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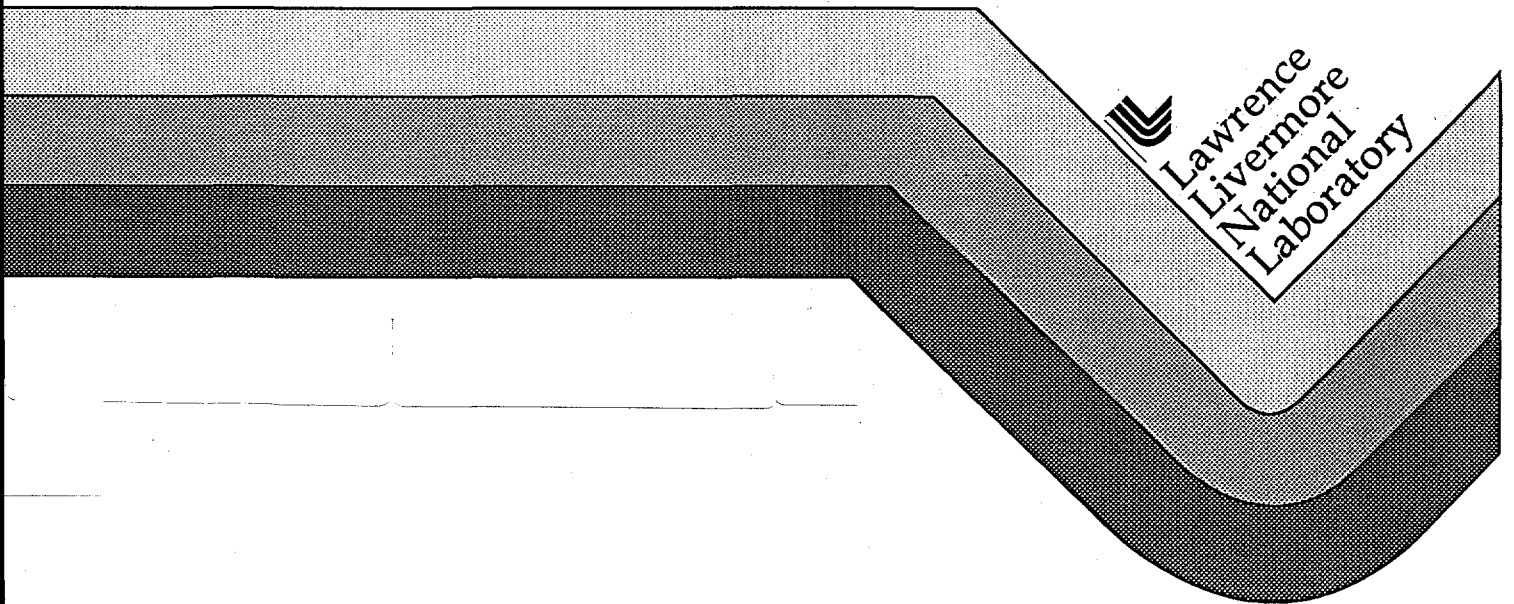
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Oxide Suspensions Containing Organic Polymer Binders

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Preparation of dielectric HR mirrors from colloidal oxide suspensions containing organic polymer binders

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ABSTRACT

Colloidal suspensions of oxides have been used to prepare dielectric HR mirrors, specifically for high power fusion case applications, on substrates up to 38 cm square using a meniscus coater. These coatings consist of porous quarterwave layers of alternating high and low refractive index oxides. Silica was used exclusively as the low index oxide and AlOOH, ZrO₂ or HfO₂ as the high index material. Coatings were weak because of low particle-to-particle adhesion. The use of organic polymer binders in the high index component in particular, was found to increase strength thereby improving the laser damage threshold and also reducing the number of layers required for 99% reflection due to increase in the refractive index.

2. INTRODUCTION

Sol gel high reflective (HR) coatings, prepared by stacking alternating quarterwave layers of porous high and low index oxides, have been under investigation for a number of years. All efforts to date have been directed towards the preparation of mirrors for high power fusion lasers. It was hoped that the great success of Sol gel AR coatings in this field could be repeated but so far this goal has not been attained. These HR coatings are prepared from colloidal suspensions of oxides by conventional liquid coating methods at room temperature. Colloidal silica has been used exclusively for the low index component and colloidal AlOOH, ZrO₂, or HfO₂ for the high index material.

ZrO₂ and HfO₂ have been the preferred oxides because of their high refractive index but HR samples have been weak and have a tendency to flake off because of low adhesion between particles. This low adhesion is also thought to contribute to the comparatively low laser damage thresholds. The flaking tendency with AlOOH has been much less but more coating layers are required for 99% reflection. A higher damage threshold for the AlOOH samples appears to confirm the greater adhesive strength. This information is summarized in Table I.

Table I

	AlOOH	ZrO ₂ /HfO ₂
Coating refractive index	1.45	1.53
Layers for 99% reflection	36	26
Damage threshold 1.06μm/3ns	15 J/cm ²	5 J/cm ²

Higher damage thresholds have been obtained when the coating strength is increased by the incorporation of soluble binders into the colloidal suspensions. Binders serve to increase particle-to-particle adhesion when the coating dries. One other very important point is that the refractive index is increased because the binder reduces

porosity by taking up some of the air space between particles. This is advantageous for systems with binders in the high index component only because fewer layers will be required for 99% reflection.

3. COLLOIDAL SUSPENSIONS CONTAINING BINDERS

There are four critical properties that are required for the binder:

- (a) It must be soluble in the suspending medium.
- (b) It must not flocculate the colloidal suspension i.e. the dispersion must be maintained.
- (c) It must not wash out or dissolve on subsequent application of more coating suspension.
- (d) Last, but not least, it must have a high laser damage threshold.

In our early investigations we found that two organic polymers, polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) were suitable as binders. As expected, both increased the refractive index and laser damage threshold of single layers of the high index oxide. This is shown in Table II.

Table II

Coating	Index	Damage Threshold
ZrO ₂	1.55	5 J/cm ²
ZrO ₂ + PVA	1.70	25 J/cm ²
ZrO ₂ + PVP	1.70	23 J/cm ²
HfO ₂	1.55	6 J/cm ²
HfO ₂ + PVA	1.70	30 + J/cm ²
HfO ₂ + PVP	1.70	19 J/cm ²
AlOOH	1.45	15 J/cm ²
AlOOH + PVA	1.55	30 + J/cm ²
PVA	1.55	35 J/cm ²
PVP	1.50	50 J/cm ²

PVA is only soluble in water and later we found that water in our coating suspensions gave problems with coating uniformity because of its high surface tension. This was especially the case when using a meniscus coater. PVP, which is soluble in lower alcohols, therefore became our binder of choice.

Our preliminary work indicated that a binder in the silica component was unnecessary because the coating strength (and laser damage threshold) was excellent and we did not want to increase the refractive index. All work with binders was carried out on the high index components only. PVP conforms to the solubility, damage threshold and non-flocculation criteria but the washing out and soaking in property required some investigation. In all mirror preparations only the first coating is applied to a dense substrate. All subsequent coatings are put down on the previous underlying porous layer and the liquid component of the suspension will therefore soak into the underlying layer on application. Components in solution may therefore be carried into the sub-layer. The major effect of this is to increase the refractive index of the sub-layer (silica) and

decrease the index of the applied upper layer. More layers will therefore be required for high reflection.

We found that the penetration effect could be minimized if we used the smallest particle size silica suspension and the highest molecular weight PVP. Coatings prepared from small particles have small pores through which large polymer molecules may have difficulty penetrating. A silica suspension prepared from tetraethyl silicate in methanol gave the smallest particle size (~8 nm) and the highest molecular weight PVP available had coiled polymer molecules approximately 70nm long (MW 350,000). This system gave the highest reflection for the fewest number of layers at an optimum binder-to-oxide ratio of 2:3 by volume. Ratios greater or smaller than this gave inferior results presumably because of lower refractive index (smaller ratio) for polymer migration (higher ratio).

4. PREPARATION OF HR COATINGS

Our most recent coatings were prepared on 6" x 6" x 1/2" fused silica substrates using a meniscus coater. This type of coater is shown diagrammatically in figure 1 and the principle of operation has been described in detail by Britten and Thomas. The coater contains a horizontal cylinder with a longitudinal slit through which coating fluid is pumped. The cylinder is thus completely coated with a thin liquid film and a meniscus can therefore be formed when a substrate is brought into near contact. Material can be continuously transferred and a coating formed if the substrate is then moved slowly horizontally.

Coatings prepared in a meniscus coater take a few minutes to dry and are sensitive to the surface tension of the liquid component. The best uniformity is obtained with low surface tension systems. Unfortunately all our high index materials are prepared in water suspension and the high surface tension of water makes it undesirable as a coating solvent. We were able to completely replace the water in the ZrO_2 and HfO_2 systems with methoxyethanol (b.p. 124°) by distillation. The $AlOOH$ suspension however required some water for stability but we were able to replace 80% of it with methanol. With these modified suspensions we were able to obtain excellent uniform coatings on the meniscus coater.

The silica suspension is prepared in ethanol or methanol and we found that both of these alcohols were a little too volatile and evaporated too fast to give high uniformity in spite of low surface tension. It was a simple matter to replace the solvents with sec-butanol by distillation and this proved quite satisfactory.

Mirrors have been prepared using $AlOOH$, ZrO_2 and HfO_2 with PVP as the high index components. Less layers were required with ZrO_2 and HfO_2 because of the higher index and the reflection peak is broader which allows a greater margin of error in thickness control. This is illustrated in figure 2 which shows typical transmission spectra of all systems. The additional advantage of the ZrO_2 and HfO_2 systems being completely anhydrous made these the systems of choice. We preferred ZrO_2 because it is less expensive than HfO_2 .

We have just recently prepared a mirror on a 38cm x 38cm substrate with SiO_2 - ZrO_2 /PVP on a meniscus cooler. This is the size of cavity mirror in the new Beamlet laser now in operation at LLNL. Similar sizes will be required for the proposed 192 beam NIF laser now in the design stage.

5. EXPERIMENTAL

5.1 Preparation of Colloidal Silica Suspension

The Silica Suspension was prepared by the base catalyzed hydrolysis of tetraethyl silicate as described by Stober et al. The silicate was first fractionally distilled under nitrogen (b.p. 167°) and then hydrolyzed in dry methanol using a Si/H₂O ratio of 1.0/2.3 at an equivalent Si/O₂ concentration of 3%. All water was added in the form of 30% ammonia solution which also provided the catalyst for the reaction. The reaction time was a minimum of three days at room temperature after which time all the methanol and the ethanol liberates from hydrolysis were exchanged for sec-butanol by distillation. The final suspension contained 3% silica with a particle size of about 8nm.

5.2 Preparation of Colloidal AlOOH Suspension

The AlOOH suspension was proposed by the hydrolysis of aluminum sec-butoxide as described by Yoldar. Vacuum distilled Al (OC₄H₉)₃ was added to vigorously stirred water at 70° at a Al/MH₂O ration of 1/100. Sec-butanol was removed by distillation and concentrated HCL added at a Al/HCL ratio of 1.0/0.07. A fluid colloidal suspension was obtained after refluxing for 16 hours. The acid was then removed from the product by dialysis and 75% of the water removed by distillations and replaced with methanol. The final suspension contained 5% AlOOH with a particle size of about 7nm.

5.3. Preparation of Colloidal ZrO₂ and HfO₂ Suspension

ZrO₂ and HfO₂ suspensions were prepared by the ammonia neutralization of the metal oxychlorider followed by hydrothermal crystallization similar to the method described by ZrOCl₂ .8H₂O or HfOCl₂.8H₂O were dissolved in water and added to a vigorously stirred solution of 20% excess ammonia in water. The amorphous hydrated oxide precipitate was removed by filtration, washed with water, and then heated in water to 220° for 10 hours in a pressure reactor. The solid crystalline oxide was suspended in water by the addition of hydrochloric acid to PH~3 followed by ultrasonic treatment. Finally the water was replaced by methoxyethonol (b.p. 124°) by distillation. The product was monoclinic with a particle size of about 7nm.

5.4. Preparation of Oxide-PVP Suspensions

Suspensions containing PVP binder were proposed by adding a solution of PVP (M.W 360,000) in methoxyeltonol to the oxide suspension followed by ultrasonic treatment until a fluid dispation was obtained. A volume ration of 3/2:oxide/PVP was used in all cases.

Total solid concentrations of 3-4% were found to be satisfactory for coating preparations on a meniscus crater.

5.5. Acknowledgements

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