Liquid Precursor Plasma Spraying of Functional Materials: A Case Study for Yttrium Aluminum Garnet (YAG)

B.G. Ravi, Ashutosh S. Gandhi, X.Z. Guo, J. Margolies, and S. Sampath

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RF precursor plasma spray synthesis (RFPPS) is an innovative and rapid technique to deposit functional oxide coatings by starting from liquid inorganic precursors and directly producing ceramic coatings. RFPPS offers excellent opportunities in exploring the nonequilibrium phase evolution during plasma spraying of molecularly mixed precursors to form multicomponent oxides. A detailed discussion of progress, critical issues and consideration in precursor development, RF plasma spraying, coating development, and phase evolution of yttrium aluminum garnet (YAG) is presented as a case study. Appropriate selection of precursors and proper tuning of spray parameters resulted in amorphous or crystalline coatings in the as-sprayed condition. YAG phase selection has also been investigated using a discrete, low-density combinatorial synthesis approach.

1. Introduction

Precursor-based synthesis of inorganics is an efficient method of synthesis of inorganic high-temperature materials and also allow exploration of compositional/phase space, helping to identify regions of interest for functionality (Ref 1, 2). Thermal spray (TS) expands the potential of precursor routes by offering access to thermal excursions with extreme temperature-time profiles, coupled with the capability for deposition of novel materials in useful forms as thin films and coatings (Ref 3-11). Traditional TS utilizes powder feedstock of premixed compositions to produce ceramic coatings. However, when complex multicomponent oxide films are desired wide ranging issues associated with composition and phase stability arises and makes it difficult to achieve the requisite functionality, explore the compositional field, and its effect of film characteristics. For instance, one of the early investigations of precursor-based processing was initiated

in late 1980s at Stony Brook University during the efforts to produce oxide superconductor films of the Y-Ba-Cu oxide family. Powder-based method indicated preferential CuO vaporization during plasma spraying pointing to need for over compensation of CuO in the powder. However, to focus in on the chemistry sweet spot required extensive evaluation of a variety of starting powder compositions (Ref 12, 13). The precursor approach allows a much more rapid method to explore the chemistry field and was briefly investigated with limited success. Since then a number of studies have been conducted with varying fundamental and applied interests, but new capabilities in both solution chemistry, precursor injection, and plasma spray processes have led to renewed interest in this area (Ref 3-11). Given the extreme conditions in the thermal spray process (in terms of large gradients in exposure temperature and very small time scales), one would anticipate formation/stabilization of metastable phases and, therefore, represents a unique synthetic tool for solid-state chemistry. The advent of nanotechnology has further expanded the field considerably with opportunities to create materials and surface with unique functionality enabled by nanoscale phenomena.

Multipronged efforts at various institutions during the '90s witnessed trials of solution/suspension spray. In early trials at University of Sherbrooke, Canada, several materials were evaluated with varying success using axial-feed liquid suspension plasma spray (SPS) (Ref 3, 4). Recently, SPS has been widely used to make ceramic powders and coatings using RF and DC plasma spraying approaches (Ref 5, 6, 14-16). Here the inorganic material was introduced in a liquid suspension and generally does not utilize any chemical modification that results from precursor decomposition. Combustion CVD (CCVD), a complementary process using combustion rather than plasma, was employed at Georgia Institute of Technology to synthesize

B.G. Ravi, X.Z. Guo, J. Margolies, and **S. Sampath**, Center for Thermal Spray Research, Department of Materials Science and Engineering, State University of New York, Stony Brook, NY; **B.G. Ravi**, GT Solar Inc., 243 Daniel Webster Highway, Merrimack, NH 03054; **Ashutosh S. Gandhi**, Metallurgical and Materials Engineering, Indian Institute of Technology–Madras, Chennai 600 036, India; **X.Z. Guo**, Boston Applied Technologies, Inc., Woburn, MA 01801; and **J. Margolies**, GE Energy, Schenectady, NY. Contact e-mail: bgravi2000@gmail.com.

coatings of metals, oxides, and polymer composites (Ref 17).

Solution precursor plasma spray (SPPS), based on DC plasma, has been developed for synthesizing nanostructured powders and coatings (Ref 7-11). In DC plasma approaches, a precursor solution is injected radially into the plasma since the contamination of the product by arc erosion of the DC electrodes is often considered as a disadvantage. Additionally, external radial injection of feedstock leads to nonoptimal material injection into the plasma flame and can produce less homogeneous thermal processing as well as reduced material processing efficiency. Although there have been efforts in this area since the 1980s and early 1990s with the goal of synthesizing nanoparticles, only recently has the work progressed in the area of functional systems. At the Center for Thermal Spray Research (CTSR), Stony Brook University, an integrated, and multidisciplinary investigative strategy has been conducted to explore the benefits and limits of this synthesis strategy.

Studies at CTSR have focused on RF induction plasma spraying of molecularly mixed precursors to deposit thin/thick films of: relatively simple systems such as γ-Al_2O_3, Y_2O_3, and Y-stabilized zirconia (YSZ) and complex systems such as yttrium aluminum/iron garnets (YAG, YIG, YAG-YIG, and Eu-doped YAG), lanthanum strontium manganate (LSM), and Zr-substituted $Y_2Ti_2O_7$ pyrochlores (Ref 18-24). To differentiate this approach from other solution or suspension spraying through plasma it was named as RFPPS (Radio frequency Precursor Plasma Spraying). In RFPPS, the coatings were made directly from liquid phase. When the temperature of the plasma and liquid precursor feed rate are appropriate enough almost all atomized liquid droplets would dehydrate, crystallize, and form a crystalline coating. On the other hand, relatively low-temperature plasma coupled with higher liquid feed rate would favor a situation where majority of the droplets reach the substrate before they completely dehydrate and from a quasi-amorphous coating.

The important advantages of RFPPS include: axial feeding of precursor solution/sol into the larger hot zone which would provide a longer particle residence time, and electrode-free nature of RF plasma which avoids the contaminations from the electrodes. RFPPS offers much greater operational temperature, large temperature gradients, very short exposure time in the flame which facilitates investigation of opportunities/implications of metastable phases, stoichiometries, and microstructures. Our integrated approach in the development of functional oxides from precursors is both science based (precursor development, exploratory synthesis, process understanding/modeling) and technology based (property assessment for potential application, identifying key barriers to implementation, and perspective paths to overcome the barriers). Systems of particular interest studied and being developed include large area luminescence coating (based on doped garnets), electrode/electrolyte for solid-oxide fuel cells and gas separation membranes (based on YSZ systems), and advanced ferrites and dielectrics for magnetic/electromagnetic applications.

Although the development of coatings of the above-mentioned functional oxides had varying successes, many challenges remain and require continued interdisciplinary collaborations. This article reports the progress, critical observations, and challenges in developmental work of RFPPS YAG coatings, as a case study. Several other systems have been investigated with this approach and are reported elsewhere (Ref 18-24). The development and decomposition characteristics of various precursor types and associated phase evolution of YAG are described. In addition to direct deposition of functional oxide films from precursors, thermal plasma also offers opportunities to examine structure evolution and functionality through a discrete combinatorial type strategy. RFPPS has been utilized to investigate metastable phase selection by screening out a narrow composition range in Al_2O_3-Y_2O_3 systems. Compositions around garnet phase field were sprayed to form coatings and their phase stability over temperature was investigated. Since this strategy was used for rapid screening of only fewer compositions (low-density library vs. high-density library in a conventional combinatorial approach) we call it as a *discrete combinatorial approach*.

2. RF Precursor Plasma Spraying of YAG—A Case Study

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) has been extensively investigated for the high-temperature engineering applications, such as refractory, insulating coating, optical devices, and phosphors for various display panels in recent years (Ref 25-27). In the Y_2O_3-Al_2O_3 system, apart from the end-member phases, there are three widely accepted compounds stable at ambient temperatures and pressure: $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), and $Y_4Al_2O_9$ (YAM), belonging to cubic garnet, orthorhombic, or hexagonal perovskite and monoclinic structural families, respectively (Ref 28, 29). Figure 1 illustrates the phases in the Y_2O_3-Al_2O_3 phase diagram. It is evident from the literature that the synthesis of single-phase YAG powder is difficult mainly due to the favored formation of perovskite and the monoclinic phases rather than single-phase YAG. Formation of these transient phases has been ascribed to inhomogeneity of the precursors in a majority of studies, implying that yttrium-aluminate compounds do not tolerate deviations from their stoichiometry. Conversely, it has been claimed that metastable phases form in a homogeneous material and thus represent deviations from stoichiometry; for example, the YAH phase field was reported to extend down to the YAG composition. Furthermore, YAG appears to tolerate greater off-stoichiometry on the Y_2O_3-rich side of Y_2O_3-Al_2O_3 system (Ref 30). The selection of metastable phases during soft chemical synthesis processing is often considered as a problem, requiring additional heat treatments to transform the systems into desirable equilibrium structure. On the other hand, the metastable compositions can also provide unique attributes with potential applicability. For
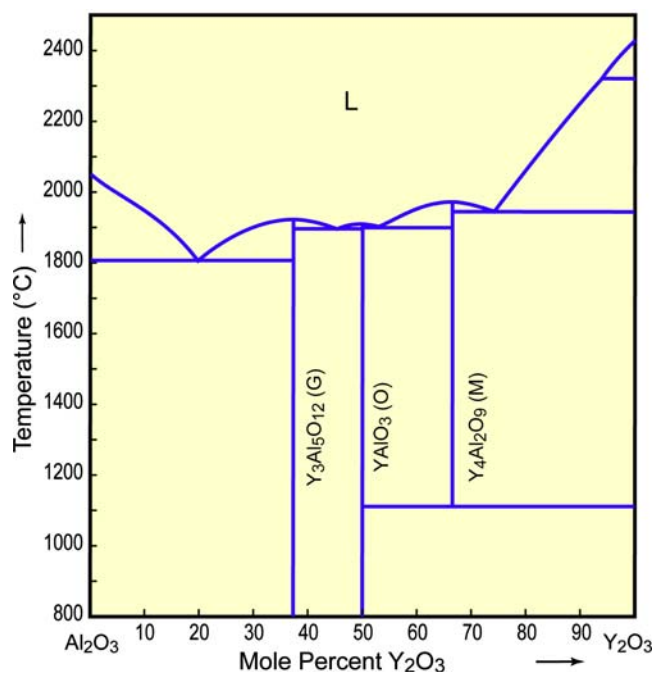
Fig. 1 Phase diagram shows various phases associated with Al_2O_3-Y_2O_3 system

example, amorphous Al_2O_3-Y_2O_3 compositions have potential applications as thin film optical waveguides (Ref 30).

Considering the challenges involved in single-phase garnet formation and the extreme conditions of plasma spraying which could potentially result in kinetically stabilized metastable phases, we have selected the YAG system as an illustrative case study to critically examine precursor processing, phase evolution, and plasma spray deposition effects. The implications of these scientific studies on potential applications are also considered. Several inorganic precursors and precursor-solvent compositions have been used to achieve compositional homogeneity and YAG phase formation.

2.1 Plasma Spraying of Hybrid Sol

Nanostructured YAG coatings were developed for the first time using precursor plasma spray of a hybrid sol-mixture of Boehmite and yttrium nitrate in water (Ref 19). A hybrid sol such as this, where one component is a colloid and the other is a soluble metal salt expected to offer advantages including better yield and production rate. To produce the coatings, the hybrid YAG sol, which had a Y:Al ratio of 3.5 and a final solid concentration of 25 g/L, was sprayed using a TAFA RF plasma torch (Model 66, TAFA, Concord, NH). The spray conditions used to make the coatings are summarized in Table 1. X-ray diffraction (XRD) analysis of the as-sprayed coatings confirmed that a metastable hexagonal yttrium aluminate (H-YAlO$_3$) was the major phase. These coatings when further heated with plasma flame for 10 s converted into cubic garnet phase with minor amount of orthorhombic YAlO$_3$ (O-YAP)

Table 1 RF plasma spray parameters

Parameter	Hybrid sol and citrate-nitrate solution	Co-precipitated sol
RF Plasma Torch	TAFA	Tekna
Power, kW	65	60
Chamber pressure, Torr	100-250	100-120
Plasma swirl gas (argon), slpm	25	25
Plasma radial gas (argon/helium), slpm	70/140	85/150
Atomized gas	Helium	Helium
Feed rate, ml/min	10-30	10-30
Substrate-Torch distance, mm	100-150	200 & 250
Traverse speed, cm/s	2.5	2.5
Number of passes (preheat/deposit)	10-20	5/20

slpm: standard litter per minute

phase. Absence of any XRD reflections of yttria (Y_2O_3) or Al_2O_3 in the as-sprayed coatings indicates exclusion of any selective decomposition of $Y(NO_3)_3$ or AlO(OH) during the atomization and spray process (Ref 19).

2.2 Plasma Spraying of Citrate-Nitrate Solution

Citrate-nitrate gel combustion technique has been widely used to synthesize nanocrystalline ceramic powders. Citric acid (fuel) and nitrates (oxidants) when added together become a potent flammable mixture and self-combusted to form many complex oxide powders at relatively low temperatures. We had expected a similar advantage when a mixed precursor solution of nitrates (aluminum nitrate + yttrium nitrate) and citric acid in water was sprayed through RF plasma to form YAG coatings (Ref 20). A YAG precursor solution, mixture of stoichiometric ratio of Y:Al = 3:5 in a 1:1 ethanol deionized water and citric acid and having a final oxide content of 7 wt.%, was sprayed using a TAFA plasma torch (Table 1) to form the coatings. Most of the observed XRD lines in the as-sprayed coating were identical to the reported hexagonal yttrium aluminate phase; H-YAlO$_3$, except for a few reflections corresponding to the O-YAlO$_3$ phase and YAG phase. A systematic growth of the YAG phase and a disappearance of the YAP phase are clearly evident as noted by the change in the relative intensities of the low angle reflections distinct for YAG, H-YAP, and O-YAP. The H-YAP phase almost disappears on calcination at 1000 °C for 1 h; however, a small amount of the O-YAP phase still remains in the material and a higher calcination temperature (>1000 °C) and a longer time was necessitated to remove the impurity phase completely (Ref 20).

When the same above precursor solution was static pyrolyzed in a furnace, a direct formation of YAG phase was observed without any intermediate phases. Since we have observed an in situ ignition during the synthesis, a similar reaction was expected to happen within individual droplets during the thermal spraying of the corresponding precursor thereby controlling the phase formation in the plasma spray. Unfortunately, the results suggest that the

expected pathway was not followed in this case. Only nucleation of the YAG phase was observed in the sprayed coatings but not a complete transformation. Nevertheless, the formation of H-YAP and O-YAP phases during spraying confirms that irrespective of the precursor chemistry, the reaction temperature and the time of the spray process favors only *kinetically stable phases*, which in turn could be due to the fast heating rates and short residence times (Ref 20).

2.3 Plasma Spraying of Co-Precipitated Sols

Precursor plasma spraying of above described hybrid sol and citrate-nitrate solution led to reasonably adherent coatings (anticipated for low-velocity RF plasma spray deposition), but the phase evolution sequence was complex. Other precursors that were solutions rather than sols, e.g., aqueous aluminum nitrate and yttrium nitrate solution, did not lead to acceptable coatings during plasma spraying, in addition to experiencing nozzle corrosion. Therefore, a different approach was adopted—a combination of chemical co-precipitation and plasma spraying of sols—to form the coatings. Reverse and normal co-precipitation was used for making the sols. Supersonic and subsonic nozzles were used within the RF torch for depositing coatings on a variety of substrates. The coatings were subjected to pos-theat treatments up to 900 °C and characterized using differential thermal analysis (DTA), thermogravimetry (TG), powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The details of synthesis of sols and coating deposition are as follows:

2.3.1 Experimental Procedure for YAG Precursor Preparation and Plasma Spraying. YAG precursor sol was prepared by chemical co-precipitation method using reagent-grade nitrates purchased from Aldrich, Milwaukee, WI. Yttrium nitrate [$Y(NO_3)_3 \cdot 6H_2O$, 99.95% purity], and aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$, 98+% purity] in 3:5 mol ratio were dissolved in excess of deionized water and mixed thoroughly using a magnetic stirrer. Two types of YAG precipitates viz., Regular co-precipitated sol and Reverse co-precipitated sol were prepared. In the case of Regular co-precipitated sol, the mixed nitrate solution turned into a gelatinous mass with the drop wise addition of ammonia solution (25% ammonium hydroxide, assay 28.0-30.0% NH_3). The gel was washed, filtered out, and re-dispersed ultrasonically in de-ionized water. To prepare a Reverse co-precipitated sol, the mixed nitrate solution was added drop wise into diluted ammonia solution having a pH of 10. In this case, fresh ammonia solution was constantly added to maintain the pH at 10 throughout the precipitation process. Gel so obtained was then washed and ultrasonically dispersed in de-ionized water similar to Regular co-precipitated sol preparation.

Precursor sol's concentration was adjusted to have a final solid content of 30 g/L. For depositing the coatings, the feedstock sol was sprayed on alumina (Al_2O_3), stainless steel (304-SS), and single crystal Si and Ti substrates ($65 \times 25 \times 2$ mm) using a RF plasma torch (Model PL-100, TEKNA Plasma Systems Inc., Sherbrooke,

Canada). The precursor sol was fed into the RF plasma torch and directly gas-atomized into the argon/helium plasma through an atomistic probe. The spray conditions used to form the coatings are presented in Table 1. The substrate holder was designed to have two base plates so that the substrates were conveniently placed at two different substrate-torch distances (200 and 250 mm). In the spray experiment, the RF torch was held stationary and the substrate holder was moved horizontally back and forth. Prior to deposition the substrates were preheated to a temperature of 400 °C with plasma flame. In a typical spray run, about 250 mL of sol was sprayed continuously to produce a coating thickness of ∼160 μm. The reproducibility of the coating with desired composition was ensured by repeating as many as five spray experiments. With an optimum spray condition the coating thickness was mainly dependent on the concentration of sol and number of passes made. Tekna RF torch has the provision of using different interchangeable plasma jet exit nozzles. In this study, a regular convergent nozzle (subsonic) and a supersonic nozzle (Mach 1.5) were adopted for depositing the coatings. The combination of nozzle design and the axial injection capability of the torches allow us to study the difference in heating the particles in the high-pressure region of discharge while accelerating the particles in the low-pressure region.

2.3.2 Results and Discussion. Regular and Reverse co-precipitated sols sprayed using subsonic nozzle exhibited good adherence (substrates: 304 SS and Ti) in the as-sprayed condition. On the Si-single crystal substrate only the regular co-precipitated sol sprayed using supersonic nozzle displayed good adherence. Powder XRD patterns of as-sprayed and post-heat-treated coatings sprayed using subsonic and supersonic nozzles coatings are shown in Fig. 2. The XRD patterns indicate all the as-sprayed coatings predominantly having an amorphous structure. Heat treatments were carried out on the adherent as-sprayed coatings to study their crystallization. All the sprayed materials crystallized into YAG upon heat treatment at 900 °C for 1 h (10 °C/min heating and cooling).

To gain better insight into the extent of precursor feedstock pyrolysis at the plasma plume, thermal analysis was performed on the overspray coatings made from Regular and Reverse co-precipitated sols and their respective DTA-TG curves are shown in Fig. 3. Small endothermic peaks seen below 100 °C are attributed to the adsorbed moisture. DTA curves (Fig. 3a and b) indicate both the coatings interestingly exhibiting exothermic peaks at around 880 °C. This result suggests that irrespective of having slightly different onset of crystallization, subsonic spraying of both regular and reverse co-precipitated sol precursors resulted in coatings which have undergone a similar amorphous-crystallization transformation. The TGA plots show that the as-sprayed coatings have substantial amount of volatile matter, presumably OH^- ions. However, subsonic-sprayed coatings lost less weight than the supersonic-sprayed coatings. It appears that the relatively longer residence times in subsonic spraying led to a greater extent of pyrolysis of the sols.
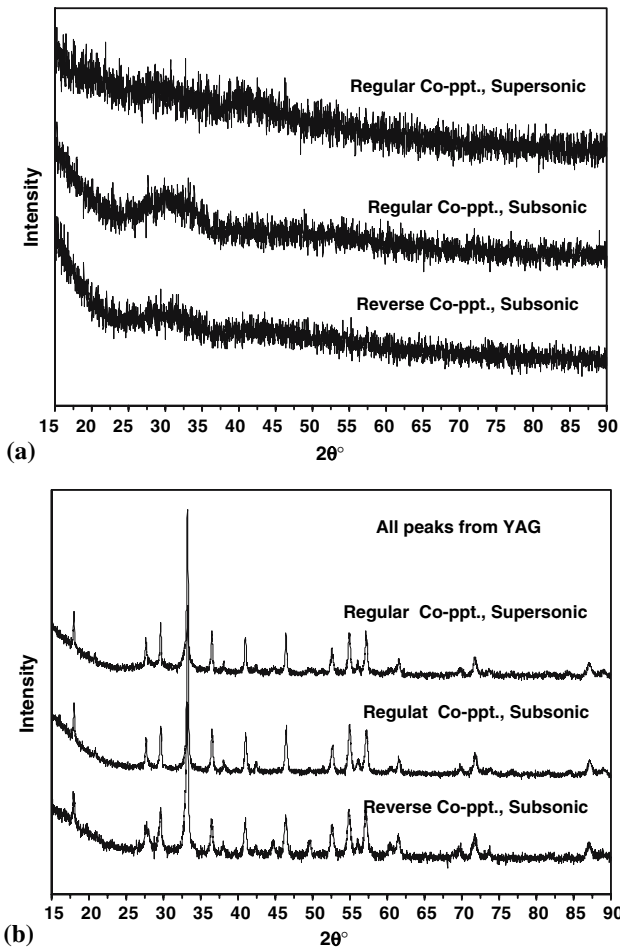
Fig. 2 X-ray diffraction (XRD) results of YAG coatings (a) as-sprayed; (b) coatings post-heat treated at 900 °C/1 h

Fig. 3 Combined TGA and DTA curves of coatings obtained by (a) regular co-precipitated sol sprayed using subsonic nozzle, (b) reverse co-precipitated sol sprayed using subsonic nozzle, and (c) regular co-precipitation sol sprayed using supersonic nozzle

Optical microscope and SEM images reveal that a denser surface morphology of the as-sprayed coatings and a relatively porous and mud-cracking pattern was observed in the heat-treated samples (not shown). A polymer impregnation (M-bond) was done for structural integrity of heat-treated (900 °C, 1 h) coatings while preparing the SEM specimens. A surface finish up to 6 μm was achieved in the polished cross-sectional samples. Cross-sectional SEM images of YAG coatings are shown in Fig. 4. Fine-grained spherical and nanometric features are evident in the reverse co-precipitated-subsonic coatings (Fig. 4c). Regular co-precipitated sol sprayed using both subsonic and supersonic nozzles formed dense and hard ceramic coatings (Fig. 4a, d), respectively.

For TEM specimen preparation, coating was scraped off the substrates and was crystallized, ground in an alumina mortar and pestle, and suspended in dry isopropyl alcohol. Fine particles from the suspension were mounted on a carbon-coated copper grid for TEM examination. TEM micrographs of the reverse and regular co-precipitated, subsonic-sprayed material show nanometric grain size of YAG (Fig. 5).
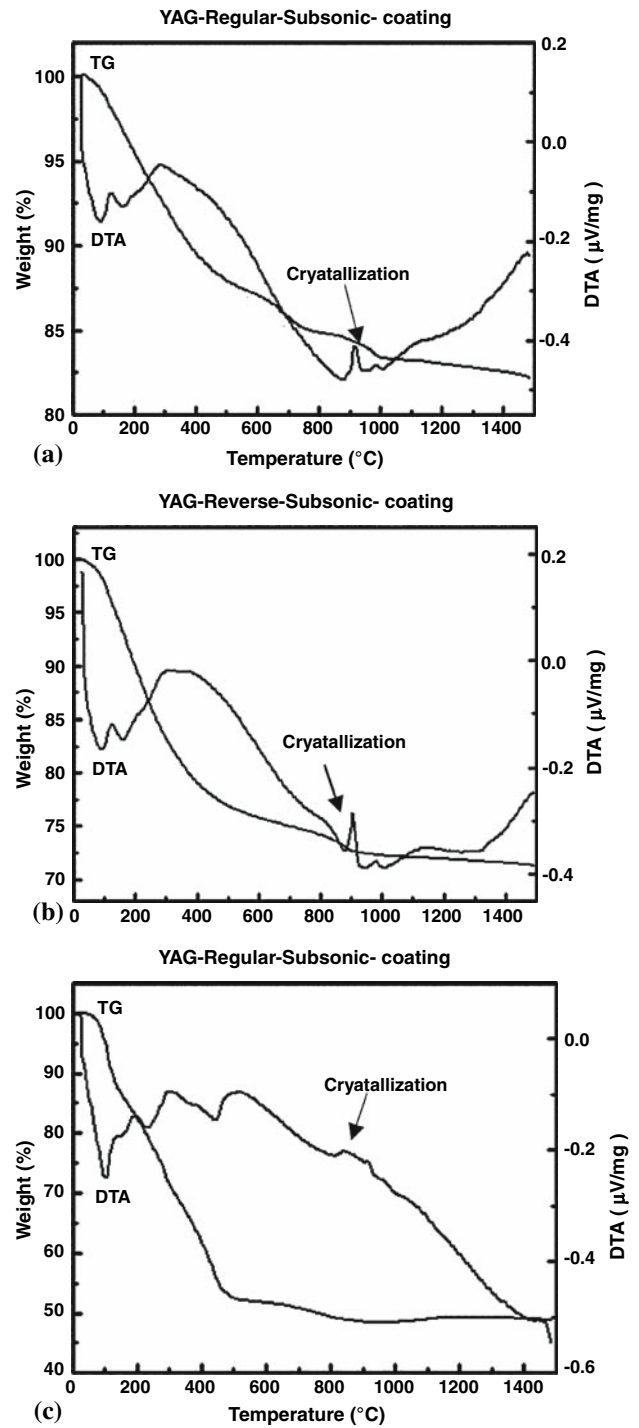
In both hybrid sol (Ref 19) and citrate-nitrate solution (Ref 20) spray approaches, irrespective of high degree of homogeneity in precursor mixtures, crystalline coatings with only kinetically stable phases were formed. In chemical synthesis of oxide compounds from inorganic
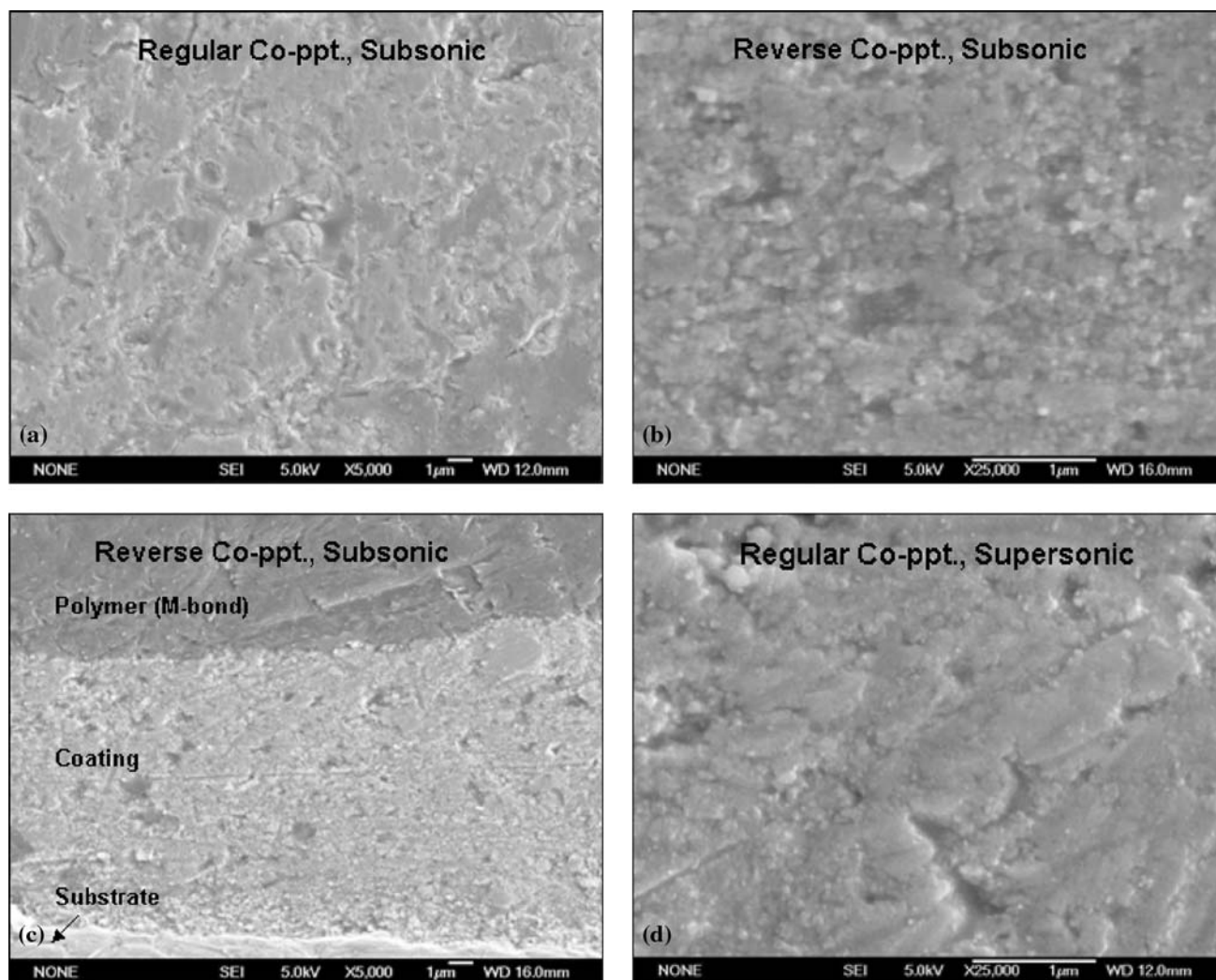
Fig. 4 Scanning electron micrograph of RFPPS YAG coatings heat treated at 1200 °C/1 h: (a) Regular co-precipitated sol, 304 SS substrate, and subsonic nozzle, (b) and (c) Reverse co-precipitated sol, 304 SS substrate, and subsonic nozzle, and (d) Regular co-precipitated sol, Si single crystal substrate, and supersonic nozzle

precursor constituents, often the phase that first form from amorphous state is a metastable or a transient phase. The transient phase so formed is stable only in certain narrow temperature range and eventually transform into a thermodynamically stable phase upon a high-temperature exposure. Similarly, in thermal plasma spraying of liquid precursors, extreme temperature and high velocity (plasma residence time less than 1 s of atomized droplet particles) favor only certain crystalline phases to form. These transient phases so formed are referred here as kinetically stable phases.

In the co-precipitated sol spraying approach, the spray parameters were intentionally adjusted to have an amorphous structure in the as-sprayed coatings. Nevertheless, a nanostructured grain feature resulted in all the approaches initiated our further interest to develop large-surface area luminescent coatings using RFPPS. Best luminescent Y_2O_3:Eu coatings were obtained for relatively lower amount of Eu substitution in garnet structure when a mixture of Yttrium nitrate and Europium nitrate in water was sprayed through RF plasma (Ref 18). Luminescent YAG:Eu coatings were also obtained by RFPPS of YAG:Eu precursor solution. Luminescent coatings produced by this approach have shown better thermal stability, superior adhesion, and high-contrast emission due to high degree of uniformity and crystallinity over traditional discrete powder coatings. RFPPS also offer potential opportunity to find new phosphor compositions with different amount of activator substitution which were never identified by the traditional processing approaches. It is also important that understanding the phase evolution paths in this system is essential for optimum control of chemistry and coating microstructure. Toward this direction, a novel low-density discrete combinatorial RFPPS approach has been developed and is being explored at Stony Brook.
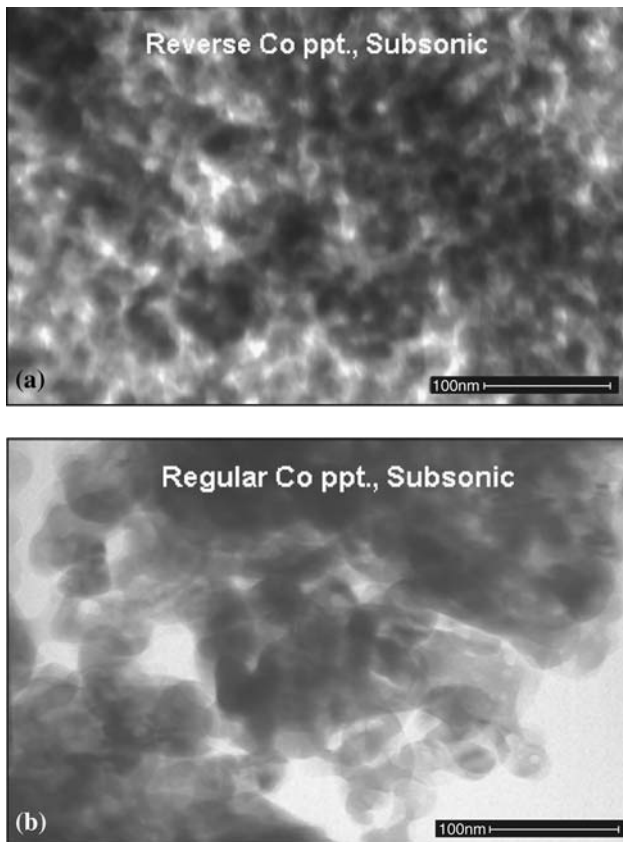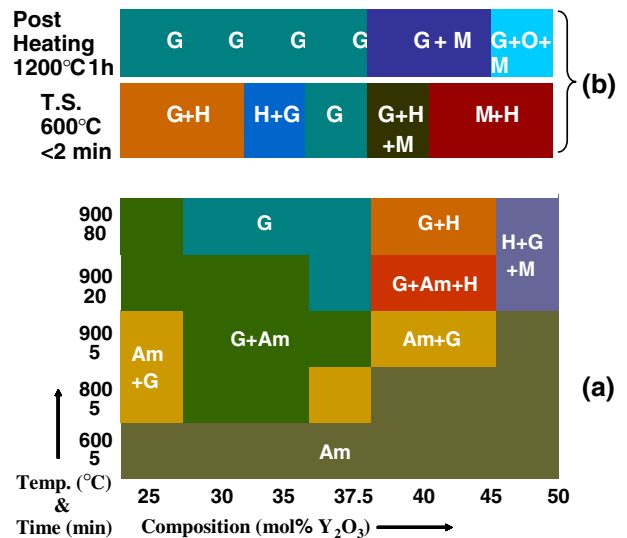
Fig. 5 (a) Bright-field TEM images from reverse co-precipitated subsonic-sprayed coating (HT 900 °C, 1 h) and (b) Bright field TEM images from regular co-precipitated subsonic-sprayed coating, HT 900 °C, 1 h

Am: Amorphous, G: YAG Garnet, H: Hexagonal YAlO₃, M: Monoclinic Y₄Al₂O₉, O: orthorhombic YAlO₃

Fig. 6 (a) Phase evolution of powder compositions prepared by reverse co-precipitation method and calcined at different temperatures (Ref 28) is shown for comparison. (b) Phase evolution of RFPPS Y_2O_3-Al_2O_3 coating compositions around stoichiometric YAG (37% Y_2O_3) in as-sprayed and post-heat-treated (1200 °C/1 h.) conditions. Am: Amorphous, G: YAG Garnet, H: Hexagonal YAlO₃, M: Monoclinic $Y_4Al_2O_9$, O: orthorhombic YAlO₃

3. Discrete Combinatorial RFPPS

Discrete Combinatorial RFPPS studies focused on gaining a fundamental insight into the potential for metastable phase selection and solubility extension in Al_2O_3-Y_2O_3 compositions about the stoichiometric $Y_3Al_5O_{12}$ compound, using reverse co-precipitation of nitrates solution and a discrete combinatorial approach using liquid precursor plasma spraying. Recently, Gandhi et al. have reported a detailed phase selection study on Al_2O_3-Y_2O_3 powders synthesized by reverse co-precipitation (Ref 30). The phase evolution sequence in all powder compositions from 25Y to 55Y (Y = mol% of Y_2O_3) is mapped in Fig. 6(a). The phase evolution in the same composition range studied in the RFPPS discrete combinatorial approach is also compared in Fig. 6(b).

In the powder-based study (Ref 30), all starting powders were amorphous and progressively heat-treated at higher temperatures. Garnet was the first crystalline phase in compositions 25Y to 45Y (see Fig. 6a). In this range, as the composition moved away from stoichiometric garnet (37.5Y), crystallization required progressively greater thermal exposure. When crystallized at low homologous temperatures the garnet phase shows significant extension of solid solubility, especially on the Y-rich side. Possible defect structures accommodating the solubility extension were examined. Phase selection results indicate that compositional inhomogeneity is not the only reason behind the appearance of hexagonal YAlO₃ that is frequently reported during YAG synthesis (Ref 30).

In the discrete combinatorial synthesis approach, mixed nitrate sols of different Al_2O_3-Y_2O_3 compositions having same final solid concentration were sprayed through RF plasma. Liquid feedstocks of compositions from 25Y to 50Y were sequentially delivered to the injector using a liquid feedstock pump. The shutters placed above the substrate holder and the liquid feedstock pump is programmed in such a way that a particular composition was deposited on the alumina substrate in a chronological order. The chemical homogeneity of each precursor composition was measured from the ratio between Y and Al atoms using EDX (energy dispersive X-ray analysis) technique. The powder sample for EDX analysis was obtained by water evaporating the gel derived from the precursor solution. In this work the ratio between Y and Al of each composition was measured as greater than or equal to 95% of actual values. For example, in the case of stoichiometric YAG composition (actual Y:Al = 3:5), the measured Y:Al ratio was 2.95:5.15.

A schematic of the combinatorial RFPPS is shown in Fig. 7. XRD revealed that crystalline phase was obtained in all the compositions in the as-sprayed condition. The typical substrate temperature measured during plasma spraying was around 600 °C. Single-phase garnet was formed only in the YAG (37.5 Y) composition while garnet + metastable phases observed in other compositions
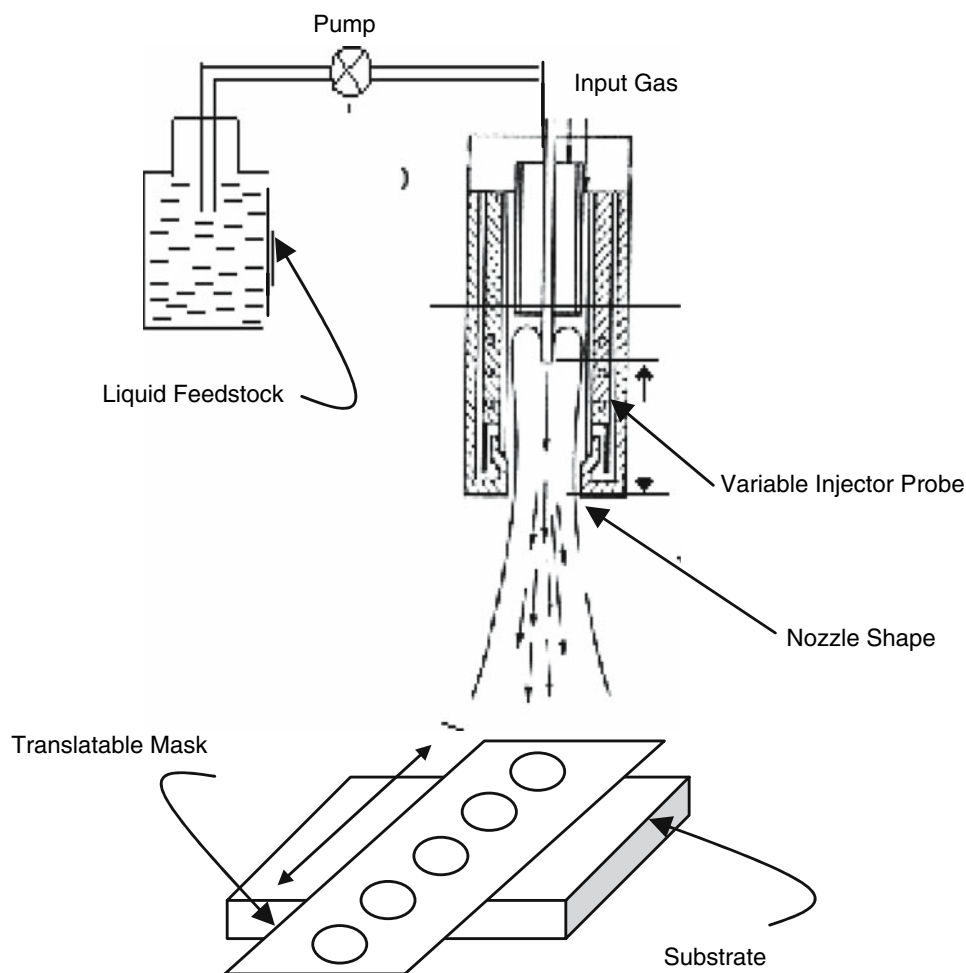
Fig. 7 Schematic of the discrete RFPPS approach used to make different composition of Al_2O_3-Y_2O_3 coatings

are mapped in Fig. 6(b). Metastable hexagonal yttrium aluminate was formed with garnet phase in 25-40% Y which completely transformed into garnet after a heat treatment (1200 °C/1 h). After the heat treatment of the coatings, XRD results indicate that YAG phase field was metastably extended away from stoichiometry which is in confirmation with powder-based study (Fig. 6a) (Ref 30). Discrete combinatorial approach by precursor plasma spraying provides an economically viable way to quickly scan through a vast range of compositions to select a composition of required properties. A limited solubility range of Europium and Chromium in YAG has been reported in conventional synthesis approaches. But an examination of metastability extension in these materials through the present combinatorial approach will potentially enable discovery of new luminescent compositions with higher efficiency.

reported. Plasma spraying of hybrid sol (mixture of boehmite and yttrium nitrate in water) or citrate-nitrate solution (mixture of yttrium nitrate, aluminum nitrate, and citric acid in water), irrespective of high degree of homogeneity, resulted in kinetically stable crystalline phases. On the other hand, regular and reverse co-precipitated sols (sol derived from mixture of nitrates using chemical co-precipitation method) resulted in amorphous coatings which transformed into single-phase YAG upon postheat treatment. A Discrete Combinatorial RFPPS method was developed and adopted to investigate metastable phase selection and solubility extension in Al_2O_3-Y_2O_3 compositions about the stoichiometric $Y_3Al_5O_{12}$ compound. XRD results of combinatorially obtained coatings indicate that YAG phase filed was metastably extended away from stoichiometry in conformation with a recent powder-based study.

4. Summary and Conclusions

Progress, critical observations, and challenges involved in the development of RFPPS of YAG coatings are

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