CHARACTERISTICS OF PARTICLE GROWTH IN A THERMAL PLASMA JET

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ABSTRACT

An argon arc plasma reactor is used to vaporize and react injected metal powders with CH_4 or N_2. Condensation and particle growth in the decaying plasma jet are studied by varying the reaction conditions such as powder injection location and mass injection rates. The particle growth rate in hetereogeneous nucleation is determined to be proportional to the vapor phase concentration of the condensing material.

1. INTRODUCTION

An arc plasma reactor has been previously developed (1)which can vaporize and react injected solid particles. This processing is well suited for refractory materials due to the high heating rates available in a thermal plasma. The refractory metal carbides and nitrides are commonly used as cutting tool materials or as sintered compacts for high temperature structural materials. Both of these applications require specific particle sizes. If control of the product powder size distribution is possible, the high purity plasma processing of materials could be very useful. This paper presents work done as part of a study on condensation and particle growth in a decaying thermal plasma jet.

A field-free plasma jet cools rapidly after passing the anode, resulting in a rapid temperature drop ΔT. For vaporized refractory metals with high boiling points, high supersaturation levels are reached in such decaying plasmas. Supersaturation is defined as the ratio of the vapor phase partial pressure to the partial pressure over a flat surface of the bulk solid. The unstable vapor phase system self-nucleates on atomic clusters of critical size. These clusters form in the vapor through random collisional processes. Below the critical size, the clusters are unstable for a given supersaturation, while above the critical cluster size the free energy of the cluster is negative (2). Calculations by Burton (3) have shown that a critical cluster can be

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as small as 25 atoms. This small critical cluster size allows rapid relief of the supersaturation by condensation on the many larger-than-critical clusters. The result is a high number density of ultrafine particles.

If the supersaturation ratio, p/p_o, of the cooling vapor can be kept at a low level the vapor phase material will condense hetereogeneously on the particles or ions already in the plasma. As hetereogeneous nucleation and condensation does not rapidly deplete the vapor phase material, the particles can grow larger than those which are homogeneously self-nucleated.

In the arc-plasma reactor used for this work, low mass injection rates of W powder are vaporized and condense in the decaying plasma jet, forming powders 30-40 Å in diameter. Due to the rapid quench of 10^5-10^6 °C/sec and the observed ultrafine uniform particle sizes, it is infered that this condensation is dominated by homogeneous nucleation. For increased particle growth the quench rate of the decaying jet should be reduced to prevent the vapor from reaching a high supersaturation ratio and to allow hetereogeneous condensation and particle growth. Since the vaporized and condensing material is in the reactor for only 20 msec, rapid growth of the condensing particles is desirable. The particle growth rate in hetereogeneous condensation depends on the rate at which individual atoms strike the condensing nuclei. At thermal plasma temperatures and pressures, the mean free path of the vapor phase material is much larger than the condensing nuclei diameters. This allows the application of a simple kinetic growth law for the nuclei (4), first order in the concentration of the condensing phase.

$$\frac{d\, v_p}{dt} = \frac{\pi d_p^{\,2} v_m (p_1 - p_o)}{(2\pi m k_B T)^{\frac{1}{2}}}$$

where v_p and v_m are the particle and molecular volumes respectively, d_p is the particle diameter, p_1 is the vapor phase pressure and p_o is the pressure above the surface of the bulk solid phase. This growth law indicates that if the vapor phase concentration can be increased while still maintaining the supersaturation level below the homogeneous nucleation realm, the final powder particle size will increase.

2. EXPERIMENTAL STUDIES

The reactor design includes a graphite reaction tube, 1 cm in diameter, extending from the torch anode and variable in length (Figure 1). This tube stabilizes the jet and, by preventing premature mixing with the cold argon in the collection chamber, helps to reduce the quench rate in the plasma. The plasma jet also strongly heats the reaction tube and this hot wall reduces the temperature gradient at the plasma jet fringes. Transferring the arc to the secondary anode allows injection of the powders into a current-carrying plasma. The cold material injection and vaporization causes a field strength increase in the plasma. The resulting higher power level compensates for high cold material injection rates.

The effect of varying the length of the reaction tube is investigated using 1-2 micron W and CH_4 as reactants. Figure 2

shows the atomic percent of W_2C and W in the product for different reaction tube lengths. As the reaction tube length increases, less W is found and the amount of W_2C increases. The longer tube encourages chemical equilibrium in the product by reducing the cooling rate. The material collected from these experiments is a three phase product, the phase not shown in Figure 2 is the high temperature phase β-$WC_{0.6}$. The 8 cm reaction tube data shows some 65% of the product is this high temperature phase, indicating the quench is rapid from approximately 2600°C to approximately 1200°C. At 16 cm this carbide has transformed to the low temperature W_2C, indicating the quench has now slowed enough for condensation to be complete before mixing with the cold gas of the collection chamber.

X-ray line profile analysis is used to characterize mean particle sizes of the product powders. In comparing the mean particle size of the transferred arc products with the nontransferred arc material, the nontransferred arc operating mode results in larger particle sizes. Figures 3a and 3b are X-ray diffractometer line profiles of the products from a transferred and a nontransferred arc processing of 1-2 micron W powder and CH_4. The mass injection rate is similar for both, but the extreme line broadening of Fig. 3a indicates a very small crystallite size. The mean particle size for the transferred arc case is calculated to be 35 Å, while in the nontransferred arc case it is 450 Å.

The importance of the metal vapor concentration is demonstrated with a reactor experiment made without removing condensed material deposited in the reaction tube during a previous run. This produces a temporary increase in the vapor phase concentration by constricting the reaction duct. Figure 4 shows the x-ray diffractometer trace of the product. This run was identical to that of Figure 3b except for the constricted reaction tube. The narrow peak profiles indicate a large particle size calculated to be 1600 Å.

Further increases in the W mass injection rate reveal unvaporized material, i.e. the vapor phase concentration cannot be further increased with this reactor. A wider range of injection rates can be tested if a lower boiling point material, such as Ti, is used. Up to 4 g/min of 44 micron Ti powder can be completely vaporized in this reactor. The larger starting powder particle size also allows for accurate metering of the injection rate. Figure 5 shows the results of a series of nontransferred arc Ti + N_2 experiments, revealing a linear increase in the product particle size with increasing Ti mass injection rates. Above 4 g/min Ti injection, further Ti is not vaporized and the vapor phase concentration remains constant.

3. DISCUSSION

Use of the transferred arc is effective in vaporizing injected material, however the rapid decay of the plasma jet downstream from the anode yields quench rates high enough to homogeneously nucleate the condensing material. The result is extremely fine product particle sizes. The nontransferred arc injection modifies the quench characteristics of the reactor. Injecting the reactants in the plasma jet produces local cooling as the material vaporizes. The vapor continues to cool but since the quench rate is diminished the very high supersaturation which occurs in the

transferred arc process may not be achieved. Without high supersaturation the vapor phase material will not self-nucleate but instead will hetereogeneously condense on the existing particles and ions in the plasma

An alternative explanation for the increased product particle size of the nontransferred arc processing is possible. If the local cooling in the nontransferred plasma jet by the injection and vaporization of powders is great enough, the injected material may not be entirely vaporized. These particles, even if they are quite small, would serve as nucleation sites for the condensing vapor as the plasma continues to cool. In the W + CH_4 reaction, unvaporized W would nucleate the condensing W and C atoms before the vapor phase concentrations reached high supersaturation levels, and the final particle size would be determined by hetereogeneous and not homogeneous nucleation rates.

In this closed reactor system it is difficult to experimentally verify the condensation mechanisms. Powder injection into a free burning arc would allow unobstructed viewing resulting in improved diagnostics of the vaporization and condensation process.

The Ti-N experiments confirm that the particle growth rate is first order in the concentration of the vapor phase material, as predicted by the kinetic growth law. When in a hetereogeneous nucleation realm (nontransferred arc mode), increasing the condensing phase concentration increases the rate at which the particles grow.

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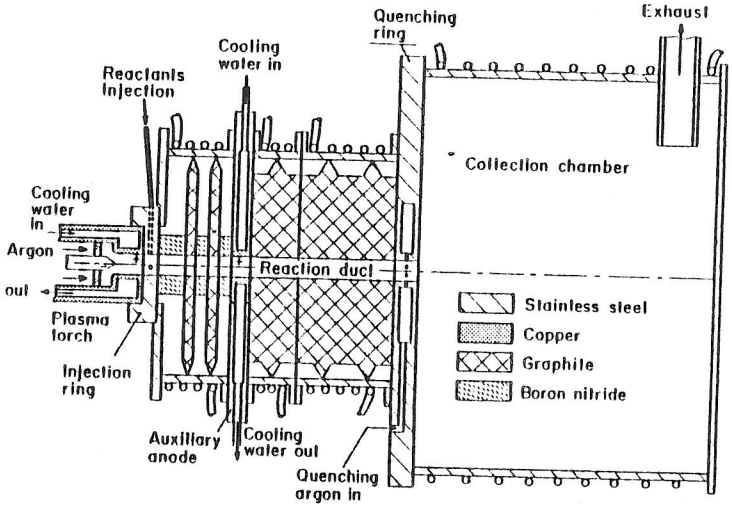

Fig. 1: Schematic of the experimental reactor.

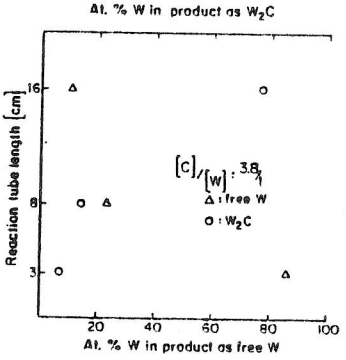

Fig. 2: Effect of varying the reaction tube length on the W-C reaction products.

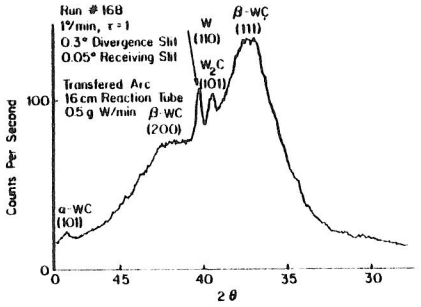

Fig. 3a: X-ray diffractometer trace of W-C transferred arc products. 1-2μmW+CH_4.

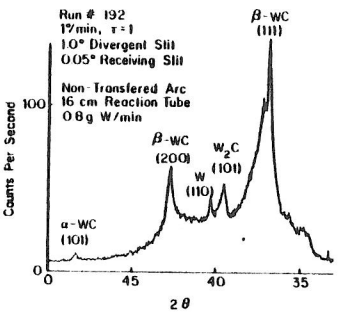

Fig. 3b: X-ray diffractometer trace of W-C nontransferred arc products. 1-2μmW+CH_4.

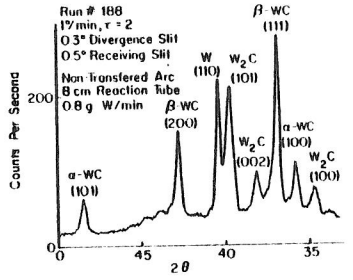

Fig. 4: X-ray diffractometer trace of W-C nontransferred arc products with constricted reaction tube.

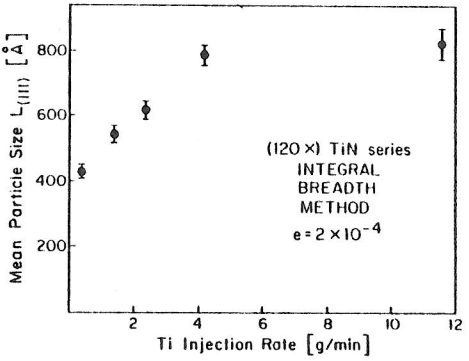

Fig. 5: Effect of varying the mass injection ratio for nontransferred arc plasma processing.