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Obtaining of aluminum nano-powders by thermal treatment

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It is known that the formation of a dispersed phase under extreme conditions (high temperatures and process speed) leads to the formation of a non-equilibrium structure of particles. Therefore, the first to attract attention are technologies based on pulsed processes with high rates of change in the thermodynamic parameters of the system. One of these promising methods for obtaining a wide range of nano-powders of inorganic materials is the technology based on the process of electrical explosion of a conductor (EVP, EVP technology) [1-5]. Unfortunately, this method is not applicable on industrial scales. In this thesis, production of Al nanoparticles by hydrogen reduction of metal chlorides in gas phase was studied. Nanoparticles have unique properties not found in bulk or micron-scale materials. These enable new products or reduced use of raw materials. Metal nanoparticle production has been studied widely, but especially for coated metal particles, research of coating mechanisms and economic production methods is still needed. The used method combines a high yield, a high production rate, low production costs, high particle quality, and a good range of available particle number average diameters and other properties. Control of the product parameters has been carried out by using a special quenching system and plasma reactor configuration. Highly hydrogen enriched Al nanopowder were collected in metal form and tested for different applications.

Key words: RF plasma, hydrogen, nano-aluminum, quenching.
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1 Introduction

Metals, such as aluminum have high combustion energies and have been employed as energetic additives in propellant and explosives [6-9]. Ultrafine aluminum powder with the size range of 300 to 15000 Angstroms may be produced by electrical explosion of aluminum wire in the hydrogen and argon containing media. Mass spectroscopy and thermal desorption analytical methods of powder produced from wires showed that aluminum powder consisted of spherical particles with distorted crystal lattice, and contained amorphous phase, surface gases, and gases inside of particle volume of about 5 to 7% mass [10]. Those results are in agreement with our results. However, the electrical explosion procedure of Al powder is not applicable for industrial production of such powder. Different chemical processes and properties of metals saturated with argon and hydrogen and aluminum hydrides are described in literature [11-16]. The properties of chemical aluminum hydride, AlH_3 (calorific value of about 9500 kcal/kg) are well known. The drawback of conventional materials is their low stability when exposed to the atmospheric air and poor temperature stability, tending to dissociate at temperature above 105 C^0. The powder produce by using RF plasma process has a similar size range, but narrower particle size distribution. The plasma process of saturation of aluminum powder with hydrogen is not well known and the efforts have been made to increase the calorific value and stability of the product [17-20].

2 Experimental set up

The RF plasma system used for this experiment consist five major parts: inductive plasma torch, reactor, feeder, quenching device and powder collector. The plasma torch include gas forming block, water-cooled copper discharge chamber, exit nozzle and is mounted on the top of the reactor. Plasma gas system is capable to mix argon and hydrogen at different ratio starting from pure argon and ending by pure hydrogen. Exit nozzle is combined together with the powder input device. High purity aluminum powder (average particle size of 5 μm) is feeding into plasma stream by quartz feeder and water cooled probes with the controller and carrier gas system. The following quenching units were used: 28 mm diameter and 92 mm diameter cylinder type quench devices; spraying liquid argon directly into the reactor and a quench system combining liquid argon spraying and a heat exchanger consisting of a 40 turn coil. Calorific value was determined using a Parr Model 1261 calorimeter; the unburned aluminum was determined by solution with sodium hydroxide on the residue in the calorimeter using and analyses by Perkin Elmer ICP 3000. The hydrogen was determined using a LECO CHN 1000 instrument.

3 Calculation and theoretical predictions

The following parameters were calculated: surface area of the quenching components, quenching rate of the product on water-cooled surfaces, quenching rate of the product with liquid argon spray in the reactor, thickness of the collected powder on the quenching surfaces and cartridge filter. Variable parameters are: initial Al powder rate, argon-hydrogen ratio of plasma gas, Al powder quality, RF discharge power, plasma gas flow rate, carrier gas flow rate, and quenching rate. Plasma processed aluminum powder can contain approximately 2.2 times more hydrogen than chemically obtained AlH_3 [11]. Oxidation of this hypothetical substance is as follows:

$$2(AlH_{6.7}) + 4.85O_2 = Al_2O_3 + 6.7\ H_2O$$

The thermal effect of this reaction is 1435 kcal/mol or 21300 kcal/kg. Molecular hydrogen is absorbed on the surface of the melted aluminum particles. The hydrogen then dissociates into atoms and diffuses into the depth of the metal. The atomic nature of hydrogen diffusion in metals was experimentally verified during the research of hydrogen diffusion in a deuterium mixture. Having diffused into the metal, the gas is distributed among atoms of metal. The absorption of hydrogen by aluminum is endothermic. This is why the amount of absorbed hydrogen increases with the increase of temperature and reaches a peak at 2000 to 3000 K. Thus, hydrogen absorbed by aluminum is present in various states, such as:

1. Dissolved in the metal,
2. Segregated of imperfections of the crystal structure,
3. Absorbed on the surface of micro-cavities and on the particles of secondary phases,
4. Accumulated in micro-cavities in molecular form,
5. Creates metal hydrides,
6. Interact with secondary phases,
7. Dissolved in hydride of metal,
8. Dissolved in amorphous metal,
9. Dissolve in amorphous hydride of metal.

Hydrogen may exist in various states inside ultra-fine aluminum powder. However, it is the atomic hydrogen that provides the greatest improvement in available power. A hydrogen saturated aluminum powder with the formula of ($AlH_{6.7}$), has a theoretical Specific Calorific Power (SCP) above 20000 kcal/kg. Quantum theory restricts the degree of saturation of crystalline aluminum with hydrogen above AlH_3. These restrictions are removed by the transition of aluminum into an amorphous state through thermal treatment of Al powder in hydrogen RF plasma at atmospheric pressure.

4 The process and experimental results

The technology is based on direct vaporization of powdered aluminum in an RF hydrogen plasma discharge at atmospheric pressure. The resulting matrix is rapidly quenched into ultra-fine aluminum powder. SCP is not directly measured in bomb calorimeter. Standard procedure includes the burning of samples and measurement of temperature increase. The coefficient of bomb calorimeters and accurate weight of samples are taken into consideration to calculate the SCP. If the weight of incombustible components is deducted from the total weight of the sample, the SCP of combustible component can be obtained. Of course, the more content of incombustible component in the samples such as oxides, the grater the difference between SCP of sample and SCP of combustible component. One of the typical plasma sample (FM2-1) content: Al = 51.4%; Total Al = 69.5%; free carbon = 2.15%. SCP presents the total calorific value for both combustible (0.64 gr.) and incombustible (0.36 gr.) components in 1 gram of sample: 3799 (Al) + 168 cal (C) + 2995 cal (H_2) = 6962 cal. The combustible components should include: 0.514g (Al) + 0.0215g(C) + 0.1045g (H_2) = 0.64 g. The content of H_2 is calculated based on SCP of the sampleFM2-1. SCP of 1 gram of combustible components in the sample FM2-1 based on experimental data: 6962: 0.64 =10878 cal/g = 19577 BTU/lb. The composition of combustible components in sample FM2-1 is 80.31% (Al) + 3.3% (C) + 16.33% (H_2) = 100%. The gross formula for produced combustible components is $Al*5.5H_2*0.08C$. In case the hydrogen in the sample FM2-1 is in atomic state, the 0.037g of H would provide the same 2995 cal as 0.1045 g of molecular hydrogen. The combustible components would include: SCP for all combustible components in 1 gram of sample: 3799 cal (Al) +168 cal(C) + 2995 cal (H) = 6962 cal. The combustible components would include: 0.514g (Al) + 0.0215g(C) + 0.037g (H) = 0.5725 g. The composition of combustible components in sample FM2-1 would be: 89.8% (Al) + 3.75 %(C) + 6.45% (H) = 100 %. SCP for all combustible components for sample FM2-1 assuming the atomic state of Hydrogen would be: 6962: 0.5725 = 12160 cal/g = 21888 BTU/lb.

There are several stages of Aluminum powder processing in plasma reactor:

Stage I (Heating process) includes:

a – heating of solid particles from T_0 to T_{melt};

b – melting of particles;

c – heating of the melted particles from T_{melt} to $T_{boiling}$;

d – evaporation of Al particles;

e – heating of Al vapor from T_{boil} to T_{plasma};

f -dissociation of Al molecules/clusters;

and g – ionization of Al atoms.

Stage II (cooling process) includes:

a – bulk or volume recombination of Al ions;

b – association of Al atoms in Al molecules;

c – formation of clusters and nucleation in amorphous states;

d – capture of Hydrogen by Al particles both on its surface and in its body;

e – increase of the particle size in amorphous state;

f – increase of hydrogen content;

g – formation of crystal lattice of Al particles;

h – stopping the increase of the Al particle size in crystal form;

i – release of most captured hydrogen

and j – final cooling of the solid particles.

In order to produce Al particles saturated with hydrogen and interrupt the increase of particle size (i.e. to fix the particle in its meta-stable form) the quenching procedure is required. The A-type samples were obtained as a consequence of quenching of Al powder on cooled surface after stage II-f (see above) and before stage II-g. The B-type samples were obtained by volume liquid Argon quenching of Al particles after stage II-c and before stage II-d. The quality of the plasma processed aluminum depends of quenching procedure. The quenching rate has a decisive importance for retention of captured hydrogen. The volume quenching procedure is widely used in plasma-chemical processes. Most plasma-chemical products have meta-stable form, which is achieved by rapid quenching.

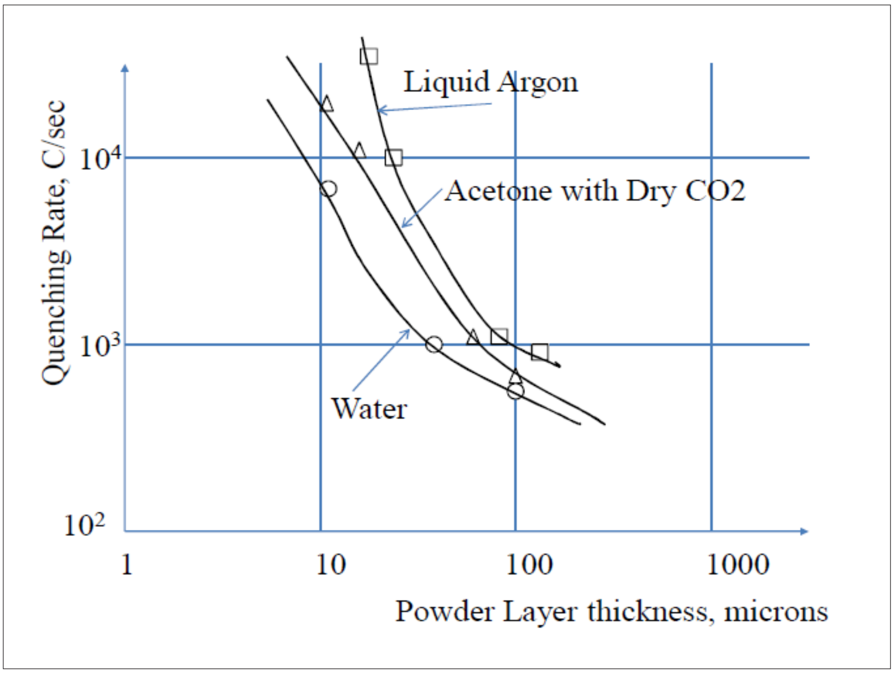

Figure 1 – Quenching Rates for the Liquid Cooled Reactor using: liquid Argon, acetone with dry CO_2 and water

Rapid solidification can be achieved by imposing a high cooling rate (103 – 109 C^0/sec) for the layer thickness not more than 10 microns. When the powder layer thickness becomes more than 10 microns, the quantity of produced powder per surface unit is increased, but the quenching rate goes down to 103 C^0/sec (see Figure 1 and Figure 2) and the upper layers of powder on the well cooled metallic surface release the captured Hydrogen. Brushing off the 100 microns thick layer led to a mixture of a high quality 10 microns layer with a "bad" quality 90 microns upper layer powder in the same sample. We apply this quenching procedure to the RF plasma method of saturation Al powder with Hydrogen and fixation of saturated Al powder in its meta-stable state. The quenching rate for three different types of cooling substances is shown in Figure 1. The following tests were performed on each sample: Aluminum content, % mass (indicate the efficiency of the Aluminum Hydrogen reaction); Hydrogen content, % mass (indicate how much Hydrogen is trapped in Aluminum particles); Carbon content, % mass (indicate impurities from other sources); Oxygen content, % mass (indicate the stability of the product) and Specific calorific power (SCP), kcal/kg (indicate the quality of the product) and Nitrogen content, % mass. As a result, the average quantity of captured Hydrogen in was about 1 % to 3.2% (see Table 1).

Figure 2 – SEM of aluminum – hydrogen saturated powder

Typical SEM of the sample is shown in Figure 2. Average particle size is 250 nm. Surface area is approximately 40 m^2/g (based on BET analysis). It is important to know the stability of the hydrogen saturated aluminum powder. The experiment was performed in special calorimeter, which could control the gas extraction depends of the sample temperature. The temperature was increased by 10 degrees per minute. Typical hydrogen release curve is shown in Figure 4. The material is very stable up to the temperature of 600 C^0.

The degree of the saturation of Al particles by Hydrogen depends of the quenching rate and is shown in Figure 3.

The best technique for the scale up to industrial production was determined. The necessary plasma power for Al powder (initial particle size 1 to 10 microns) rate equal of 1 g/sec will be in the range of 16 to 18 kW. Taking in account that the total efficiency of RF generator, RF torch and the heat transfer from plasma to the solid-liquid Al particles is about 10%, we have determined that RF power output of the production system could be in the range of 160 to 175 kW.

Table 1 – Experimental data on the amount of elements for different samples.

Name	FM2-11	FM2-12	FM2-13	FM2-14
Calorific Value, BTU/lb	11884	11259	11922	12855
Total Aluminum, %wt	96.76	97.85	96.31	98.05
Unburned Aluminum, % wt	5.46	3.52	2.44	2.30
Hydrogen, % wt.	3.18	0.86	0.78	0.44

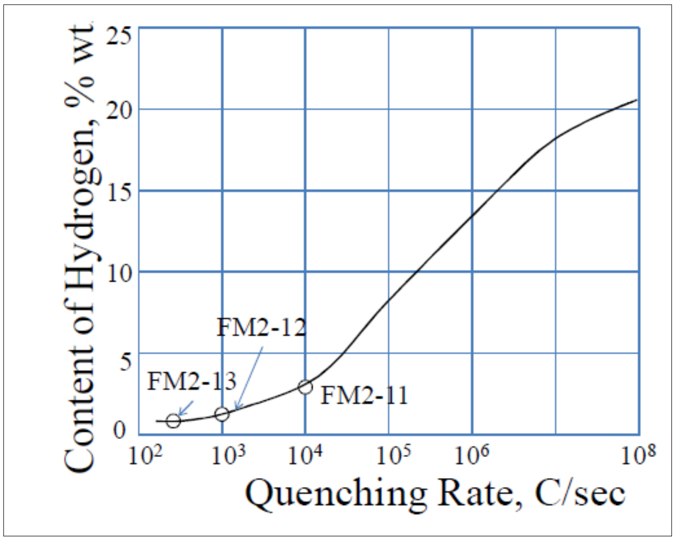

Figure 3 – The degree of the hydrogen saturation vs quenching rate for FM2-11, FM2-12 and FM2-13

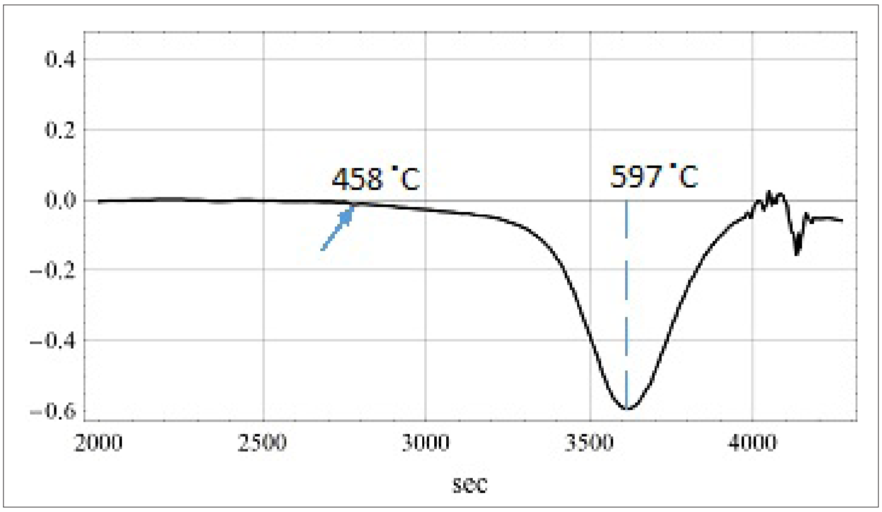

Figure 4 – Typical Hydrogen release curve

5 Conclusions

The technology to produce a new high energy hydrogen saturated aluminum powder using RF plasma process at atmospheric pressure is successfully demonstrated. Standard methods of product analysis such as bomb calorimeter, derivatograph and differential scanning calorimeter (DSC) need to be modified to provide adequate analysis for meta-stable Al powder. The measured quantity of captured Hydrogen was 3.18% wt. Heat of combustion for combustible components of produced Al powder was in the range of 10878 to 12160 cal/g. This value overcome the SCP of chemical AlH_3 and can be increased up to 20000 cal/g. The optimum processing conditions were ascertained, and the best techniques for scale up to industrial production of 8 lbs/Hr of AlH* powder at 160 to 175 kW RF plasma system were determined.

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