

Anisotropic Thermal Expansion Behaviour of Thermally Sprayed Coatings

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1. INTRODUCTION

It has been reported [1] that plasma sprayed materials exhibit anisotropic thermal expansion effects. The results of a zirconia containing 8wt.% yttria show that the longitudinal coefficients of thermal expansion are approximately constant at $10 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$; regardless of prior heat treatment. On the other hand, the transverse coefficients of thermal expansion range from 2.9 to $23.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [1]. Thermal expansion differences between the first and second heat cycles have been observed [1,2]. It was believed that these differences arise from phase redistribution within the sprayed materials [2]. Heat treatment of the coating may not only influence the phase transformation but also the relaxation of residual stresses and/or redistribution of the microcrack network. The latter may also contribute to the difference in the thermal expansion coefficient, in both the longitudinal and transverse directions. It is necessary to investigate such anisotropic thermal expansion effects to optimize potential industrial applications of plasma sprayed coatings.

2. EXPERIMENTAL PROCEDURES AND RESULTS

Plasma spraying has been performed on degreased, sand blasted and cleaned steel substrates with dimensions of 50 mm in diameter and a uniform thickness of about 2 mm. The substrates were coated with salt prior to spraying to facilitate the specimen removal. The free standing plasma sprayed samples were cut with a fine diamond saw to form square specimens of about 10×10 mm. The flat samples were used for X-ray analysis and porosity measurements.

The alumina powders were sintered, crushed and sieved to produce a free flowing product with a particle size range from 28 μm to 56 μm . Plasma spraying was carried out at 40 V and 900 A. The argon gas and nitrogen carrier gas were set to flow rate of 50 l min^{-1} and 30 l min^{-1} respectively. The torch to substrate distance was 120 mm and the powder flow rate was 30 g min^{-1} . Thermal expansion behaviour of the plasma sprayed samples was investigated under a constant heating rate of $5 \text{ }^\circ\text{C/min}$; using an Amadel-Lhomargy dilatometer (Model No. DI-24).

The experimental results for alumina show that there was little difference in thermal expansion along the longitudinal direction for different cycles of the heat treatment.

They are essentially the same below 500 °C; with a linear thermal expansion of about 0.3% and thermal expansion coefficient of $5.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for the first cycle and about $5.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for other cycles (see Fig. 1). The measurements from the first cycle show different behaviour from the following cycles above 500 °C⁻¹. The thermal expansion of samples during the first cycle were non-linear and shrank from 0.20 to 0.25 % up to 1000 °C. The alumina specimens show stable and repeatable thermal expansion behaviour after the first cycle. The average linear thermal expansion was 0.62 % up to 1000 °C and the overall thermal expansion coefficient was $6.98 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.

The thermal expansion behaviour of alumina coatings in the transverse direction is more complex than that in the longitudinal direction. The thermal expansion coefficient of the first cycle was usually very low. An overall thermal expansion of 20 to 30 x 10⁻⁴ °C was obtained below 500 °C⁻¹ and the thermal expansion coefficient was $5.20 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The sample did not exhibit linear thermal expansion behaviour and began to shrink above 500 °C. This shrinkage rate increases at about 600 °C and occasionally the samples changed from a net expansion into a net contraction at about 930 °C. The thermal expansion measurements of the first cycle can be repeated and the standard deviation of 8 tests is 0.3 with a variance of 8% below 500 °C and 0.6 with a variance of 21.5% up to 950 °C. The thermal expansion behaviour of other cycles is quite different from measurements performed in the longitudinal direction. A linear thermal expansion up to 1000 °C is obtained which gives an overall thermal expansion coefficient of about $7.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. A sudden increase in expansion within a short period was observed for the following cycles. This large expansion occurred between 270 °C to 850 °C and was quite stable for the same sample. No general trend between samples was observed.

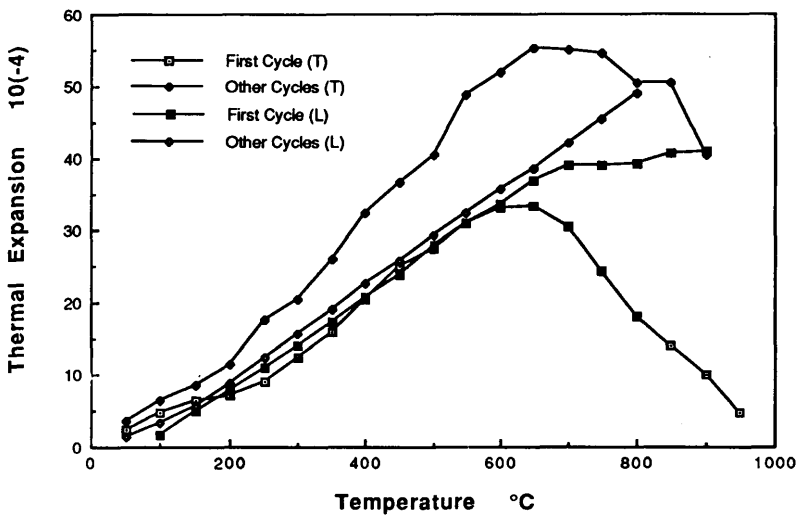


Figure 1: Comparison of thermal expansion in longitudinal (L) and transverse (T) direction for the different cycles of alumina coatings

The experiments show that anisotropic thermal expansion existed in plasma sprayed alumina coatings during thermal cycling. Shrinkage in the transverse direction was much more than that in the longitudinal direction for as-sprayed samples during the first cycle. The longitudinal coefficient of thermal expansion is approximately constant at $7.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for the following cycles; regardless of the number of thermal cycles. However, the transverse coefficient of the sample is not stable; being around $7.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ with a sudden increment up to $18.5 \sim 24.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ within a range of 270 to $850 \text{ }^\circ\text{C}$. These results suggest that the thermal expansion coefficients are related to the thermal history of the samples since there may be changes in microstructure, relaxation of residual stresses or **rearrangement** of the microcrack network.

The XRD patterns before and after the experiments of thermal expansion show no phase changes occur during heating and cooling up to $1000 \text{ }^\circ\text{C}$. This conclusion was confirmed by DTA work since no peak differences were detected. The γ alumina phase is produced after plasma spraying. Broadened lines were obtained for the as-sprayed sample. It was found that as the cycle number increased then the broad peaks become distinct and move towards the standard $\gamma\text{-Al}_2\text{O}_3$ pattern. These broad lines are thought to be caused by the distorted lattice which is formed during rapid solidification and are associated with the residual stresses of the sprayed coating. The change of XRD patterns indicates that residual stress is released by any subsequent thermal cycling.

3 THEORETICAL ANALYSIS AND DISCUSSION

3.1 Stress in the coating

Thermally sprayed coatings which are processed by the usual means are in a state of stress. A thermal stress is produced at the interface between the first layer of the coating structure and the substrate. Plastic deformation of the substrate can be ignored because the thickness of splats is much less than that of the substrate. This stress can be expressed in the form of [3];

$$\sigma_t = E(\alpha_c - \alpha_s)(T_{sp} - T_{me}) \quad (1)$$

where E is the Young's modulus, α_c and α_s , are the average thermal expansion coefficients for the splats and substrate respectively. T_{sp} and T_{me} are the temperatures during spraying and when the measurement is performed. A positive value of σ_t corresponds to a tensile stress. This stress is introduced by the change of temperature or materials, such as the stress formed at the interface of the coating/substrate system. Thermal stress can also be produced between identical materials which have the same thermal expansion coefficients. For example, these materials may be bolted together at different temperatures. A thermal stress would be produced between the materials after a homogenous temperature is reached. This is the case in the thermal spray coating in which splats overlap and are pinned together at different temperatures [4]. This condition can be expressed by letting α_s equal zero in equation 1.

The residual stress can be defined as the self-equilibrating internal stress which exists in a free body when no external traction is applied [5]. Residual stress can arise, for example, when a material is subjected to heat treatment. If the material is cooled quickly from the heat treatment, such as happens in the solidification of splats during deposition,

then surface and interior experience different cooling rates. This is a **real** effect; for example, bulk alumina ceramics may yield a stress of 272 MPa per degree centigrade temperature difference between two regions. The residual stress can be expressed in the following form [5];

$$\sigma_r = -E(\epsilon_u - \epsilon_s) \quad (2)$$

where E is the elastic modulus of the substrate. The residual stress, σ_r , is positive if it lies in the normal direction to the surface on which it acts. Hence, compression is negative. The residual stress is thus proportional to the difference between the "actual" local reversible strain " ϵ_r " and the free local strain " ϵ_u ".

3.2 Stress distribution within splats

The detail of the stress distribution between splats and a substrate can be very complex. However for an idealized representation the stress distribution is determined by the requirement that the sum of the normal stress and bending moments over the total cross section be zero [3].

Consider the situation of two splats which are pinned together at the edge, Fig.2. A tensile stress will be produced in splat A after cooling if splat B solidified before A and acted as its substrate. **This** occurs because splat A tends to contract more than B during cooling. Two boundary conditions need to be satisfied. The first is that splat

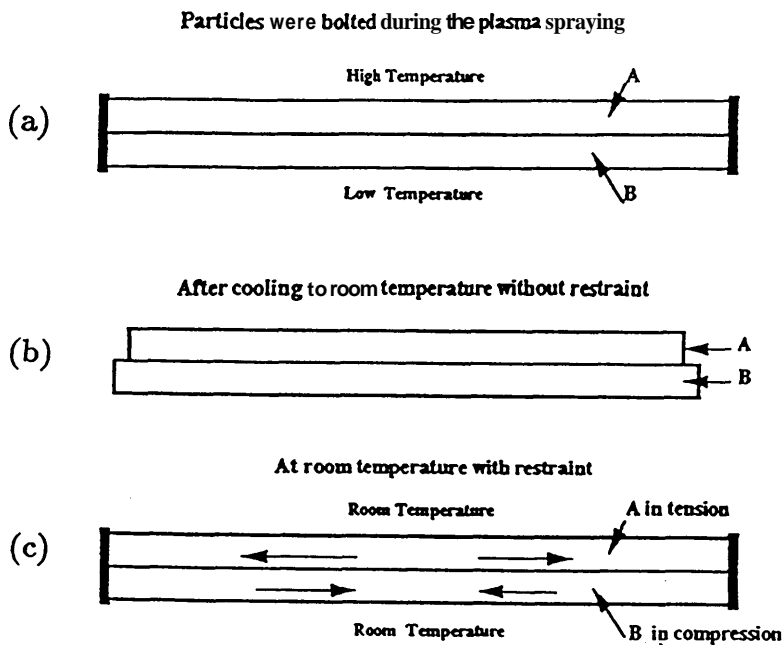


Figure 2: Illustration of two pin model: (a) two particles are bolted at high temperature; (b) after cooling without restraint; (c) at room temperature with restraint

B produces compressive stress between two pins to produce a zero normal force. The second condition is that splats which have solidified before B produce a bending moment which prevents splat B from spalling. It can be noted that the pinned splats will be partially restrained and residual stress is produced after cooling from high temperature. This can be expressed by introducing a restraint coefficient, K , in equation 1.

$$\sigma_t = -K\alpha E(T_{sp} - T_{si}) \quad (3)$$

where T_{si} is the initial substrate temperature. Let the substrate temperature be uniform throughout each splat. Thus from the requirements for the pinned splats, equations 2 and 3 can be combined to find;

$$K_A = \frac{1 - \frac{\alpha_B(T_A^A - T_A)}{\alpha_A(T_{si}^B - T_B)}}{1 + \frac{h_A E_A}{h_B E_B}} \quad (4)$$

where K_A is a restraint coefficient which is introduced to express the influence of splat B on A. T_A is the spraying temperature of splat A. The above equation can be simplified if splats A and B have the same final room temperature, thermal expansion coefficient and Young's modulus. However they are subjected to different initial temperatures when they are pinned together during the spraying process. It can be concluded that a tensile stress will exist in any new solidified particle which overlaps others. The melted particle may be pinned at many locations within two single splat discs. Therefore the multi-pinned splats can be divided into a number of two pin systems. Each of these is illustrated in Fig. 2 and can be considered to be independent from each other.

3.3 Stress distribution within the coating

The stress of the top nth layer splat of plasma sprayed coatings after cooling to room temperature is given by equation 5, i.e.; (see Fig. 3)

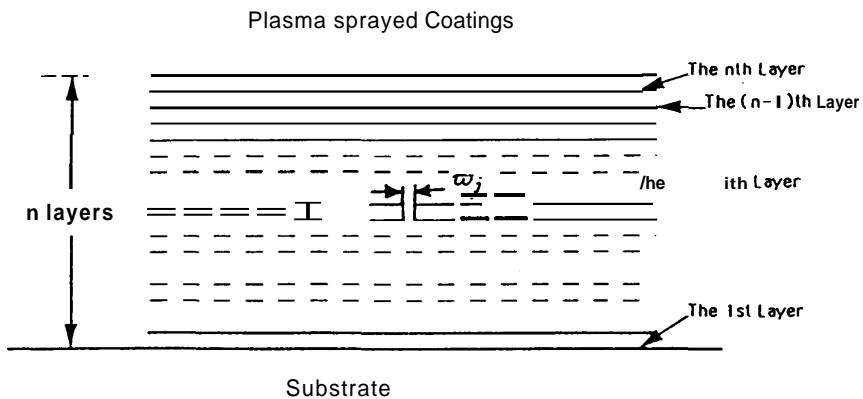


Figure 3: Illustration of lamellar pin model with microcracks; pore and cracks are presented by ω_j .

$$\sigma_n = -\alpha_n K_n E_n (T_n - T_r) \quad (5)$$

where T_r and T_n are the room and solidified temperature for the top layer of material. K_n , α_n and E_n are the restraint coefficient, thermal expansion coefficient and Young's modulus, respectively. K_n is the restraint coefficient of the nth layer of splats and is evaluated by a similar expression to equation 4.

$$K_n = \frac{1 - \left(\frac{\alpha_{n-1} E_{n-1} (T_r - T_n)}{\alpha_n E_n (T_r - T_n)} \right)}{1 + \frac{h_n E_n}{H_{n-1} E_{n-1}}} \quad (6)$$

where

$$H_{n-1} = \sum_{i=1}^{n-1} h_i \quad (7)$$

The stress is composed of two parts for the next splat layer. The first part comes from the stresses produced when the splat is pinned to prior solidified particles. The second part arises from the contribution of the nth layer. This can be expressed as;

$$\sigma_{n-1} = -\alpha_{n-1} K_{n-1} E_{n-1} (T_r - T_{n-1}) + \left(-\frac{h_n}{h_{n-1}} \sigma_n \right) \quad (8)$$

or

$$\sigma_{n-1} = -\alpha_{n-1} K_{n-1} E_{n-1} (T_r - T_{n-1}) + \frac{h_n}{\sum_{i=1}^{n-1} h_i} \alpha_n K_n E_n (T_r - T_n) \quad (9)$$

The stresses of the (n-1)th splat layer can be written in the form of;

$$\sigma_{n-1} = -\alpha_{n-1} K'_{n-1} E_{n-1} (T_{n-1} - T_r) \quad (10)$$

where

$$K'_{n-1} = \frac{\alpha_n E_n (T_n - T_r)}{\alpha_{n-1} E_{n-1} (T_{n-1} - T_r)} \frac{h_n}{H_{n-1}} K_n - K_{n-1} \quad (11)$$

Therefore the stress of the ith layer of splats can be written in the form of;

$$\sigma_i = -\alpha_i K'_i E_i (T_i - T_r) \quad (12)$$

where

$$K'_i = \sum_{i+1}^n \frac{\alpha_{i+1} E_{i+1} (T_{i+1} - T_r)}{\alpha_i E_i (T_i - T_r) h_i} \frac{h_{i+1}}{H_i} K_{i+1} - K_i \quad (13)$$

If all layers of the coating are made of the same materials and have the same Young's modulus and thermal expansion coefficient, then the above equations may be simplified. For any ith layer, K_i can be written as;

$$K'_i = \sum_{i+1}^n \frac{(T_{i+1} - T_r) h_{i+1}}{(T_i - T_r) H_i} K_{i+1} - K_i \quad (14)$$

Equation 13 or 14 can be used to evaluate the residual stress distribution in a plasma sprayed coating. The positive restraint coefficients correspond to compressive stresses

and negative coefficients to tensile stresses. The equations 13 and 14 are developed from an idealized situation where all the layers are aligned in the longitudinal direction. The splats, however, are not continuous in the real situation. For example there may be pores and cracks within splats between two splats; as schematically illustrated in Fig.3. The restraint coefficient formula can be obtained by using the same method and procedures determined in section 3.3. It is obtained in the form of;

$$K'_i = \sum_{i+1}^n \frac{\alpha_{i+1} E_{i+1} (T_{i+1} - T_r) h_{i+1}}{\alpha_i E_i (T_i - T_r) H_i} K_{i+1} - K_i \quad (15)$$

where K_i is given by

$$K_i = \frac{1 - \left(\frac{\alpha_{i-1} (T_r - T_i)}{\alpha_i (T_r - T_i)} - \frac{\sum_j^m \varpi_j}{\alpha_i d_i (T_i - T_o)} \right)}{1 + \frac{h_i E_i}{h_{i-1} E_{i-1}}} \quad (16)$$

where m is the total number of cracks and pores covered by the splats in the “ i th” layer; d_i and α_i are the thermal expansion coefficients and diameters of splats when solidified on the substrate, ϖ_j is the width of the cracks on the i th layer splats and j is the corresponding number of cracks covered by the splat.

It has been experimentally shown that the surface coating after spraying is usually in tension [6] and it has been estimated that the residual stresses within zirconia coatings changed gradually from negative to positive as the thickness of the coating increased.

4. GENERAL DISCUSSION

4.1 Thermal expansion in longitudinal directions

Consider a coating sample that is heated to a temperature T . The average stress on the coating, σ , is given by two terms, such that;

$$\sigma = \sigma_t + \sigma_r \quad (17)$$

where σ_t is the thermal stress produced by the heating or cooling cycle and σ_r is the residual stress produced during the formation of the coating.

$$\sigma = \alpha E (T - T_o) + [-E \alpha K'_\alpha (T_m - T_s)] \quad (18)$$

or by letting $\alpha' = \alpha E (T - T_o)$, then

$$\alpha' = \alpha \left[1 - K'_\alpha \frac{(T_m - T_s)}{(T - T_o)} \right], \quad (T > T_o) \quad (19)$$

where α' is the measured thermal expansion coefficient, and K'_α is the average restraint coefficient of the coating. T_m is the average solidification temperature during the spraying and T_s is the average substrate temperature. T_o is the initial temperature of the heated coating.

Equation 19 shows that the measured thermal expansion coefficient is also related to thermal spray processes. It can be noted that $(T_m - T_s)/(T - T_o) > 0$, therefore the

measured thermal expansion coefficients of coatings may be larger or smaller than that of the bulk material of the coating and are determined by the sign of the average restraint coefficient of the coating. A positive restraint coefficient corresponds to the average compressive stresses in the coating. A negative restraint coefficient corresponds to an average tensile stresses in the coating. Therefore, the measured thermal expansion coefficients will be less than the intrinsic material property of the coating if the average residual stresses are compressive. Likewise the measured thermal expansion coefficients will be larger than that of the coating if the average residual stress is tensile.

The derivative of the ratio of thermal expansion coefficient to temperature is not zero, therefore:

$$R_\alpha = \frac{d}{dT} \left(\frac{\alpha'}{\alpha} \right) = K'_\alpha \frac{(T_m - T_s)}{(T - T_o)^2} \neq 0 \quad (20)$$

where R_α is a mono-function of temperature. R_α will decrease as the temperature increases if the average restraint coefficient is positive.

4.2 Thermal expansion in transverse direction

The thermal expansion behaviour in the transverse direction can be analyzed by a similar method for the longitudinal direction. The only difference is that thermal expansion in the transverse direction of coatings is not the sum of thermal expansions of all splats in the thickness since the structure of coatings is anisotropic. The deflection of all splats in the thickness direction should be considered. Thus the original deflection of the splat is given in the form of [7];

$$w_e = \frac{\delta_o}{2} \left[1 + \cos \left(\frac{2\pi x}{l} \right) \right] \quad (21)$$

Then, the deflection of the splat will be given in the form of [8];

$$\delta = \frac{\delta_o}{1 - \left(\frac{p}{p_{cr}} \right)} \quad (22)$$

where the p_{cr} is the critical Euler load and p is the applied load. In the case of temperature change the load p is determined by strain so that equation 22 becomes;

$$\delta = \frac{\delta_o}{1 - \left(\frac{\epsilon}{\epsilon_*} \right)} \quad (23)$$

where ϵ_* is the critical buckling strain and ϵ^* is the strain in the middle of splats. The thermal expansion of the coating in the transverse direction can thus be written in the form of;

$$\Delta h = \sum_i^n \Delta h_i + \sum_i^m \delta_i \quad (24)$$

where δh_i is the thickness change of splat i and δ_i is the deflection of splat i . The parameters n and m are the number of splats in the cross-section and number of deflected

splats respectively. The thermal expansion coefficient can be written as;

$$\alpha = \frac{\Delta h}{h} \frac{1}{T_{av} - T_0} \quad (25)$$

where T_{av} and T_0 are the average temperature and initial temperature respectively, and h is the thickness of the coating. Therefore, the measured thermal expansion coefficient in the transverse direction can be given in the form of;

$$\alpha' = \frac{1}{h(T_{av} - T_0)} \left(\sum_{i=1}^n h_i \alpha_i (T_i - T_0) + \sum_{j=1}^m \delta_j \right) \quad (26)$$

where T_i is the i th layer's temperature and α_i is the thermal expansion coefficient of these splats in the transverse direction. The above equation indicates that the total thermal expansion of coatings in the transverse direction is the sum of thermal expansion of all layers and the total buckling deflection of all splats.

If it is assumed that all splats have the same thermal expansion coefficient and thickness, then the equation becomes

$$\alpha' = \alpha \frac{1}{n(T_{av} - T_0)} \sum_{i=1}^n (T_i - T_0) + \frac{\delta_o}{h(T_{av} - T_0)} \sum_{i=1}^m \frac{1}{1 - \left(\frac{\epsilon_o}{\epsilon^*}\right)} \quad (27)$$

The first term on the right hand side of equation 27 indicates the influence of temperature gradient between lamellae. The second term indicates the influence of deflection. For the idealized uniformly heated materials without lamellar structure, $T_i = T_{av}$ and $\delta_i = 0$. Under these conditions the measured thermal expansion coefficient will equal the bulk thermal expansion coefficient of the material. The deflection in the lamellar structure can be positive or negative and depends on the stress distribution which is determined by the spray and heat treatment conditions. Positive deflection will increase the measured thermal expansion coefficient and negative deflection decreases the measured thermal expansion coefficient. Thus the measured thermal expansion in the transverse direction can not be repeated for different samples and different heat treatment conditions [1].

5. SUMMARY

The thermal expansion behaviour of the coating is anisotropic due to the anisotropic lamellar structure. A restraint coefficient has been introduced to express the residual stress distribution within each splat. A positive restraint coefficient indicates compressive stress and a negative coefficient indicates tensile stress in the splats. The residual stress distribution can thus be discussed by an average restraint coefficient.

It was found that the measured thermal expansion coefficient is related to the average restraint coefficient in the coating. The measured thermal expansion coefficient will either increase if the coating is in a state of average tensile stress or decrease if the coating is in a state of average compressive stress. This is especially significant in the first cycle of heat treatment. The thermal expansion of coatings becomes stable after the first cycle since most of the residual stress has been released during the first thermal cycle. The expansion in the longitudinal direction is more stable than that in the transverse direction.

The thermal expansion behaviour in the transverse direction is different from that in the **longitudinal** direction. The deflection of splats in the lamellar structure should be considered since the measured thermal expansion is the sum of the total thermal expansion in thickness and the total deflection of all splats during heat treatment. Thus the thermal expansion in the transverse direction is related to the lamellar structure formed during the spraying process. The measured thermal expansion varies for different samples and is relatively stable for the same sample after the first thermal cycle.

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