Journal of the European Ceramic Society **17** (1997) 147–152

PII: S0955-2219(96)00176-8
0955-2219/97/$17.00

Glasses and Bioglasses: Synthesis and Coatings

J. A. Helsen,[a] J.Proost,[a] J. Schrooten,[a] G. Timmermans,[a] E. Brauns[b] & J. Vanderstraeten[c]

[a]Metallurgy & Materials Engineering, de Croylaan 2, B-3001 Leuven, Belgium
[b]VITO, Materials Division, Boeretang 200, B-2400 Mol, Belgium
[c]Vanderstraeten b.v.b.a., E3-laan, 9 Deinze, Belgium

(Received 15 September 1995; revised version received 16 August 1996; accepted 19 August 1996)

Abstract

In this paper a production technique is described for the application of glass coatings on diverse substrates, more particularly bioglass coatings on titanium. The glass is synthesized from base chemicals in a plasma torch and is applied as a coating in the same operation. In this way well-adhering coatings with controlled composition and amorphicity are obtained. Adhesion strengths above 40 MPa are easily obtained. © 1996 Elsevier Science Limited.

Introduction

In the early sixties it was found that some phosphate-containing glasses were prone to bond to bone. The most important papers are reviewed by Hench and Wilson.[1] Despite the long history, the great flexibility in composition and the excellent biological performance of bioglasses commercialized applications remained restricted to just a few. In load-bearing applications exclusively glass-ceramics are used. Examples, summarized by Kobubo,[2] are the glass-ceramic Ceravital[R] as an artificial middle-ear bone substitute and Cerabone[R] A-W in vertebral surgery. Bioglass shows with respect to the above mentioned ceramics the highest bioactivity but lower mechanical properties. As a consequence bioglasses are used in non- or low load-bearing applications or as a coating on a substrate responsible for the mechanical strength. A recent successful application is described by Schepers[3] for granular bioglass used for bone repair.

One of the limiting factors affecting widespread application is the difficulty experienced in producing well-adhering coatings by an industrially feasible process. Various techniques have been used but three are more common: enamelling or glazing, flame or plasma spraying and rapid-immersion coating.[4,5] The flame spraying is done using bioglass powder. This can be produced by powdering conventional bioglass and processing it until a free-flowing powder is obtained.

In this communication an alternative technique is proposed. The coating is performed by plasma spraying. The basic chemicals are processed to a free-flowing powder and the glass is synthesized in the torch itself. When the spraying is performed in a closed vessel the glass can be collected as a powder. When directed to a substrate, either metallic, ceramic or polymer, it is applied as a coating. The technique, however, applies in general to many other glasses as well. Potential applications of the technique to bioglass are all types of prostheses in hard tissue and some in soft tissue. Other applications are glass coatings for protection of metal surfaces from corrosion, decorative coatings or, when appropriately formulated, coatings with enhanced abrasion resistance. The advantages of the proposed process are: the composition can easily be modified without having to make a new glass as was the case in the previous flame or plasma spraying methods; low energy consumption with respect to the process starting from powdered glass; easy control of composition with respect to immersion coating. A patent application has been deposited for the process.

Experimental

The basic chemicals are various alkaline or alkaline earth silicates and phosphates (if aimed at the production of bioglass). Other compounds of calcium and sodium, e.g. carbonates, are added in order to obtain the desired final composition. Fluoride is added for co-controlling the solubility. If necessary, other compounds are added for giving the glass special properties such as a modification of the expansion coefficient, an improvement of the osteoconductive properties, integration of insoluble particles for improving the abrasion resistance or of ions for colouring the coating.

Table 1. Examples of composition (% w/w) of the mixture of the basic chemicals

Calcium silicate	*Sodium silicate*	*Calcium carbonate*	*Sodium carbonate*	*Tricalcium phosphate*	*Calcium hydroxy apatite*	*Calcium fluoride*
58·81	—	16·87	12·81	10·36	—	1·15
58·98	—	15·80	12·85	—	11·22	1·15
22·12	38·79	27·18	—	10·73	—	1·15

Table 2. Final composition (% w/w) after plasma spraying the mixture of Table 1

SiO_2	CaO	Na_2O	P_2O_5	CaF_2
52·0	30·5	9·8	6·2	1·5

Powder conditioning

A key step in the whole process is the conditioning of the basic chemicals to a homogeneous free flowing powder suitable for feeding to the torch. All compounds are milled to particle sizes smaller than 20 μm. The compounds are mixed in an attritor to form an aqueous slurry. This slurry is fed to a spray dryer. A very homogeneous mixture is obtained: the dissolved phases (e.g. carbonates) reprecipitate during the spray drying. Subsequently, the spray-dried powder is densified by uniaxial or isostatic compression, sintered and/or calcined, milled and fractionated. The fraction of 30–63 μm was used for spraying. In this step a free-flowing powder is obtained. Examples of compositions of the mixture of the basic chemicals are given in Table 1 which will produce after plasma spraying a bioglass of the final composition given in Table 2. Merck products of p.a. quality were used throughout.

Plasma spraying

Considering the number of parameters which can be varied during the plasma spraying, the optimization is performed through a factorial scheme. This scheme is discussed below. The instrument used is from Metco. The primary arc gas was argon and the secondary gas hydrogen.The substrates were in all cases pure titanium rods of 5 mm diameter, reduced over a length of 15 mm to a diameter of 3 mm (Goodfellow, ref. Tl007920). The rods were sandblasted using Al_2O_3 grits and cleaned ultrasonically during 5 min in distilled water and 5 min in acetone. During spraying the rods were spun at 10 rev. min^{-1}.

Evaluation of the coatings

A factor of major importance was the crystallinity of the coating. This was tested using a conventional X-ray diffraction goniometer (Cu-tube, 34 kV, 20 mA, nickel filter, step mode, 0·02° 2Θ per step, counting time 2 s). The chemical analysis was done by X-ray fluorescence and by classical wet analysis. For the latter silicon and phosphate were determined gravimetrically, calcium and sodium by atomic absorption (using appropriate conditions for the relatively high concentrations). Homogeneity was controlled by electron probe microanalysis (EPMA). Adhesion strength was measured on test coatings sprayed on titanium rods of 20 mm diameter. The section of the rods was pretreated in the same way as the small titanium rods. A coated section was glued by an epoxy glue to a non-coated and after curing fitted to an Instron Tensile Tester. Both ends were carefully aligned in the Instron.

Optimisation of the Plasma Spraying

In order to simplify the test plan a fractional factorial was chosen. A full factorial for four factors would require 24 tests. A half factorial of the four factors reduces this number to eight. To maximize the information produced, the choice of tests to retain or to discard is not arbitrary. The way to perform this was taken from Box *et al.*[6]

The selected factors for our purposes were arc current, argon arc gas flow, argon carrier gas flow and spray distance (a,b,c,d). Levels were chosen based on published data[7] and instrument capabilities and are summarized in Table 3. This table represents the half 24 factorial test plan of resolution IV (selection rule I = 1234). It is generally assumed that higher order interactions can be neglected and as a consequence the main effects of the four selected parameters can be estimated correctly.[6,8] Voltage and torch power are added to the table as well but these are dependent variables because a constant secondary gas flow was selected.[9]

For the optimization procedure using the fractional factorial plan, the degree of crystallinity of the coating was considered as the critical property, a fully amorphous coating being the optimum. In order to estimate the main effects and hence to optimize the plasma spraying process, a quantitative evaluation of the recorded diffractograms was necessary. For the sake of simplicity, eight test specimens were evaluated through ratings from 1 to 10, 10 being most completely amorphous, 1 being

Table 3. Factorial design matrix

Test	*Current* (A)	*Arc gas flow* (*litre/min*)	*Carrier gas flow* (*litre/min*)	*Spray distance* (*cm*)	*Voltage* (*V*)	*Power* (*kW*)	*Rating*
1	500	40	4	8	59·8	29·9	5
2	700	40	4	10	58·2	40·7	10
3	500	50	4	10	63·3	31·7	6
4	700	50	4	8	60·9	42·6	4
5	500	40	6	10	60·0	30·0	8
6	700	40	6	8	58·9	41·2	1
7	500	50	6	8	63·8	31·9	3
8	700	50	6	10	61·1	42·8	9

almost crystalline. These ratings are included in the last column of Table 3. Note that these figures are ratings, not rankings, describing the degree of crystallinity. How the ratings were attributed is illustrated by Figs 1 and 2. Figure 1 represents the powder diffractogram of a completely amorphous coating; the combination was ad, i.e. arc current and spray distance on a high level (cf. Table 3, test 2), and was given a rating of 10, while Fig. 2 (cf. Table 3, test 6) is relative to combination ac, i.e. high arc current and argon carrier gas flow, which still had a high degree of crystallinity and to which a rating of 1 was attributed. Figure 1 has to be compared with Fig. 3 which represents a diffractogram of a flat polished block of bioglass produced in the conventional way, i.e. by melting the basic chemicals in a platinum crucible at about 1500°C and casting in a graphite die. The die was heated to 300°C to avoid too rapid cooling. This sample is expected to be amorphous. The diffractogram is equal to that of Fig. 1 and was therefore attributed the highest rating. The low intensity peaks at the low angle side in Figs 1 and 2 are from the sample holder of the powder. To estimate the four main effects, these ratings were summed for each level of a given factor. For comparing a carrier gas flow of 4 with a flow of 6 litre/min, the ratings of tests 1 to 4 (4 litre/min) and those of tests 5 to 8 (6 litre/min) are summed. Both sums are then expressed as a ratio with the highest factor level used as numerator. In the example we have 21/25=0·84 which means

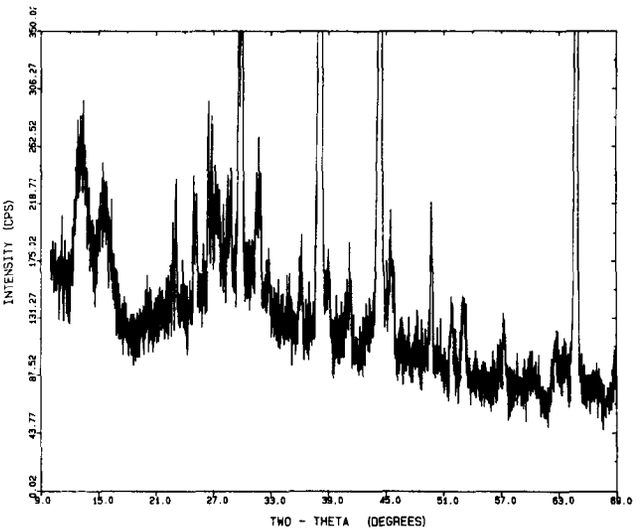

Fig. 2. X-ray diffractogram of a coating to which the lowest rating (=1) was attributed. Axes as Fig. 1.

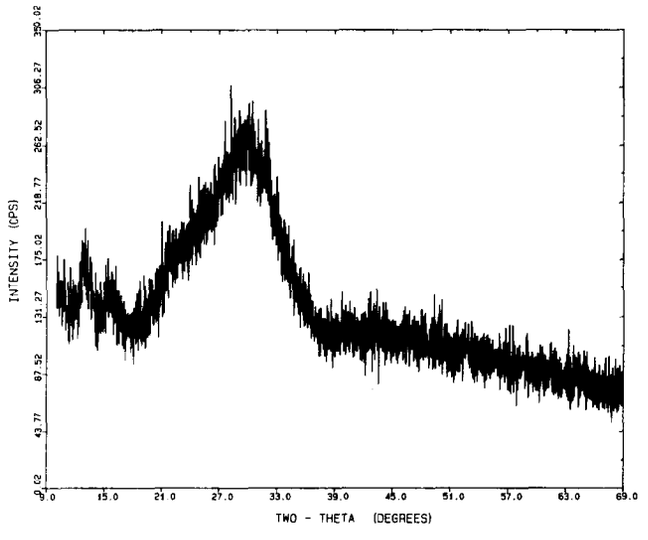

Fig. 1. X-ray diffractogram of a coating to which the best rating (=10) was attributed. The x-axis is expressed in °2Θ (Cu anode tube); intensity on the y-axis in 1000 × counts/s.

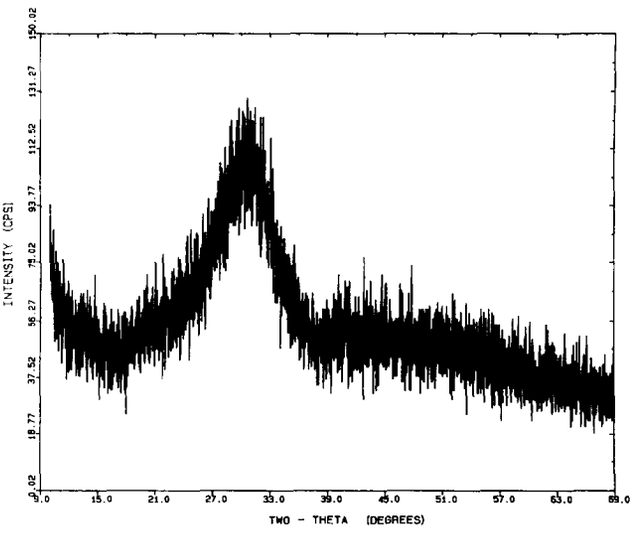

Fig. 3. X-ray diffractogram of a conventional bioglass. Axes as Fig. 1.

Table 4. Ratios and favoured factor levels for the four parameters

	Current	*Arc gas flow*	*Carrier gas flow*	*Spray distance*
Effect	1·09	0·92	0·84	2·54
Favoured level	700 A	40 l/min	4 l/min	10 cm

that the lower flow (4 litre/min) is preferred. The effects of all four parameters are given in Table 4. As a non-replicated factorial design was used, the significance of the effects cannot be calculated using variances.[6] However, factorial testing experience suggests that a ratio above 1·20 (or below 0·83) is necessary to result in a significant benefit.[10] In that case the spray distance only appears to affect significantly the degree of crystallinity of the coating at the levels chosen.

Other properties such as porosity, surface roughness, hetero- or homogeneity, etc., may require optimization and in this case the factorial scheme should be adapted accordingly.

Other Results and Discussion

Composition and adhesion strength

Two aspects are important here: the composition of the end product should be the same or at least predictable from the composition of the mixture of the basic compounds, and the composition should be homogeneous throughout the coating. Table 5 summarizes a set of results for one coating. The relation between starting and end product is acceptable for silicon, calcium and phosphorus. Sodium was thought to be the most volatile element and in fact a loss of sodium during the spraying is observed. The initial concentration is somewhat different from the proposed composition but that is due to deviations in composition of the starting products, especially the silicates. The commercially available sodium and calcium silicates do not have stoichiometric composition and consequently the concentration might be slightly different from one lot to another. Fluoride was not determined in the coating. The small loss is easily compensated for by correcting the composition at the start of the production process.

Table 5. Comparison between the theoretical concentration, the concentration measured in the free-flowing powder and the coating

	SiO_2	CaO	Na_2O	P_2O_5	CaF_2
Theoretical	52·0	30·5	9·8	6·2	1·5
Powder	52·26	31·57	8·34	5·32	n.d.[a]
Coating	53·04	31·93	7·38	5·30	n.d.

[a]n.d. = not determined.

In order to control the efficiency of the mixing, individual powder particles from the free-flowing powder were analyzed by EPMA. Figure 4 shows for the four elements concerned the results for one set of 20 particles. The weight percentages have to be considered as relative values; they are not converted to oxide and not corrected. The homogeneity is not perfect but acceptable and values for Ca, Si and P are correlated. That is explained by agglomeration of tricalcium phosphate particles and adhering on silicate particles. Their average particle diameter is well below 10 μm but these particles are not easily disagglomerated. All elements are, however, present in each particle. In Table 6 averages and standard deviations of the results shown in Fig. 1 are tabulated.

The adhesion strength of a number of test coatings, measured as explained above, is variable but in all cases above 35 MPa.

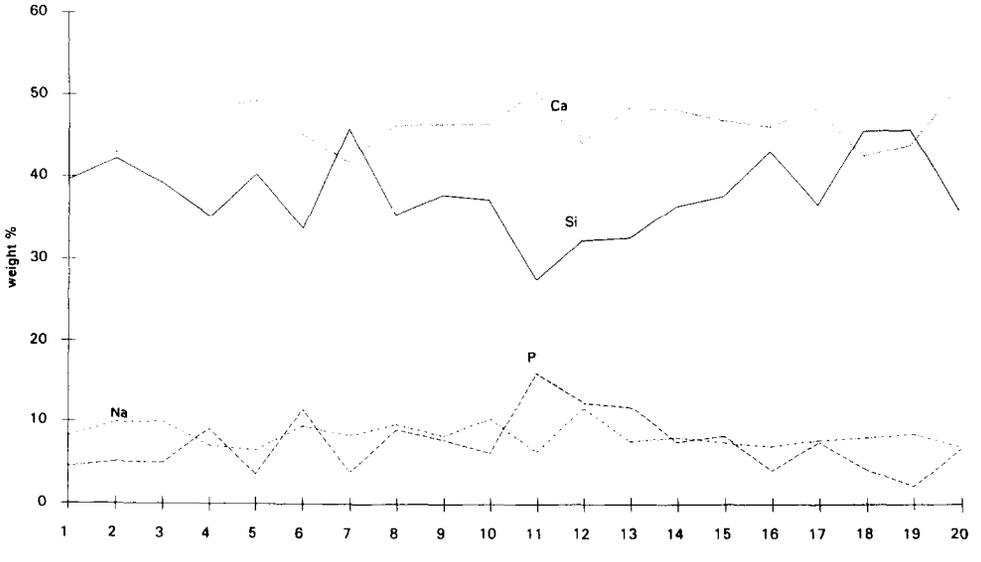

Fig. 4. EPMA analysis for Si, Ca, Na and P of a free-flowing powder for 20 spots. y-axis: weight % for the elements (pure elements, intensities not corrected).

Table 6. EPMA spot determinations of Si, Ca, Na and P on 20 particles of the free-flowing powder

	Silicon	*Calcium*	*Sodium*	*Phosphorus*
Average	37·94	46·37	8·35	7·34
S.D.	4·83	2·53	1·35	3·47

Porosity

Figures 5 and 6 show SEM pictures of the external aspect of the coatings obtained and of a section through a coating. The aspect shows that we have to do here with a glassy coating. Small cracks are seen on the surface and a number penetrate to the metal surface. We are currently working on cooling rate and composition in order to avoid this cracking. The porosity seems to be acceptable and is probably lower than usually obtained for crystalline coatings. No complete characterization of the porosity has been done yet.

Summary and Conclusions

In this paper we comment on a new technique for the application of glass coatings by synthesizing the glass from basic chemicals in a plasma torch. The technique allows production of a powder or direct production of a coating on diverse substrates. Here we discuss an application of coatings

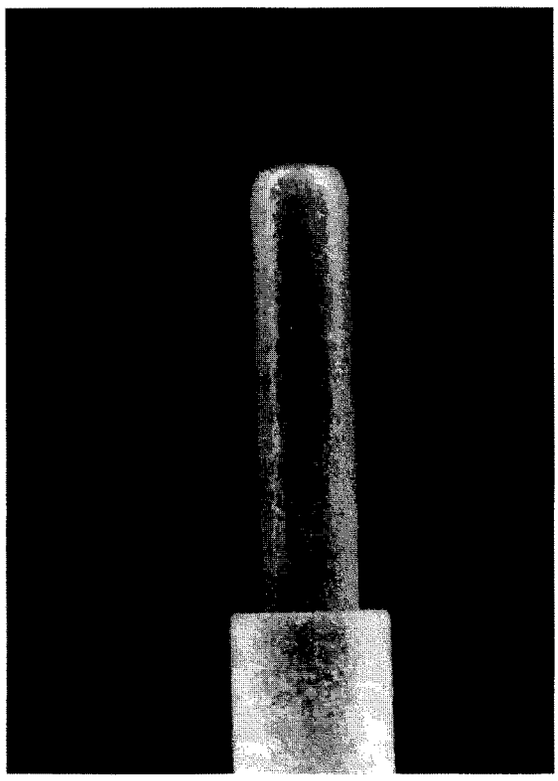

Fig. 5. Photograph of a titanium rod (diameter 3 mm) coated with 150 μm bioglass.

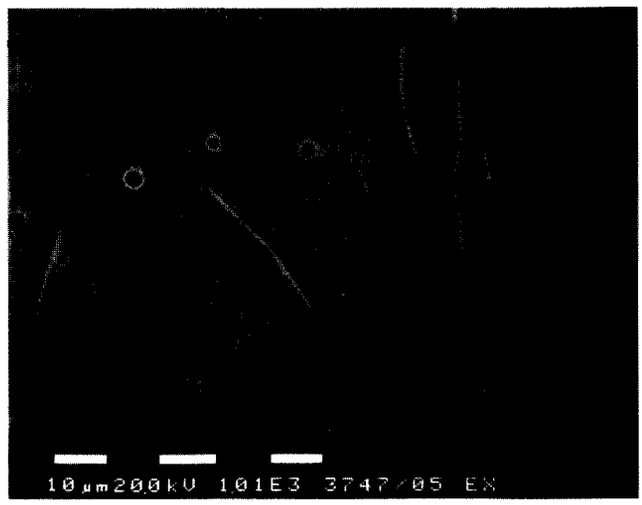

Fig. 6. SEM image of a section through a coating similar to that of Fig. 5.

with the composition of bioglass. Hydroxyapatite coatings have to be crystalline in order to perform well. Glass, and bioglass in particular, has to be amorphous.

The first step in the production process is the preparation of an aqueous slurry for obtaining an optimal mixing of the different compounds. After spray drying and further granulation a free-flowing powder was obtained suitable for feeding to the plasma torch. The powder was tested for homogeneity. According to EPMA measurements the composition does not seem to be perfectly homogeneous but the deviations remain within reasonable bounds.

A plasma spray process requires a great number of parameters to be optimized. Amorphicity was considered here as the main parameter. The plasma parameters were optimized according to a factorial scheme aiming to obtain the highest rating for amorphicity. Ratings were attributed based on the 'macroscopic' aspect of the X-ray diffractograms. It was found that glassy coatings can be obtained which adhere well to the metal substrate, in the case described a titanium rod.

It was shown that composition of the free-flowing powder and the coating match fairly well although not perfectly. Tests runs will always be necessary for adapting the composition of the initial mixture to the required composition for the coating.

The main aspects that are subject to improvement are the mixing procedures, the efficiency of the powder conditioning and the conditions for cooling the substrates after spraying.

Bioglass coatings are currently being tested on animal models and the first results seem to be encouraging.

References

1. Hench, L. L. & Wilson, J. (eds), *An Introduction to Bioceramics*. World Scientific, Singapore, 1993.
2. Kobubo, T., Bioactivity of glasses and glass ceramics. In *Bone-Bonding Biomaterials*, ed. P. Ducheyne, T. Kobubo & C. A. van Blitterswijk. Reed Healthcare Communications, Leiderdorp, 1992.
3. Schepers, E., Clercq, M. De, Ducheyne, P. & Kempeneers, R., Bioactive glasses particulate material as a filler for bone lesions. *J. Oral Rehabil.*, **18** (1991) 439–452.
4. Ravaglioli, A. & Krajewski, A., *Bioceramics*. Chapman & Hall, London, 1992, pp. 198–244.
5. Hench, L. L. & Andersson, Ö., Bioactive glass coatings. In *An Introduction to Bioceramics*, ed. L. L. Hench & J. Wilson. World Scientific, Singapore, 1993, pp. 239–259.
6. Box, G. E. P., Hunter, J. S. & Hunter, W. G., *Statistics for Experimenters*. John Wiley & Sons, New York, 1978. ch. 10–13, 15.
7. Timmermans, G., Optimalisatie van het Produktieproces van Plasmagespoten Deklagen uit Bioglas. Graduate Thesis, Dept. Metallurgy & Materials Engineering, University of Leuven, 1993.
8. Heimann, R. B., Lamy, D. & Sopkow, T. N., Parameter optimization of alumina–titania coatings by statistical experimental design. In *Proceedings of the Third National Thermal Spray Conference*, Long Beach, California, 1990. pp. 491–496.
9. Fisher, I. A., Variables influencing the characteristics of plasma sprayed coatings. *Int. Metallurgical Rev.*, **17** (1972) 117–129.
10. Van Doren, S. L., A statistical method of plasma spray parameter testing. *Thermal Spray Res. Applications* (1987) 113–117.