3.C Development of Metal-Doped Polymer Ablation Materials

Some inertial-fusion target designs specify ablator coatings with a high average atomic number (Z), in order to minimize the fusion-fuel preheat caused by superthermal electrons or radiation originating in the target corona.[1] Low-Z materials with up to several atomic percent of a high-Z element uniformly dispersed on an atomic scale are desirable in this type of target.

We have investigated two polymeric materials for incorporating high-Z metallic elements into ablation layers. Although each method utilizes solution-coating techniques, the materials and the resulting structures are basically different. The first, sulfonated polystyrene, which has a metal content of up to 5 atomic percent, is easily prepared and can easily be coated from solution. The second material is a styrene-butadiene copolymer in which stable iron colloids are dispersed. In sulfonated polystyrene the metal atoms are expected to be homogeneously dispersed in the polystyrene matrix on the molecular scale. In the metal-colloid-seeded polymer the metal dispersion is less uniform, but a broader range of average Z is possible.

We have also investigated two methods for coating the polymer solutions onto glass-microballoon targets. One technique involves dipping a stalk-mounted target into the solution; the other uses an acoustic-levitation device,[2,3] wherein the target is placed into an acoustic potential well. The solution-dipping technique has the advantage of simplicity, but is limited by the difficulty of obtaining uniform coatings thicker than 0.5 μm. Using the acoustic-levitation approach special care must be taken to ensure concentricity of the coating and the target, but thicker coatings are achievable.

Metal-Loaded Polymeric Materials

The first material, fully sulfonated polystyrene, is easily soluble in water. The acid form, in 30% aqueous solution with an average molecular weight of 120,000 and a high degree of substitution (90 to 100%), was obtained from the National Starch and Chemical Company.[4] It was neutralized with hydroxides of various alkali and alkaline-earth metals.

The polymer contains five atomic percent metal if neutralized with alkali metals, and 2.5 atomic percent if neutralized with alkaline earth metals. Average Z's range from 4.8 to 7.5, the largest value occurring with Cs neutralization. This is in contrast with $Z=2.7$ for polyethylene and $Z=3.5$ for parylene. Full neutralization of sulfonated polystyrene was performed by adding a stoichiometric amount of a metal hydroxide. The reaction proceeded rapidly at room temperature. The viscosity of the 30% aqueous sulfonated polystyrene was 150 cps. For our experiments, the viscosity was increased to 300 cps by freeze-drying and redissolving in water to a 75% concentration. In addition to cesium, we have also used Rb, K, Ba, and Ca.

To obtain the second coating material, thermolysis of a metal carbonyl in solution with a functional polymer has been used to produce a dispersion of stable metal colloids in the polymer solution.[5] Colloid particle sizes range from 10 to 1000 Å. Smith and Wychick[6] have reported metal colloids of diameter 60–80 Å uniformly dispersed in styrene-butadiene copolymer. A sample of Fe-colloid dispersion with styrene-butadiene copolymer in decalin was obtained from Smith and Wychick and contained 4.5 atomic percent Fe per polymer after evaporation of the solvent. Oxidation of the colloid particles changes the resulting structure significantly.[6] This can be avoided or minimized by carrying out the thermolysis in an inert-gas atmosphere. The colloidal particles embedded in the polymer matrix are protected against oxidation in air.

Coating Methods

Metal-doped polymer materials have been solution-coated onto stalk-mounted laser-fusion targets. To be suitable for laser-fusion targets, the coating must satisfy exacting geometrical requirements including thickness uniformity, surface smoothness, absolute thickness, and in this case metal-dispersion homogeneity.

Simple solution dipping of targets has proved successful for coating thicknesses less than 0.5 μm. Here a stalk-mounted glass microballoon was immersed into a metal-neutralized sulfonated-polystyrene solution or a decalin solution of Fe-colloid dispersion of styrene-butadiene copolymer. For proper solution wetting of the microballoon, 0.1% of a surfactant, Photoflow, was added to the solution. With the decalin solution of Fe-colloid dispersion of styrene-butadiene copolymer, the surfactant was not necessary. After immersion, the solution-coated glass microballoon was suspended in air. For the Fe-colloid solution, the suspension was performed in an Ar-atmosphere glove box to minimize oxidation of the colloids. After drying, a polymer film encapsulated the glass microballoon.

The wetting agent decreased the contact angle between the solution and the stalk, causing a nonuniform coating as shown in Fig. 29. This was minimized by immersing the microballoon into the solution until its top surface was level with the solution surface. The final coating thickness depends primarily on solution viscosity and concentration. This functional relationship is presently being studied.

As the glass microballoon is removed from the solution in the dip coating, the surface tension of the solution causes the layer to sag, resulting in a nonuniform coating. This becomes pronounced for coatings thicker than 0.5 μm. Gravitational effects also contribute to the nonuniform coating, since the solution can flow singificantly during the time required for solvent evaporation. Uniform coatings thicker than 0.5 μm can be obtained by applying a centering force to a sagged coating during solvent evaporation. Viscosity, density,

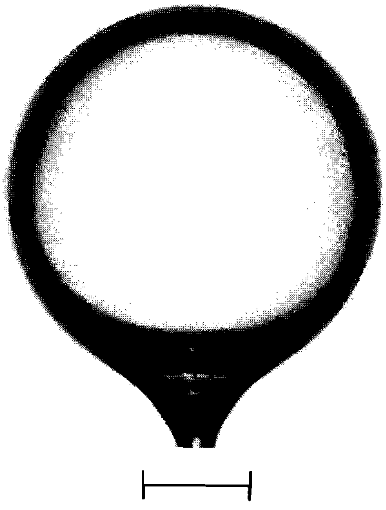

Fig. 29
Sulfonated-polystyrene Cs-salt coating produced by the dip method. The solution concentration was 40%, and the coating thickness was 14 μm. Notice the extra coating on the stalk due to surface tension.

coating thickness, and other factors of the solution determine the magnitude of the force required to form the concentric coating. This centering force can be produced by periodically inverting the target. A detailed study of this coating method is in progress, and preliminary results are very encouraging.

An alternative coating technique involves using an acoustic-levitation scheme. This method has previously been used to coat non-stalk-mounted levitated inertial-fusion targets with ablation layers. To coat a levitated microballoon, a glass microballoon is injected into an acoustic force field and trapped in a potential well. Subsequently, a drop of polymer solution, injected into the acoustic force field with a liquid atomizer, concentrically coats the glass microballoon. The solvent evaporates, leaving the microballoon coated with the polymer. In using acoustic levitation for coating a stalk-mounted balloon, the balloon was positioned in a stationary location. However, perturbations in the acoustic field caused a shift of the center of the acoustic potential well relative to the center of the microballoon, necessitating constant manual position adjustment.

Results and Discussion

The results of the present study are evaluated in terms of the coating requirements previously mentioned. Some coating properties, such as surface finish and homogeneity of the metal dispersion, are primarily functions of the materials utilized. Other properties, such as coating uniformity and thickness, depend strongly on the viscosity and concentration and, therefore, on the coating technique.

The typical surface structure of sulfonated-polystyrene coatings, as observed by Scanning Electron Microscopy (SEM), is shown in Fig. 30. The surface is extremely smooth and completely featureless. Similar surface smoothness was obtained with styrene-butadiene copolymer containing metal-colloid dispersions in the polymer matrix. Smooth surfaces are characteristic of non-

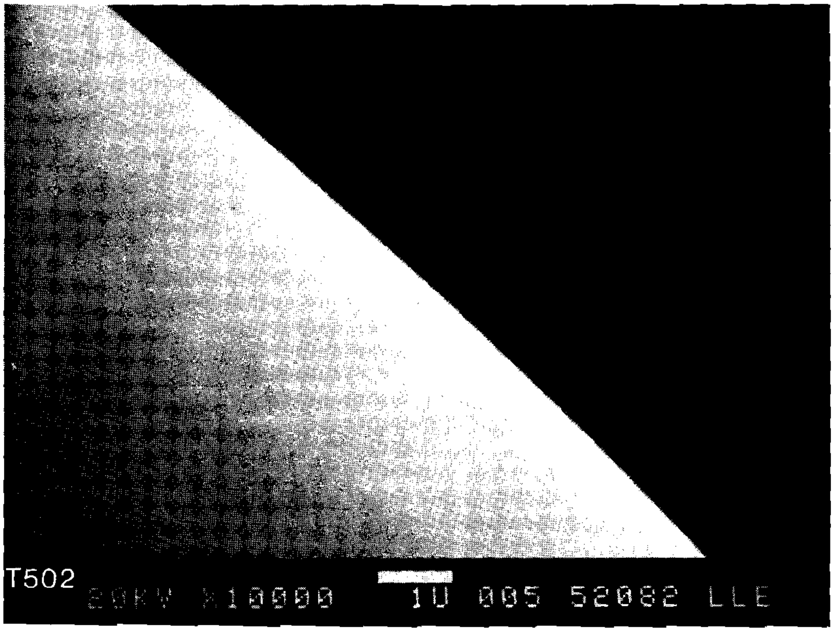

Fig. 30
Scanning electron micrograph of the surface of a sulfonated-polystyrene Cs-salt coating.

crystalline polymer-solution coatings because surface tension is the primary force forming the surface. This is in contrast with crystalline polymer-solution coating and vacuum-deposition methods. The surfaces of crystalline polymers frequently show crystal facets, and substrate defects are substantially amplified with vacuum-deposition methods, such as parylene coating or plasma polymerization. This results in cone defects or a wrinkled surface resembling "orange peel".

Most of the published work[7,8] on the morphology and structure of sulfonated polystyrene involves lightly sulfonated polystyrene (sulfonation level less than 8 mole percent). The state of ionic aggregation has not been completely elucidated in this polymer, but it is generally believed[9] that above a critical ion concentration of ca. 3 mole percent, ion-rich aggregates or clusters are formed, while below this critical concentration, ionic species are homogeneously dispersed. There is, however, no work reported on the structure of ionic aggregates of fully sulfonated polystyrene. Because of the very close ion proximity in the fully sulfonated polystyrene, a phase separation of ion-rich aggregates is extremely unlikely. In other words, metal atoms are expected to be homogeneously dispersed in the polystyrene matrix on the molecular scale.

With the metal-colloid-seeded polymers, metals are not dispersed homogeneously but phase-separated into colloids. We have not investigated the size of Fe colloids in a styrene-butadiene copolymer matrix, but it has been reported[5] that the size of Fe colloids is about 50 Å. Dispersion of these colloids may not be homogeneous on a molecular scale. Since any transition-metal carbonyl can be reduced to metal colloids, this method provides a broader range of average Z than does the sulfonation method.

Concentricity of thick coatings was investigated by contact x-ray radiography. For coatings with thicknesses less than 0.5 μm, simple solution dipping provided sufficiently concentric coatings. However, for thicker coatings, satisfactory concentricity was obtained only when performed with acoustic levitation. Figure 31 shows a contact x-ray radiograph of a glass microballoon coated with Cs-neutralized sulfonated polystyrene in an acoustic-levitation apparatus. A detailed description of the acoustic-levitation coating process is presented elsewhere.[10] From Fig. 31, the non-concentricity, defined as the difference between the thickest and the thinnest coatings divided by the average coating thickness, is calculated to be 0.08. Coating concentricity by acoustic levitation can be improved[10] using an automated position-adjustment system to center the microballoon in the liquid polymer layer. The Fe-colloid-seeded styrene-butadiene copolymer gave results similar to Fig. 31.

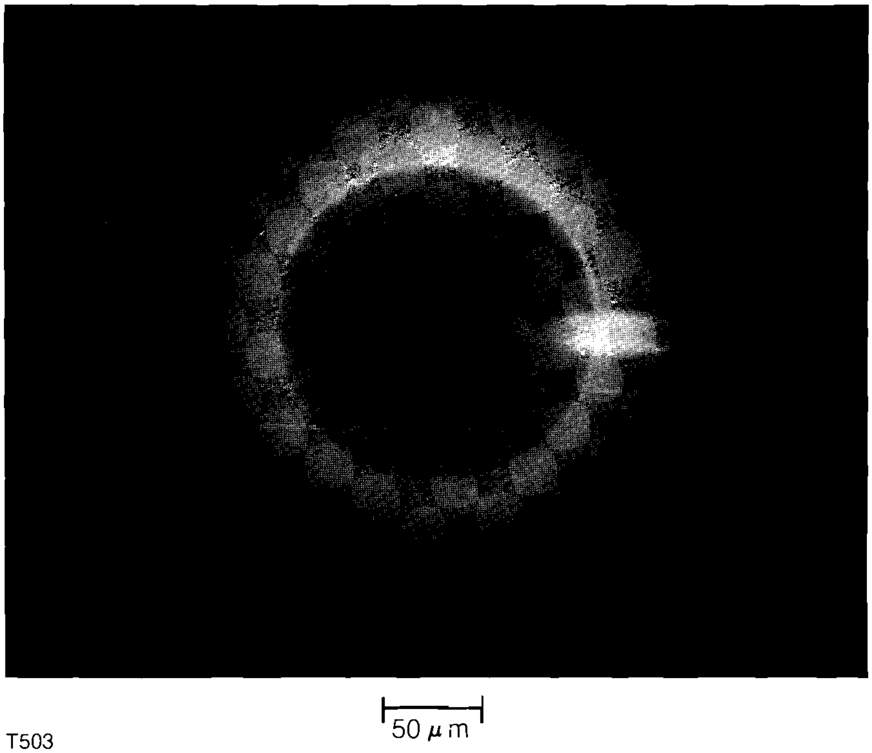

Fig. 31
Contact radiograph of a sulfonated-polystyrene Cs-salt coating on a glass microballoon, produced by the acoustic-levitation scheme.

In vacuum-deposition methods, particularly the parylene-coating method, real-time monitoring and control of coating thickness are possible using a laser reflectometer, and control of coating thickness to several hundred angstroms has been demonstrated.[11] In the solution techniques described in the present work, precise control of the thickness has not been achieved. The coating thickness depends on the viscosity and concentration of the solution, and the relationships are presently being studied.

Summary

Two polymer materials loaded with high-Z elements, and two solution-coating techniques, have been investigated for fusion-target coating. Sulfonated polystyrene neutralized with various alkali and alkaline-earth metals has been coated onto glass microballoons by solution-dipping, and produced an atomic-scale dispersion of the metal in the polymer with an extremely smooth surface. This characteristic is usual for solution coating of non-crystalline polymers.

A metal-colloid-seeded polymer was also coated by solution dipping. Although a homogeneous dispersion of metal was not achieved, metal colloids are dispersed as small particles of size ca. 50 Å. This techique has an advantage in that practically any metallic element can be used for the colloid, thus providing a wider range of Z for the fabricated ablation layer.

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