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PREPARATION OF NANOPHASE MATERIALS BY THERMAL SPRAY PROCESSING OF LIQUID PRECURSORS

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ABSTRACT

Thermal spray processes were modified to spray liquid feedstocks. Nanophase Al_2O_3, Mn_2O_3, ZrO_2 and Y_2O_3 stabilized ZrO_2 powders and deposits were produced. Ceramic particles of **1-150 nm** size were collected at a rate of **~ 20 mg/min.**, with **~ 20-35** % collection efficiency. Organometallic precursors produced oxide deposits with a powdery morphology, while aqueous solutions yielded hydroxide deposits, requiring post spray heat treatments for producing oxide coatings. Spray feedstock and processing conditions affected the size, shape and phase composition of the synthesized nanomaterials. Particles with wider distributions of larger size grains were produced from aqueous solutions, while a narrow distribution of fine-grained materials were produced when organometallic precursors were used. @1997 *Acta Metallurgica Inc.*

INTRODUCTION

Nanomaterials exhibit unique properties and these features are expected to find applications in high technology industries (1). A variety of techniques such as inert gas condensation and mechanical milling have been developed to produce various nanomaterials. A novel technique, viz., thermal spraying of liquids (TSL), has been developed to produce nanoceramic powders and deposits (2,3).

In conventional thermal spray process, a high temperature flame is produced employing either electrical or chemical energy and this flame is used to process solid feedstock material. In the TSL process, Fig. 1, liquid precursor chemicals are atomized and injected into a thermal spray jet. Nanomaterials, synthesized in the flame, are collected as powder in an electrostatic precipitator or as a deposit on a substrate. The TSL technique has many advantages such as low cost, simplicity, versatility to produce nanostructured powders and deposits of a variety of materials, high rate of synthesis, high collection efficiency and the flexibility to produce complex composites with chemical homogeneity.

EXPERIMENTAL

Precursor salts (isopropoxide, butoxide, acetate and nitrate) were dissolved in organic solvents

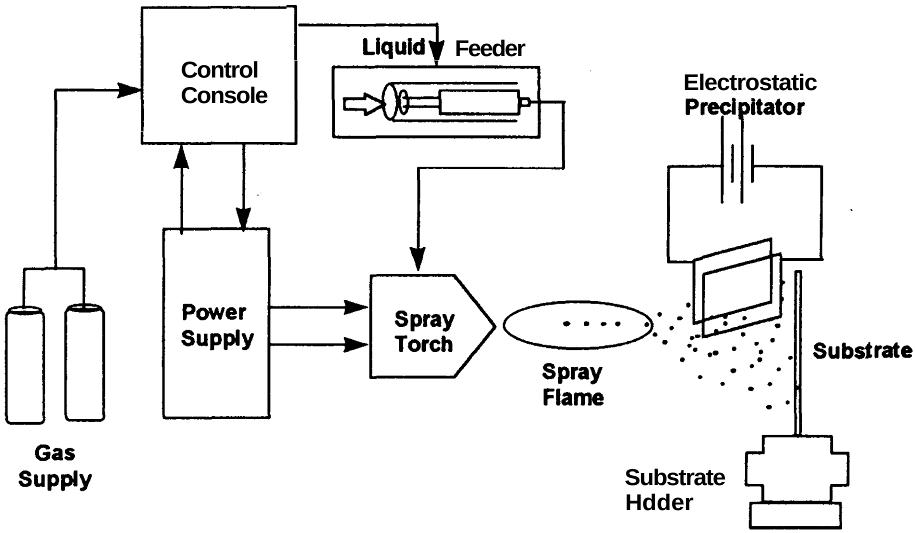

Figure 1: Schematic of the Experimental System.

(isopropanol or butanol) to obtain organic solutions. Aqueous solutions were produced by dissolving appropriate salts in distilled water. Grit blasted stainless steel coupons were used as substrates. Conventional thermal spray systems, including plasma, electromagnetically coalesced (EMC) plasma, flame and high velocity oxy-fuel (HVOF), with modified torches, incorporating the liquid injector, were used for spray synthesis of nanomaterials.

A series of process characterization experiments were carried out by varying the feedstock, atomizer and spray parameters to optimize the process parameters (4). Deposits were heat treated at 1273 K for one hour with heating and cooling rates of 5 K/min. The specimens were characterized using microscopy, SEM, XRD and TEM. Scherrer analysis was carried out to estimate the grain sizes (2,3).

RESULTS AND DISCUSSION

Ceramic particles (Al_2O_3, Mn_2O_3, ZrO_2 and Y_2O_3 stabilized ZrO_2) particles of 1-150 nm size can be collected at a rate of ~ 20 mg/min., with ~ 20-35 % collection efficiency. TEM images of typical powders are shown in Fig. 2, and the particle size distributions (PSD) of various powders are presented in Fig. 3. A slight increase in the partcicle size was observed when the spray jet was changed from combustion flame to plasma. Varying the flame conditions from stoichiometric to oxidizing produced a small decrease in the PSD of manganese oxide. Spray feedstock had a strong effect on the PSD of synthesized powders; particles with wider distributions of larger size grains were produced by aqueous solutions, while a narrow distribution of fine-grained materials were produced by organometallic precursors. The powder XRDs contained the peak patterns of only oxide phases, indicating that all the chemical reactions have been completed during the spray synthesis.

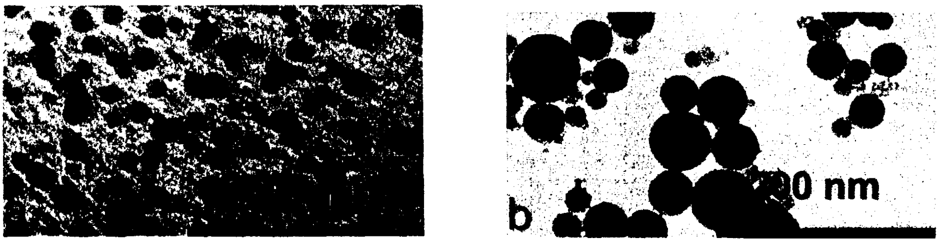

Figure 2: TEM Images of Plasma Synthesized Zirconia and Flame Synthesized Alumina

Spray processing of liquid feedstocks yielded **nanograined** deposits at a deposition rate of around **3-15 μm/min.**, with about **10-25** % deposition efficiency. **XRDs** of typical deposits are compared in Fig. 4. Strong, dense and adherent hydroxide deposits, which required post spray heat treatments for producing oxide coatings, were obtained with aqueous solutions. Organometallic precursors produced flame **pyrolyzed** oxide deposits with a powdery morphology and low adhesive and cohesive strengths.

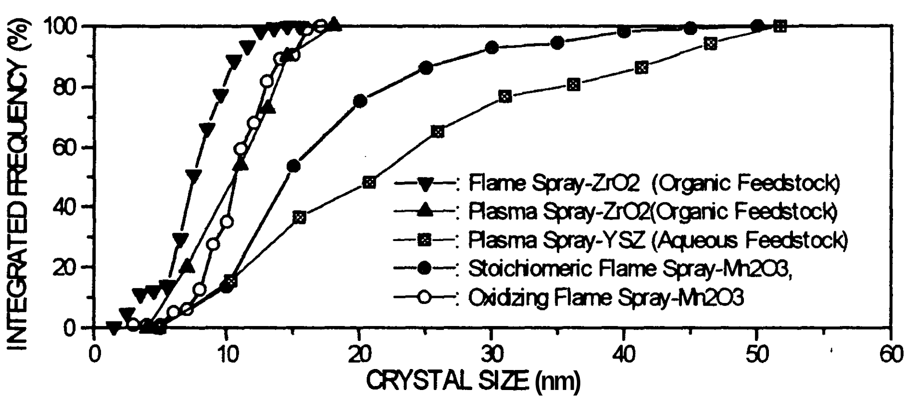

Figure 3: Particle Size Distribution of TSL Synthesized Powders

In the TSL process, liquid droplets are injected into the spray flame, and as they are accelerated by the flame, heat transfer from the flame into the droplet leads to evaporation of the solvent, condensation of the precursor, chemical reaction and synthesis, nucleation and growth of the grains and densification of the particles **(2,3,5)**. Since organic solutions produce finer droplets (4) and increase the enthalpy and thermal conductivity of the flame (2,3), all the reactions noted above are completed in the flame. This leads to the formation of a narrow range of small sized particles, and produce deposits formed by the flame pyrolysis process (5). Aqueous solutions produce relatively larger sized droplets (4). They cool the flame and also require more heat for evaporation of the water. Hence, only evaporation and condensation reactions are completed in the flame when aqueous solutions are used. This leads to chemical reactions occurring at or near the substrate surface and results in the formation of strong and adherent hydroxide deposits. Larger droplet size, coupled with **affinity** of the water vapor to increase the particle size (6), result in a wider distribution of larger sized particles.

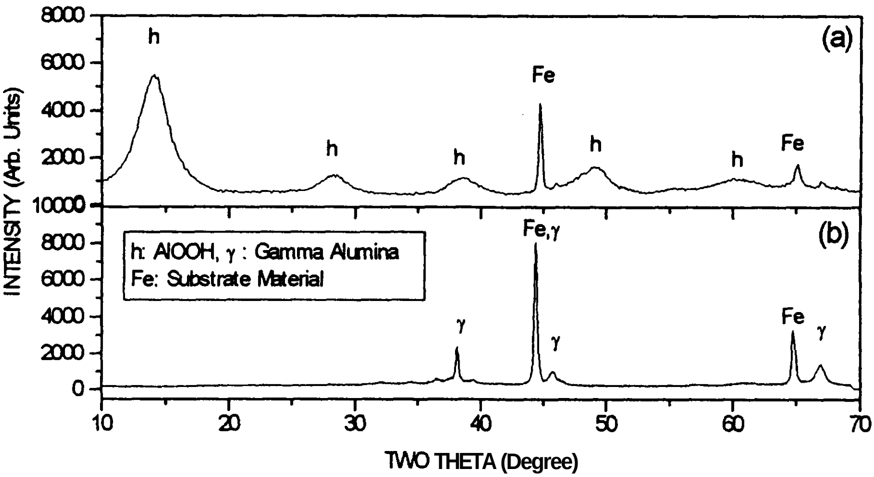

Figure 4: XRD of Alumina Depositrs: (a) EMC Sprayed with Aqueous Solution and (b) Flame Sprayed with Organic Feedstock.

CONCLUDING REMARKS

Conventional thermal spraying has been modified to spray liquid precursors and produce nanophase Al_2O_3, Mn_2O_3, ZrO_2 and Y_2O_3 stabilized ZrO_2 powders and deposits. Characteristics of the synthesized nanomaterials depend on the spray feedstock and processing conditions.

ACKNOWLEDGMENTS

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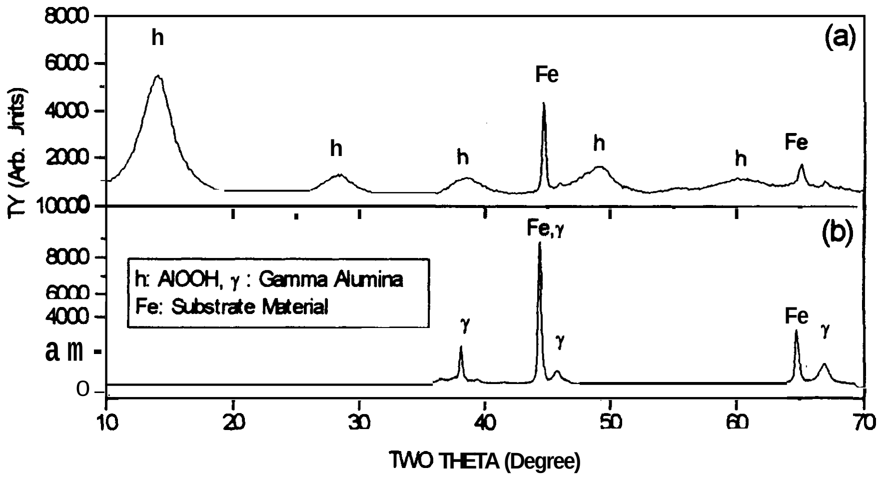

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