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Plasma-sprayed coatings of 62W bioactive glass: Mechanical properties and in vitro behavior

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ARTICLE INFO	A B S T R A C T		
Keywords: Bond strength Bioactive glass Magnesium oxide Bioactivity Thermal spray	Bioactive glasses, due to their chemical and biological properties, are promising materials for being used in orthopedic applications. In this study, coatings of the novel 62W glass, with a composition in the system SiO ₂ -CaO-P ₂ O ₅ -MgO, were analyzed. The 62W feedstock powder was prepared from a mixture of reagents by the melt- quenching route and deposited onto titanium alloy substrates by atmospheric plasma spray (APS) technique. The cross-section and the phase of the coatings were analyzed by scanning electron microscopy and X-ray diffraction. Mechanical and in vitro tests were conducted on the obtained coatings to evaluate their bioactive ability. The results of the cross-sections show dense coatings with the absence of the characteristic pores that appear when spraying the usual bioactive glasses. The obtained coatings present a bond strength of 32 ± 3 MPa with the substrate without crystalline phases on the microstructure. The presence of magnesium oxide in the composition favours the glass's processing and increases its crystallization temperature and, thus, the proper stacking of the deposited particles. The bioactive capacity of the 62W coatings was demonstrated at short periods after in vitro		

1. Introduction

Bioactive glasses are materials based on silicate glasses containing sodium, calcium, and phosphate in their composition. Since their discovery by L.L. Hench in 1967, different combinations of bioactive glasses have been studied, including other elements such as magnesium, boron, or potassium. New compositions of bioactive glasses are still being developed, as these materials have potential applications in biomaterials and tissue engineering. In recent years, different formulations of glasses have been used for enhancing cement and bone wax [1-3], as a phase for 3D printing techniques [4,5], and even for the regeneration of soft tissues [6,7]. However, the mechanical properties of bioactive glasses are poor, and it is a determinant disadvantage for bone substitution applications. Because of that, these biomaterials found an interesting field in composite materials, providing a combination of a tougher phase that simultaneously provides a bioactive response. Metallic implants are a reference in orthopedic surgery due to their excellent mechanical response. Specifically, titanium and its alloys have a series of combined advantages, such as proper strength, a suitable Young's modulus, and biocompatibility, which make them the perfect metallic candidate [8]. Combining the mechanical response from titanium with the high bioactivity of bioactive glasses opens the possibility of obtaining materials suitable for load-bearing applications, establishing a chemical bonding with surrounding bone tissue. From this premise, many studies have been developed to provide bioactivity on the surface of metallic implants. One of the most widespread forms of processing coatings is its deposition by thermal spray techniques [9]. Many of these studies have focused on studying the spraying of ceramic and vitreous bioactive materials using techniques such as high-velocity suspension flame sprav (HVSFS) [10–13], suspension plasma sprav (SPS) [14,15], and atmospheric plasma spray (APS) [16–19] that are the most common. For the response of the coating to be the desired one, it must be well adhered to the substrate, and the interface must be resistant so that the bioinert metallic substrate remains entirely covered by the bioactive phase after implantation in the body. In addition, the coating must be thick enough so that the ionic exchange and the hydroxyapatite formation process do not involve the whole coating, compromising the implant's stability. The bioactive glasses approved by the FDA, which are used commercially in other applications, have insufficient adhesion to the substrate when applied as coatings and cannot be used for load-

evaluation in SBF and TRIS/HCl solutions. The study reveals the potential use of 62W glass coatings for bone

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Table 1

Composition of the 62W glass powder in % wt.

	CaO	SiO ₂	P_2O_5	MgO
Theoretical	46	40	10.6	2.8
Analyzed	47.5	40.6	8.6	2.7

Table	2
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Plasma spraying parameters.

1 9 01	
Argon plasma gas flow rate (slpm)	30
Hydrogen plasma gas flow rate (slpm)	15
Spray distance (mm)	125
Current (A)	650
Spray cycles	5
Torch speed (mm/s)	500

bearing implants.

In this work, a bioactive glass, named 62W and designed in the SiO₂-CaO-P₂O₅-MgO system [20], was used as feed-stock powder for being deposited on a titanium alloy substrate by APS. The effect of the composition on the coating's microstructure was analyzed, and the mechanical properties of the coatings were evaluated. Finally, an in vitro characterization was performed to validate the bioactivity and biodegradation rate of the new 62W coatings.

2. Materials and methods

2.1. Feedstock powder and substrate

The 62W glass composition was prepared following the indications of Rodrigo et al. [20]. Its chemical composition was quantified using X-ray Fluorescence spectrometry (XRF) (MagicX PW-2424, Malvern Panalytical Ltd., Malvern, UK) with an RX tube and a generator of 2.4 kW. For the analysis, the sample was prepared as a pearl, and a Pt—Au crucible was used. The result is detailed in Table 1.

The obtained glass was milled using a tungsten-carbide vibrating cup mill to get glass powder, and it was sieved using a vibrating sieve with different meshes. Finally, the powder between 63 and 100 μ m was collected for spraying. The powder in the selected size offered a suitable flow ability for spraying.

Titanium alloy grade 5, Ti_6Al_4V , specimens were used as substrate material. In particular, for the adhesion strength, the specimens used had a diameter of 25 mm, and for the in vitro tests, plane discs of 10 mm diameter and 1 mm thickness were used.

2.2. Atmospheric plasma spray (APS)

Coatings were deposited using the plasma spray equipment (Plasma-Technik A3000S, Sulzer Metco AG, Wohlen, Switzerland) with an F4 plasma torch. Argon was used as the primary carrier gas and hydrogen as the secondary gas for the plume formation. The spraying parameters were evaluated to achieve a good melting of the particles that results in homogeneous coatings. For this purpose, the spray distance was modified from 100 to 125 mm; the argon and the hydrogen gas flow rate were modified from 30–35 slpm and 12–15 slpm, respectively, and the current between 600 and 650 A. The carrier gas flow rate for this powder was adjusted to 4 slpm. The parameters selected after optimizing the coating deposition of 62W powder are detailed in Table 2.

The powders were deposited onto substrates, previously grit-blasted (MAB-4, MAB industrial, Barcelona, Spain) with corundum G24 (grit size 800 μ m) at 0.5 MPa. Before the spraying process, the substrates were cleaned with ethanol. The characteristic roughness values (Ra and Rz) were recorded using a surface roughness measurement device (Surftest 301, Mitutoyo, Kawasaki, Japan). The substrate roughness after grit-blasting was Ra = 4 \pm 1 μ m and Rz = 31 \pm 4 μ m.

2.3. X-ray diffraction (XRD)

XRD patterns were recorded on a diffractometer with a monochromator (D8 Advance, Bruker, Karlsruhe, Germany) using Cu ka₁ radiation. Data were collected in the Bragg-Brentano vertical geometry ($\theta/2\theta$) between 20 and 70° (2 θ) in 0.05° counting for 153 s per step. The EVA-version 6.0 diffract plus software (Bruker, Karksruhe, Germany) was used to analyze the crystalline phases.

2.4. Scanning electron microscopy (SEM)

Microstructural analysis was performed using a scanning electron microscopy system (SEM, Hitachi TM-1000, Tokyo, Japan) with a backscattered electron detector (BSE).



Fig. 1. SEM micrographs representative of (a) cross-section and (b) surface of the as-sprayed 62W coating.



Fig. 2. XRD patterns of 62W powder and 62W as-sprayed coating.

Moreover, the coating composition was determined from the crosssection, using a scanning electron microscopy (Quanta-200, FEI, Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray detector (UltraDry, Thermo Fisher Scientific, Madison, USA).

2.5. Adhesion test

The bond strength of the sprayed coatings was evaluated by using a mechanical test machine (ME-402/10, Servosis, Madrid, Spain) according to the ASTM C633-13 (Standard test method for adhesion or cohesion strength of thermal spray coatings). Thus, a tensile strength at 0.02 mm/s was applied to the samples previously glued to a counter-test piece with HTK ULTRA BOND 100® glue (HTK, Germany). The value that caused the fracture was recorded for as-sprayed coatings.

2.6. In vitro tests

Bioactivity was evaluated in vitro following the standard ISO 23317 (Implants for surgery - In vitro evaluation for the apatite-forming ability of implant materials) by preparing a simulated body fluid solution (SBF) fixed in a pH of 7.4. Plane discs were immersed in 15 mL of SBF solution at 37 $^{\circ}$ C for seven days using clean conical flasks.

The biodegradation rate (ISO 10993-14 Biological evaluation of medical devices - Part 14: Identification and quantification of degradation products from ceramics) was evaluated by preparing a buffer solution TRIS/HCl 0.05 M with a pH of 7.4. Plane discs were immersed in 15 mL of TRIS/HCl solution at 37 °C for 7, 14, 21, 35, and 70 days using clean conical flasks. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Iris Advantage, Thermo Jarrel Ash. Boston, USA) was used to measure the quantification of elements released with time.

2.7. Raman spectroscopy

Analysis of the samples, before and after the bioactivity test, was

Table 3

Composition of the 62W coating in % wt.	
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1	6				
	CaO	SiO ₂	P_2O_5	MgO	
Analyzed	48.6	39.8	8.8	2.8	

carried out by Raman spectroscopy. The spectra were obtained using a confocal Raman microscope (inVia Raman Microscope, Renishaw, Wotton-under-Edge, England) equipped with a red laser working at 785 nm and a 10 % of power and a microscope's objective $50\times$. The measuring conditions were 10 s exposure time over 300-1100 nm.

3. Results and discussion

3.1. Coating characterization

Fig. 1a shows the cross-section of the 62W glass coating. It reveals a dense coating with interparticle fusion with few cracks and holes. Dense coatings with flat areas result from well-molten particles, which have reached enough temperature to achieve this state during the deposition process. In bioactive glass coatings obtained by plasma it is expected to observe some porosity [16,21,22]; however, in this coating, the presence of pores is minimal. This fact can be related to the specific composition of the glass powder. On the one hand, magnesium oxide can promote good fusion of the particles, and the absence of sodium oxide in the composition should also be highlighted, since sodium oxide is related to the porosity in glass coatings because it can volatilize during spraying [23].

The measured thickness of the coating is $105 \pm 18 \,\mu$ m. Fig. 1b shows a SEM micrograph of the surface microstructure of the as-sprayed 62W glass coating, where most of the cracks observed occurred due to the fast cooling and the residual stress generated; also, some cracks and porosity were produced by the gas leak. Besides, at the surface, it can be seen large flattened splats (disc shape) and partially melted or re-solidified particles (spherical shape).

The XRD patterns of 62W powder and coating are shown in Fig. 2. In both cases, a wide band at the $30^{\circ} 2\theta$ range with no crystalline peaks implies a completely vitreous state of the materials. The high temperatures used in this technique can cause partial devitrification of a glass material [24], and the appearance of crystalline phases may affect essential variables such as the bioactive response or the degradation rate. It has been reported that including magnesium oxide in the composition can favor the processing of bioactive glasses since it reduces its crystallization tendency [25,26]. In particular, the thermal stability of 62W glass allows us to work at very high temperatures without any undesired crystallization. The XRD analysis confirms that it has been



Fig. 3. Fracture morphology of 62W coatings. Samples below correspond to coated samples, and above to counter-test pieces.

obtained plasma coatings without generating crystallization for this composition.

The results from the EDS analysis are detailed in Table 3. The chemical composition of the coating is quite similar to the glass powder composition (Table 1), thus the proportion of oxides is kept after deposition.

3.2. Mechanical response

The bond strength of the substrate - 62W glass interface was tested, and the obtained result was 32 \pm 3 MPa, which is higher bonding strength than the minimum required (15 MPa) for thermally sprayed coatings of hydroxyapatite coatings according to ISO 13779-2:2018. The fractured surfaces after the test, shown in Fig. 3, indicate a cohesive



Fig. 4. XRD patterns of the as-sprayed coating after one, three and seven days of immersion in SBF. (A Hydroxyapatite characteristic peaks).



Fig. 5. SEM micrographs of as-sprayed 62W coating (a) untreated, (b) one day in SBF, (c) three days in SBF, and (d) seven days in SBF.

failure at the 62W glass coating since the coating remains on both surfaces (the coated samples and the counter-test pieces). The result obtained is close to some of the highest bonding strength values reported for bioactive ceramic coatings deposited by APS onto titanium alloy, as a heat-treated glass ceramic coating in the system CaO-MgO-SiO₂ with 35.4 MPa [27], or a glass coating in the system SiO₂-Al₂O₃-CaO-Na₂O with 41.2 MPa [28].

The bonding strength is a fundamental parameter for the final application, as it is related to the long-term stability of the coating.

3.3. In vitro test: bioactivity

Bioactive response of the coating was studied by immersion in a SBF solution for seven days. The appearance of a new layer of a hydroxyl carbonate apatite (HCA) on the surface indicates that the material is suitable to bond the surrounding bone tissue after its implantation. The precipitation of this crystalline phase is the result of an initial ions exchange process between H⁺ from the SBF solution, and Ca²⁺ and Mg²⁺ from the glass, and a second step where PO_4^{3-} groups and Ca²⁺ migrate to the surface forming this phase.

The coating surface was initially studied by XRD, and the obtained patterns are shown in Fig. 4. Samples examined after one and three days reveal an amorphous profile, with a wide band centered at 30° 20. However, after seven days, some characteristic peaks related to a hydroxyapatite phase are identified (Reference number: 00–009-0432), indicating that the crystallization of the formed layer already started.

The surface evolution before and after the immersion in SBF is shown in Fig. 5. The comparison between the surface before (Fig. 5a) and after one day of SBF immersion (Fig. 5b) shows a clear change in the microstructure, where plates of apatite are formed on the flat parts of the coating, and these are delimited by the cracks of the glass coating. After three days of immersion (Fig. 5c), the surface of the glass appears



Fig. 6. Raman spectrum of the coating before and after seven days immersed in SBF compared to theoretical hydroxyapatite (HA) spectrum.

completely covered by plates of apatite forming a continuous phase. Finally, after seven days of immersion (Fig. 5d), a globular microstructure corresponding to the typical apatite layer can be observed.

Further information about the new layer formed onto the glass coating after the SBF immersion was obtained using Raman microspectroscopy. The Raman spectrum of the coating before and after the SBF test can be observed in Fig. 6; also, the spectrum corresponding to



300 µm

300 µm

Fig. 7. SEM micrographs of as-sprayed 62W coating (a) untreated, (b) 7 days, (c) 21 days, and (d) 70 days immersed in TRIS/HCl solution.



Fig. 8. Release of silicon, calcium, magnesium, and phosphorous ions in TRIS/HCl with immersion time.



Fig. 9. XRD patterns of the as-sprayed coating after 7, 14, 21, 35, and 70 days immersed in TRIS/HCl 0.05 M solution. (A Hydroxyapatite characteristic peaks).

hydroxyapatite was included for comparison purposes. The spectrum acquired on the surface of the coating after the immersion in SBF shows a marked change. In particular, peaks in the 423 cm⁻¹ and the interval 950–965 cm⁻¹ are detected, corresponding to phosphate ions' vibrations. These peaks are distinctive of hydroxyapatite peaks, as can be observed in the HA profile included in the graph. These results corroborate the formation of an apatite layer.

3.4. In vitro test: biodegradation

The ability of the coatings to release ions was studied using a TRIS/ HCl buffer solution. The gradual dissolution of the coating in a physiological environment is an essential variable for a third-generation material, where the coating should favor the formation of new bone tissue and, at the same time, gradually disappear to be replaced by neoformed bone. For this purpose, samples were immersed in the solution for 7, 14, 21, 35, and 70 days. Fig. 7 shows the coating surface before the degradation test and after immersion on TRIS/HCl.

According to the SEM analysis, it can be seen an initial dissolution, which occurs mainly in the peaks located in the highest plane of the rough surface. Further degradation could be appreciated at samples after 21 days of immersion, where the degradation located at the peaks grows, generating little holes and even emptying the inside of the granules at more extended immersion periods. The main surface changes



Fig. 10. SEM micrographs of 62W coating surface after seven days of immersion in (a) SBF and (b) TRIS/HCl solution.

due to dissolution processes are observed during the first steps when the degradation effect is stronger.

The percentage of ion release from the coatings related to the initial amount of Ca, Si, P, and Mg in the composition is presented in Fig. 8.

TRIS/HCl buffer is used for studying the ion release kinetics as it does not contain ions from the glass, so all the Ca, Si, P, and Mg ions detected come from the coatings [29]. ICP data revealed that higher ions release from the coatings occurred in the first two weeks, and then the rate decreased with time. In particular, the release of Ca and Mg ions showed a similar trend, being higher for Ca, as it is found as a network modifier in the glass structure, and consequently, Ca ions are weakly bound. It can be observed in other silicates that the release of Mg is less than that of Ca [30]; the same behavior is observed in the present case. In the case of Si, the release shows a different behavior to Ca and Mg, where it suffers a stronger release the first two weeks and, from that point, decreases the lixiviation rate; probably, this decrease with time is due to its participation in the apatite precipitation mechanism, where initially a Si-rich layer is formed on the coating surface. Finally, the release of P is very low compared to the other ions as it works as a network former and because the precipitation of the Ca-P layer partially consumes P. Although Ca ions also precipitate to form the Ca-P layer, these are still present in the solution since only a part are consumed to form the layer.

In TRIS/HCl, the ions needed to start the apatite formation mechanism must be released from the material since the solution does not contain them. The XRD patterns of the coatings after immersion in TRIS/ HCl buffer for 7, 14, 21, 35, and 70 days are plotted in Fig. 9.

At all the studied periods, typical peaks corresponding to hydroxyapatite phase are detected, confirming the formation of the apatite layer after immersion of the coatings in this solution. At 7 days the low intensity of the peaks suggests that most of the formed apatite layer is still in an amorphous state. However, at later points, from 14 days, more hydroxyapatite characteristic peaks are identified, corroborating the crystallization of the layer.

Fig. 10 shows a direct comparison of TRIS/HCl and SBF concerning apatite formation on the glass coating surface. It can be seen that after seven days, the apatite formation is delayed in the sample immersed in TRIS/HCl compared to SBF, where fewer apatite deposits are detected, and not all the surface is covered by the formed layer. As the TRIS/HCl solution does not contain elements from the glass, the kinetics of HCA formation needs more time than in the SBF solution since the ions that start the process need to be released from the coating in an initial stage [31]. Furthermore, this delay in TRIS/HCl solution is corroborated with the XRD profiles at seven days (Figs. 4 and 9), where a more ordered apatite is formed in samples immersed in SBF, causing more peaks in this XRD pattern.

4. Conclusions

In this work, the 62W bioactive glass material, based on the system SiO_2 -CaO- P_2O_5 -MgO, was deposited as a coating onto titanium alloy using APS. The obtained coating maintains an entirely amorphous structure due to the high processability of this composition caused by network disruption that provides MgO. The coating exhibited a proper bond strength (32 \pm 3 MPa) for the desired application.

The coating exposed to SBF and TRIS/HCl solution formed an apatite crystalline layer, proving its ability to bond bone and biodegradability, which is more pronounced at the beginning of the dissolution process.

This preliminary work with the 62W material represents a starting point for future investigations to assess the chance of this composition since, considering the properties mentioned, it has exciting potential in the orthopedic field.

CRediT authorship contribution statement

The authors confirm their contribution to the paper as follows:

Beatriz Garrido: Conceptualization, Methodology, Investigation, Writing- Original draft preparation.

Carmen-Sara Rodrigo: Investigation, Data curation.

Miguel Angel Rodríguez: Supervision, Resources, Writing-Reviewing.

Antonio H. de Aza: Funding acquisition, Conceptualization, Supervision, Writing- Reviewing.

Irene Garcia-Cano: Funding acquisition, Resources, Writing-Reviewing.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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