

# An Analysis of the Porosity Producing Mechanism

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## Abstract

It is well-known that thermal spray coatings have porosity, but the reason why the porosity is produced in thermal spray coating processes is not known. Although many qualitative discussions have been done about porosity in thermal spray coatings. This paper proposes a physical and mathematical model of the porosity producing mechanism, and flattening process of the molten particle on the surface of the substrate or the coating after the molten particle impinges onto the substrate or the coating in thermal spray processes. This paper theoretically describes that atmospheric gas contributes to producing porosity in the thermal spray process and that there is a distribution of pores between the splat and the substrate or between splats.

IT IS KNOWN that the boundary structure between splats or between the substrate and splats greatly affects the physical characteristics of thermal spray coatings. In particular, porosity in the coating is an important factor in understanding characteristics of coatings. At present, the structures of splat interfaces are being clarified by various studies (1 - 4); but there is no established theory on the formation mechanism of pores between splats or between the substrate and splats. In this paper, the porosity formation mechanism of coatings is mathematically analyzed under several assumptions.

## Theory

*Definition of porosity.* The structure of coatings is considered to be lamellar shown in Fig. 1. An enlarged interface between splats or between the substrate and splat is shown in Fig.2. The porosity  $f_p$  of coatings is defined as follows,

$$f_p = \frac{V_g}{V_s + V_g} \quad (1)$$

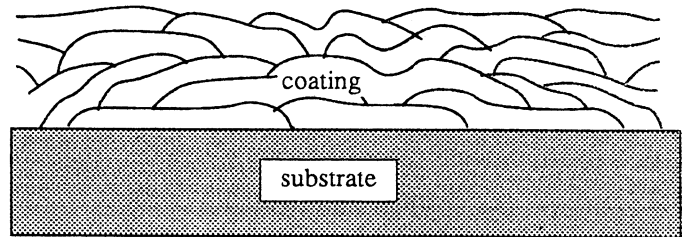


Fig. 1 - Cross section of a thermal spray coating.

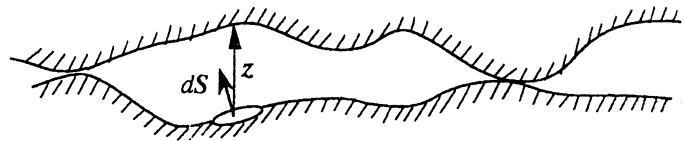


Fig. 2 - Interface between splats or between a splat and a substrate.

where

$V_g$  = the total volume of pores between splats, and between splats and the substrate in the coating,  
 $V_s$  = the total volume of solid in the coating.

The total volume of pores  $V_g$  in coatings is defined as follows,

$$V_g = \frac{1}{2} \int_S z \, dS \quad (2)$$

where

$z$  = the vector which is parallel to the  $z$  axis and has a length of  $z$ ,

$dS$  = the vector which is perpendicular to the splat surface and positive to the outer direction of the splat and has a length equal to a surface area of  $dS$  of the splat,

$S$  = the total surface area of all splats in the coating.

According to Eq. 2, the integration is carried out for the surface area of every splat, so integration is performed twice for every splat interface. Therefore, the resultant value divided by 2 represents the total volume of pores.

A mathematical model of porosity formation. The cross section profile of the surface of a substrate or a thermal spray coating is assumed to be as shown Fig.3; namely, there are many holes on both surfaces. The total volume of holes on a unit surface area is assumed to be  $V_0$ .

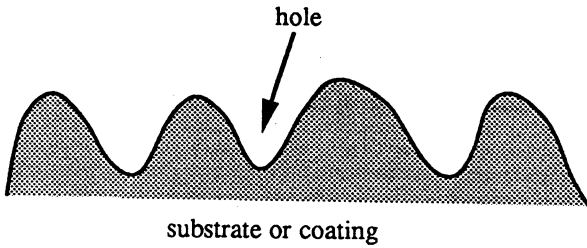


Fig. 3 - Cross section of surface profile of substrate or coating.

A molten disk particle impinges onto the surface at velocity  $v_0$  as shown in Fig.4. It is assumed that molten particle flows only perpendicularly to the surface, but not parallel to the surface. The molten particle compresses the gas in the holes on the surface. Then, the gas volume changes from  $V_0$  to  $V$ . Also, it is assumed that the gas is an ideal gas and the pressure and volume of the gas change in a polytropic action. The gas pressure  $P$  in the holes is;

$$P = k_1 V^{-n} \quad (3)$$

where

$V$  = the volume of gas in the holes on a unit surface area,  
 $k_1$  = a constant,  
 $n > 1$ .

It is assumed that no gas is released from the molten particle and the substrate, the compressed gas is completely released through the interface between splats or between the substrate and splat after the solidification of the molten particle. Also, it is assumed that the work to compress the gas from  $V_0$  to  $V$  in the holes on a unit surface area is proportional to the kinetic energy of molten particles whose volume equals the compressed volume ( $V_0 - V$ ) of the gas. Then, the next equation can be derived as

$$\int_{V_0}^V -P dV = \frac{1}{2} k_2 \rho (V_0 - V) v_0^2 \quad (4)$$

where

$v_0$  = the impinging velocity of molten particle,  
 $\rho$  = density of molten particle,  
 $k_2$  = a constant.

On substitution of Eq.3 into Eq.4 the next equation is;

$$\frac{\left(\frac{V}{V_0}\right)^{1-n} - 1}{1 - \frac{V}{V_0}} = \frac{(n-1)k_2 \rho v_0^2}{2P_0} \quad (5)$$

where

$P_0$  = the initial pressure of the gas in the holes.

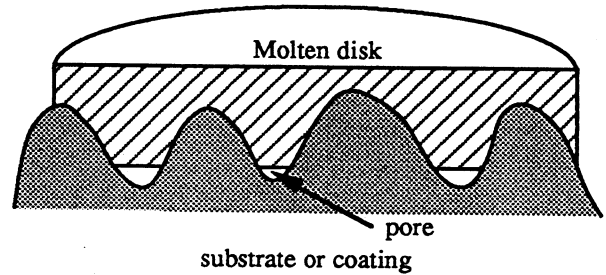
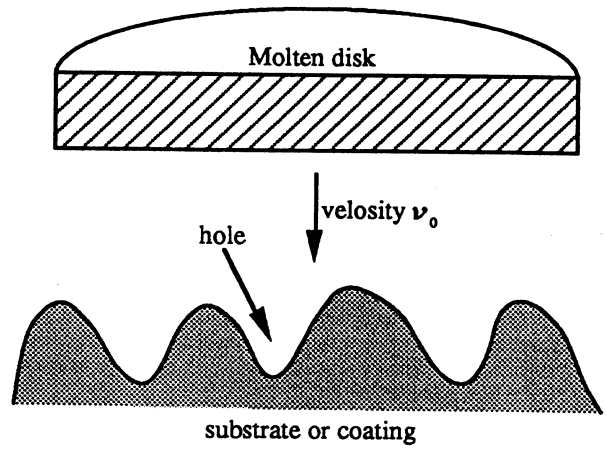


Fig. 4 - Cross section before and after impingement of a molten disk onto a substrate or a coating.

If  $V/V_0 \ll 1$ , then Eq. 5 can be written as;

$$\left(\frac{V}{V_0}\right)^{1-n} = \frac{(n-1)k_2 \rho v_0^2}{2P_0} \quad (6)$$

Eq.5 and 6 describe that the volume of pores depends on the impinging velocity of a molten particle, the initial pressure of gas in the holes and the density of molten particles.

**The flattening process of molten particle.** In the preceding paragraph, the gas compression process in holes was described without consideration of the parallel flow of a molten particle to the surface of the substrate or the coating after impingement. The flattening process of a molten particle must be considered in the porosity producing model. It is assumed that the molten particle is flattened after impingement on the substrate or the coating as shown in Fig.5. Further assumptions are;

- 1) The impinging particle is completely molten.
- 2) The particles impinge perpendicularly on the substrate or the coating.
- 3) The density and viscosity of the molten particles are constant during flow and deformation processes.
- 4) Flattening is completed before solidification.
- 5) The thickness  $h$  of a flattening particle is constant in the region of  $r \geq R_0$  during the flattening process.

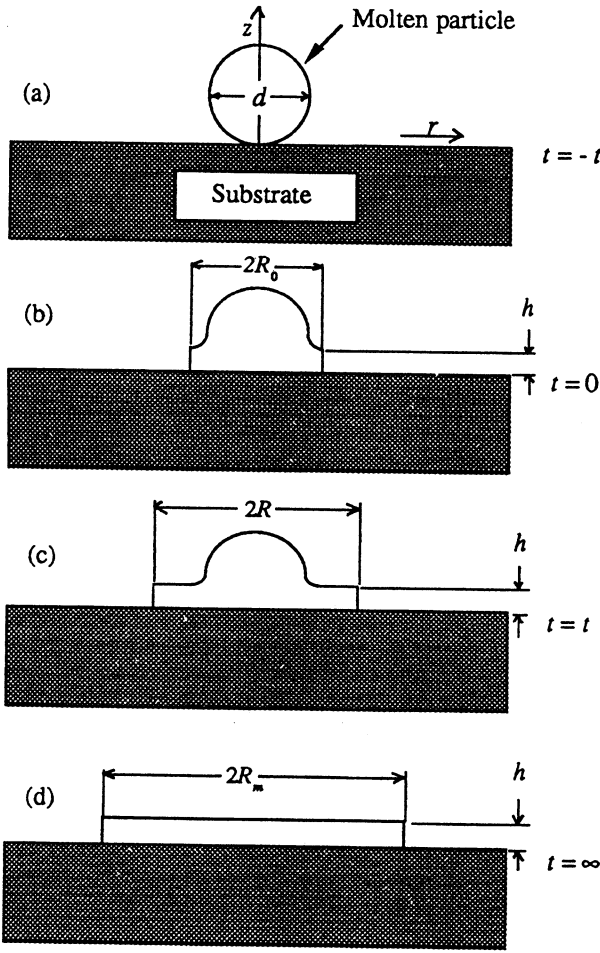


Fig. 5 - Flattening process of molten particle.

6) The energy dissipation of a molten particle by viscous work is negligible in the region of  $r < R_0$ .

7) Gravity can be neglected.

A cylindrical coordinate is used, and the flow velocity field  $\mathbf{v} = (v_r, v_\theta, v_z)$  in the region of  $r \geq R_0$  assumed to be as follows. Since the flow of a molten particle is symmetrical around the  $z$  axis, then  $v_\theta = 0$ , and there is no flow in the  $z$  direction, i.e.  $v_z = 0$ .  $v_r$  is assumed to be represented by the next equation, as  $C(t)$  is a function of time.

$$v_r = C(t) \frac{z}{r} \quad (7)$$

$C(t)$  is assumed to be;

$$C(t) = \frac{R_0 v_0 e^{-\alpha t}}{h} \quad (8)$$

where

$t$  = time,

$v_0 = |\mathbf{v}_0|$ .

Velocity  $\mathbf{v}$  fulfills the continuous equation as follows;

$$\text{div } \mathbf{v} = \frac{1}{r} \frac{\partial v_r}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z} = 0 \quad (9)$$

The volume of fluid in the range of  $R_0 \leq r \leq R$  is equal to the volume flowing out of the region of  $r < R_0$  in time from  $t = 0$  to  $t = t$ . Therefore, the next equation follows.

$$\begin{aligned} \pi h (R^2 - R_0^2) &= 2\pi R_0 \int_0^t \int_0^h v_r (r = R_0) dz dt \\ &= 2\pi R_0 \int_0^t \int_0^h \frac{v_0 e^{-\alpha t} z}{h} dz dt \end{aligned} \quad (10)$$

Eq.10 is calculated as follows;

$$\pi h (R^2 - R_0^2) = \frac{\pi R_0 v_0 h}{\alpha} (1 - e^{-\alpha t}) \quad (11)$$

with the assumption that  $R = R_m$  when  $t = \infty$ ,

$$\alpha = \frac{R_0 v_0}{R_m^2 - R_0^2} \quad (12)$$

If the velocity field in the region of  $r \geq R_0$  is  $v_r$ , then the viscosity coefficient of the fluid is  $\mu$ , and the volume of the fluid in the region  $r \geq R_0$  is  $V$ . This dissipated energy  $\dot{\Phi}$  of the fluid per unit time due to viscous work is written as follows;

$$\dot{\Phi} = \int_V \mu \left( \frac{\partial v_r}{\partial z} \right)^2 dV \quad (13)$$

When the surface tension of the molten particle against atmospheric gas, interfacial tension between the molten particle and substrate or coating, and kinetic energy of the molten particle at the time of impingement are  $\gamma$ ,  $\gamma_{SL}$  and  $E_k$  respectively, Eq.14 holds.

$$E_k - \int_0^\infty \dot{\Phi} dt - \int_{S_0}^{S_0 - S_1} \gamma dS - \int_0^{S_1} \gamma_{SL} dS = 0 \quad (14)$$

Where

$S_0$  = the surface area of the molten particle before impingement,

$S_1$  = the contact area of the splat on the substrate or the coating after the flattening process is completed.

If the contribution of surface tension and interfacial tension can be negligible, Eq.14 can be written as Eq.15,

$$\int_0^\infty \int_{R_0}^R \int_0^h 2\pi\mu \left\{ \frac{\partial}{\partial z} \left( \frac{R_0 v_0 e^{-\alpha t} z}{hr} \right) \right\}^2 r dz dr dt = \frac{1}{12} \pi \rho d^3 v_0^2 \quad (15)$$

where  $d$  is the diameter of the molten particle before impingement. Since  $h = d^3/6R_m^2$ , the solution of Eq.15 leads to

$$\begin{aligned} \frac{6\pi\mu v_0 R_0 R_m^6}{(R_m^2 - R_0^2) d^3} \left( \ln \frac{R_m}{R_0} + \frac{R_0^2}{R_m^2} - \frac{1}{4} \frac{R_0^4}{R_m^4} - \frac{3}{4} \right) \\ = \frac{1}{12} \pi \rho d^3 v_0^2 \end{aligned} \quad (16)$$

When  $R_0/R_m$  is small, Eq.16 can be written as

$$\left( \frac{D}{d} \right)^4 \left( \ln \frac{D}{\epsilon d} - \frac{3}{4} \right) = \frac{4}{9\epsilon} \frac{\rho d v_0}{\mu} \quad (17)$$

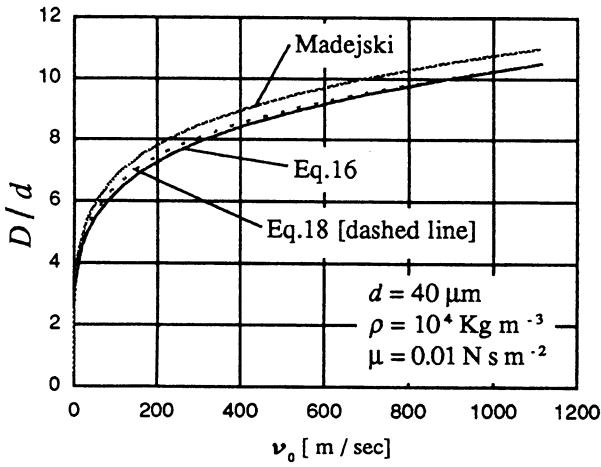


Fig. 6 - The relation between  $D/d$  and impinging velocity  $v_0$ .

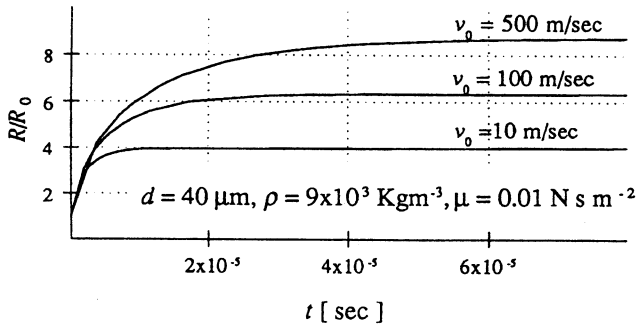


Fig. 7 - The relation between  $R/R_0$  and  $t$ .

where

$$D = 2R_m,$$

$$d = 2R_0/\varepsilon.$$

When  $\varepsilon = 1$ , then approximation of the formula within the second parenthesis of Eq.17 by a line proportional to  $D/d$  in the range from about 3 to 10 of  $D/d$  results in;

$$\frac{D}{d} = 1.234 \left( \frac{\rho d v_0}{\mu} \right)^{0.2} \quad (18)$$

Fig. 6 shows the relations between impinging velocity  $v_0$  and  $D/d$  in Eq.16, Eq.18 and Madejski's theory (5). Calculation of the expansion rate  $v_R$  of the splat radius from Eq. 11 and 12 leads to;

$$v_R = \frac{dR}{dt} = \frac{R_0 v_0}{2(R_m^2 - R_0^2)} \cdot \frac{R_m^2 - R^2}{R} \quad (19)$$

And calculation of  $R/R_0$  from Eq.11 and 12 leads to;

$$\frac{R}{R_0} = \left[ \frac{R_m^2}{R_0^2} + \left( 1 - \frac{R_m^2}{R_0^2} \right) e^{-\frac{R_0 v_0}{R_m^2 - R_0^2} t} \right]^{\frac{1}{2}} \quad (20)$$

On substitution of Eq.18 into Eq.20,  $R/R_0$  can be calculated. Fig.7 shows the time dependence of  $R/R_0$  during about  $10^{-5}$  sec required for the molten particle to spread.

**Compression of gas in the flattening process.** The mechanism of porosity formation during impingement and the deformation flow of molten particle is described in this subsection. The porosity formation model described in the preceding paragraph is applied to the flow process in which the splat is formed. The figure of the particle after a very short time at impingement is shown in Fig.5 (b) where  $t = 0$ . When the contact area between the particle and substrate is small like this case; the theory described in the preceding paragraph can be directly applied to the process by which the gas in holes on the surface of the substrate is compressed. Then, it is assumed that  $v_z = v_0$  in the region of  $r < R_0$ . On the other hand, in the region of  $r \geq R_0$ , it is assumed that the compression energy of the gas in holes corresponds to the kinetic energy of the expansion of the splat radius. The volume of pores between the splats or between the splat and the substrate  $V_g$  is written as Eq.21 using Eq.6. When  $v_R \rightarrow 0$ , Eq.5 instead of Eq.6 must be used, i. e., in the neighborhood of  $R = R_m$ , so the parameter  $\xi$  is used. This is a positive number close to 1.

$$V_g = \int_0^{R_0} V_0 \left\{ \frac{k_2(n-1)\rho v_0^2}{2P_0} \right\}^{\frac{1}{1-n}} 2\pi R dR$$

$$+ \int_{R_0}^{\xi R_m} V_0 \left\{ \frac{k_2(n-1)\rho (k_3 v_R)^2}{2P_0} \right\}^{\frac{1}{1-n}} 2\pi R dR$$

$$+ \int_{\xi R_m}^{R_m} 2\pi R dR \quad (21)$$

Substituting Eq.19 into Eq.21 results in;

$$V_g = \int_0^{R_0} V_0 \left\{ \frac{k_2(n-1)\rho v_0^2}{2P_0} \right\}^{\frac{1}{1-n}} 2\pi R dR$$

$$+ \int_{R_0}^{\xi R_m} \left[ \frac{k_2 k_3^2 (n-1)\rho}{2P_0} \left\{ \frac{R_0 v_0}{2(R_m^2 - R_0^2)} \cdot \frac{R_m^2 - R^2}{R} \right\}^2 \right]^{\frac{1}{1-n}} 2\pi R dR$$

$$+ \int_{\xi R_m}^{R_m} 2\pi R dR \quad (22)$$

Calculating Eq.22 to substitute  $n=1.5$ ,  $n=2$ , when  $n=1.5$ , Eq. 22 results in;

$$V_g = \pi R_0^2 V_0 \left( \frac{4P_0}{k_2 \rho} \right)^2 \frac{1}{v_0^4} \left[ 1 + \frac{16}{k_3^4} \left( \frac{\rho v_0 d}{\mu} \right)^{1.2} \left\{ \frac{3\xi^4 - 3\xi^2 + 1}{3(1-\xi^2)^3} \right\} \right]$$

$$+ \left( \frac{k_2 \rho}{4P_0} \right)^2 v_0^4 \left( \frac{\rho v_0 d}{\mu} \right)^{0.4} (1 - \xi^2) \quad (23)$$

when  $n = 2$ , Eq. 22 results in;

$$V_g = \pi R_0^2 V_0 \frac{2P_0}{k_2 \rho} \frac{1}{v_0^2} \left[ 1 + \frac{4}{k_3^2} \left( \frac{\rho v_0 d}{\mu} \right)^{0.8} \left\{ \frac{\xi^2}{1-\xi^2} + \ln(1-\xi^2) \right\} \right]$$

$$+ \frac{k_2 \rho}{2P_0} v_0^2 \left( \frac{\rho v_0 d}{\mu} \right)^{0.4} (1 - \xi^2) \quad (24)$$

Since the values of  $k_2$  and  $k_3$  are less than 10 at most, the first and third terms within the parentheses in Eq.23 and Eq.24 can be negligible as compared to the second terms. Eq.23 and Eq.24 can be written as follows, respectively;

$$V_g = \frac{256\pi AV_0}{k_2^2 k_3^4} \left( \frac{dP_0}{\rho} \right)^2 \left( \frac{\rho v_0 d}{\mu} \right)^{1.2} \frac{1}{v_0^4} \quad (25)$$

$$V_g = \frac{8\pi BV_0}{k_2 k_3^2} \left( \frac{d^2 P_0}{\rho} \right) \left( \frac{\rho v_0 d}{\mu} \right)^{0.8} \frac{1}{v_0^2} \quad (26)$$

where;

$$A = \frac{3\xi^4 - 3\xi^2 + 1}{3(1 - \xi^2)^3} \quad (27)$$

$$B = \frac{\xi^2}{1 - \xi^2} + \ln(1 - \xi^2) \quad (28)$$

Since the volume of solid splat is approximately equal to the volume of the molten particle, then the volume of splat  $V_s$  is  $\pi d^3/6$ .  $V_g/V_s$  can be written as Eq.29 and Eq.30, respectively.

$$\frac{V_g}{V_s} = \frac{1536AV_0}{k_2^2 k_3^4} \left( \frac{P_0^2}{d\rho^2} \right) \left( \frac{\rho v_0 d}{\mu} \right)^{1.2} \frac{1}{v_0^4} \quad (29)$$

$$\frac{V_g}{V_s} = \frac{48BV_0}{k_2 k_3^2} \left( \frac{P_0}{d\rho} \right) \left( \frac{\rho v_0 d}{\mu} \right)^{0.8} \frac{1}{v_0^2} \quad (30)$$

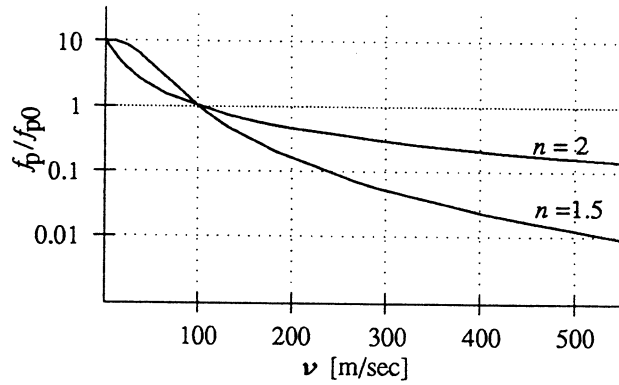


Fig. 8 - The relation between porosity ratio and impingement velocity.

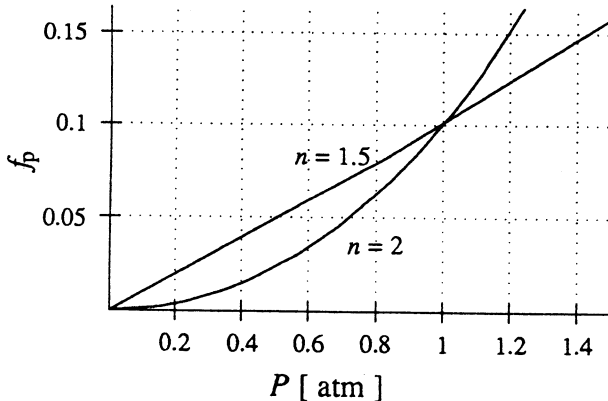


Fig.9 - The relation between porosity and coating pressure.

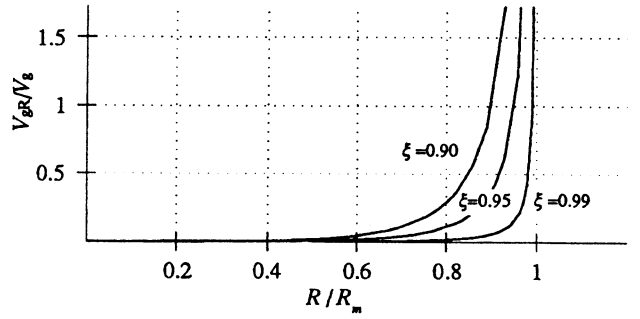


Fig. 10 - Distribution of volume of pores.

If  $f_p$  and  $f_{p0}$  denote the porosity of coatings at the impingement velocity  $v$  and  $v_0$ , then the porosity ratio  $f_p/f_{p0}$  is;

$$\frac{f_p}{f_{p0}} = \frac{V_g}{V_{g0}} \frac{1}{1 + \left( -1 + \frac{V_g}{V_{g0}} \right) f_{p0}} \quad (31)$$

where

$V_g$  = the volume of pores after solidification when the impinging velocity is  $v$ ,

$V_{g0}$  = the volume of pores after solidification when the impinging velocity is  $v_0$ .

Fig. 8 shows the relation between impingement velocity  $v$  and porosity ratio  $f_p/f_{p0}$  which is normalized under the condition of  $f_{p0} = 0.1$  at an impingement velocity of 100 m/sec, i.e. by expressing 10% porosity as 1. Fig. 9 shows the porosity dependence of the atmospheric pressure in the thermal spray process.

When the total volume of pores from the splat center to its radius  $R$  is defined as  $V_{gR}$ ,  $V_{gR}$  can be written as;

$$V_{gR} = \int_0^{R_0} V_0 \left\{ \frac{k_2(n-1)\rho v_0^2}{2P_0} \right\}^{\frac{1}{1-n}} 2\pi R dR + \int_0^R V_0 \left\{ \frac{k_2(n-1)\rho(k_3 v_R)^2}{2P_0} \right\}^{\frac{1}{1-n}} 2\pi R dR \quad (32)$$

When  $n = 2$ , calculation of the ratio  $V_{gR}/V_g$  results in Eq. 33.

$$\frac{V_{gR}}{V_g} = \frac{\frac{(R/R_m)^2}{1 - (R/R_m)^2} + \ln\{1 - (R/R_m)^2\}}{\frac{\xi^2}{1 - \xi^2} + \ln(1 - \xi^2)} \quad (33)$$

The results are given in Fig.10, indicating that most of pores exist in the area from 0.6 to  $1 R_m$  of the splat.

## Discussions

The relations shown in Fig.8 and Fig.9 seem to be very close to empirical facts. The polytropic exponent  $n$  is probably between 1.5 and 2.

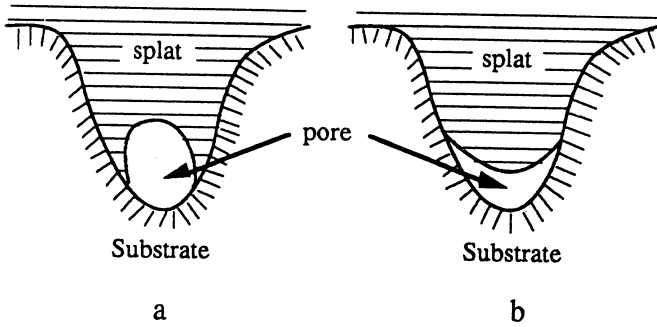


Fig. 11 - Shapes of pores depending of the wettability between the splat and the substrate.

According to this theory, most of the pores between the splats or between the splat and the substrate exist in the periphery of the splat. Figure 10 indicates that most of the pores are distributed outside  $0.6 - 0.8 R_m$  of the splat. Accordingly, the volume of pores is very little in the central 36 to 64% area of splat, existing mostly in the peripheral 36 to 64% area. However, this does not mean that no pores exist in the central areas; but refers only to the relative amounts of pores existing in the interface between the splats or between the splat and the substrate. The above fact suggests that the real contact area which is effective for bonding between the splat and the coating or between the splat and the substrate becomes larger in the central part of the splat. The splat central area equivalent to the diameter of the molten par-

ticle before impingement onto the substrate contributes to bonding between the splat and the substrate or between the splat and the coating. Then the bonding force becomes smaller in the peripheral part of the splat.

It must be considered that the action of wetting between the splat and the substrate contributes to the bonding force. If wetting action between the molten particle and the substrate is not taken into account, in the assumption for compressing the gas in the hole, then the end of the molten particle in the hole will solidify into the shape shown in Fig.11-b. On the other hand, if the splat and the substrate are easy to wet, then the particle will solidify into the shape shown Fig. 11-a. The contacting area between the splat and the substrate in Fig. 11-a is larger than that in Fig. 11-b. Because the time required from impingement to flattening is probably about  $10^{-5}$  sec, then the degree of progress of wetting is an important problem associated with the bonding strength of thermal spray coatings. The analysis of dynamic phenomena on the wetting process is therefore necessary.

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