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SUBJECT: Arc Calcination of Thorium Oxide

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ABSTRACT

An overall description of the background material on the use of electrical arcs for heating of powders is presented as well as a summary of experimental studies on the arc calcination of thoria made at Oak Ridge National Laboratory. Favorable results have been indicated both with heating thoria powder in an arc heated gas and with thoria formed into a consumable electrode. Use of a consumable electrode produces thoria particles $0.1 - 0.01\mu$ in diameter. It is recommended that additional electrodes be fabricated and further arc calcination tests be run to produce a quantity of product sufficient for evaluation.

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812 001

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1.0 INTRODUCTION

In considering electric arc heating or calcination of a material there are three principal modes of operation. One, the method used in steel and smelting operations as well as regular metal-arc welding, depends upon forming the arc between an electrode and a pool of molten metal. This method would certainly not appear to be suitable in the case of thorium oxide. Another method utilizes a gas to transfer the energy from an electrical arc to the material to be heated. This method is employed in Heliarc welding or in the atomic hydrogen torch. Heating dispersed thoria particles in a gas by this method does show promise.

The third method of heating consists of dispersing the solid to be heated in a carbon matrix in the form of a consumable electrode, a relatively new process if the material added to the carbon is the desired product. Carbon with rare earth compounds added has been used for many years as a light source. Recent experiments in this laboratory show that a consumable electrode containing thoria can be used to produce very small ($<0.1\mu$) thoria particles.

2.0 ATOMIC HYDROGEN TORCH

The high temperature obtained with an atomic hydrogen torch is possible due to the high "heat capacity" of hydrogen in dissociating from H_2 to $2H$. The electrical energy of the arc is used to dissociate the hydrogen and then is recovered at temperatures in the order of $4000^\circ K$ when the recombination of the hydrogen atoms takes place a few centimeters away from the arc. By using the hydrogen as a carrier gas for thoria dust, it has been possible to fuse some of the thoria particles as they were suspended in the recombination zone of the hydrogen atoms. An electron micrograph of such particles is shown in Fig. 1. The arc in this run was formed between $1/16$ " tungsten electrodes at 30 amperes and 40 volts with a hydrogen flow of 10 cfh.

The major problems in this form of heating is getting a reasonable fraction of the thoria particles through the high temperature zone. In order to prevent melting of the electrodes it is necessary to remove the heat from the arc as it is generated. This heat removal requires an excess of molecular hydrogen gas which will not be dissociated and recombined but which will form an envelope around the atomic hydrogen flame. (If the excess hydrogen is open to the atmosphere, it will burn at a temperature which is not nearly so high as the recombination reaction temperature).

According to H. G. MacPherson, while a member of the National Carbon Research Laboratories, "It is more difficult than one might assume to heat a gas stream to high temperatures by normal-transfer methods. Where such a hot gas is needed, it is easiest to heat it directly by an arc discharge

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FIGURE 1. Thorium Oxide Passed Through Atomic Hydrogen Flame.

812 003

occurring in the gas."¹

The atomic hydrogen flame has been used at Mallinckrodt^{2,3} for the preparation of fused UO_2 . The process was aimed at forming maximum density UO_2 by a process similar to the Verneuil process for the preparation of monocrystalline sapphires. The product was a fused solid rod or boule rather than fine particles.

3.0 CONSUMABLE ELECTRODES

The high intensity carbon arc is a very suitable means for reaching extremely high temperatures. This type of electrical discharge is established above the sudden transition from an ordinary type of arc when the current density on the electrodes is increased beyond a critical point. This form of arc is familiar to illumination engineers since it is marked by a sudden increase in the brilliance of the arc. Another change, observed when the current density is increased beyond this critical value, is a rapid increase in temperature with increasing current from 3900°K to 7000°K or more.

It has been found possible by incorporating a metal salt or oxide in the electrode material to subject the material to the high temperature of the arc. This technique has been used on a pilot plant as well as a laboratory scale by the Vitro Laboratories with materials such as boron⁴, silica⁵, and manganese⁶. For illumination use, additives such as rare earth oxides have long been used mixed with the carbon of electrodes to stabilize the arc and increase its brilliance. The Vitro Laboratories report that virtually any material which is incorporated into the electrodes can be vaporized and heated to temperatures in excess of 7000°K at a power consumption of between 3 and 7 kwh per pound.⁵ Their studies indicated that for operation in air, electrode carbon is oxidized and passes off as carbon monoxide, whereas a metal oxide becomes a vapor and condenses as a fine fume. Their product condensed as solid spherical particles $0.01 - 0.1 \mu$ in diameter.⁷

3.1 Carbide Formation

One factor to consider in a high temperature operation with carbon and a metal oxide is the possible formation of carbides. In the case of thorium, this reaction could be:

Calculations show that for this reaction, $\Delta F_{2000^\circ\text{K}}^\circ = 4.7 \text{ kcal}$ and $\Delta F_{3000^\circ\text{K}}^\circ = -38.3 \text{ kcal}$ indicating that ThC_2 would be more stable than thorium at temperatures somewhat over 2000°K and in the absence of other reactants. In Vitro's work on boron⁴ they were troubled with carbide formation; however, they were operating

in an inert atmosphere in an effort to produce boron metal. If oxygen were present, the reaction:

must be considered. Here calculations show that $\Delta F^\circ_{2000^\circ\text{K}} = -47,196$ kcal and $\Delta F^\circ_{3000^\circ\text{K}} = -72,694$ kcal, favoring the oxidation of any carbide formed. Sheer⁷ reports no carbide formation with metals when operating the arc in air. No documented evidence has been found establishing the formation of carbides of thorium with an arc operating in an oxidizing atmosphere.

3.2 Production Rate

In order to obtain some conception of the size of equipment required for small scale production of fused thoria spheres, some conservative estimates have been made on the production from a single small unit. Vitro⁴ operated an arc at 300 amperes and 65 volts using an electrode 5/8" diameter containing 35% carbon (65% borax) and obtained an electrode erosion rate of 3 1/2" per minute. Making the following assumptions for a thoria-containing electrode:

Electrode diameter	1.0 cm
ThO ₂ content (by wgt)	50 %
Electrode density	6.0 gm/cc
Consumption rate	3.0 cm/min

there would be vaporized 3.5 gm per minute of ThO₂ or approximately 11 pounds per 24 hour day.

3.3 Tests Made at Oak Ridge National Laboratory

Some arc calcination tests were made about a year ago by C. E. Curtis of the Ceramics Research group. His method consisted of dusting ThO₂ powder through a hollow refractory tube into an arc using carbon electrodes. The product consisted of a mixture of solid and hollow spheres 100 - 300 μ in diameter. This material was not considered suitable for reactor slurry use.

Recently a test was made by C. S. Morgan¹⁰ and C. E. Curtis using a hollow carbon electrode for feeding 15 - 30 μ agglomerates of ThO₂ particles into the arc. The product appeared unchanged by x-ray analysis but proved much poorer than the feed material in a Waring Blender degradation test.

Experiments in the Unit Operations Section have consisted of burning 3/16" carbon electrodes having a 1/8" core packed with a thoria-carbon mixture. It

has not been possible to collect significant amounts of the product but samples of the "smoke" from the arc have been taken. A photomicrograph of such a sample is shown in Fig. 2. Most of the particles appear to be spheres with a diameter of 0.02 - 0.04 μ . Sheer⁷ feels that particles up to 0.1 μ diameter can readily be obtained by surrounding the arc with an insulated chamber and diluting the ThO_2 vapor stream (lowering the dew point).

3.4 Electrode Preparation

It is reported^{4,5,7} that satisfactory operation cannot be obtained with a loosely packed cored electrode but that a compact homogeneous electrode is needed. Vitro reports^{4,7} that satisfactory electrodes can be made using as much as 80% metal oxide content while MacPherson⁹ feels that with a refractory material like ThO_2 the oxide content should be limited to 10 - 15%.

Experimental work will be necessary to produce a satisfactory electrode since the ThO_2 present will affect the electrical and physical properties of the electrode. Apparently the best mixture of one of the many types of carbon (coke flour, coal flour, carbon black, etc.) with binder and oxide must be determined by trial and error.

4.0 RECOMMENDATIONS

It is felt that arc calcination using consumable electrodes shows significant promise for the preparation of thorium microspheres. At present the fabrication of suitable electrodes containing thorium is the major problem in obtaining sufficient product to evaluate its usefulness. No data are available describing the behavior of slurries of thorium spheres having diameters of less than 0.1 μ . Enough material should be collected to permit determination of particle size, shape, composition, yield stress, and surface area.

An attempt to fabricate a few electrodes should be made at Oak Ridge National Laboratory and at the same time inquiries should be made regarding having experimental quantities of electrodes made by an outside vendor such as Stackpole Carbon Company or National Carbon Company.

The off gas and collection system in use for flame calcination should prove adequate for test use and an electrode feed mechanism can be easily devised. A 150 ampere AC welding machine on hand can be used although it is understood that there might be some advantages to using direct current.

FIGURE 2. Thorium Oxide from High Intensity Arc Vapor.

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