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Evaluation of Strength for Borosilicate Glass Coated with Ceramic Materials by Sputtering

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The durability of coated materials with high performance should be adequately evaluated prior to their application. This study aims at establishing a procedure to estimate the durability of such materials. In this study, a borosilicate glass was coated with ceramic films by a radio-frequency (RF) magnetron sputtering method, and mechanical properties of materials coated with single ceramic materials, alumina (Al_2O_3), silicon carbide (SiC), or titanium nitride (TiN), were investigated. Roughness and hardness were measured as surface characteristics of coated glass. The strength of coated glass was evaluated under three-point bending mode. It was found that the strength properties were improved by coating ceramic materials on glass. As for the strength properties, TiN-coated glass was superior to Al_2O_3- or SiC-coated glass, although the surface of TiN-coated glass was rougher compared with that of Al_2O_3- or SiC-coated glass. A new procedure to estimate the strength of coated materials was proposed by incorporating relative hardness and roughness variations with sputtering time. The strength in experiments was adequately estimated by using the proposed procedure.

Keywords alumina, bending strength, borosilicate glass, coated glass materials, mechanical properties, silicon carbide, sputtering, titanium nitride

1. Introduction

Glass coated with ceramic materials by sputtering has applications in various engineering apparatuses. Recent studies reported that glass sputtered with ceramic thin film is functionally used as magnetic/electronic device materials (Ref 1-3) as well as optical ones (Ref 1, 4-7). In functional and/or mechanical applications of coated glass materials, it is anticipated that they suffer serious damages which may be caused by unexpected forces in anomalous operations or the inconsistency in their equipping. Consequently, to improve the durability in their practical applications, the structural design of systems using coated glass materials requires a good understanding of their strength properties.

In this study, mechanical properties of a borosilicate glass coated with alumina, silicon carbide, or titanium nitride were experimentally investigated to clarify the difference in the properties attributed to different kinds of ceramic coating materials. A radio-frequency (RF) magnetron sputtering method was adopted in producing thin ceramic films on glass. Coated glass materials were prepared by changing a combination of RF output power and film thickness for each ceramic coating material. Roughness and hardness of coating ceramic film as surface properties are important factors for tribological usage (Ref 8). Roughness and hardness were measured for coating film and the substrate glass. The information on material strength is also required to guarantee the integrity during service. Since tensile tests of brittle glass or ceramic materials are very difficult to be performed in evaluating their strength characteristics adequately (Ref 9), bending tests of the glass coated under several conditions were conducted instead of tensile tests in this study. The dependencies of mechanical properties of coated materials on the thickness of ceramic film and on the RF output power were also investigated to clarify a suitable sputtering condition. Finally, a new procedure to estimate the strength of coated glass was proposed by using the surface properties of coating film as well as sputtering time, and its applicability was discussed in comparison with experimental results.

2. Experimental Procedures

2.1 Material Processing

A commercial borosilicate glass was used as a substrate material. Alumina (Al_2O_3) of 99.99% purity, silicon carbide (SiC) of 99.8% purity, and titanium nitride (TiN) of 99.0% purity were adopted as target materials. The geometry of glass substrate was a disk type with a diameter of 100 mm and a thickness of 2 mm. In this study, each ceramic film was coated by sputtering as mentioned below, and the thickness t_f of coated film was controlled to be 1, 3, or 5 μm.

An RF magnetron sputtering apparatus of upper deposit type was used in the coating process. The distance between substrate and target materials was set to be 40 mm in this apparatus. Metallic supporting or bonding plates, on which substrate and target materials were fixed, respectively, were being water-cooled during the processing. Before starting a steady sputtering,

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presputtering was carried out for 300 s so that a contaminated layer of target material could be removed. The initial degree of vacuum in a processing chamber was kept $< 1.3 \times 10^{-4}$ Pa. The flow-rate and pressure of argon gas, which was used to activate the sputtering process in the chamber, was controlled to be 167 mm^3/s and 1.3 Pa, respectively. In sputtering of ceramic target materials, the initial temperature of substrate was not controlled, and two levels of RF output power P were selected as $P = 400$ and 600 W.

2.2 Measurements of Film Surface Characteristics

Images of surface areas on each coating film were taken through a laser scanning microscope (LSM), and the images were processed into digital data by using a personal computer in which software for image-processing was installed. Data in individually measured areas were used to evaluate porosity and roughness of their respective areas by using the images processed by the software. The center-line-average roughness, R_a, was measured as the roughness of specimen surface in this study.

The surface hardness of coated materials is one of important factors in characterizing the strength of coated materials. To avoid the influence of the substrate hardness on the film hardness, it has been recommended that a penetrating depth D of indenter should be kept one-tenth or one-fifth of the film thickness (Ref 10). For this situation, a dynamic microhardness tester with the applicable range of indentation force F from 98 μN to 1.96 N is appropriate to measure the film hardness. It has been found that the aforementioned condition is properly satisfied in ceramics-coated materials by using a dynamic microhardness tester (Ref 11, 12). The dynamic microhardness H is defined as

$$H = 371\left(\frac{F}{D^2}\right) \qquad \text{(Eq 1)}$$

In Eq 1, units of H, F, and D are GPa, N, and m, respectively. The film hardness may present not only the resistance of microplastic deformation, but also the effect of residual stress in a coated film.

2.3 Bending Test

For bending tests, plate type specimens with dimensions of 10 mm in width and 40 mm in length were cut out from coated glass specimens and the glass substrates themselves. No damage, such as de-bonding between glass substrate and coated ceramic film, was found after the cutting process of ceramics-coated glass.

In evaluating bending strength, a three-point or four-point bending test is usually adopted. In this study, a three-point bending test is used to achieve more reduction of friction points in a supporting system. The span length in three-point bending test was 20 mm. The loading rate was controlled so that the rate of nominal stress at the position subjected to the maximum tensile stress in a specimen should be 100 MPa/s. In setting a coated specimen on supporting equipment, the coated surface of the specimen was located in the tensile side. Fifteen specimens were prepared for each sputtering conditions. All tests were carried out in an ambient atmosphere, i.e., at temperature of 294 ± 6 K and in relative humidity of $73 \pm 2\%$. The bending strength of coated and non-coated specimens was calculated as the maximum nominal stress, which was monitored at final failure, irrespective of the actual breaking position.

3. Experimental Results and Discussions

3.1 Characteristics of Coating Film

The observation by LSM revealed that the average of porosities measured on surfaces of coated ceramic films was $< 0.1\%$. The result suggested that sufficiently dense films were formed under the sputtering conditions adopted in this study.

Table 1 summarizes statistical parameters of surface roughness R_a measured on coated ceramic films. In Table 1, the coefficient of variation, which is defined as the standard deviation divided by the mean value, is also indicated as a reference factor of statistical scatter. Larger coefficient of variation is corresponded to larger scatter. The coefficient of variation is hereafter abbreviated to COV. Compared with the mean surface roughness of glass, $R_a = 3.92 \times 10^{-2}$ μm, the surface coated with ceramics in any case is clearly rougher than the glass surface. Figure 1 presents the variation of the mean roughness with respect to the film thickness t_f. The roughness of coated film is found to increase with increasing the film thickness. It is well recognized that such a tendency is caused by a shadowing effect during a coating process of physically

Table 1 Surface roughness R_a on coated ceramic films

RF output power	Film thickness t_f	1 μm	3 μm	5 μm
(a) Coated alumina films				
$P = 400$ W	Mean of R_a, μm	4.63×10^{-2}	4.83×10^{-2}	5.19×10^{-2}
	Coefficient of variation	0.194	0.236	0.183
$P = 600$ W	Mean of R_a, μm	5.26×10^{-2}	5.77×10^{-2}	6.44×10^{-2}
	Coefficient of variation	0.207	0.201	0.179
(b) Coated silicon carbide films				
$P = 400$ W	Mean of R_a, μm	6.11×10^{-2}	6.69×10^{-2}	6.73×10^{-2}
	Coefficient of variation	0.175	0.159	0.171
$P = 600$ W	Mean of R_a, μm	6.28×10^{-2}	6.57×10^{-2}	6.04×10^{-2}
	Coefficient of variation	0.160	0.185	0.166
(c) Coated titanium nitride films				
$P = 400$ W	Mean of R_a, μm	6.66×10^{-2}	6.00×10^{-2}	7.12×10^{-2}
	Coefficient of variation	0.228	0.183	0.281
$P = 600$ W	Mean of R_a, μm	6.60×10^{-2}	8.47×10^{-2}	9.23×10^{-2}
	Coefficient of variation	0.206	0.162	0.173

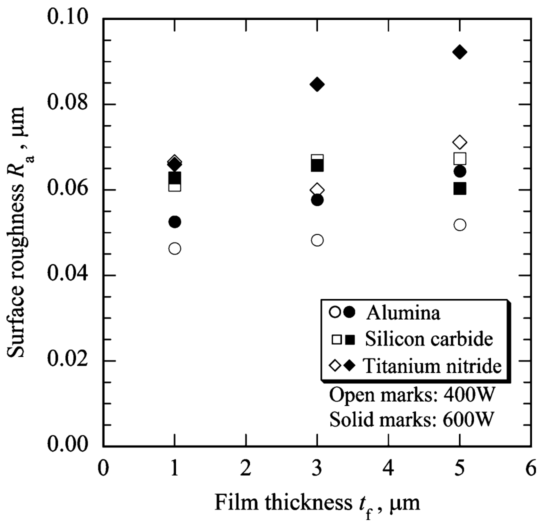

Fig. 1 Surface roughness of coated ceramic film correlated with film thickness

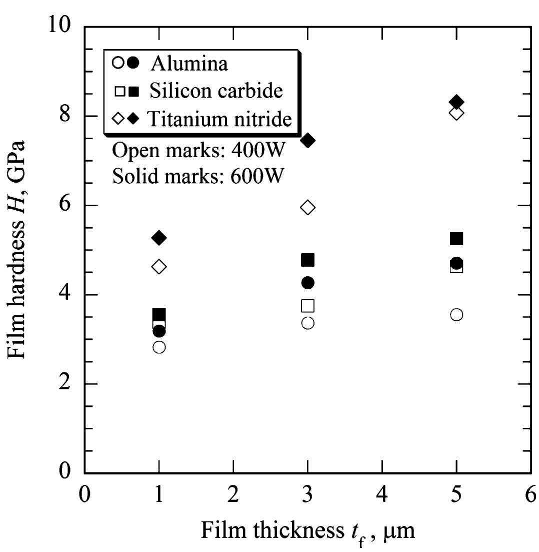

Fig. 2 Hardness of coated ceramic film correlated with film thickness

vaporized deposit type. As a whole trend in Al_2O_3- or TiN-coated materials, the surface coated under lower RF output power P is smoother than the surface coated under higher power. In SiC-coated materials, however, the film roughness does not always change systematically with respect to P. As seen clearly in Fig. 1, thicker TiN films formed under higher P are particularly rougher than films of the others. Since COV values of surface roughness on coated glass are around 2×10^{-1} as indicated in Table 1, a scatter of roughness is almost the same independently of film material and coating condition. COV values of roughness measured on coated films are a little smaller than COV = 2.41×10^{-1} in substrate roughness.

Figure 2 shows the relation of film hardness H to film thickness. The mean value and COV of H are listed in Table 2. Since the mean value of dynamic hardness of the glass substrate is 2.21 GPa, every coated film is found to be harder than the substrate glass. However, COV values of hardness measured on coated films are larger than COV = 1.10×10^{-1} in the substrate

Table 2 Film hardness H on coated ceramic films

RF output power	Film thickness t_f	1 µm	3 µm	5 µm
(a) Coated alumina films				
P = 400 W	Mean of H, GPa	2.83	3.37	3.56
	Coefficient of variation	0.135	0.164	0.113
P = 600 W	Mean value, GPa	3.19	4.27	4.71
	Coefficient of variation	0.113	0.139	0.172
(b) Coated silicon carbide films				
P = 400 W	Mean of H, GPa	3.38	3.75	4.63
	Coefficient of variation	0.120	0.164	0.159
P = 600 W	Mean of H, GPa	3.56	4.78	5.26
	Coefficient of variation	0.113	0.129	0.158
(c) Coated titanium nitride films				
P = 400 W	Mean of H, GPa	4.63	5.96	8.08
	Coefficient of variation	0.362	0.336	0.361
P = 600 W	Mean of H, GPa	5.28	7.46	8.32
	Coefficient of variation	0.314	0.305	0.335

hardness. Such a trend is most remarkable in coated TiN films. This implies that the hardness of coated films has a larger dispersion compared with that of the glass substrate. In each ceramic film, thicker film has higher hardness, because the effect of the substrate hardness, which is softer than those of coated ceramic films as aforementioned, is reduced in thicker film. It is also clarified that the surface hardness of films coated under a higher RF power P is larger. It is suggested that higher RF power brings denser film.

3.2 Strength Properties of Coated Material

By observations of fracture surfaces through SEM, fracture surfaces of coated and non-coated materials were found to be featureless unlike those of high-strength ceramic materials, on which mirror, hackle, and/or mist patterns are sometimes observed. Such a featureless fracture surface made us unable to identify fracture origins.

It is well known that a large dispersion is often observed in the strength of brittle materials. At first, statistical properties of strength σ_f are investigated. Figure 3 presents strength distributions plotted on Weibull probability papers. As seen in Fig. 3, the strength distributions of all coated glass shift toward higher strength region compared with the strength distribution of the glass substrate. This implies that the strength of glass is improved by ceramic coating even if the dispersion of strength is considered in the comparison between strengths of glass substrate and coated glass. Straight lines in Fig. 3 are drawn by fitting the strength data to the two-parameter Weibull distribution function $F(\sigma_f)$, which is expressed as follows.

$$F(\sigma_f) = 1 - \exp\left\{-\left(\frac{\sigma_f}{\sigma_S}\right)^m\right\} \quad \text{(Eq 2)}$$

In the above equation, σ_S and m are, respectively, the scale and shape parameters. The shape parameter m, as like as COV, is also associated with a range width of scatter; i.e., smaller m is corresponded to larger scatter. It is found from Fig. 3 that the strength distributions are well approximated by Eq 2. The statistical parameters of bending strength are summarized in Table 3. As seen in Table 3, COV increases and m decreases for thicker film in TiN-coated glass. This implies that, in TiN-coated glass, the strength scatter increases as the film thickness becomes thicker. On the other hand, COV and m do not clearly depend on the film thickness in Al_2O_3- or SiC-coated glass.

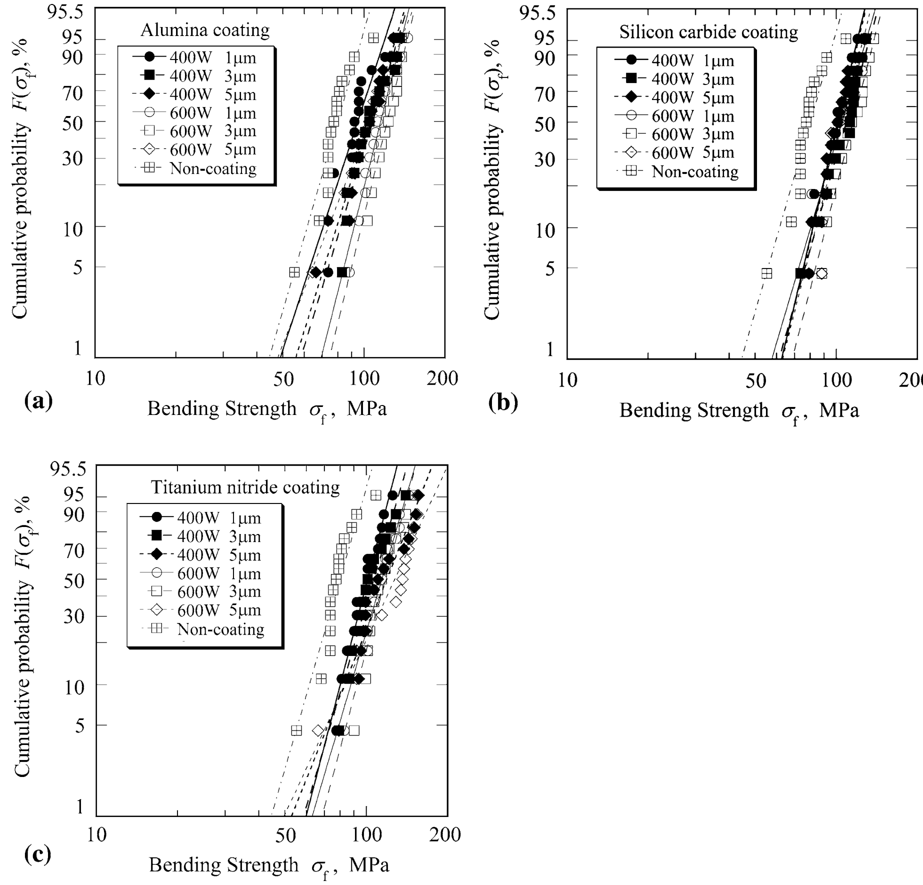

Fig. 3 Weibull plot of bending strength of ceramic-coated glass

Table 3 Bending strength σ_f of ceramics-coated glass

RF output power	Film thickness t_f	1 μm	3 μm	5 μm
(a) Alumina-coated glass				
P = 400 W	Mean of σ_f, MPa	93.5	106	104
	Coefficient of variation	0.166	0.157	0.152
	Shape parameter m	7.41	7.51	6.97
	Scale parameter σ_S, MPa	99.2	113	111
P = 600 W	Mean of σ_f, MPa	114	120	103
	Coefficient of variation	0.131	0.119	0.195
	Shape parameter m	8.81	8.84	5.45
	Scale parameter σ_S, MPa	120	127	112
(b) Silicon carbide-coated glass				
P = 400 W	Mean of σ_f, MPa	100	107	101
	Coefficient of variation	0.121	0.139	0.124
	Shape parameter m	9.14	7.58	9.13
	Scale parameter σ_S, MPa	105	114	106
P = 600 W	Mean of σ_f, MPa	103	114	104
	Coefficient of variation	0.150	0.131	0.126
	Shape parameter m	7.50	8.41	9.70
	Scale parameter σ_S, MPa	110	120	109
(c) Titanium nitride-coated glass				
P = 400 W	Mean of σ_f, MPa	99.8	105	118
	Coefficient of variation	0.134	0.155	0.204
	Shape parameter m	8.37	7.55	5.74
	Scale parameter σ_S, MPa	106	112	126
P = 600 W	Mean of σ_f, MPa	113	116	126
	Coefficient of variation	0.149	0.138	0.208
	Shape parameter m	7.42	8.49	4.82
	Scale parameter σ_S, MPa	120	123	137

The mean strength σ_f is correlated with the thickness t_f of coating film in Fig. 4. Error bars in the figure present standard-deviation ranges. As for TiN-coated glass, it is found that the strength increases monotonically as the film thickness is increased. On the other hand, it seems that the strength in Al_2O_3- or SiC-coated glass has a peak around a film thickness of 3 μm. It is speculated that such an anomalous behavior may be attributed to a competition between two phenomena as follows. The strength may be improved by coating of hard ceramic film, whereas the strength is probably degraded by softening of substrate which is caused by heating during long-time sputtering process. Therefore, in the next section, a strength evaluation will be discussed by considering the sputtering time as well as the surface properties of coated film such as hardness and roughness. Of course, the residual stress in coated film is important factor for strength, though it is very difficult to measure the residual stress in amorphous ceramic thin film. Therefore, the effect of residual stress is considered to be reflected by the film hardness in this study.

4. Estimation of Strength Improvement by Ceramic Coating

Several factors may affect the strength improvement of glass by ceramic coating. In this study, however, a simple procedure is aimed at in estimating such a strength improvement. In the

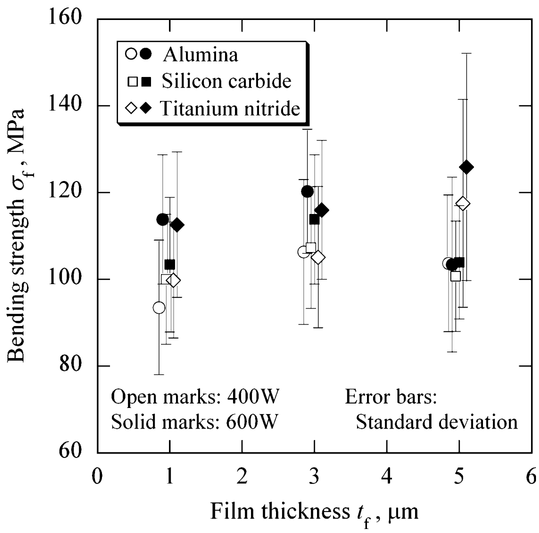

Fig. 4 Strength correlated with thickness of coated film

following, hardness, surface roughness and sputtering time, especially, are considered as parameters dominating strength improvement, because these parameters can be easily measured.

First, a higher hardness of coating film on specimen surface is considered to improve the strength of coated glass under loading mode of a bending type. Actually, the proportional relationship of the strength to the hardness is well recognized in metallic materials. In ceramic materials too, a similar relation has been reported elsewhere (Ref 13). On the analogy of such an empirical fact as aforementioned, it is suggested that the strength may be proportional to the film hardness.

Second, the roughness is considered to act as an origin of surface defect. Such defects in brittle materials are usually treated as cracks, and discussed based on the framework of fracture mechanics. Consider an infinite and brittle plate including a crack. In this case, a fracture mechanics criterion is described as follows.

$$\sigma_f (\pi a)^{1/2} = K_C \qquad \text{(Eq 3)}$$

In the above equation, σ_f and a are, respectively, the strength of the plate and the half length of the crack, and K_C is a constant toughness. The criterion (3) can be rewritten as

$$\sigma_f = K_C (\pi a)^{-1/2} \qquad \text{(Eq 4)}$$

Equation 4 implies that the strength is proportional to the inverse of root square of the flaw size. Considering surface roughness as a kind of surface flaw, it is presumed that strength is proportional to the inverse of root square of roughness.

Third, the effect of sputtering time on strength is taken into account. It is found that the strength decreases for longer sputtering time irrespective of the RF output. Longer sputtering time brings the elevation of temperature of coated material, which results in the softening of glass substrate. The glass softening has been observed in a heat treatment by elevating the initial substrate temperature in the chamber of sputtering apparatus (Ref 14). In the present estimation, a function of exponential type is assumed as one of functions which can

Table 4 Parameters in estimating strength improvement

Film material	α	β	γ
Alumina	1.10	−0.0713	1.16
Silicon carbide	1.03		
Titanium nitride	0.838		

express such a strength degradation with respect to the sputtering time τ; i.e., a function $\exp(\beta t^{\gamma})$ is considered as a simple form. The parameters β and γ in the exponential function are negative and positive constants, respectively. This function represents a phenomenon as follows; there is no strength degradation at the beginning of sputtering with $\tau = 0$, though the degradation occurs during sputtering process with $\tau > 0$. It should be noted that the exponential term is determined by the sputtering time and the kind of substrate glass independently of coating film materials.

As mentioned above, the aim of this study is a proposal of a simple procedure for the estimation of strength improvement by ceramic coating. In this study, a procedure formulated by multiplying the aforementioned three parameters together is adopted as one of simplest procedures; i.e., a new procedure to estimate the rate of strength improvement (σ_c/σ_s) by ceramic coating is proposed by incorporating relative hardness (H_c/H_s) and roughness (R_{ac}/R_{as}) with sputtering time τ in a time unit of ks. Subscripts "s" and "c" imply, respectively, parameters related with substrate glass and coated glass. Finally, an estimation of strength improvement by coating is proposed as follows:

$$\frac{\sigma_c}{\sigma_s} = \alpha \left(\frac{H_c}{H_s}\right) \left(\frac{R_{ac}}{R_{as}}\right)^{-1/2} \exp(\beta\tau^{\gamma}) \qquad \text{(Eq 5)}$$

The parameters α, β, and γ are finally determined by the most suitable fitting, and their values are summarized in Table 4. As mentioned previously, the parameters β and γ are the same irrespectively of film materials. In Eq 5, the parameter α should be unity considering the consistency throughout sputtering process starting from $\tau = 0$, because $\sigma_c = \sigma_s$ results from relations of $H_c = H_s$, $R_{ac} = R_{as}$, and $\exp(\beta\tau^{\gamma}) = 1$ given in the case of $\tau = 0$. As seen in Table 4, however, the α value deviates a little from unity, and it depends on a combination of substrate and coating materials.

The rate of strength improvement observed in experiments is correlated with that estimated by using Eq 5. Figure 5 shows the comparison between both values of strength improvement rates in a logarithmic graph. In the figure, lines indicating the deviation of ±10% from the exact estimation are also drawn. As seen in Fig. 5, most of all data are well estimated by the proposed procedure. Of course, if the α-values are reduced adequately less than those listed Table 4, a conservative estimation can be obtained.

5. Conclusion

The improvement in durability of coated glass is desired in practical applications of such a material. In this study, the effect of coating material kind was evaluated on strength properties of

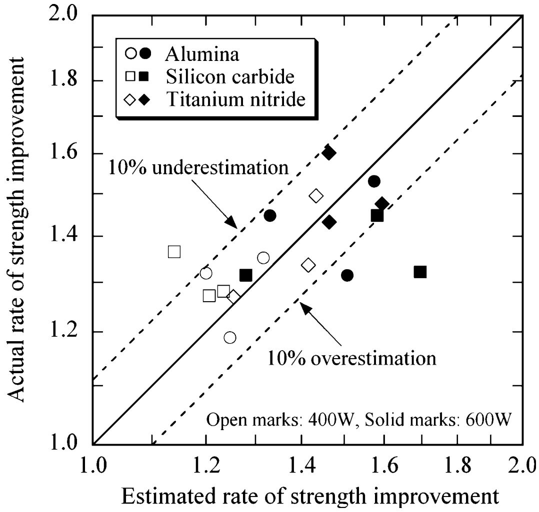

Fig. 5 Estimation of strength improvement by ceramic coating

coated glass. The borosilicate glass was actually coated with three ceramic materials, i.e., alumina, silicon carbide, and titanium nitride. The coating was processed by the RF magnetron sputtering method under two different RF output powers. Mechanical properties of coated materials were investigated with respect to the thickness of sputtered ceramic film. By measuring surface roughness and porosity on coating film, it was found that relative smooth and dense coating films were produced irrespective of the sputtering condition examined in this study. The hardness of coating film was measured by using a dynamic microhardness tester. Observations in hardness test revealed that the coating film became harder for thicker film and/or higher RF output power. Strength tests of coated materials were also conducted under three-point bending mode. The strength properties of ceramics-coated materials were improved in comparison with those of the glass substrate. It was found that the film hardness became higher and the strength was increased in thicker films. To estimate a rate of strength improvement by ceramic coating, a new procedure was proposed by incorporating relative hardness and roughness with sputtering time. The rates of strength improvement in experiments were well estimated by using the proposed procedure.

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