

with a siliceous material are cathode sputtering, plasma deposition, and electron beam evaporation, all of which are known techniques, especially in the semi-conductor arts. FIG. 9 is a schematic representation of apparatus suitable for sputter coating silica onto the surface of a crystalline alumina orthodontic bracket. The apparatus, shown generally as 62, includes a sputtering chamber 64 (which is vacuum tight), a target 66, in this case silicon metal, which is brought to cathode potential, an RF or DC power supply 68, and a plate 70 for holding the cleaned and dried substrate 72 to be coated, in which the plate 70 is brought to anode potential. A source of oxygen (not shown) introduces oxygen into the chamber 64 so that the silicon metal 66 will be converted to silicon dioxide on the substrate 72. Reactive sputtering, such as is briefly outlined here, is known. For instance, see "The Basics of Sputtering", printed in December 1980 by Materials Research Corporation, Orangeburg, New York 10962.

The crystalline alumina bracket having its base surface 74 (see FIG. 2) sputter coated with silica or other siliceous material such as a glass, has a greatly enhanced affinity for silane or silicone coupling agents such as gammamethacryloxypropyltrimethoxysilane, and by using such coupling agents the adhesion of the bracket to acrylic orthodontic cements is greatly enhanced. This is illustrated in the examples, below:

EXAMPLE 1 AND CONTROL EXAMPLES 1-6

The purpose of the experiments described below was to measure the shear strength between various materials and a plug of adhesive. The experiments were carried out by inserting a crystalline alpha-alumina 0.2 inch diameter rod (or a steel rod, to simulate a steel orthodontic bracket) treated in various ways into the end of a short length of "Tygon" laboratory tubing, and then building up a plug of an acrylic orthodontic cement on the end of the rod by tamping it into the tubing against the end of the rod. After the cement hardened, the shear strength between the rod and the cement was measured by the test procedure described below.

The acrylic orthodontic cement used was a two-paste formulation having the following composition:

Component	Weight Percent	
	Universal	Catalyst
2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane ("Bis-GMA")	12.60	12.80
Bisphenol-A Dimethacrylate	1.40	1.42
Triethyleneglycol Dimethacrylate	6.09	6.09
2-Hydroxy-4-methoxybenzophenone	0.20	0.20
Butylated hydroxytoluene	0.01	0.03
N,N-di(2-hydroxyethyl)-p-toluidine	0.50	—
Benzoyl Peroxide	—	0.40
Quartz powder-silane treated	75.00	75.86
Fumed Colloidal Silica	3.20	3.20
Pigments	1.00	—

Approximately equal quantities of the two pastes are mixed just before use, and a total of about 0.5 gram of the mixed cement is spatulated into the open end of the tubing and tamped against the end of the rod, to build up a short plug of cement. After the cement has hardened (within 3 to 5 minutes), the tubing is cut away and the sample is placed in water at 37° C. for 48 hours, after which it is tested.

An Instron Testing Machine is used. The sample is placed on its side in a "V" shaped steel block and is

clamped tightly therein. In this test, the cured cement is sheared off at the rod/cement interface with a steel blade secured to the cross head of the Instron machine. The blade was positioned as closely as possible to the interface, about ½ to 1 millimeter from the interface on the cement side thereof, and the shearing force exerted at the interface was determined using a cross head speed of 0.05 inch/minute.

The various samples tested were the following:

Control 1—Mesh bonded stainless steel rod. The rod was stainless steel having an 80 mesh, square weave metal wire vacuum brazed onto the end of the rod.

Control 2—Crystalline alpha-alumina rod, etched in sulfuric acid (20% aqueous) by boiling for 2 minutes (all of the crystalline alpha-alumina rods were etched in sulfuric acid to thoroughly clean them prior to treatment, unless otherwise specified). This rod had no further treatment.

Control 3—Crystalline alpha-alumina rod, treated with a 1% solution in ethanol of Z-6032 silane from Dow Corning. This silane has the following structure:



Control 4—Crystalline alpha-alumina rod, treated with a 1% ethanol solution of gamma-methacryloxypropyltrimethoxysilane (A-174). Control 5—Crystalline alpha-alumina rod, treated with a 1% ethanol solution (based on weight of silane) of an epoxy/silane primer prepared as follows:

6.13 grams of A-1100 silane (gamma-aminopropyltriethoxysilane) and 19.3 grams of the diglycidyl diether of bisphenol-A were added to a reaction vessel and heated to 60° C. 4.77 Grams of methacrylic acid was dripped into the mixture over a period of three hours. When the mixture became quite viscous, ethanol was added. At the conclusion of the methacrylic acid addition, more ethanol was added to reach a 1% solution, based on the silane.

Control 6—Crystalline alpha-alumina rod treated with a Bis-GMA/silane primer that was prepared in the following manner:

91.9 millequivalents of Bis-GMA was reacted with 22.85 millimoles of A-1100 silane in the presence of 5 drops of acetic acid, in ethanol solution in a Michael addition. The reaction product was applied to the sapphire in a 1% ethanol solution.

Example 1—Crystalline alpha-alumina rod coated with a layer of silica about 10,000 Angstroms thick by electron beam evaporation. (This rod was not acid-etched, since the electron beam treatment cleans the surface adequately). Prior to treating the silica-coated rod with a silane coupling agent, the coated rod is heated in air at 350° C. for one hour. This converts the silica surface to a form that has a greater affinity for the silane. (It appears that silanol groups are thereby formed, the moisture content of air being sufficient to promote their formation.) Heating in ethylene chloride also has the same effect, for reasons that are not clear. The silica coated rod was treated with a ½% ethanol solution of A-174 silane by spraying, followed by air drying. The silane is then hydrolyzed by immersion in water for one hour at room temperature.

The results of the shear tests are displayed below in Table 1: