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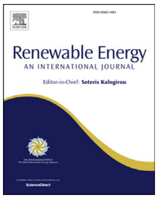

Susceptibility to corrosion of aluminium alloy components in ethanol adsorption chiller

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ABSTRACT

Methanol, and more recently ethanol, have been deeply employed as adsorbate phase (refrigerant) in adsorption chiller and heat pump applications (e.g. refrigerator adsorption ice maker). The use of anhydrous alcohols however can cause several problems related to the corrosiveness of such molecules towards light alloys (from titanium to aluminium). The problem was already highlighted in bio-fuel technology where bio-ethanol was considered as a promise alternative to fossil hydrocarbons. Water content was observed as one of the main factors influencing corrosion rate. In the present works several accelerated corrosion tests on 6061 Aluminium alloy have been carried out in autoclave in a temperature range from 110 to 135 °C with different ethanol to aluminium mass ratio. Highly exothermic reactions related to aluminium oxidation, coupled to hydrogen evolution, have been recorded. The main drawback of hydrogen evolution is the formation of a stagnant layer over the heat exchangers surface, which can limit the ethanol vapour diffusion, thus reducing adsorption/condensation rate.

1. Introduction

During last years, thermally driven adsorption heat pumps increased their attractiveness as they appear to be promising technologies to reduce greenhouse gas (GHG) emissions and Ozone layer depletion problems [1]. Indeed one of the main challenges in environmentally-friendly energy systems lies in the development of low Global Warming Potential (GWP) and low ozone-depleting potential (ODP) heat transformation systems. In this context, adsorption heat pumps (AHPs) that can be driven by low grade heat such as industrial waste heat or solar thermal collectors have been considered as one of the best candidates since they employ zero GWP and zero ODP refrigerants like water, alcohols and ammonia. Other advantage of adsorption refrigerating system is the absence of vibrating or moving parts, which consequently reduces control and operating costs [2].

Watanabe et al. [3], studied the possibility to produce cold energy by a super active carbon (SAC)/ethanol adsorption system. The SAC/ethanol adsorber system enables to increase the heat transfer fluid operating temperature range, while the amount of cooling energy production is the same as the conventional silica gel-water based adsorption system [4].

Saha et al. [5] presented the transient modelling for a two-bed, activated carbon fibre (ACF)/ethanol adsorption chiller using low grade heat sources characterised by temperature between 60 and 95 °C with a coolant at 30 °C. Furthermore in Ref. [6] it is reported that active carbon – ethanol cooling cycle can achieve a specific cooling effect as high as 420 kJ kg−1 at the evaporator temperature of 7 °C in combination with heat source and heat sink temperatures 80 and 30 °C, respectively. Analogously Kanamori et al. [7] proposed activated carbon–ethanol adsorption heat pump with a disk-module type adsorber for refrigeration applications. The results evidenced that the present system properly works employing regeneration temperatures of around 77 °C generating cooling effect around −3 °C. Considering the high adsorption uptake of ethanol onto activated carbon and low regeneration temperature needed for the working pair (below 100 °C), the proposed

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configuration of AHP seems to be attractive for solar adsorption cooling application. Recently, Frazzica et al. [8] have proposed a small-scale adsorption refrigerator employing activated carbon and ethanol as working pair. The prototype demonstrate to be able to deliver specific cooling power around 50 W/kg with a COP about 0.15, thanks to the use of highly efficient aluminium finned flat tubes heat exchangers in the adsorbers.

However, with regard to the challenge of using ethanol in AHP, it is important to verify the impact of this alternative fluid on the metallic components durability. such as heat exchangers, valves and vacuum chambers. Corrosion of metal alloys in methanol is indeed a well known problem since the early studies carried out on this subject [9,10]. More recently, with the increasing demand of bio-fuels production and consumption corrosion problems related to the use of aluminium alloys in internal combustion engine in presence of ethanol have been highlighted [11–14]. Some research studies evidenced that ethanol with water content below 0.2% vol at temperature as low as 70 °C triggers corrosion phenomena [15] i.e. in same operative range of adsorption heat pump [16]. Furthermore, in these systems another big concern is represented by the evolution of gaseous hydrogen produced by the corrosion reaction. Hydrogen evolution, significantly alters the absolute pressure inside the system affecting efficiency of the heat pump itself [17,18].

The components of an adsorption heat pump are usually based on materials that can be considered compatible with ethanol, such as stainless steel, polymer or light metal components, particularly aluminium alloys. However aluminium alloys in the typical AHP operating environmental conditions, can corrode resulting in a deterioration of the durability and safety of AHP.

This study examined the corrosion characteristics and mechanisms of the 6061 aluminium alloy, in ethanol solution varying temperature and ethanol contents. Morphological analysis of corroded surfaces was used to better identify the interface interaction between metal substrate and liquid/vapour phase and to relate that with the mechanisms that can cause corrosion in medium temperature ethanol conditions.

2. Experimental

2.1. Materials

A 6061 aluminium alloy was used as reference lightweight material to investigate the corrosion susceptibility in ethanol solution. All samples were obtained from an extruded 35 Ø mm diameter bar. The major alloying elements of the alloy were magnesium (1.10%), silicon (0,61%) and copper (0,25%).

2.2. Immersion corrosion test

In order to perform accelerated corrosion tests a specific set-up to assess the corrosion phenomena on 6061 aluminium alloy samples in anhydrous ethanol was developed by fitting aluminium specimens inside a temperature controlled PTFE lined 316L stainless steel autoclave (Fig. 1).

Preliminarily, the surface of the samples was mechanically ground with emery paper up to grade 1200, then cleaned in a diluted nitric (15%) and hydrofluoric (1%) acid solution for 180s, washed in distilled water and finally with ethanol. Afterwards the aluminium samples were placed into the autoclave under nitrogen flux. The anhydrous conditions were guaranteed until the stainless steel autoclave was closed and ethanol was introduced in the chamber.

The effect of temperature (ranging from 110 to 135 °C) and ethanol to aluminium mass ratio were studied in order to evaluate how these parameters can affect the kinetics of degradation. Table 1 summarizes the experimental testing conditions. After the immersion tests, the corrosion degradation of aluminium samples was evaluated by mass weight loss. The corroded surface, pit morphology and microstructure were observed by scanning electron microscopy (ZEISS SEM/FIB crossbeam 540) and 3D optical stereo-microscopy (Hirox KH 8700).

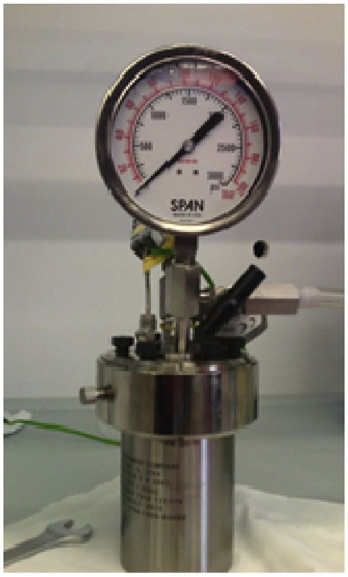
Fig. 1. Temperature controlled stainless steel autoclave.

3. Results and discussion

Fig. 2 shows, as a reference, the results of the test A11E30_135, carried out with 30 ml of ethanol and 11.12 g of aluminium at a temperature of 135 °C. Four regions can be identified:

3.1. Heating stage

a first phase (up to about 20 min) during which a gradual increase of the temperature inside the autoclave up to the set point temperature of 135 °C was observed. In this phase, no appreciable pressure increase in the vessel was observed.

3.2. Activation stage

In this stage, the corrosion phenomenon is not yet activated, but the progressive thinning of the protective oxide layer on the aluminium surface could take place [13]. Once the protective aluminium oxide layer has been removed, the aluminium substrate is directly exposed to the aggressive environment. In this stage the temperature is quite constant. The slight increase of autoclave

Table 1
Summary of experimental tests details.

CODE	Aluminium [g]	Ethanol [ml]	Temperature [°C]
A06E30_135	6	30	135
A11E30_135	11	30	135
A14E30_135	14	30	135
A06E15_110	6	15	110
A06E30_110	6	30	110
A06E50_110	6	50	110

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