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Evaluation of Spherical Grains in Flame-Sprayed Coatings for Medical Purposes by Stereological Methods

B. Gueorgiev[1], **I. Iordanova**[2], **C.M. Sprecher**[1]

[1]AO Research Institute, Clavadelerstrasse 8, 7270 Davos, Switzerland

[2]Department of Solid State Physics, University of Sofia, 5 J. Bouchier Blvd., 1164 Sofia, Bulgaria

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Abstract. An adopted stereological method has been implemented to characterize spherical grains, analysed by scanning electron microscopy (SEM) in flame-sprayed bioceramic two-layered coatings, consisting of a titania (TiO_2) transition layer (200 μm) and a hydroxylapatite (HA) top layer (200 μm), deposited on titanium-aluminium-vanadium alloy (TAV) substrates. In addition, optical microscopy measurements were combined with image analysis of the initial powders to explore the relationship between the volume parameters of the spherical grains and the dimensions of the respective powder particles. The results revealed that most of these grains were mainly distributed between the lamellae in the transition layer with a volume share of less than 1%. They were probably resultant from powder particles, which have reached the substrate in a semi-molten state. The small amount of the spherical grains in the TiO_2 transition layer and their almost full absence in the top HA layer indicate proper selection of the technological conditions during the flame-spraying, which contributes to achieve coatings with potentially good exploring properties for medical purposes.

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1 Introduction

Thermal spraying comprises a group of advanced technological surface engineering methods, using a large variety of materials to deposit a wide range of coatings on different substrates. These techniques are extensively investigated at present, being main topics at a number of scientific meetings. One of the most important aims of the modern surface engineering industry is to develop precise,

preferably non-destructive methods for characterization and control of the technological conditions, microstructure characteristics and macroscopic properties of the finished deposits.

Plasma- and flame-spraying are two thermal-spraying techniques, where the coating material, in the form of a powder, is injected into high-temperature fields, created by a high-temperature gas plasma torch (plasmotron) or by an oxy-acetylene flame spray gun, respectively. The heated powder particles, melted and propelled toward the substrate, solidify on its surface in strongly non-equilibrium conditions and transform into solid lamellae which form the deposit [1, 2]. The thermo-chemical equation, describing the combustion of 1 mol acetylene in the oxy-acetylene flame, is represented in Ref. [2] as follows:

$$\mathrm{C_2H_2} + 2.5\mathrm{O_2} = 2\mathrm{CO_2} + \mathrm{H_2O} + 301.4\ \mathrm{kcal}. \qquad (1)$$

In the same reference it is pointed out that the maximum temperature reached in the flame, due to the above reaction, is about 3000°C.

During plasma-spraying, a stream of gas (argon, nitrogen, *etc*. or their mixture with hydrogen) is introduced into the plasma-spray torch, where, due to the electric arc, the working gas attains a plasma state with high enthalpy and temperatures in the range of 10 000–15 000°C and even 30 000°C in some regions [1,3-6]. Although the injected powder particles are exposed to this high temperature influence for a very short time (10^{-3}–10^{-4} s), most of them are heated to sufficiently high temperatures to become molten [1].

However, as it has been pointed out in Ref. [1, 2, 6, 7], regarding both thermal-spraying methods discussed above, the individual particles can differ in shape, dimensions, temperature and velocity. For this reason evaporation, not complete but only partial melting or even absence of melting of the different powder particles could occur at the same time during the thermal-spraying. The evaporated particles do not take part in the coating formation. However, the partially melted and some of the completely unmelted particles can get incorporated between the lamellae. As it has been shown in Ref. [1, 3, 8] the shape of the grains, resultant from the semi-molten particles, is spherical. During the practical use these grains can get depleted or become sources of stress fields in the coating, thus influencing the properties and as a result the coating performance. That is why it is of a great importance to know the reasons for availability of such grains in each particular coating and also to estimate their parameters. This can help in optimizing the technology in order to minimize the concentration and dimensions of the spherical grains.

Since the mid 1980s thermal-spraying is considered as the most promising technique to apply bioactive films on metallic implants for orthopaedic and dental applications. Particularly important among them are hydroxylappatite (HA) coatings on titanium-aluminium-vanadium alloy (TAV) substrates. The hydroxylappatite is a calcium phosphate with chemical formula $\mathrm{Ca_5(PO_4)_3(OH)}$. Con-

tacting with bones, it enables an increased uniform bone growth at the bone-implant interface, a stable fixation of the implant and a decreased release of metal ions from the implant to the body [9, 10]. That is why Ti and its alloys, coated with HA, are intensively investigated at present.

In this paper the basis of a stereological method for estimation of volume parameters of spherical grains, distributed between the lamellae in thermally-sprayed coatings, is described. The method has been adopted and applied for characterization of flame-sprayed HA and titania (TiO_2) deposits on TAV substrates.

2 Description of the Samples and the Applied Stereological Method

2.1 Samples preparation

The analyzed samples consist of two-layered coatings applied by flame-spraying of HA and TiO_2 powders on TAV substrates. The initial powders were supplied by Sulzer Metco Europe GmbH. The TAV material was delivered in the form of a rod with diameter $\oslash$ 36 mm, which was then sawed to prepare the circular substrates with 4 mm thickness. Prior to spraying, their surfaces were grit-blasted with 450 μm SiC particles under 0.4 MPa air pressure. The flame-spraying was performed on Castolin Eutectic Rototec 80 equipment. During the spraying the samples were rotated (50 revs/min) around the normal to their surfaces. The spraying conditions are given in Table 1.

Table 1. Parameters of the flame-spraying process.

powder	pressure, MPa		gas flow, l/h		spraying distance, mm
	O_2	C_2H_2	O_2	C_2H_2	
HA	0.4	0.07	650	600	130
TiO_2	0.4	0.07	550	600	220

Firstly a TiO_2 layer with a thickness of about 200 μm was sprayed onto the substrate. Then a HA coating, having a thickness of 200 μm, was deposited on the top of this transition layer. Thus, several samples representing heterostructures HA/TiO_2/TAV were prepared.

2.2 Description of the used stereological method

Stereological methods allow estimation of volume parameters of the microstructure elements on the basis of their two-dimensional cross-section parameters, which can be experimentally evaluated by standard metallographic methods. All quantitative stereological analyses are based on the principle, according to which

the share of a phase (or any other structure element) in a volume is equal to the surface or linear share of its cross-sections with a plane or line intersecting this volume. Only structure elements that can be represented as convex bodies are suitable for stereological analyses, as a concave body can be crossed more than once by the intersecting plane or line. In addition, stereological methods are applicable when the distribution of the analyzed structure element (*i.e.* spherical grains in the present investigation) in the volume is close to random [11].

The adopted in this study method, known as Scheil–Schwartz–Saltikow's method, is based on the fact that the plane, which is observed in a microscope, intersects the spherical grains at random, thus forming circular cross-sections with varying radii. The cross-section with the maximum radius is assumed to correspond to the biggest spherical grain, whose diameter is defined as $D^{\max}$. The actual size distribution of the spheres is approximated by assuming that their diameters form series of discrete values, *i.e.* Δ, 2Δ, $3\Delta, \ldots, k\Delta$, where the step size Δ is given by the following relation: $\Delta = D^{\max}/k$ (k is the number of dimensional groups in which the array of diameters dimensions is distributed). According to the analysis performed in Ref. [11], values of k in the range $5 \leq k \leq 12$ are high enough to give a good approximation to the real distribution.

If the volume number density of the grains (*i.e.* their number per 1 mm^3 unit volume) with constant diameter D_j is N_j ($1 \leq j \leq k$) and if the total volume number density (*i.e.* the number of all spherical particles with different radii in 1 mm^3) is N, then the mean diameter $\bar{D}$ of the spherical grains can be represented as follows:

$$\bar{D} = (D_1 N_1 + D_2 N_2 + \cdots + D_k N_k)/N. \tag{2}$$

It follows from equation (2), that for estimation of $\bar{D}$ it is necessary to know the size distribution function, *i.e.* $D_j = f(N_j)$ and the total volume number density (N).

As it is already mentioned, the aim of the stereological methods is to calculate the volume parameters *via* the corresponding experimentally measured plane parameters, namely the diameters of the observed circular cross-sections d_i ($1 \leq i \leq k$) and their plane number densities n_i (*i.e.* the number of the circular cross-sections per 1 mm^2 unit area). In order to obtain the volume size distribution $D_j = f(N_j)$, it is necessary to know the corresponding plane size distribution $d_i = f(n_i)$, where d_i are the experimentally measured diameters of the circular cross-sections and n_i are their plane number densities (which can also be experimentally evaluated).

To define the plane size distribution function $d_i = f(n_i)$, a procedure for grouping of the measured diameters d_i, similar to that described above for D_j, must be performed. In this case the number of the plane dimensional groups is also k, but in contrast with the volume distribution, where D_j has a constant value in the

j^{th} volume dimensional group (*i.e.* $D_j = j\Delta$, $1 \leq j \leq k$), the corresponding d_i in each plane group varies as follows: $0 < d_1 \leq \Delta$ in the first dimensional group ($i = 1$), $\Delta < d_2 \leq 2\Delta$ in the second one ($i = 2$), $\ldots$, $(k-1)\Delta < d_k \leq k\Delta$ in the last k^{th} dimensional group ($i = k$).

As the d_1 values are the smallest, the cross-sections included in the first plane dimensional group could correspond to all spherical particles having diameters D_j, varying from the minimum $D_1 = \Delta$ to the maximum $D^{\max} = k\Delta$. These spherical grains, being crossed at random by the plane, observed in the microscope, form circular cross-sections with diameters d_1, varying within the above mentioned limits and defining the first plane dimensional group.

The second plane dimensional group will contain cross-sections with varying diameters d_2 within the above mentioned limits. The circular cross-sections, included in this group, are formed as a result of the intersection of particles with diameters D_j, obeying the relation $2\Delta \leq D_j \leq k\Delta$.

The third plane dimensional group corresponds to spherical grains with diameters D_j, varying within the limits $3\Delta \leq D_j \leq k\Delta$, *etc*. And the last, k^{th}, plane dimensional group will be formed as a result of the intersection of only the grains with $D^{\max} = k\Delta$.

It follows from the discussion above that the plane number density n_i, corresponding to each of the introduced plane dimensional groups, is a function of unknown parameters n_{ij} ($i \leq j \leq k$), whose values indicate the number density of the circular cross-sections, included in the i^{th} plane group, which have been formed when the spheres, belonging to the j^{th} volume dimensional group, have been crossed with the intersecting plane. Thus, from the description above, it can be written

$$\begin{aligned} n_1 &= n_{11} + n_{12} + n_{13} + \ \ldots\ + n_{1k}\,, \quad (i = 1,\ 1 \leq j \leq k) \\ n_2 &= n_{22} + n_{23} + n_{24} + \ \ldots\ + n_{2k}\,, \quad (i = 2,\ 2 \leq j \leq k) \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ n_k &= n_{kk}\,, \quad (i = j = k). \end{aligned} \tag{3}$$

Figure 1 shows schematically the principle of formation of circular cross-sections belonging to the i^{th} plane dimensional group (*i.e.* those with cross-section diameters d_i within the interval from $(i-1)\Delta$ to $i\Delta$), which have been formed from intersected grains belonging to the j^{th} volume dimensional group (*i.e.* those with diameter $D_j = j\Delta$). From this scheme it follows that the spherical particles with diameter D_j will form cross-sections belonging to the i^{th} plane dimensional group only if the distances between particles' centers and the intersecting plane are in the range from h_{i-1} to h_i. Thus, the centers of the discussed spherical grains must be positioned within a rectangular parallelepiped with the following parameters:

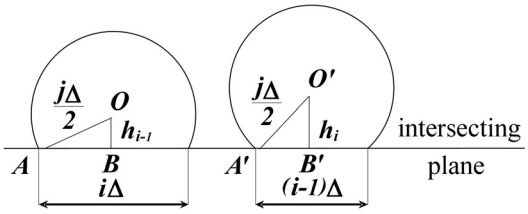

Figure 1. Scheme representing the formation of circular cross-sections belonging to the i^{th} plane dimensional group and formed via intersection of the spherical grains included in the j^{th} volume dimensional group.

- a base laying in the intersecting plane with 1 mm^2 area, *i.e.* the area over which the corresponding plane number densities are experimentally estimated;
- a height equal to $(h_i - h_{i-1})$.

As the area of the base is 1 mm^2, then the volume of such a parallelepiped is $(h_i - h_{i-1})$. Taking into account the fact that each particle could be crossed in an identical manner from both sides in respect to its centre, then the total volume, containing spherical grains, belonging to the discussed j^{th} dimensional group will be $V = 2(h_i - h_{i-1})$.

If the volume number density of these spherical grains is N_j, then according to the main stereological principle, the relation between the introduced parameter n_{ij} and the corresponding volume number density N_j will obey the following equation:

$$n_{ij} = 2(h_i - h_{i-1})N_j. \tag{4}$$

From the triangles AOB and $A'O'B'$ in Figure 1, it follows that

$$h_i = (\Delta/2)\sqrt{j^2 - (i-1)^2}; \qquad h_{i-1} = (\Delta/2)\sqrt{j^2 - i^2}. \tag{5}$$

Then substituting Eq. 5 in Eq. 4, the following relation is obtained:

$$n_{ij} = N_j\Delta\left(\sqrt{j^2 - (i-1)^2} - \sqrt{j^2 - i^2}\right). \tag{6}$$

Now if each parameter n_{ij} in the system of equations (3) is substituted by the corresponding expression from equation (6), a defined system of linear equations, where the number of equations (k) is equal to that of the unknown variables, can be obtained. The solution of this system in respect to N_j can be represented by the following general expression:

$$N_j = \left(A_j n_i - A_{j+1}n_{i+1} - A_{j+2}n_{i+2} - \cdots - A_k n_k\right)/\Delta, \quad (i = j) \tag{7}$$

where n_i are the plane number densities, experimentally estimated by the standard metallographic methods; A_j are coefficients, which have real numerical values in the obtained solution for the system of equations (3). The analysis can be speeded up by using the values of the coefficients A_j, that have been previously estimated and published in Ref. [11].

In the present investigation the method of Scheil–Schwartz–Saltikow has been adopted and applied to evaluate the volume parameters of the spherical grains, observed in the transition TiO_2 layer of the analysed heterostructures HA/TiO_2/TAV.

3 Results and Discussion

The analysed samples were cryofractured in liquid nitrogen and the prepared fractured cross-sections were observed under a Hitachi S-4100 FESEM (Kyoto, Japan) scanning electron microscope (SEM). A typical picture of the flame-sprayed HA/TiO_2 deposit microstructure is shown in Figure 2.

The observations of all the samples over the whole fractured area showed that the microstructure is lamellar and the circular cross-sections, corresponding to spherical grains, are mainly contained in the transition TiO_2 layer, while in the top HA coating they are hardly seen. This is probably due to the fact, that the TiO_2 melting temperature (1850°C) is higher than that of the HA (1650°C) and thus, at the selected technological conditions, full melting of almost all HA powder particles has occurred during their flight through the flame, whereas some of the TiO_2 powder particles have probably reached the substrate only partially molten.

The stereological analysis of the spherical grains in the transition TiO_2 layer was performed on the basis of 200 measured diameters which have been grouped into six dimensional groups according to the procedure described above.

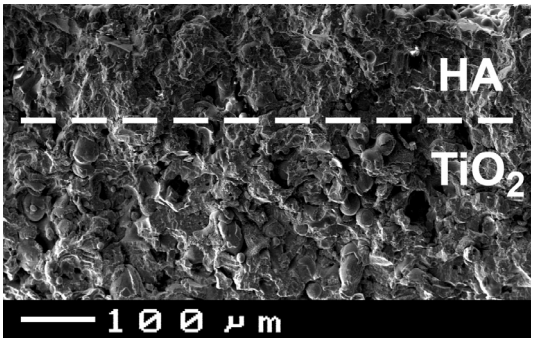

Figure 2. SEM micrograph of the outer part of the fractured cross-section of the HA/TiO_2 deposit.

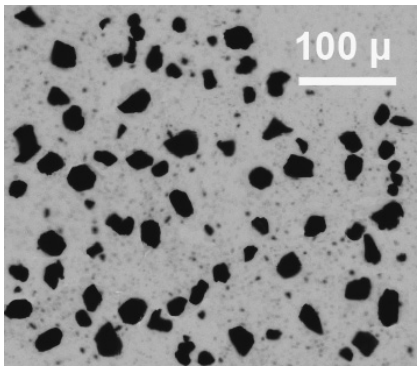

Figure 3. Picture of the initial TiO_2 powder particles used for flame-spraying of the transition layer.

In order to explore the relationship between the volume parameters of the spherical grains in the transition layer and the dimensions of the particles in the initial TiO_2 powder, some additional optical microscopy measurements, combined with image analysis of these powder particles, were performed by a Carl Zeiss Axiovert 200M (Göttingen, Germany) transmission light microscope. In Figure 3 a picture of the TiO_2 powder particles is presented.

It is obvious that the majority of them have an irregular, non-spherical shape. The image analysis was made using a Carl Zeiss Axiovision software package (Version 4.5) to evaluate the focal plane projection area s_{opt} of each observed particle. Further, an equivalent circle diameter d_{opt} was calculated and defined as a particle size according to the following relation:

$$d_{\text{opt}} = 2\sqrt{s_{\text{opt}}/\pi}. \tag{8}$$

The statistics of the equivalent circle diameters was based on measurements of more than 500 randomly selected powder particles. Six dimensional groups were applied to obtain the size distribution of the initial TiO_2 powder.

In Figure 4 both size distributions curves, corresponding to the initial TiO_2 powder and the spherical grains in the flame-sprayed transition TiO_2 layer are shown. It is obvious that the curve corresponding to the spherical grains is shifted to lower dimensions in respect to those of the initial powder particles. This confirms the expectation that the observed spherical grains are probably resultant from some initial powder particles, which have reached the substrate only partially molten. Those may be particles with higher dimensions, very irregular form, or particles whose trajectories pass through relatively lower temperature regions of the flame, or which fly faster through the high temperature field.

The parameters of the initial TiO_2 powder particles and spherical grains in the

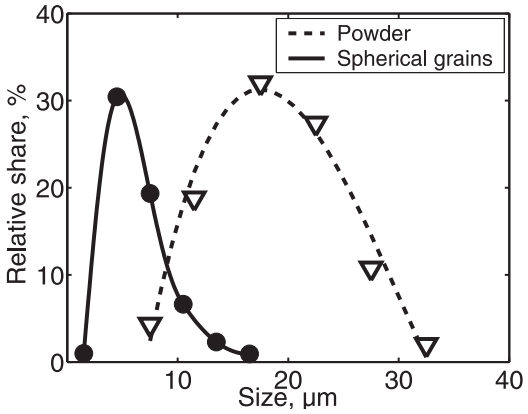

Figure 4. Size distribution curves of the initial TiO_2 powder and spherical grains in the TiO_2 transition layer.

transition layer, evaluated by the performed metallographic analyses, are given in Table 2.

Table 2. Evaluated parameters of the initial TiO_2 powder particles and spherical grains in the transition layer.

parameters of the initial TiO_2 powder particles			parameters of the spherical grains in the transition TiO_2 layer			
$d_{\min}$ μm	$d_{\max}$ μm	$\bar{d}$ μm	$D_{\min}$ μm	$D_{\max}$ μm	$\bar{D}$ μm	N mm^{-3}
5.65	33.52	18.05 ± 5.15	1.5	16.5	6.6 ± 2.8	28.1

The evaluated relative volume share of the spherical grains in a unit volume of the TiO_2 layer is less than 1%. This small amount, together with the almost full absence of spherical grains in the top HA layer of all investigated coatings, indicates that the technological conditions during the flame-spraying are properly selected.

4 Summary

In this study the essential of the Scheil–Schwartz–Saltikow stereological method is described. The method has been adopted and applied for characterization of spherical grains in two-layered HA/TiO_2 coatings applied by flame-spraying on TAV substrates. It has been found that the microstructure of both investigated layers (TiO_2 and HA) is predominately lamellar. Spherical grains, distributed

between the lamellae, have been observed only in the transition TiO_2 layer. Their dimensional characteristics point out that they are probably resultant from some initial powder particles that have reached the substrate in a semi-molten state. The performed quantitative stereological analysis showed that the volume share of the spherical grains is very low (less than 1%) which confirms that the technological conditions are properly selected to produce coatings with potentially good exploring properties for medical purposes.

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References

[1] F. Brossa, E. Lang (1992) in *Advanced Techniques for Surface Engineering*, Kluwer Academic Publishers, Dordrecht/Boston/London, **1** 199.

[2] A. Hasuy (1975) *Tehnika napileniya*, Moscow, Mashinostroenie (in Russian).

[3] H. Herman (1988) *Sci. Am.*, **259** 112.

[4] B.J. Gill, R.C. Tucker (1986) *J. Mater. Sci. Technol.*, **2** 207.

[5] A. Vardelle, J.M. Barnot, M. Vardelle, P. Fauchais (1980) *Trans. Plasma Sci.*, PS-8, **4** 417.

[6] M. Vardelle, A. Vardelle, P. Fauchais (1983) *Proc. 10 Internat. Thermal Spray Conf.*, Essen, DVS-Berichte, **80** 88.

[7] A.R. Nicoll, H. Gruner, R. Prince, G. Wuest (1985) *Surf. Eng.*, **1** 59.

[8] I. Iordanova, M. Surtchev, K.S. Forcey (2001) *Surf. Coat. Technol.*, **139** 118.

[9] W.F. Morris (1998) *J. Oral Maxillofac. Surg.*, **56** 1303.

[10] Yu-Peng Lu, Mu-Sen Li, Shi-Tong Li, Zhi-Gang Wang (2004) *Biomaterials*, **25** 4393.

[11] S.A. Saltikow (1970) *Stereometric Metallography*, Moscow, Metallurgia (in Russian).