$$P_f = \int_0^\sigma \frac{N!}{(N_f - 1)!\,(N - N_f)!}\,[F(\sigma)]^{N_f - 1} \times [1 - F(\sigma)]^{N - N_f} \frac{dF}{d\sigma}\, d\sigma \qquad (5)$$

where a proportion of N_f/N out of a total of N cracks have failed. The expression for P_f can be evaluated numerically for different combinations of N and N_f/N, and the average strength, $\bar{\sigma}$, is then computed from

$$\bar{\sigma} = \int_0^\infty (1 - P_f)\, d\sigma. \qquad (6)$$

For large N, the sampling distribution of σ is approximately normal with mean μ given by $F(\mu) = N_f/(N+1)$ and variance inversely proportional to N. This is confirmed by the numerical computations of Equations 5 and 6. Table I shows that the average compressive strength is fairly independent of the number of cracks for a given proportion. Thus if the proposed model for the failure of a brittle material under compression is realistic, then the observed compressive strength of a given material should closely follow a normal distribution with mean independent of volume and variance inversely proportional to volume, as the volume is proportional to the number of cracks in a given material. Experimental observations on the compressive strength of two brittle materials support the theoretical predictions.

TABLE I Normalized average compressive stress, $\bar{\sigma}_c/\sigma_I$, for $N_f/N = 2\%$ and 8%. $\bar{\sigma}_T/\sigma_I$ is the normalized average tensile strength based on the failure of one crack. $\sigma_I = K_{IC}/\sqrt{\pi c}$.

N	$m = 2 (n = 2)$			$m = 10 (n = 6)$		
	$\bar{\sigma}_T/\sigma_I$	$\bar{\sigma}_c/\sigma_I$		$\bar{\sigma}_T/\sigma_I$	$\bar{\sigma}_c/\sigma_I$	
		2%	8%		2%	8%
200	0.0870	0.558	1.174	1.145	3.996	5.060
400	0.0615	0.567	1.179	1.051	4.025	5.069
600	0.0502	0.570	1.181	1.001	4.034	5.073
1000	0.0389	0.573	1.182	0.941	4.042	5.075

The above model enables the compressive strength to be related to the tensile strength provided that the Weibull modulus, the number of cracks per unit volume and the exact proportion of cracks that should fail prior to material failure are known. This information may be experimentally forthcoming, in the near future, using acoustic emissions devices. The theory described can also be applied to biaxial systems by using the appropriate value of $U(\beta)$. For an engineer, who is interested in designing with a brittle material, it should in the future be possible to derive "safety factors" on the basis of the probabilities of failure.

References

1. G. C. SIH., *Int. J. Frac.* **10** (1974) 305.
2. A. De S. JAYATILAKA, I. J. JENKINS and S. V. PRASAD, 4th International Conference on Fracture, June 1977, Waterloo, Canada.
3. A. De S. JAYATILAKA and K. TRUSTRUM, J. *Mater. Sci.* **12** (1977) 1426.
4. *Idem, ibid* **12** (1977) 2043.
5. W. J. WEIBULL, *Appl. Mech.* 18 (1951) 293.
6. W. F. BRACE and E. G. BOMBOLAKIS, *J. Geo. Phys. Res.* 68 (1963) 3709.

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Fritted thick film conductor adherence: role of firing atmosphere

Previous studies showed that the adherence of a fritted Pt/Au thick film conductor fired in air on alumina substrates is a function of the thick film peak firing temperature and time and the character of the alumina substrate [1, 2]. In these studies, a fracture energy approach was used to determine thick film adherence as well as to relate this to the thick film-substrate microstructure. It was demonstrated that the above parameters altered the formation of the interpenetrating thick film glass–metal interface required for maximum adherence by affecting the thick film metal sintering and glass flow behaviour.

Besides the above parameters, changes in the thick film firing atmosphere may also be a factor in the adherence of such systems. In fact, reducing, rather than oxidizing (air), firing conditions can be generated either within the thick film due to incomplete organic binder pyrolysis, or inadvertently within the furnace atmosphere. Altering the glass-to-metal wetting and thus altering the glass–metal interface is one possible effect reducing conditions can have on the thick film adherence. For example, contact angles of glasses on noble metals are increased in reducing versus oxidizing atmospheres [3]. Furthermore, Holmquist and Pask showed that the wetting of platinum by glass is degraded when the oxidizing conditions are insufficient to remove residual surface carbon on the platinum [4]. The effects of firing in reducing conditions on the adherence of the fritted Pt/Au thick film conductor have been examined.

Thermal graviametric analysis (TGA) of the thick film composition, after drying at 150° C in air for 2 h using a heating profile similar to that used for actual firing, was used to determine the effects of firing atmosphere on binder pyrolysis and loss of other volatile constituents. TGA data to 1000° C indicate comparable initial weight losses (~ 3.5 wt%) in both oxygen and argon-4 mol% hydrogen atmospheres. However, in oxygen, the initial loss occurs spontaneously at $\sim 200°$ C while in argon–H_2 this loss occurs in two steps: ~ 2.5 wt% at about 340° C and ~ 1 wt% from 350 to about 600° C. Furthermore, a slight (< 1 wt%) weight gain (which is dependent on sample size) is observed from ~ 220 to 1000° C in oxygen versus a small (< 0.5 wt%) weight loss from 900 to 1000° C in argon–H_2. This data suggests that there are not substantial differences in thick film behaviour in oxidizing or reducing conditions. However, subsequent scanning electron microscopy of these samples fired to 1000° C revealed that the samples fired in oxygen were composed of a porous, sintered metal wet by glass, i.e. similar to the microstructure observed in previous studies [1, 2]. On the other hand, little metal sintering and very poor wetting of the metal by the melted glass occurred in the argon–H_2 atmosphere.

Samples were prepared for adherence tests by screen printing (200 mesh) a conductor strip pattern (~ 1.9 cm long × ~ 0.2 cm wide) of the fritted Pt–Au conductor paste onto alumina substrates and drying in air at 150° C for 15 to 20 min. The alumina substrates employed included the 96 wt% and 99 + wt% as-fired polycrystalline alumina and polished 0° sapphire substrates described earlier [2]. The printed and dried samples were then fired using conventional firing profiles in a covered 99.98 wt% alumina tray into which 4 mol% H_2/argon gas (0.5 l min^{-1}) was introduced. Peak firing conditions included 10 min hold times at 850, 950, and 1050° C. After firing, the adherence fracture energy was measured at 22° C, 50% r.h. at a deflection rate of 2×10^{-2} cm min^{-1} using the procedures previously described [1, 2, 5] and the resultant separation surfaces examined using scanning electron microscopy employing stereo-pair photographs to determine the locus of failure (separation).

The adherence results (Fig. 1) show that there is a substantial reduction in the adherence fracture energy, γ_{IC}, for all peak firing temperatures and substrates with a reducing versus oxidizing firing atmosphere. Note that with the 96 wt% alumina substrate and reducing conditions, the maximum adherence γ_{IC} value of 3.6 J m^{-2} obtained with air firing is not achieved and that the minimum adherence γ_{IC} values ($\leqslant 0.5$ J m^{-2}) occur at lower firing temperatures. Based on the previous studies

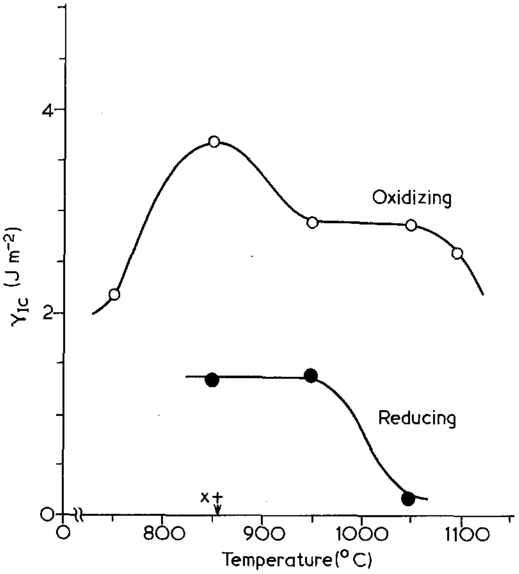

Figure 1 Thick film adherence fracture energy for various thick film peak firing temperatures. The curves represent thick film adherence to 96 wt% alumina substrates after firing in air (○) and argon-4 mol% hydrogen (●). Also shown is the adherence to 99 wt% alumina (X) and 0° sapphire (+) substrates after firing on argon-4 mol% hydrogen.

[1, 2], the adherence γ_{IC} values obtained in reducing firing conditions should be indicative of the lack of a strongly interpenetrating thick film glass–metal interface. This is confirmed by the separation (fracture) surface analysis. The locus of separation of thick film-96 wt% substrate samples fired in $Ar\text{-}H_2$ to 850 and 950° C primarily involves separation at the smooth glass–metal interface together with fracture of the limited number of glass fibrils that penetrate into the conductor metal. The samples fired to 1050° C separated entirely along the smooth glass–metal interface which is devoid of interlocking glass fibrils.

In comparison to the data for the 96 wt% alumina, adherence is negligible after firing at 850° C in the reducing atmosphere when the 99+ wt% alumina and 0° sapphire substrates are used. The locus of thick film separation is along the glass/metal interface for both the 99+ wt% alumina and sapphire substrates. This behaviour is similar to the loss of adherence in air with the purer substrates where the loss of an interpenetrating glass–metal interface is futher promoted by greater glass-to-substrate wetting [2].

Thus, the adherence of the fritted thick film conductor is significantly degraded by the introduction of reducing versus oxidizing firing conditions. This is due to the decrease in the interpenetrating microstructure of the metal–glass interface brought on primarily by the poor glass-to-metal wetting and in part by the poor metal sintering. It is felt that residual carboneous contamination from incomplete binder pyrolysis in $Ar\text{–}H_2$ is responsible for the poor glass-to-metal wetting. Such effects of carbon contamination of the metal on wetting have been noted [4] and could also result in the observed decrease in metal sintering. On the other hand, loss of metal surface oxide film, while it might cause poor glass-to-metal wetting, would lead to enhanced metal sintering. Finally, loss of thick film glass or flux constituents (notably B_2O_3, CdO, or Bi_2O_3) are not felt to be factors in the degraded adherence for reducing atmosphere firings as the glass still wets and flows on the alumina substrates and the TGA data does not indicate any related weight loss until temperatures > 900° C.

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References

1. P. F. BECHER and W. L. NEWELL, *J. Mater. Sci.* **12** (1977) 90.
2. P. F. BECHER and J. S. MURDAY, *ibid* **12** (1977) 1088.
3. J. A. PASK and F. M. FULRATH, *J. Amer. Ceram. Soc.* 45 (1962) 552.
4. G. A. HOLMQUIST and J. A. PASK, *ibid* 59 (1976) 384.
5. P. F. BECHER, W. D. BASCOM, J. L. BITNER and J. S. MURDAY, proceedings of the International Microelectronics Symposium (International Society for Hybrid Microelectronics, Montgomery, Ala., 1975) p. 279.

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Control of stress sensitivity in gadolinium yttrium iron garnets

$Y_{2.01}Gd_{0.99}Fe_{4.925}O_{12}$ has been shown to have good magnetic properties for microwave applications, but the remanent magnetization is small [1]. Remanent magnetization and coercive force in garnets can be altered by stress developed in the specimens [2], and stress in the garnet toroid can result in a serious degradation in performance of remanent devices [3]. It is intended to show in this letter that the remanent magnetization, coercive force and sintered density are improved by a small addition of manganese ion.

A study was undertaken to investigate the effect of manganese ion concentration on properties of $Y_{2.01}Gd_{0.99}Fe_{4.925}O_{12}$ $Y_{2.01}Gd_{0.99}Fe_{4.925-x}Mn_xO_{12}$, where $x = 0$, 0.03, 0.05, 0.07 and 0.09. Samples were prepared by spray-drying precursory solutions followed by rotary calcining,