liquid Al-Ga 98-2 weight% alloy and achieved theoretical hydrogen evolution. Woodall further claims solid alloys with 18, 28 and 80% Al evolved hydrogen although experimental results are not offered. This paper looks experimentally at aluminium-gallium alloys for hydrogen evolution and evaluates the environmental and economic consequences. The usefulness of aluminium as an energy storage method is also discussed.

2. EXPERIMENTAL

2.1 Experimental Method

The aluminium-gallium phase diagram is shown in Figure 1 [12].



Figure 1: Aluminium(α)-gallium(β) phase diagram [12]

If a fully liquid alloy of 35 wt% Ga is cooled below the liquidus a solid phase of gallium in an aluminium matrix appears first. This α -phase grows until below 26.6°C a solid pure gallium phase emerges. This β -phase appears in the grain boundaries.

The purpose of the experiments was to investigate Woodall's claims of hydrogen evolution from solid aluminium-gallium alloys [1,13]. Samples were prepared using commercial purity aluminium and 99.9999% pure gallium. Samples of different compositions were prepared using an induction furnace open to the atmosphere. The cast samples were cooled naturally in air. 1-2 gram pieces of these samples were cut off, weighed and placed in a test tube with 50 ml of water at room temperature for 25 minutes. The test tube was placed in a beaker with 500 ml of water to ensure an even temperature. The evolved hydrogen was measured by bubbling it through a graduated cylinder filled with water. The volume was compared to the theoretical volume possible of 1245ml/g aluminium [9].

2.2 Experimental Results

Figure 2 shows the results obtained.





The reaction proceeds according to equation 1 [4,9].

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$$
 (1)

Equation 2, as proposed by Woodall [1,13], does not occur.

$$2Al + 3H_20 \rightarrow Al_20_3 + 3H_2$$
 (2)

The quantity of hydrogen evolved was very low. Kravchenko et al. [11] reported yields between 6-100% from aluminium powders alloyed with Ga, In, Sn and Zn. Similar results were obtained by others [4,9,10]. The two differences between their approaches and those tried here are that they used powders which had not been exposed to the atmosphere.

The use of powders greatly increases the surface area on which the reaction can occur. The storage and production of powders in inert atmospheres means that the exposed surface can not react with oxygen prior to placement in water. Fan et al. [10] and Kravchenko et al. [11] reported that after the activated powders were exposed to air they immediately turned black and almost lost their reactivity. The production and storage of powders in inert atmospheres increases manufacturing costs. Storage of powders in an inert atmosphere may not be practical throughout the supply chain.

Woodall [1,13] proposes the use of aluminium-gallium pellets exposed to the atmosphere as opposed to inert powders. Pellets were also used to obtain the results in Figure 2.

2.3 Experimental Mechanism

The Al-Ga pellets were exposed to the atmosphere prior to reaction. The surface did not change colour as reported in [10,11]. The reason suggested for this is that gallium does not react

with oxygen at room temperature [14]. Any aluminium at the surface can be expected to react with oxygen to form a localised aluminium oxide layer. This was supported by the observation that hydrogen evolved only from certain spots on the surface of the pellet.

There is a large difference in standard electrode potential between aluminium and gallium of 1.1V [15]. Hence because gallium is cathodic to aluminium, micro-galvanic cells are suggested to form between exposed surface gallium and neighbouring aluminium. The hydrogen is evolved at the surface gallium which explains the evolution of hydrogen only at certain points on the pellet. Intergranular corrosion would thus be expected between the cathodic pure gallium β -phase in the grain boundaries and the anodic α -phase. Intragranular corrosion is suggested to occur by selective leaching. Evidence of these mechanisms is exhibited by Figure 3:



Figure 3: SEM image of corrosion of reacted Al-Ga 79-21wt% pellet

The dark brown precipitate that is seen to form is suggested to be gallium suboxide (Ga_2O) . Of the possible oxides and hydroxides the precipitate could be, gallium suboxide is the only compound with a dark brown colour [14]. The only pathway in the literature for the formation of gallium suboxide is given by equation 3 [16].

$$2Ga^+(aq) + 2(0H)^- \rightarrow Ga_2O \downarrow + H_2O \tag{3}$$

The dark brown precipitate was left in solution for a week and its colour turned snow white. This snow white precipitate is GaO(OH). This is suggested to occur according to equation 4 because gallium suboxide is unstable in water as reported in [16].

$$Ga_20 + 4(0H)^- \to 2Ga0(0H) + H_20$$
 (4)

Gallium suboxide evolves very slowly from pure gallium in water [16]. The reason it forms so rapidly must be due to the presence of aluminium. A possible reason is that the heat of formation of aluminium hydroxide [14] activates the reaction of gallium and water according to equations 5-7.

$$\begin{array}{ll} Al \to Al^{3+} + 3e^{-} & \Delta E^{\circ}V = 1.1V & \Delta H^{\circ}f_{25^{\circ}C} = -487kJ/mol & (5) \\ Al^{3+} + 3(OH)^{-} \to Al(OH)_{3} & \Delta H^{\circ}f_{25^{\circ}C} = -1535kJ/mol & (6) \end{array}$$

$$Ga + H_2 O \to Ga^+ + 0.5H_2 + (OH)^-$$
 (7)

With the precipitation of the surface gallium as gallium suboxide, the reason the reaction is seen to slow down dramatically is suggested to be the resulting lack of a cathode at the surface. After the gallium precipitates off, the underlying aluminium reacts to form an aluminium hydroxide layer. Hydrogen was still observed to evolve very slowly after the initial 25 minutes. The suggested reason for this is that the aluminium hydroxide layer is not fully coherent and may be destabilised by the presence of gallium.

In Figure 2 there is increased evidence of corrosion around the grain boundaries where the pure gallium β -phase was before precipitating off. This suggests that the main mode of corrosion is intergranular corrosion. In choosing an alloy, this indicates that an element or compound which is both cathodic and insoluble in aluminium may by optimal for hydrogen evolution. This may be the reason that the Al-Ga-In-Sn alloy used by Woodall [13] is effective – the Ga-In-Sn compound is insoluble and resides in the grain boundaries.

3. ECONOMICS

3.1 Aluminium fuel loop

The fuel loop would consist of separating and regenerating the spent fuel into fresh charge. A fuel loop for a general additive is considered. This is shown in Figure 4.



Figure 4: Aluminium fuel loop

3.1.1 Fuel loop energy input

The majority of the energy input would consist of reprocessing aluminium hydroxide into fresh aluminium and this element of the fuel loop is discussed. The worldwide average embodied energy of virgin aluminium is 224.1MJ/kg Al [17]. The fuel loop would include all the energy consumption associated with virgin aluminium apart from the mining of bauxite and the early stages of the alumina refining process. The bauxite mining process accounts for 0.5% of overall energy consumption and the refining process accounts for 11.3% [18]. Calcination of the aluminium hydroxide into alumina is the only stage of the refining process which would be necessary. This accounts for approximately 75% of the energy input to the refining process [19]. The fuel loop thus requires 96.7% (100 - (11.3*0.25) - 0.5) of the energy input to virgin aluminium or 216.7 MJ/kg Al (224.1*0.967). The energy density of aluminium is 29.2MJ/kg. This gives a maximum recycling energy efficiency of 13.5% ((29.2/216.7)*100).

Yang and Knickle [2], in computing the fuel loop energy input, use the figures for the thermodynamic minimum required. They apply a practical discount to these figures and proceed to use a recycling energy efficiency of 32% in their calculations. The use of thermodynamic equations neglects all the other energy and raw material inputs to the recycling process. The use of a real world embodied energy approach is considered more accurate.

Woodall's paper points to a recycling energy requirement of just 54MJ/kg Al. This uses the erroneous assumption that the byproduct is alumina, not aluminium hydroxide. It similarly does

not include the other energy inputs. It also assumes the use of a zero feedstock energy source for smelting such as hydroelectricity. 50% of the smelting electricity worldwide comes from these zero feedstock energy sources [18]. The worldwide average embodied energy figure accounts for this reduction in thermal energy requirement. Due to aluminium's fungibility a worldwide average is considered more accurate from an energy accounting perspective than using a particular smelter's figures.

3.1.2 Fuel loop carbon footprint

The fuel loop carbon footprint consists of all the greenhouse gases emitted from all activities associated with converting aluminium hydroxide into aluminium. The worldwide average carbon footprint of virgin aluminium was found to be 10.512kg CO_{2e}/kg Al [20]. From this 0.026kg CO_{2e}/kg Al is attributable to mining and 1.482kg CO_{2e}/kg Al for refining [20]. Of the refining emissions, 92% are due to calcinations [20]. Thus the fuel loop carbon footprint is 10.367 kg CO_{2e}/kg Al (10.512 – (1.482*.08) – 0.026). For carbon accounting purposes a worldwide average is most accurate, but if a clean smelting energy source is assumed, the footprint drops by 5.330kg [20] to 5.037kg CO_{2e}/kg Al. This substantial carbon footprint is due to the emissions from the calcining fuel, anode production and per fluoro carbons emitted during smelting [20].

3.2 Energy consumption per kilometre

The main fuel that aluminium is competing to replace is gasoline. The European Institute for Environment and Sustainability (IES) conducted a study comparing the performance of a wide range of fuels assuming the same vehicle performance metrics and the same drive cycle [21]. The gasoline vehicle consumed 2.1MJ/km on a well-to-wheels basis.

A hydrogen vehicle was analysed also and found to consume 7g H₂/km [21]. One kilogramme of aluminium yields a stoichiometric maximum of 111.2g H₂ [4]. One kg of aluminium is thus considered to last a maximum of 15.9km (111.2/7) for comparison purposes. From section 3.1.1 the energy consumption is a minimum of 13.6MJ/km (216.7/15.9).

3.3 CO_{2e} emissions per kilometre

The same gasoline vehicle was found to have a carbon footprint of $160\text{gCO}_{2e}/\text{km}$ on a well-to-wheels basis [21]. From sections 3.1.2 and 3.2 the carbon footprint for hydrogen derived from aluminium would be $652\text{g CO}_{2e}/\text{km}$ ((10.367/15.9)*1000) on average. If a zero feedstock source such as wind, solar or hydroelectricity for smelting is used, this drops to an average of 317g CO_{2e}/km ((5.037/15.9)*1000).

3.4 Gallium availability

Gallium is produced in very small quantities as a byproduct from alumina production each year. Total worldwide production in 2008 was 95 tons [22]. Woodall [13] proposes a 95-3-1-1wt% Al-Ga-In-Sn alloy. Kravchenko et al. [11] noted that if the powders were devoid of gallium, minimal hydrogen was evolved. Gallium is clearly a crucial ingredient for hydrogen evolution in neutral water.

The aluminium requirement for fuel is 62.9g/km travelled (1000/15.9). If a 3wt% gallium alloy is assumed, the gallium requirement is 2g/km ((3/95)*62.9). Kilometres driven per year vary by geographical location but a reasonable figure is 15,000km/year for a passenger car [23]. The gallium requirement is then 30kg/car/year ((2*15000)/1000). If all of 2008 production was used for this purpose, it would support 3200 cars (95000/30). Even if the gallium was recycled 10 times a year, this would only provide for 32,000 cars. Gallium is only produced as a byproduct, there are no gallium mines, and gallium is only found in very small concentrations [22]. The prospects for a dramatic expansion in production appear dim.

3.5 Aluminium availability

Total worldwide production of virgin aluminium in 2008 was 25,654 million kg [24]. From section 3.4 this would be sufficient for 27 million cars ($(25654*10^{6}/.0629)/15000$). Initially spare capacity in the aluminium industry could provide for the recycling of aluminium hydroxide. However with hundreds of millions of cars on the roads, any meaningful penetration would require investment in refineries and smelters.

3.6 Aluminium for grid levelling

It is proposed by Woodall [13] that the source of electricity for aluminium production would be renewable energy from the wind and the sun when this is not needed on the grid. In this way it would make wind and solar power more economic and allow for load curve flattening. This issue was investigated and it was suggested that power demand for smelters may only fluctuate by 5% [25]. This is because large fluctuations result in electrolytic cell temperature changes which may induce thermal stresses in the busbar and reduce cell life [25]. As wind power is nondispatchable, this would necessitate additional spinning reserve which would offset any potential savings. The prospect of an aluminium smelter being able to accommodate highly variable wind power as its main power source appears unfavourable.

3.7 Aluminium as energy storage for batteries

Aluminium batteries may be either rechargeable or non-rechargeable. In a 2002 paper Li and Bjerrum [3] described the prospects of a couple of molten salt aluminium batteries with the potential to be recharged. No literature since then can be found and no commercial availability is discernable. To the extent that rechargeable aluminium batteries may be developed they are subject to the normal economic factors of secondary batteries – cost, weight, recharge efficiency, durability and so forth.

More literature is available for primary non-rechargeable batteries [2-4]. These are subject to the same energetic and carbon cycle described in sections 3.1.1 and 3.1.2. They are used in submarines to save on weight or as a backup system for telephone exchanges [3]. Their expansion for use in applications such as supplying power to homes or industry would presumably be motivated by reductions in greenhouse gas emissions from electric grids. With a maximum electrical energy output of 29.2 MJ/kg and emissions of 10.367kg CO_{2e}/kg Al, this yields a CO_{2e} of 355g/MJ ((10.367/29.2)*1000) or 1,278g CO_{2e}/kWh (355*3.6). Similarly a renewable energy smelting operation yields 621g CO_{2e}/kWh ((5.037/29.2)*1000*3.6). If the battery is assumed 80% efficient [2] the figures become 1,598g CO_{2e}/kWh (1278/0.8) and 776 g CO_{2e}/kWh (621/0.8). By contrast coal produces approximately 970g CO_{2e}/kWh and natural gas produces 440g CO_{2e}/kWh [26].

CONCLUSION

Experimental analysis of aluminium-gallium alloy pellets which had been exposed to air prior to reaction indicated that the reaction was very inefficient with a low percentage of theoretical hydrogen evolved. The suggested optimal microstructure for an alloy is to have the cathodic additive in the grain boundaries.

The use of aluminium as a vector to store energy for hydrogen propulsion and stationary applications was investigated. In both cases it was found to be very energetically inefficient and to emit significantly higher greenhouse gas emissions than the current technologies.

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