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EFFECTS OF COLD-WORKING ALUMINUM PRIOR TO ACTIVATION VIA A Ga-In EUTECTIC

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ABSTRACT

The reaction of aluminum and water is among the most energy dense reactions known - producing roughly equal amounts of energy in the form of hydrogen gas and heat. Recently, a new high-efficiency method for activating aluminum was discovered that allows it to react in water. Cold-worked aluminum immersed in a bath of liquid gallium and indium allows the liquid metal to penetrate the grain boundaries of the aluminum. The treatment results in liquid metal embrittlement and activation of the bulk aluminum while using a minimal amount of gallium and indium. It is hypothesized that the highly worked grain structure of the aluminum, as a result of cold working, is a major contributing factor to the reactivity of the activated aluminum. This paper shows the importance of residual stresses on reactivity by comparing treated, stress-relieved 6mm aluminum spheres with un-annealed spheres which contain residual stresses as a result of manufacturing. Cold working the aluminum results in hardening of the material via residual stresses in the grains, providing favorable conditions for liquid metal embrittlement and thus activation of the aluminum. Hydrogen yield from the aluminum-water reaction is measured as a means to quantify energy efficiency and the effect of residual stresses on activation of the aluminum. Results show that annealing the aluminum and thus eliminating residual stresses in the aluminum bulk reduces the hydrogen yield by more than 70%.

Keywords: aluminum, hydrogen, embrittlement, gallium, indium, water.

INTRODUCTION

Aluminum is well known for its high energy density, abundance in the Earth's crust, and ability to react with water to generate heat and hydrogen [1]. However, the thin oxide coating that surrounds aluminum makes it difficult to use as an energy source since the coating forms rapidly and is stable even at elevated temperatures (1<RPB-AL<2) [3]. Eutectics of gallium, indium, and/or tin have been shown to activate aluminum as they have strong affinities for aluminum grain boundaries. Cast alloys (Woodall et al., 2011) and ball-milled aluminum powders (Ilyukhina et al., 2017) combined with these eutectics have proven effective at activating aluminum, however these methods are either too costly, impractical to handle, or pose explosivity hazards [4][5].

Recently, the present authors invented a method for activating aluminum in which 0.3g spheres of aluminum are treated in a heated Ga-In eutectic bath. The Ga-In eutectic travels along the grain boundaries, embrittling (via liquid metal embrittlement) and activating the aluminum bulk. The spheres were then cured for 7 days and reacted in water to near 90% efficiency, while containing only 3-4 wt. % Ga-In. It has been shown that stressed aluminum is a pre-requisite for liquid metal embrittlement to occur [6]. These spheres have high residual stresses as a result of forming; they were extruded, forged, and then polished. In order to determine the effect internal stresses have upon the efficiency of the aluminum once it is activated, 0.3g aluminum spheres were annealed at 412^{o}C (775^{o}F) for 3 hours then cooled at 10^{o}C/hour. The spheres were then treated and reacted in water in the same manner as the un-annealed spheres.

EXPERIMENTAL SETUP

Aluminum spheres 6mm in diameter weighing 0.3g were annealed at 412^{o}C (775^{o}F) for 3 hours. The annealed spheres were then treated in heated Ga-In eutectic baths for 2 hours then allowed to cure for 7 days. The spheres were then reacted in 5mL of deionized water and the hydrogen volume was recorded after no additional noticeable hydrogen was being generated by the reaction. SEM imaging was then done on fractured sphere sections

RESULTS

The results show that annealing the spheres has a significant effect on hydrogen yield when the spheres were reacted in water (Fig. 1). Hydrogen yield was calculated by comparing the measured H2 volume to the expected H2 volume. The extent of the annealing was also examined using scanning electron microscopy (SEM). The spheres were sectioned to compare the internal structure and grain sizes before and after annealing (Fig. 2)

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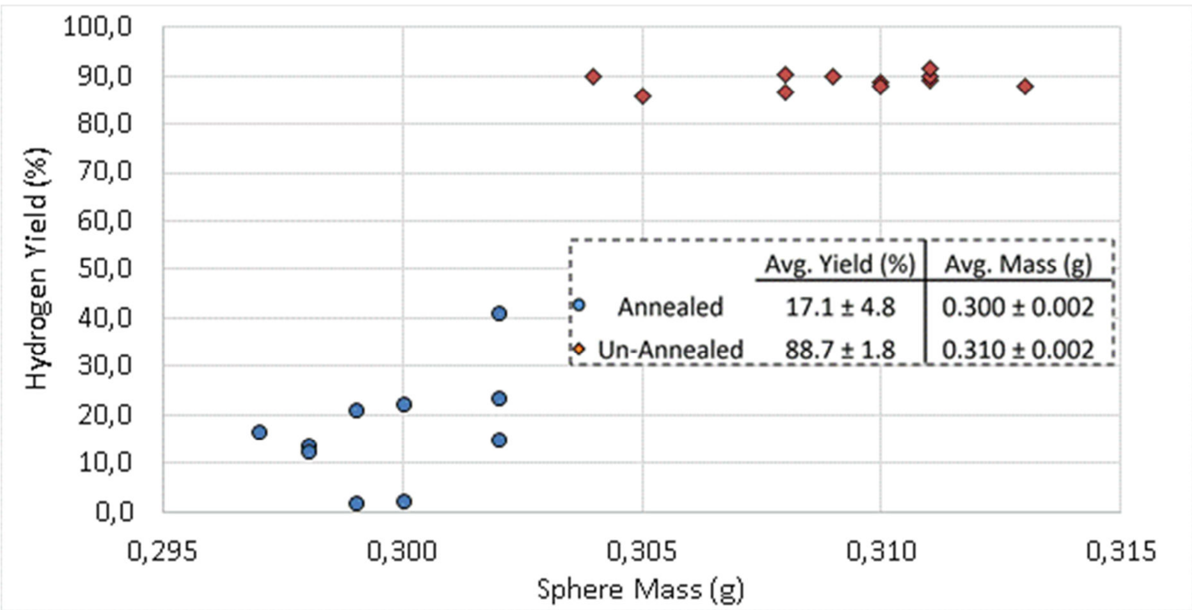
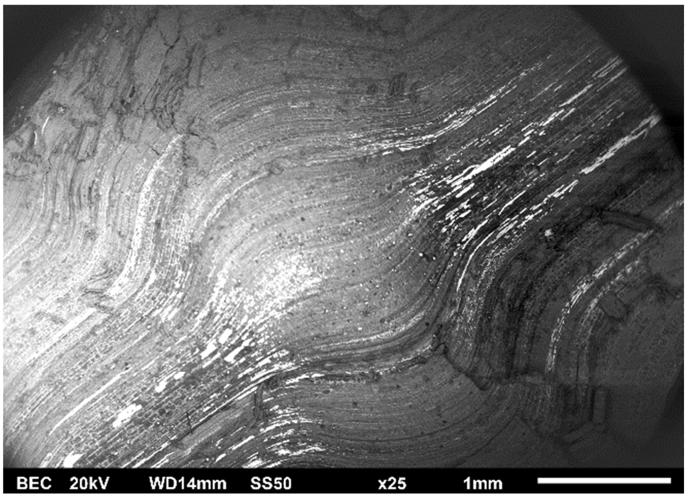
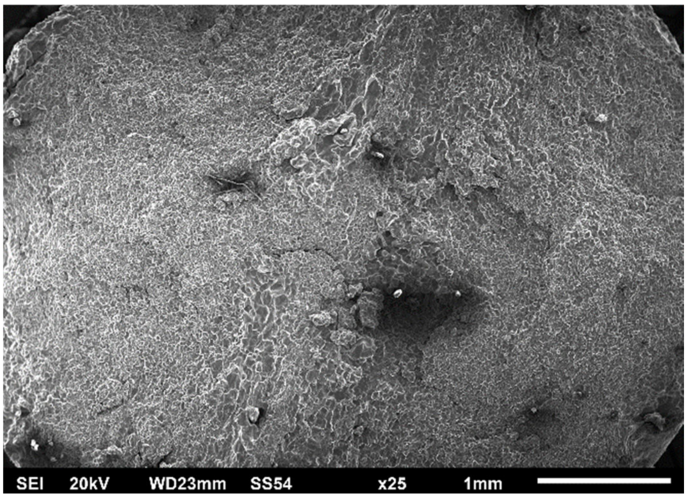


Fig. 1 - Hydrogen yield comparing annealed spheres to un-annealed spheres.



(a)



(b)

Fig. 2 - SEM images of un-annealed sphere (a) and an annealed sphere (b)

CONCLUSIONS

The process of annealing affects the internal structure of aluminum spheres, resulting in apparent grain growth as well as the disappearance of the forming lines caused by manufacturing. Annealing had a significant effect on hydrogen yield with annealed aluminum spheres producing on average 71.6% less hydrogen than un-annealed spheres. However, the mass of annealed spheres is on average 0.010g less than un-annealed spheres, indicating that the annealing also affects the treatment process. This shows that the presence of internal stresses in the aluminum, as a result of manufacturing, play an integral role in the reactivity of the aluminum once treated. Further investigation is needed to quantify the extent to which cold-working affects the treatment process and subsequently the hydrogen yield.

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REFERENCES

[1]-A. J. Downs, Ed., Chemistry of Aluminum, Gallium, Indium and Thorium, First. Springer Netherlands, 1993.

[2]-T. Campbell, R. Kalia, A. Nakano, P. Vashishta, S. Ogata, and S. Rodgers, “Dynamics of Oxidation of Aluminum Nanoclusters using Variable Charge Molecular-Dynamics Simulations on Parallel Computers,” Phys. Rev. Lett., vol. 82, no. 24, pp. 4866-4869, 1999.

[3]-J. T. Ziebarth, J. M. Woodall, R. a. Kramer, and G. Choi, “Liquid phase-enabled reaction of Al-Ga and Al-Ga-In-Sn alloys with water,” Int. J. Hydrogen Energy, vol. 36, no. 9, pp. 5271-5279, 2011.

[4]-A. V. Ilyukhina, O. V. Kravchenko, and B. M. Bulychev, “Studies on microstructure of activated aluminum and its hydrogen generation properties in aluminum/water reaction,” J. Alloys Compd., vol. 690, pp. 321-329, 2017.

[5]-M. G. G. Nicholas and C. F. Old, “Review Liquid metal embrittlement,” J. Mater. Sci., vol. 14, no. 1, pp. 1-18, 1979.