Short Communication

Modification of the shrinking core model for hydrogen generation by reaction of aluminum particles with water

S.S. Razavi-Tousi[*], J.A. Szpunar

Department of Mechanical Engineering, University of Saskatchewan, S7N 5A9, Saskatoon, Saskatchewan, Canada

ABSTRACT

The assumptions of the traditional shrinking core model cannot be adopted for the core—shell structure formed during the reaction of aluminum particles and water. The model assumes that diffusion coefficient is constant and the particle size is unchanged during the reaction. This study modifies the traditional shrinking core model by including the effect of the growing size of the particles and the changes in porosity of the hydroxide layer on hydrogen generation. The modified model is fitted to the experimental data and the results are compared to that of the traditional model. The flux of water molecules in the hydroxide layer is calculated using the parameters obtained by the hydrogen generation data.

Introduction

Aluminum—water reaction

Researchers have extensively investigated the reaction of aluminum particles with water for the purpose of hydrogen generation [1—9]. Because aluminum particles are usually covered by a thin native oxide film, the reaction does not start immediately after immersion of particles in water. The thin oxide film should be hydrated/dissolved in water and then reduction of water molecules by water initiates. The rate and byproducts of the reaction strongly depends on pH and temperature of water. The hydroxide species formed as byproduct is soluble in solutions with a pH higher than 11 or lower than 2 [10,11]. However, within a pH range of 2—11, a hydroxide layer precipitates on the aluminum surface, which makes the diffusion of ion species/water molecules a critical step in determining the kinetics of hydrogen generation.

At the presence of a hydroxide layer on the surface of aluminum particles, which results in a core—shell structure [12], three parameters can control the rate of the reaction: 1) diffusion of ion species/water molecules in the solution to the particles surface, 2) diffusion of ion species/water molecules from the particle surface to the substrate aluminum and vice versa, 3) the reaction between aluminum and water. If one

assumes that an abundant amount of ion species/water molecules is available in the solution, the diffusion in the solution is not the controlling step and thus either the chemical reaction or diffusion in hydroxide layer controls the kinetics. In a case where a chemical reaction is the controlling step, the reaction rate is explained by the "diminishing sphere" model. However the diffusion of ion species is the controlling step when a hydroxide layer is present and the reaction rate is explained by the "shrinking core" model.

Few studies attempted to fit either the diminishing sphere or shrinking core model to the measured hydrogen evolution data from the reaction of aluminum and water [13−16]. However, the results of fittings cannot be considered satisfactory because of the considerable deviation of the theoretical values from experimental data. A. I. Ratko et al. [17] developed a diffusion based model for the reaction of aluminum and water, which later was used by H. Nie et al. [18]. Although this model was developed considering the mechanism of the reaction, H. Nie et al. concluded that the diffusion coefficient changes with the time of the reaction, which indicated "inadequacy of the simplified model" [18]. Another approach to model the kinetics of reaction of solid particles with a liquid is to use empirical formula [19−21]. Although the numerical models result in a good fitting to the experimental data, they do not provide any insight to the mechanism of the reaction.

New assumptions for the shrinking core model

In this study, considering the growth of the hydroxide film on aluminum particles during the reaction, we attempt to modify the shrinking core model. There are two main differences between the assumptions of the shrinking-core model and the proposed model in explaining the growth of hydroxide layer. The first difference is that the diffusion coefficient of the shell (hydroxide layer) formed on the core (aluminum) in our model changes with time. Researchers found that the grown hydroxide layer is not uniform across its thickness [22−25]. This was explained by density of the formed hydroxide that changes during the reaction. R.S. Alwitt claimed that when the reaction starts, the formed hydroxide phase is permeable to water [26]. As reaction continues, the hydroxide densifies and pores become filled, therefore, water penetration rate through the shell reduces. The observations of pores in the hydroxide layer, the hydroxide densification during the reaction and the resulting change in the reaction rate are discussed in our previous work [27]. The change in the porosity of the shell and its influence on the reaction rate have to be incorporated into formulating the kinetics of the reaction.

The second difference between the assumptions of our model and the shrinking-core model concerns the thickness of the formed shell around the particle. The shrinking-core model was developed for the leaching process [28], in which the thickness of the shell is the same as that of the consumed core. However for the reaction of aluminum particles with water, considering the difference between the density of the produced hydroxide layer and the consumed aluminum core, the thickness of the hydroxide layer is bigger than that of the consumed core.

The main body of the model that we developed in this study is similar to the traditional shrinking core model. The above mentioned assumptions will be applied in this model and the results will be compared with the experimental data. A comparison will be made between the modified model and traditional shrinking core model, and the rate of mass transfer of species/water molecules will be calculated based on the modified model.

Experimental procedure

Aluminum powder of 99.8% purity (MFCD00134029) provided by Alfa Aeasar Company was mixed with 3 wt% of Stearic acid (97% purity, Fisher Scientific-AC17449-0010) as the process control agent (PCA), and the mixture was activated by ball milling in a planetary ball mill (Torrey Hills−ND2L) for 19 h in an argon atmosphere.

The procedure for measurement of hydrogen production rate is similar to our previous work [29]. We added 2 g aluminum powder into an Erlenmeyer flask contained 200 ml distilled water at temperature of 80 ± 3 °C with a constant stirring rate of 120 rpm. The produced hydrogen gas passed through a desiccant ($CoCl_2$) to absorb moisture, and then an ADM2000 flowmeter measured the flow with an accuracy of 0.1 ml/min. The flowmeter was connected to a computer and the ADM Trend software acquired the data. We measured the flow for the first hour of the reaction for each sample and then normalized the results for 1 g aluminum powder. The hydrogen yield curves vs. time were obtained by integrating the flow data over time. We did not continue measuring hydrogen flow after 1 h of the reaction because the collected data was sufficient for comparison with the models.

Development of the model

The schematic diagram of the model is presented in Fig. 1. The particle on the right represents the situation before the reaction, and the particle on the left shows how the reaction forms the core−shell structure. One can see that in the traditional shrinking core model the overall size of the particle is unchanged during the reaction, however, in our model the size of the particle increases and the radius of the particle changes from R_o to R. The assumption of a core−shell structure was adopted based on our SEM observations of the cross section of reacted aluminum particles [12].

Water reaches to the core of the particle and reacts with aluminum. The mass transfer equation at a given diameter within the hydroxide layer can be expressed as:

$$\{H_2O_{\text{towards the core}}\} - \{H_2O_{\text{consumed by reaction}}\} + \{H_2O_{\text{generated by reaction}}\}$$
$$= \{H_2O_{\text{accumulated}}\}$$

$$\tag{1}$$

$$H_2O_{\text{generated by reaction}} = H_2O_{\text{accumulated}} = 0 \tag{2}$$

Therefore;

$$H_2O_{\text{towards the core}} = H_2O_{\text{consumed by reaction}} \tag{3}$$

Eq. (3) means that the amount of water that diffuses toward the core should be the same as the amount of water