

GENERATION OF HYDROGEN BY CORROSION OF NEW NANOCOMPOSITE BASED ON ALUMINUM IN DILUTED ALKALINE SOLUTION

EMAD M AHMED

Materials Science and Engineering Group, Physics Department, Faculty of Science,
Taif University, Hawiya, Taif, Saudi Arabia
Solid State Physics Department, National Research Center, Dokki, Giza, Egypt

ABSTRACT

The aim of this paper was to fabricate Al matrix composites with 0-10 wt. % TiO_2 nanoparticles (TiO_2 -NPs) and examine their hydrogen generation properties from the hydrolysis of Al in 0.05M NaOH solution at room temperature. XRD, SEM, TEM and EDX techniques were used to study the structure properties of the nanocomposites before and after hydrolysis process. Powder metallurgy technology has been followed to fabricate the nanocomposite samples. Hydrolysis results exhibit a maximum hydrogen generation rate of about $20 \text{ ml min}^{-1} \text{ g}^{-1}$ for 5 wt. % NiO_2 -NP/Al composite which is higher than that of Al without TiO_2 -NP due to the synergetic effect of the porous Al matrix, which has a large reaction area and galvanic corrosion between the Al matrix and the TiO_2 -NPs. SEM photographs confirmed the homogeneity of the nanocomposites microstructure except for 10 wt. TiO_2 -Nps/Al composite since the TiO_2 -Nps are not well distributed through the Al matrix but accumulated in isolated regions leading to produce composites with less porous structure and less Al surface area subjected to the alkaline solution that leading to lower hydrogen generation rate comparing to 5 wt.% TiO_2 -NP/Al composite.

KEYWORDS: hydrogen generation Reaction, Metal Matrix nanocomposites, Aluminum, Titania nanoparticles

1. INTRODUCTION

Nowadays, large amounts of hydrogen are consumed in several industrial processes like production of bulk ammonia and methanol, gasoline refining and hydrogenation of fats and oils. Moreover, the hydrogen requirements are rising because of the growth of its application in pharmaceuticals, metallurgy, semiconductor and aerospace industries, among others. It is expected that the market growth for fuel cells will increase the demand even further [1]. Likewise hydrogen is an attractive fuel alternative for the future, an attractive method for hydrogen production must be employed in order to maintain its positive profile. Other challenges that must also be addressed include the methods of hydrogen storage and transportation. Hydrogen can be produced in many different ways, such as through direct decomposition or partial oxidation of hydrocarbon compounds [2,3], the steam reforming of hydrocarbons [3,4], chemical hydrides reacting with water [5], splitting water using metal-oxide catalysts under solar energy [6-10]. However, all of the above production methods suffer from various drawbacks. For example, the direct decomposition or partial oxidation of hydrocarbon reactants requires elevated temperatures and produces considerable quantities of CO and other byproducts. The reforming of methanol produces hydrogen at lower temperatures, with considerably less CO than the oxidation of hydrocarbons [3,4] however, this process is endothermic, and externally supplied heat is required to maintain the reaction. Chemical hydrides such as LiBH_4 , NaBH_4 , NaH , and MgH_2 react with water directly and generate large quantities of hydrogen under ambient

conditions [5]. However, the deactivation of the catalysts (Pt, Ru), the treatment of hydroxide byproducts, control of the reaction rate, and the high price of reactants are all impediments to the commercialization of this process. Splitting water using metal-oxide photo-catalysts such as TiO_2 is a promising route for the production of hydrogen [6-8]. However, the efficiency of producing hydrogen using bare TiO_2 is low, due mainly to the fast recombination of electron/hole pairs [7,8]. Noble metals such as Pt or semiconductors such as CdS-modified TiO_2 have proven highly effective in overcoming this problem [9,10]. The use of aluminum to produce hydrogen has gained interest in recent years because aluminum's low density and tri-valence state result in high effective hydrogen content per mass of reactants, and the by-products have minimal environmental impact [11-14]. The reaction of aluminum (Al) with aqueous alkaline solutions to generate hydrogen is well known [15]. One gram of Al can produce 1.36 L of H_2 when completely reacted with water in ambient conditions. A direct reaction of metallic Al with pure water is difficult due to a dense Al_2O_3 film (3-6 nm in thickness) that passivates the surface of the Al [16]. Metallic Al reacts continuously with water when the passive Al_2O_3 layer is exposed to acid or alkaline solutions however, the environmental pollution and the easy passivation of metallic Al are major concerns using this method. Several novel alternative processes permitting the direct reaction of metallic Al and pure water under ambient conditions were proposed by Woodall [17,18], Chaklader [19,20], and Czech [21]. The method invented by Woodall takes advantage of Al-Ga eutectic reaction to generate hydrogen in a straight-forward manner [17,18]. The gallium is a critical component hindering the formation of the aluminum oxide skin on the surface of the Al. In the same manner, other metals such as Bi, Sn, and In could also be used for the formation of alloys with Al to generate hydrogen gas on demand, however, caution must be exercised to prevent hydrogen gas explosions. The cost of materials is also a critical concern for the practical implementation of this process. Chaklader [19,20] patented the direct reaction of metallic Al with tap water by using α - Al_2O_3 and γ - Al_2O_3 powders as modifiers through mechanical mixing. Czech [21] reported similar direct reactions of metallic Al with tap water through the mechanical mixing of Al with chloride salts such as KCl and NaCl. The latter two methods generate hydrogen easily under ambient condition. The purpose of this study is to prepare new modified Aluminum-matrix composite with some metal oxides nanoparticle to improve the hydrogen generation in an aqueous alkaline solutions. The statement of the proposal research will be through main points. The aluminum matrix composite will be prepared using powder metallurgy rout.

The reactions of aluminum with aqueous solutions of sodium hydroxide are as the following.



Initially, the hydrogen generation reaction consumes sodium hydroxide, but when the aluminate concentration exceeds the saturation limit, aluminate undergoes a decomposition reaction (2) that produces a crystalline precipitate of aluminum hydroxide with theregeneration of the alkali. The overall hydrogen-generating reaction of aluminum in an aqueous solution is described by equation (3). The formation of the alumina layer on the surface of the Aluminum is the main reason for hindering the hydrogen production process. High surface area of metal oxides nano-crystals induces pitting on the surface of the Al, thereby accelerating the mobile defect species in the Al_2O_3 layer to maintain a continuous reaction with the alkaline solution. There are different parameters are affecting the hydrogen production by Al in alkaline solutions such as: the metallic Al particles, the modifier materials, the size of the modifier particles, the mixing duration, the reaction temperature, and the purity of the alkaline solution

2. EXPERIMENTS

Titanate nanoparticles (TiO_2 -NPs) were first prepared using a procedure described below: 2.0 g TiO_2 was added to 75 mL of 10 M NaOH solution under vigorously magnetic stirring for about 1 h to form a white suspension. This suspension was then transferred into 100 ml Teflon-lined stainless steel autoclaves, which were allowed to react at 130 °C for 24 h. After being cooled to room temperature, the titanate powders were washed with dilute HNO_3 (pH=3) and then distilled water for several times till the residue solution is neutralized. These washed powders were dried in air at 60 °C for overnight to achieve the titanate nanotubes. TNTs were calcined at 300 °C and 600 °C for 1 h to achieve TiO_2 nanoparticles.

X-ray diffraction (XRD) analysis was performed using an automated diffractometer (Philips type: PW1840), at a step size of 0.02°, scanning rate of 2° in 2 θ /min., and a 2 θ range from 4° to 80°. The powders morphology was investigated using SEM (JOEL, Model: JSM-5600, Japan.) equipped with secondary electron detector and EDX. All samples were coated with gold. The particle shape and size were studied using transmission electron microscope operated at 120 kV accelerating voltage (JTEM-1230, Japan, JEOL). The samples were prepared by making a suspension from the powder in distilled water using ultrasonic water bath. Then a drop of the suspension was put into the carbon grid and left to dry. TiO_2 -NPs/Al mixtures containing various amounts of TiO_2 nanoparticles (0-10 wt. %) were prepared by powder metallurgy route using Al powder (purity: 99.9%) and the prepared TiO_2 -NPs. The nano-composites samples were prepared under applied uniaxial stress of 300 Mpa and the sintering process was performed at 500 °C for 1 h with a heating rate of 20 C/min.. The pure Al and TiO_2 -NPs/Al composites have a disk shape with a diameter of 10 mm and a thickness of 3 mm. The hydrogen generation rate was measured in 200 ml of 0.05 M of NaOH solution at room temperature using a mass flow meter (MFM). The hydrogen volume obtained by integration of the hydrogen rate with time. The microstructure of the nano-composites were examined by XRD and SEM before and after etching in 0.05 M NaOH solution.

3. RESULTS AND DISCUSSION

3.1. Structure Properties of the Prepared Nano-Composites

The XRD patterns shows that TNTs calcined at different temperatures using microwave. In samples calcined up to 100°C, the main diffraction peaks are typical of layered titanates, especially the strong broad one

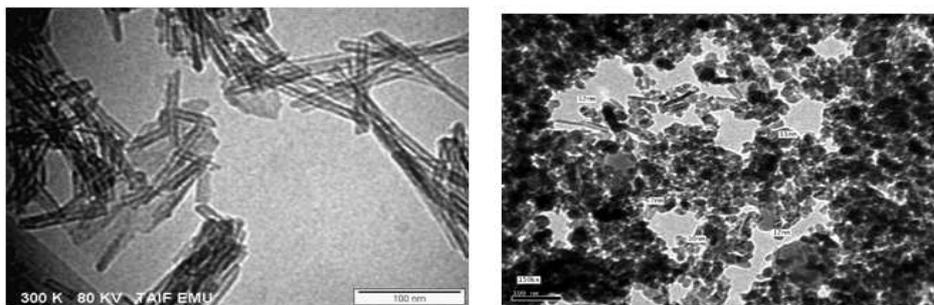


Figure 2: TEM Micrograph of TiO_2 at 300°C (a) and 600°C (b)

Around $2\theta = 10^\circ$, attributed to the interlayer distance. According to XRD of these samples, the chemical formula of TNT samples is essentially a protonic layered titanate and the structure was very close to $\text{H}_2\text{Ti}_3\text{O}_7$ [19]. However, at 300°C, this peak disappears indicated the collapse of the layer structure. However all the other peaks of hydrogen titanates

are still observed, suggesting that the tubular structures can be maintained up to 300°C. At 600°C all nanotubes were converted to anatase nanoparticles (9- 16 nm)

Figure 2 shows TEM micrographs of the prepared TiO₂-NPs. TEM micrographs confirmed that the prepared TiO₂-NPs are still in nano-size range at 600 C. Figure 3 shows SEM micrographs and EDX spectra of as prepared TiO₂-NPs/Al composites with different TiO₂-NPs contents demonstrating the effect of the TiO₂-NPs contents on the surface morphology of the TiO₂-NPs/Al composites. These nanocomposites became more porous with increase of TiO₂-NPs contents. Moreover, All TiO₂-NPs/Al composites exhibit homogeneous composition except the composite of 10% TiO₂-NPs content. This means that the TiO₂ nanoparticles are well distributed through the samples of 5% TiO₂-NP.

On the contrary, the TiO₂-NPs are not well distributed through the sample of 10%TiO₂ but accumulated in isolated regions leading to the observed non-homogeneous composition as shown in Figure (3). EDX spectra of the as prepared TiO₂/Al composites proves the existence of the Ti and O₂ in the as prepared nanocomposites and their ratios increase with increasing of TiO₂ contents. Figure 4 shows the XRD patterns of the TiO₂/Al nanocomposites with different contents of TiO₂.

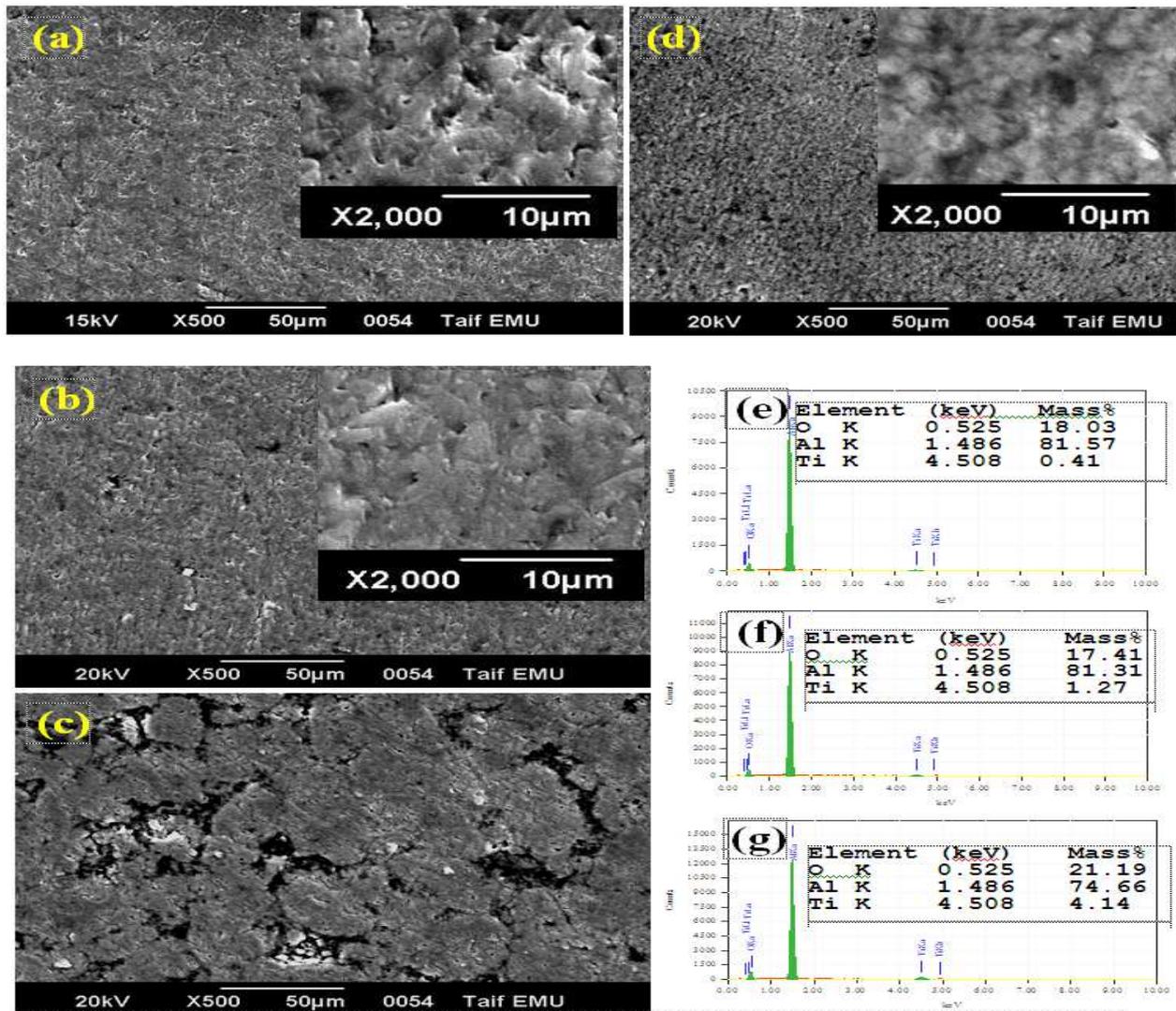


Figure 3: SEM Micrograph of Al-x wt. % TiO₂-NP, x= 1 (a), 5 (b), 10 (c) and 0 (d) and EDX analysis of x=1, 5 (f) and 10 (g)

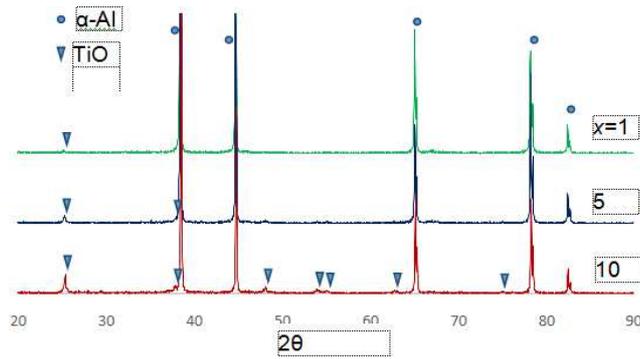


Figure 4: XRD Patterns of Al-x wt.% TiO₂-NPs nanocomposite, x= 1, 5 and 10

The XRD patterns confirmed the existence of α -Al and TiO₂ in the as prepared TiO₂/Al nanocomposites. Moreover, the corresponding XRD lines of TiO₂ increase with increasing of the TiO₂ contents.

3.2. Hydrogen Generation Properties of nanocomposites

Figure 5 shows the effects of the hydrolysis time on the accumulated hydrogen volume and hydrogen rate per unite weight for 0-10 wt.%TiO₂-NPs composites. The hydrogen generation rate enhances for 5 wt.% TiO₂-NPs/Al composite comparing to the sintered Al recording maximum rate of 20 comparing to 15 mL min⁻¹ g⁻¹ for the sintered Al without TiO₂NP. Moreover, the initial stage hydrogen generation rate of 5 wt.% TiO₂-NPs/Al composite reached the maximum value earlier than the sintered Al. Furthermore, due to its porous structure and large reaction area the sintered

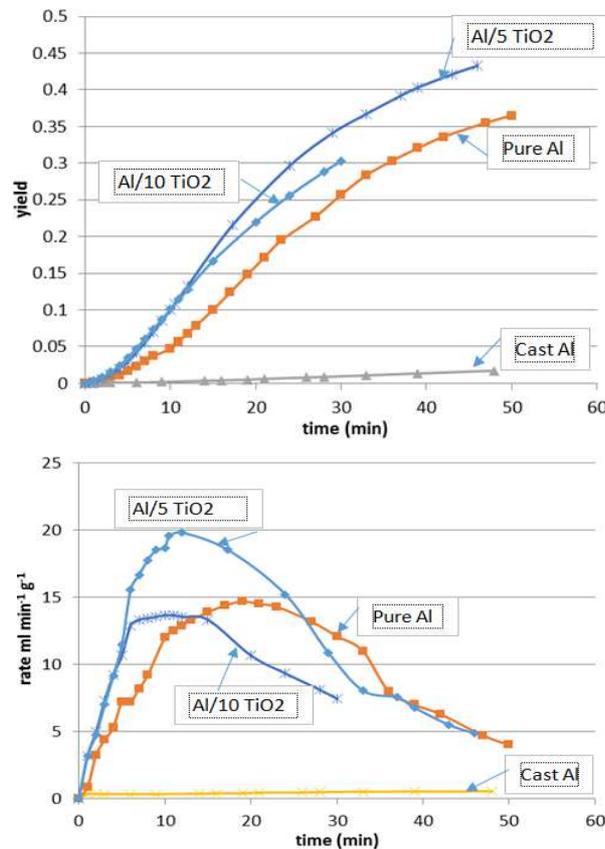


Figure 5: Comparison of H₂ Yield (top) and H₂ Rate (Bottom) at Initial Stage among the Samples: Cast Al, Sintered Al, Al-5TiO₂ and Al-10TiO₂ Nano-Composites

Al has hydrogen generation rate that is higher than that of the casted Al. The hydrogen generation rate of Al-10 TiO₂-NPs composite has the same behavior as Al-5 TiO₂NP only at the first stage of the hydrolysis (time range of 0-7 min) recording max rate of about 14 mL min⁻¹ g⁻¹. The retardation of the hydrogen generation may be attributed to the non-homogenous structure of this composition and the TiO₂-NPs are not well distributed through the sample. This result is consistent with SEM analysis since the TiO₂-NP are accumulated in isolated regions which decreases the Al surface subjected to alkaline solution. The Al matrix becomes much higher porous by distributing TiO₂-NP through it, increasing the effective surface area of the Al surface subjected to the alkaline solution. To get further improvement of hydrogen generation rate for Al-5 wt.% TiO₂-NPs composite, the applied uniaxial stress is decreased and sintering time is shortened at 500 °C. Al-5 wt.% TiO₂NP composites were fabricated at different levels of uniaxial stress (20, 40 and 100 Mpa) to investigate the effects of specific surface area on the hydrogen generation rate. A porous Al structure with high specific surface area can be achievable by applying a low stress. As can be seen in Figure. 6 the hydrogen generation rate of Al decreased with increasing stress applied. Porous Al with higher specific area produced fast hydrogen generation from the hydrolysis of Al in alkaline solution.

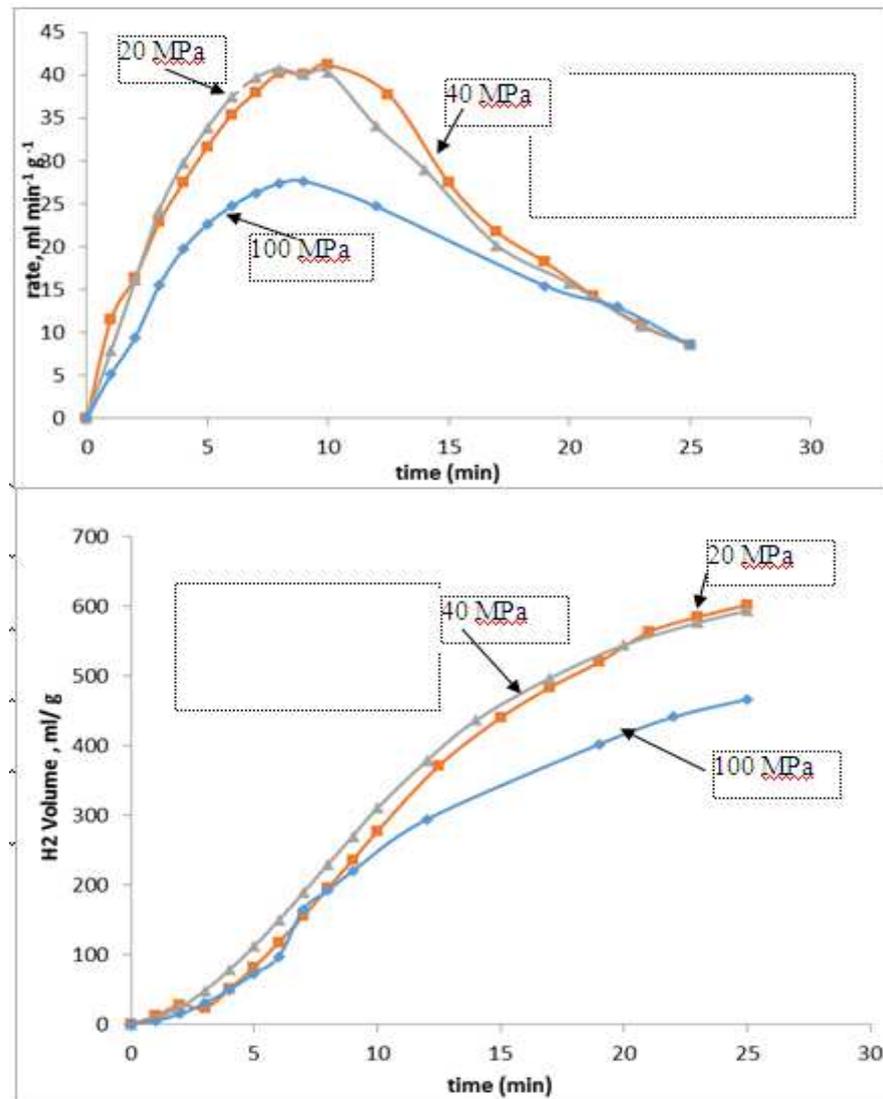


Figure 6: The Effect of the Applied Stress of the Al-5wt. %TiO₂NP Composite on the Hydrogen Volume per Unit Weight at Initial Stage

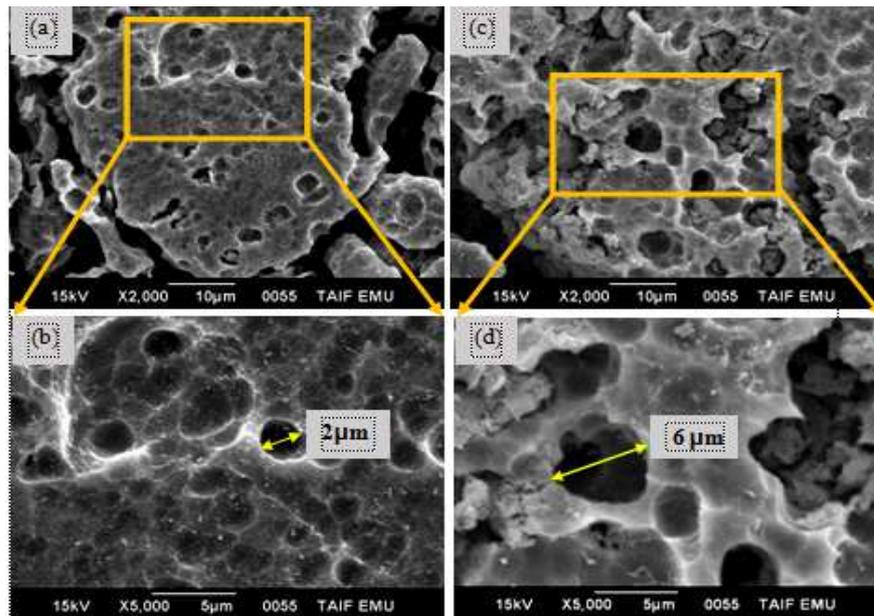


Figure 7: SEM Micrographs of Al (a and b) and Al-5TiO₂ (c and d) after 10 min Etching in 0.05M NaOH Solution at 25 °C. The Lower Images are 2.5 Times Higher Magnification of the Selected Region of the Upper Images

Figure 7 shows SEM micrographs of sintered Al (images a and b) and 5 wt.% TiO₂-NPs/Al composite (images c and d) after 10 min etching in 0.05M NaOH solution at 25 °C. The SEM images of Figure. 7 revealed, as expected, rough surfaces with high porosity as a result of the alkaline corrosion and subsequent evolution of hydrogen. Noticeable changes in morphology were observed on the surface of the composite (images c and d) as comparison to that of sintered Al (images a and b). The pores got wider and deeper after the hydrolysis of the TiO₂/Al composite due to severe dissolution of the Al matrix catalyzed by TiO₂ NPs. TiO₂ NPs remained in the composite, as they are stable in the alkaline solution solutions. It has been proposed that each TiO₂-NP can act as a localized cathode in the Al matrix during hydrolysis, and hence causes rapid hydrogen generation due to the galvanic corrosion effect between the TiO₂-NPs and the Al matrix. This reflect that porous Al with higher spesific surface area produced fast hydrogen generation from the hydrolysis of Al in alkalin solution.

CONCLUSIONS

TiO₂-NPs/Al composite was fabricated using powder metallurgy technology to achieve a rapid hydrogen generation rate in a diluted alkaline solution. A maximum hydrogen rate of 20 ml min⁻¹ g⁻¹ was obtained for 5 wt. TiO₂-NPs addition and applied stress 300 Mpa, sintered at 500 °C for 1 h, in 0.05 M NaOH solution. The fast hydrogen generation rate can be attributed to the large specific area of the porous Al matrix and galvanic corrosion between the TiO₂-NPs and the Al matrix. The hydrogen generated from the hydrolysis of the TiO₂-NPs/Al composites has high purity without any production of undesirable CO. Using of different kinds of Oxides-NPs/Al composites are strongly suggested to be used for developing the hydrogen generation of Al in alkaline solutions.

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