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Study of the Ca/P atomic ratio of the amorphous phase in plasma-sprayed hydroxyapatite coatings

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Abstract

Because of the excellent biocompatibility of hydroxyapatite (HAp), plasma-sprayed HAp is widely used to coat orthopedic protheses. During the plasma spraying process, the thermal decomposition of HAp products tricalcium phosphate (TCP), tetracalcium phosphate (TeCP), calcium oxide (CaO), oxyhydroxyapatite (OxyHAp) and a molten phase. Hence, the coating is made of different phases including TCP, TeCP, CaO, OxyHAp, HAp and an amorphous phase. According to AFNOR standards, 35 samples of plasma-sprayed HAp coatings were analyzed by X-ray diffraction. The weight fraction of each phase (TCP, TeCP, CaO, HAp and amorphous phase) was measured with calibration curves. Thus, the Ca/P atomic ratio of the amorphous phase was calculated, the different ratios were between 1.50 and 1.67. The Ca/P atomic ratio of the amorphous phase varies both with the quantity of TCP or TeCP solubilized in the molten phase and with the part of TCP and TeCP which crystallizes from the amorphous phase during cooling.

Keywords: Plasma-sprayed hydroxyapatite coatings; Ca/P atomic ratio; Amorphous phase; X-ray diffraction

1. Introduction

Calcium phosphate ceramics show a great ability to form a physical–chemical bond with human bone. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (HAp) coated implants are widely used in orthopedic surgery. They present several advantages: an excellent biocompatibility related to the osteoconductive properties of calcium phosphate coatings, as well as good mechanical resistance when associated with the substrate alloy Ti–6Al–4V. A large proportion of knee and hip protheses are coated with calcium phosphate compounds. Plasma spraying of a HAp powder is the industrial process used to coat orthopedic protheses. The calcium phosphate coatings obtained are made up of variable proportions of HAp and other calcium phosphate phases. The amounts of residual compounds, amorphous and recrystallized phases are related to the conditions of spraying [1,2] such as the gas flow, which controls the time the HAp particles spend in the plasma, the plasma temperature, the nature of the plasma gas used, the cooling conditions or the stand-off distance. They are also closely dependent on the particle size distribution and the quality of the HAp powder used [3,4], for example the powder density determines the distance the HAp particles penetrates into the plasma.

The plasma jet, which possesses high temperatures (5000–20,000°C), can decompose HAp. The following reactions may occur: at about 900°C

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x + xH_2O \qquad (I)$$

between 1100°C and 1500°C, depending on water vapour pressure [5,6]:

$$Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x \rightarrow 2Ca_3(PO_4)_2 + Ca_4(PO_4)_2O + (1-x)H_2O, \qquad (II)$$

$$Ca_4(PO_4)_2O \rightarrow Ca_3(PO_4)_2 + CaO. \qquad (III)$$

This decomposition leads, after various physical–chemical transformations, to the deposition of a coating made up of variable proportions of α and β tricalcium phosphate $Ca_3(PO_4)_2$ (TCP), tetracalcium phosphate

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$Ca_4(PO_4)_2O$ (TeCP), HAp, calcium oxide (CaO) and an amorphous phase. The chemical phase composition is altered from the original HAp. As the HAp particles go through the plasma flame, several phase configurations can possibly coexist:

- a molten phase which, when deposited onto the Ti substrate, solidifies to produce the amorphous phase observed in the coatings [7];
- phases TCP, TeCP and CaO obtained by partial decomposition of apatite under the high temperature (reactions (I)–(III));
- an OxyHAp [5,8] formed by partial "dehydroxylation" of the HAp under the effect of the temperature. This OxyHAp can be hydrolized again during cooling to return to more hydrolized OxyHAp or even transformed completely to HAp.

The interfacial bone–ceramic reactions are influenced by the chemical composition and the crystallinity of calcium phosphate coatings. Moreover, the longevity of an implant is conditioned by how well it is bound to the natural bone as well as by the bioresorption of the coating by the host organism. These two factors depend mainly on the mineral phases which are formed and their relative proportions. For example, one approach would suggest that the amorphous phase must only be present in moderate quantities as it dissolves quickly, but it must be present in sufficient quantities for the coating to adhere to the Ti alloy correctly.

Calcium phosphates are a large family of compounds characterized by their calcium/phosphorus (Ca/P) atomic ratios (Table 1). The initial HAp powder injected into the plasma has a Ca/P atomic ratio of 1.67, therefore the overall composition of all the solid phases formed, must have the same Ca/P atomic ratio: 1.67. The Ca/P atomic ratios of each crystalline phase formed is accurately known but that of the amorphous phase is not. The aim of this study was to define the Ca/P ratio of the high temperature amorphous phase present in plasma-sprayed HAp coatings.

The coatings were obtained by spraying different commercial HAp powders. Almost all the samples were treated in identical standard conditions defined by the plasma gun manufacturers, 2PS Co. Ltd. The decomposition of the HAp gives rise to the formation of several phases according to the following overall reaction:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow aCa_3(PO_4)_2 + bCa_4O(PO_4)_2 + cCaO + dCa_{10}(PO_4)_6(OH)_2 + eCa_x(PO_4)_y,$$

$Ca_x(PO_4)_y$ represents the amorphous phase. Knowing coefficients a, b, c and d makes it possible to determine the amorphous phase Ca/P atomic ratio.

The data collected related to 35 samples. HAp, TCP, TeCP, CaO and amorphous phases were identified and quantified by X-ray diffraction.

2. Material and method

2.1. Plasma spraying

The plasma spray apparatus was a 2PS device (plasma gun GT5, digitally controlled). The initial HAp powders were of various commercial origins. They all had a Ca/P atomic ratio of 1.67. Their differences lie primarily in the particle sizes and the apparent densities. The few variations of spraying conditions which were studied relate to the stand-off distance, the plasma gas (air/Ar or air/H_2 mixtures), the range of particle sizes and the density of the HAp injected, as well as the conditions of cooling. These parameters primarily influence the quantity of HAp decomposed and consequently the proportions of mineral phases formed (TCP, TeCP, CaO, HAp and amorphous phase), but in the present study only the physical–chemical processes modifying the Ca/P atomic ratio of the amorphous phase interest us.

2.2. Method of identification and determination of the ratios of the different mineral phases by X-ray diffraction

Part of the coating was scraped from the titanium surface and finely crushed in an agate mortar. The initial powders and the scraped powders were analyzed by X-ray diffraction (Fig. 1) using an Inel diffractometer

Table 1
Characteristics of the crystallized compounds present in the plasma coatings

Compounds			Ca/P	JCPDS cards	Theoretical lines	d-spacing (Å)	Peak intensity ratios
α-TCP	α-Tricalcium phosphate	α-$Ca_3(PO_4)_2$	1.5	9-348	(170)	2.905	$I_{170\alpha TCP}/I_{210Hap}$
β-TCP	β-Tricalcium phosphate	β-$Ca_3(PO_4)_2$	1.5	9-169	(0210)	2.88	$I_{0210\beta TCP}/I_{210Hap}$
HAp	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	1.667	9-432	(210)	3.08	
					(202)	2.631	
CaO	Calcium oxide	CaO	—	37-1497	(200)	2.4059	I_{200CaO}/I_{202Hap}
TeCP	Tetracalcium phosphate	$Ca_4(PO_4)_2O$	2	25-1137	(040)	2.995	$I_{040TeCP}/I_{210HAp}$

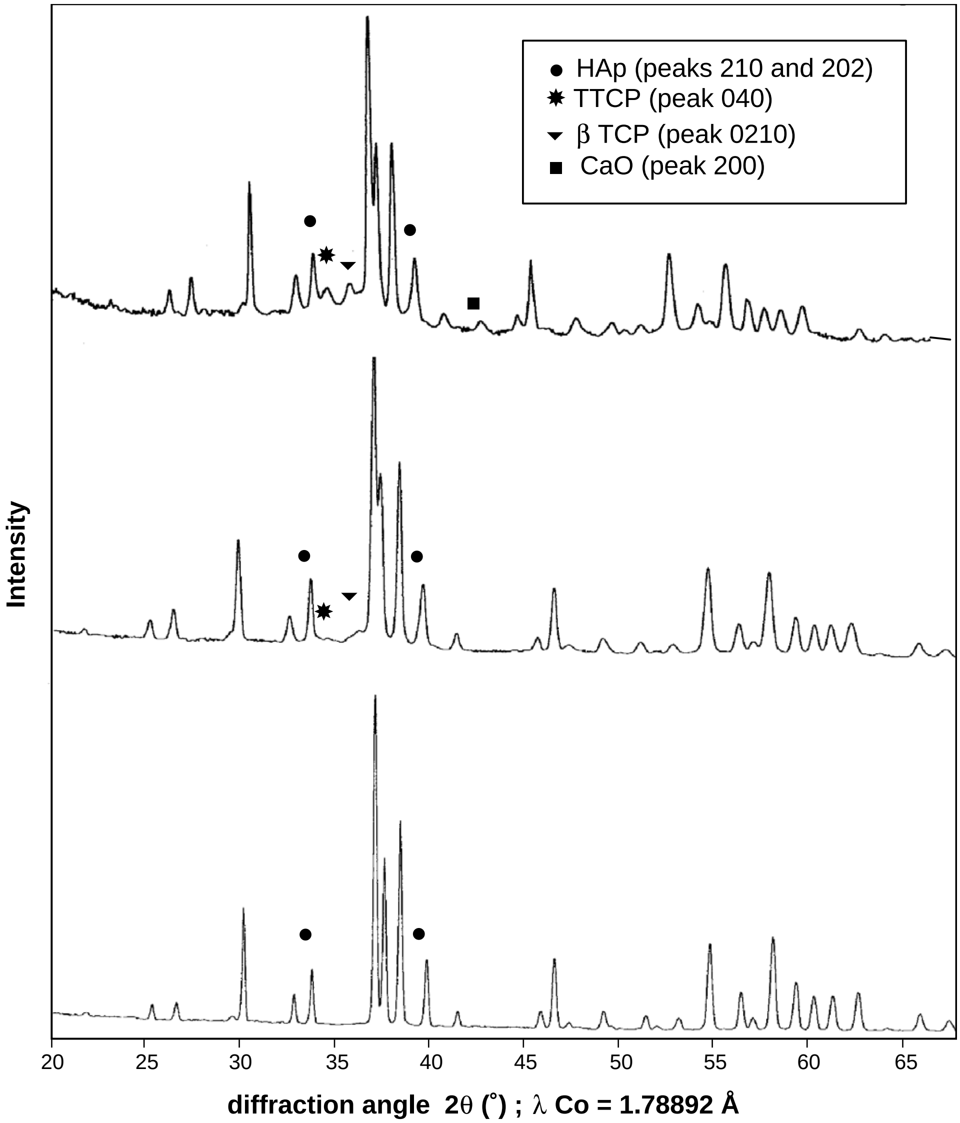


Fig. 1. XRD patterns (a) HAp as-received, (b) plasma-sprayed HAp coating with a low rate of decomposition, (c) plasma-sprayed HAp coating with a high rate of decomposition.

equipped with a curved sensitive position detector CPS 120 (λCo = 1.78892 Å).

The crystalline phases were identified according to JCPDS cards as indicated in Table 1.

The amounts of each phase were determined in accordance with AFNOR standards [9]. The calibration curves were established according to the terms of these AFNOR standards for each phase. The compounds αTCP, βTCP, TeCP, and CaO were quantified by the ratio of the integrated intensity of the significant peaks for each phase to that of the HAp peaks (210) or (202). The proportion of amorphous phase was obtained from the ratio of the integrated intensity of the HAp peak (210) and the height of the amorphous diffuse peak centered at $d = 2.97$ Å or $2\theta = 35.1°$. The integrated intensities of the peaks were obtained using an AMSLER planimeter. The weight fractions of αTCP, βTCP, TeCP, CaO, and amorphous phase were first obtained with respect to HAp, and are then expressed with respect to the total mass of the mixture.

2.3. Method of determination of the amorphous phase Ca/P atomic ratio

The calculation of the amorphous phase Ca/P atomic ratio (noted Ca/P$_{\text{amorphous}}$) can be deduced from the following reaction:

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2} \rightarrow a\mathrm{Ca_3(PO_4)_2} + b\mathrm{Ca_4O(PO_4)_2} + c\mathrm{CaO} + d\mathrm{Ca_{10}(PO_4)_6(OH)_2} + e\mathrm{Ca}_x\mathrm{(PO_4)}_y$$

with $Ca_x(PO_4)_y$ = amorphous phase.

$$Ca/P_{products} = 10/6 = (3a + 4b + c + 10d + ex)/(2a + 2b + 6d + ey),$$

$$ex = 10 - 3a - 4b - c - 10d$$

and

$$ey = 6 - 2a - 2b - 6d,$$

$$Ca/P_{amorphous} = ex/ey.$$

The errors incurred by this method of determination are an accumulation of those related to the peak measurement (relatively low between 1% and 2%), those related to the X-ray diffraction analysis technique (very low given that the equipment, and the operator were identical for all samples), and those due to calculation (these errors were higher, mainly because of the large number of mathematical formulas used).

Overall, the uncertainty induced by the error of measurement, by the error of the X-ray diffraction analysis, and by miscalculation was about 15–20%. These values led us to work on the groups of dots related to the curves presented to try to reveal any trends which may occur.

3. Results

3.1. Determination of the relative proportions of TCP, TeCP, CaO, amorphous phase and HAp in the plasma-sprayed coatings

The results of the X-ray diffraction analysis carried out on the 35 samples are presented in Figs. 2–6. The weight fractions initially calculated compared to the total mass of the mixture were translated into a number of moles per mole of HAp sprayed. The curves show an overall increase in TCP (α and β), TeCP, CaO and amorphous phases, correlated with a decrease in HAp in the coating. TCP was almost entirely in the high temperature α form. TeCP was lightly more abundant than TCP. It is noted that there is a good correlation between the variations of the 2 phases: the 2 phases increase simultaneously, which corresponds to the decomposition of HAp. CaO appears in small proportions in the coatings.

3.2. Determination of the amorphous phase Ca/P atomic ratio in coatings

The $Ca/P_{amorphous}$ ratios were calculated for each of the 35 samples starting from the weight fractions of TCP, TeCP, CaO, and HAp phases expressed with respect to the whole plasma coating. The results are presented in Figs. 7–10.

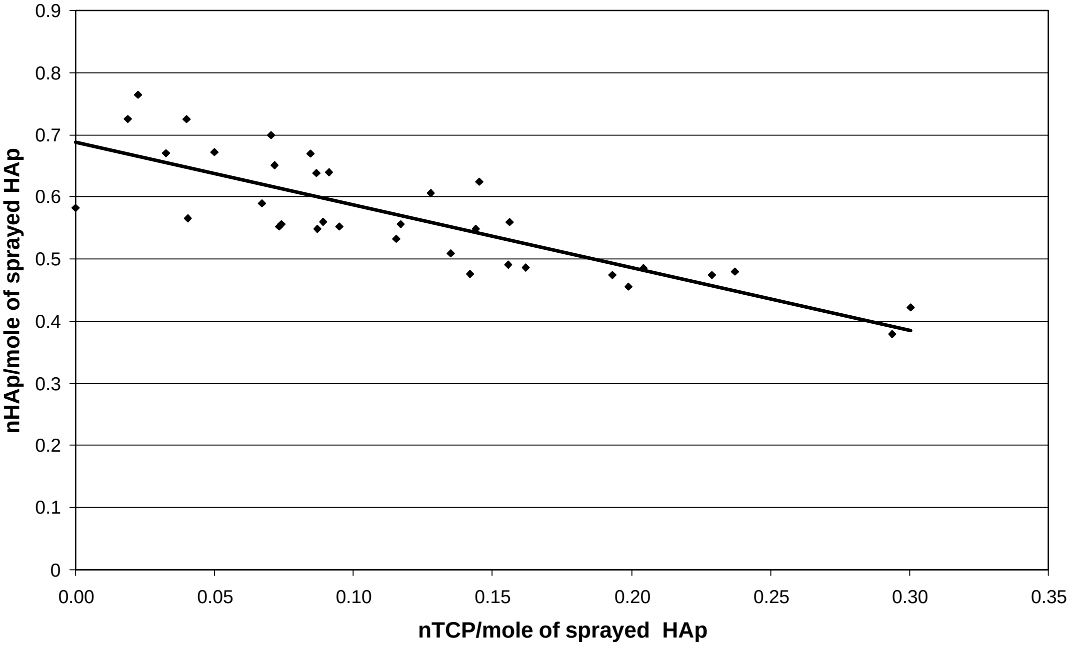


Fig. 2. Number of moles HAp in the coating versus the number of moles TCP in the coating (*n*HAp or *n*TCP is the number of moles of HAp or TCP obtained in the coating per mole of sprayed HAp).

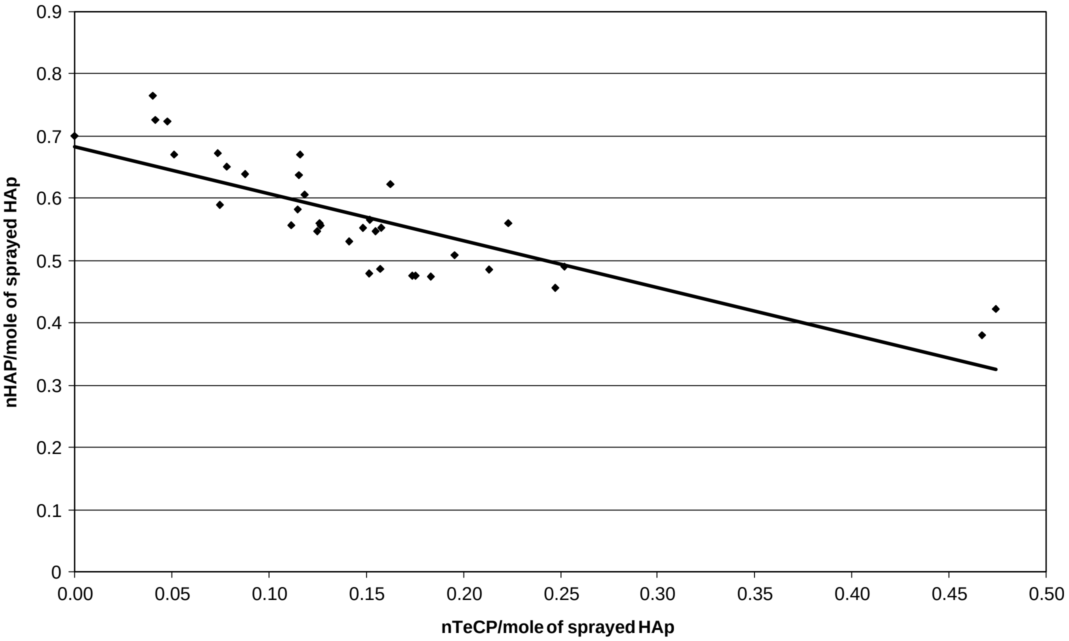


Fig. 3. Number of moles HAp in the coating versus the number of moles TeCP in the coating (*n*HAp or *n*TeCP is the number of moles of HAp or TeCP obtained in the coating per mole of sprayed HAp).

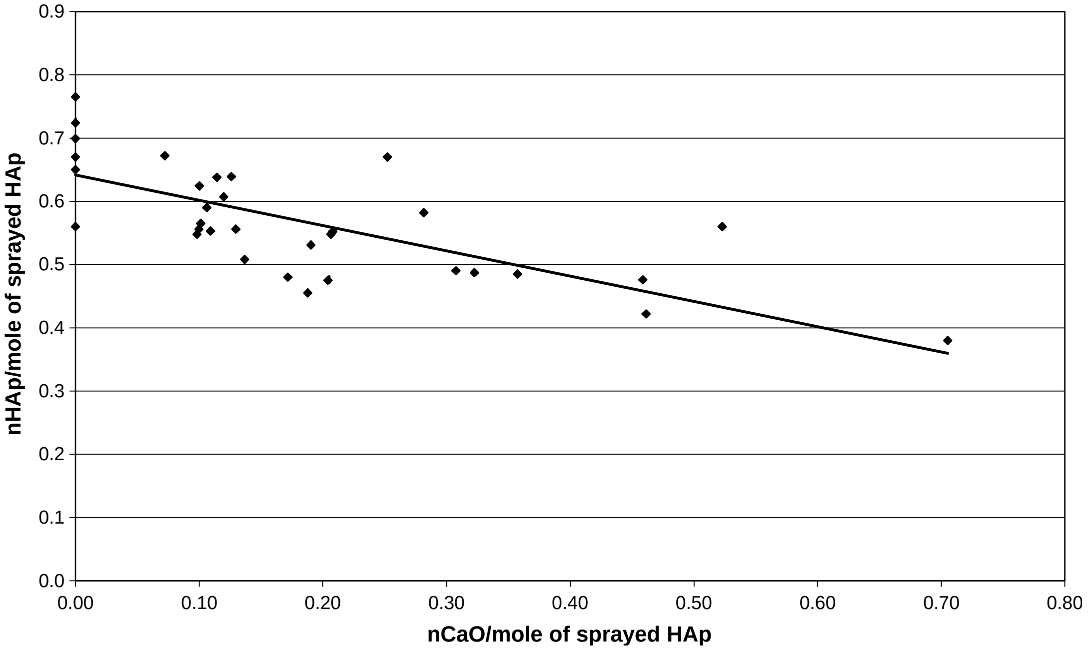


Fig. 4. Number of moles HAp in the coating versus the number of moles CaO in the coating (*n*HAp or *n*CaO is the number of moles of HAp or CaO obtained in the coating per mole of sprayed HAp).

A decrease was observed in the Ca/$P_{\mathrm{amorphous}}$ ratio and in the quantity of HAp, whereas TCP, TeCP, and CaO proportions increased. The Ca/$P_{\mathrm{amorphous}}$ ratio did not depend on the quantity of the amorphous phase.

As shown in Fig. 11, the Ca/$P_{\mathrm{amorphous}}$ ratios lie mainly between 1.50 and 1.67. A third of the samples is in the range 1.55–1.60. Three of the samples appear very distant from these values (Ca/$P_{\mathrm{amorphous}} \approx 1.3$), they were excluded from the discussion.

It can be stressed that the correlation between the Ca/$P_{\mathrm{amorphous}}$ ratio and the proportion of CaO is excellent (Fig. 7).

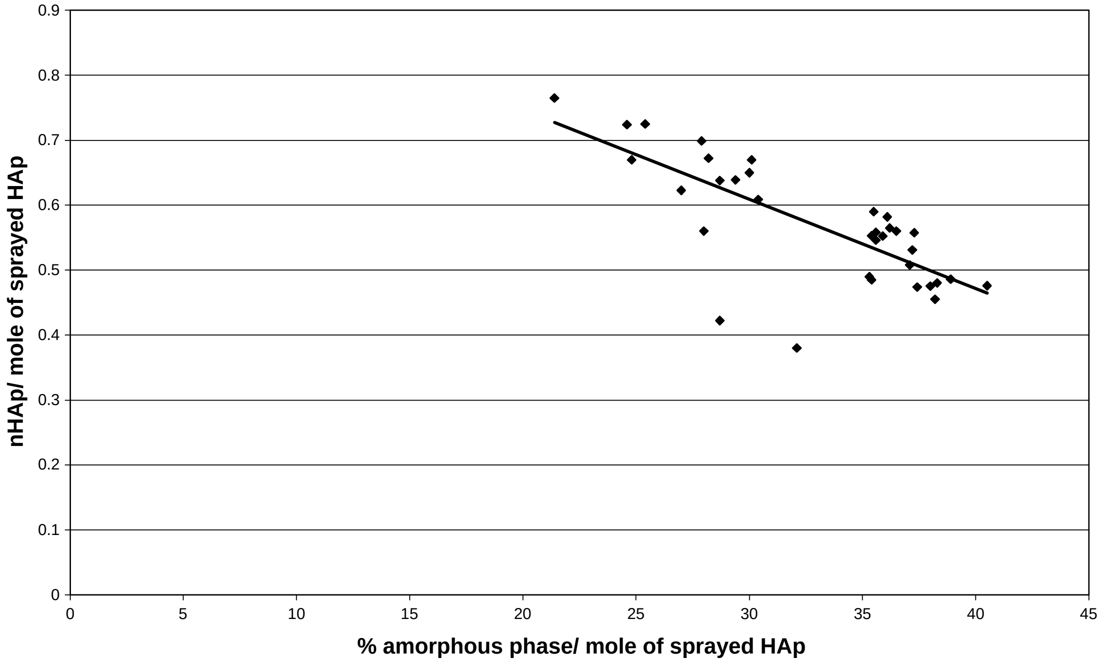


Fig. 5. Number of moles HAp in the coating versus the weight fraction of amorphous phase in the coating (% amorphous phase is the weight fraction of amorphous phase and *n*HAp is the number of moles of HAp obtained in the coating per mole of sprayed HAp).

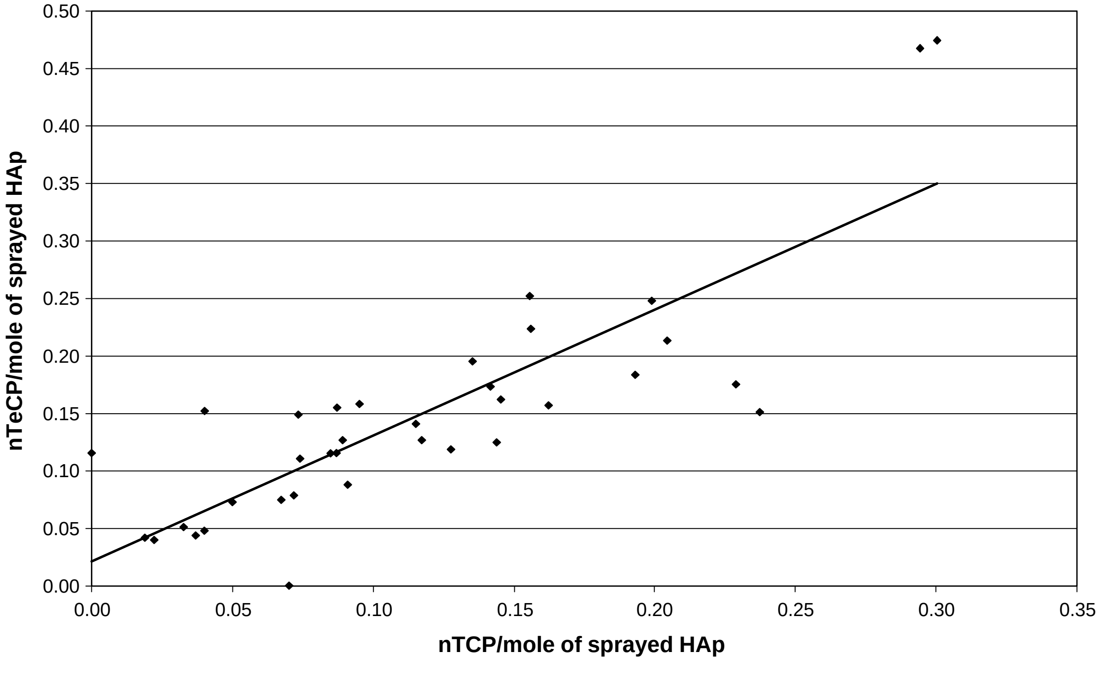


Fig. 6. Number of moles TeCP in the coating versus the number of moles TCP in the coating (*n*TeCP or *n*TCP is the number of moles of TeCP or TCP obtained in the coating per mole of sprayed HAp).

4. Discussion

The physical parameters (such as stand-off distance, gas composition, or particle size, etc.) certainly influence the decomposition of the HAp introduced in the plasma jet, the melting of the various phases formed, and consequently the ratio of all the phases present in the coating. Nevertheless, we are only interested in the physical–chemical mechanisms which occur in the plasma flame and in the coating after

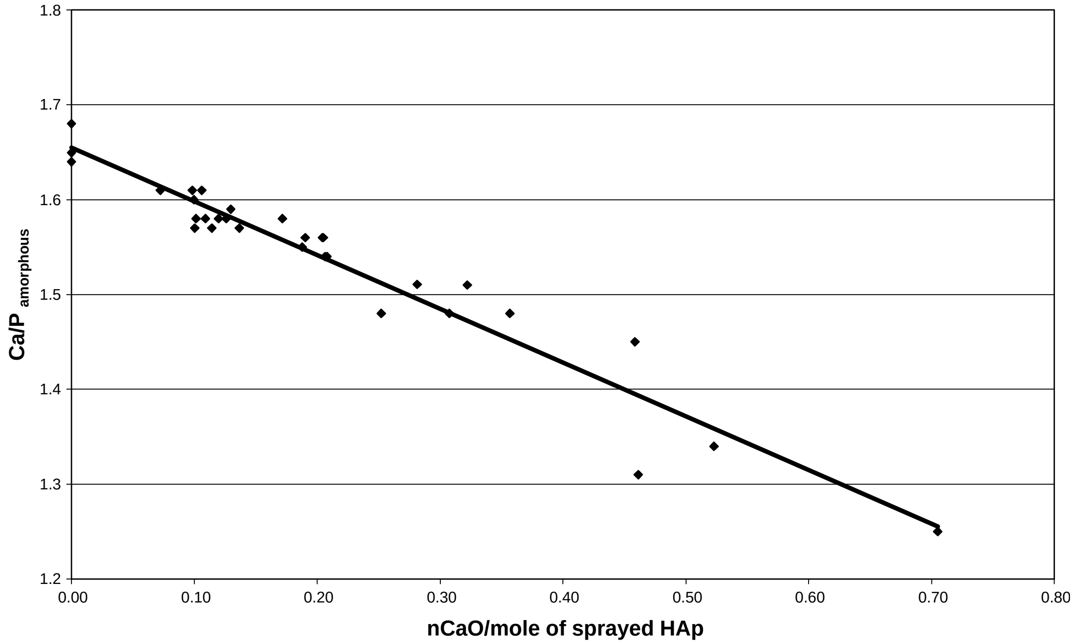


Fig. 7. Ca/P atomic ratio of the amorphous phase versus the number of moles CaO in the coating (*n*CaO is the number of moles of CaO obtained in the coating per mole of sprayed HAp).

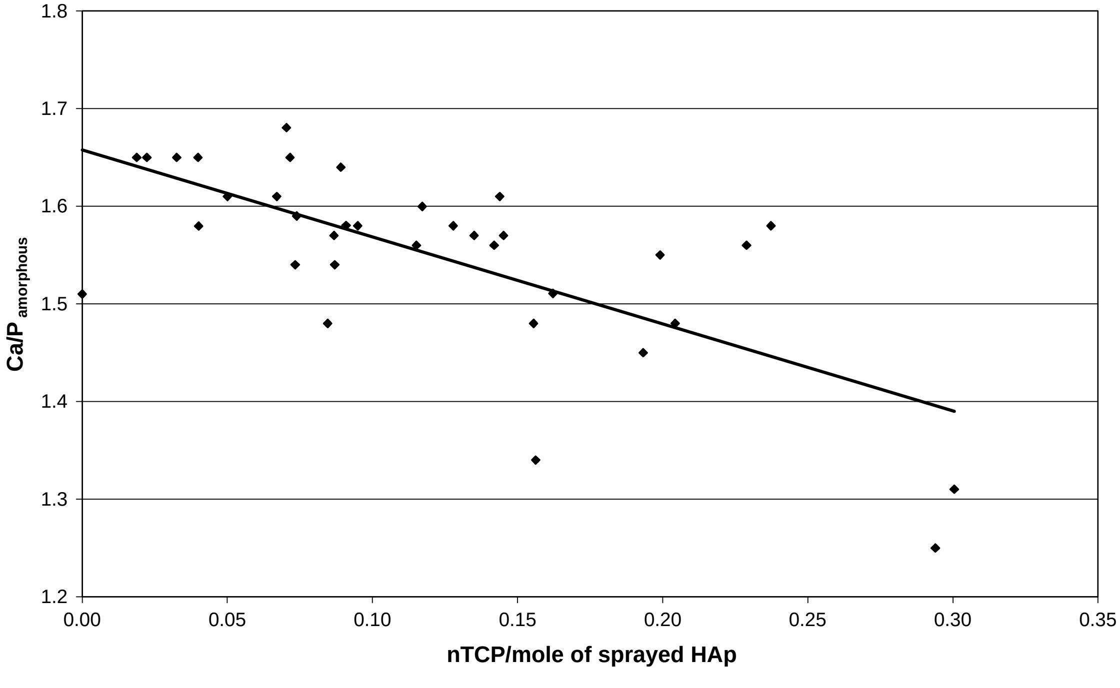


Fig. 8. Ca/P atomic ratio of the amorphous phase versus the number of moles TCP in the coating (nTCP is the number of moles of TCP obtained in the coating per mole of sprayed HAp).

its deposition on the prothesis. These mechanisms remain identical whatever the spraying conditions.

The amorphous phase is produced by the solidification of a molten phase and is representative of the molten phase at the time when it solidifies. The $Ca/P_{amorphous}$ ratio is therefore that of the molten phase. From a thermodynamic point of view, it appears impossible that a phenomenon of solification could lead to the simultaneous formation of both an amorphous phase and crystallized phases. The results obtained on the 35 samples show a $Ca/P_{amorphous}$ ratio lower than 1.67. The histogram (Fig. 11) underlines a large propor-

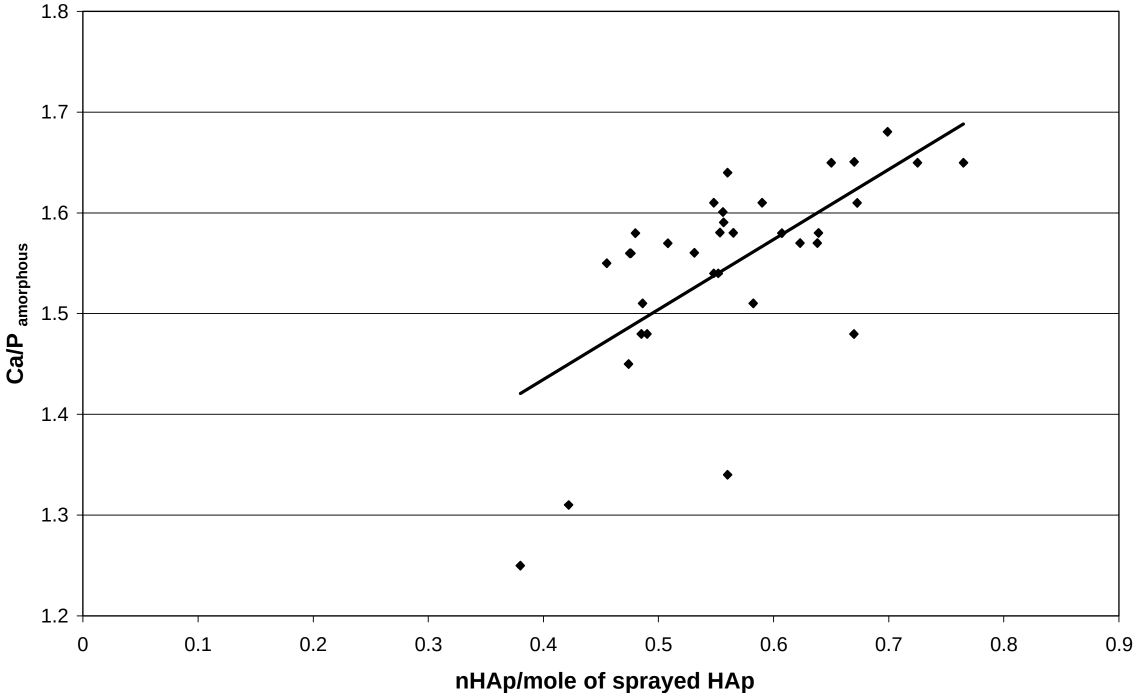


Fig. 9. Ca/P atomic ratio of the amorphous phase versus the number of moles HAp in the coating (*n*HAP is the number of moles of HAp obtained in the coating per mole of sprayed HAp).

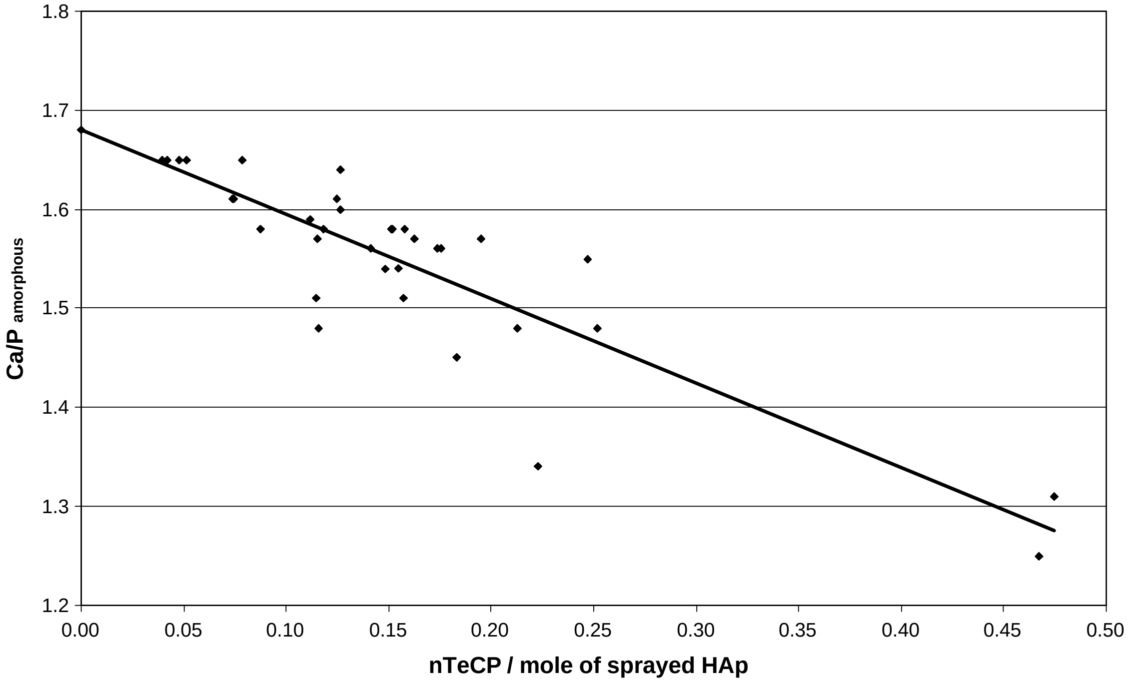


Fig. 10. Ca/P atomic ratio of the amorphous phase versus the number of moles TeCP in the coating (*n*TeCP is the number of moles of TeCP obtained in the coating per mole of sprayed HAp).

tion of the samples in the Ca/P$_{\text{amorphous}}$ ratio range 1.55–1.60, and an almost Gaussian distribution on either side. These values agree with the results suggested by Vogel et al. [10] who did not observe an amorphous phase for a Ca/P ratio lower than 1.50. In their report, the Ca/P$_{\text{amorphous}}$ ratio remained between 1.50 and 1.67.

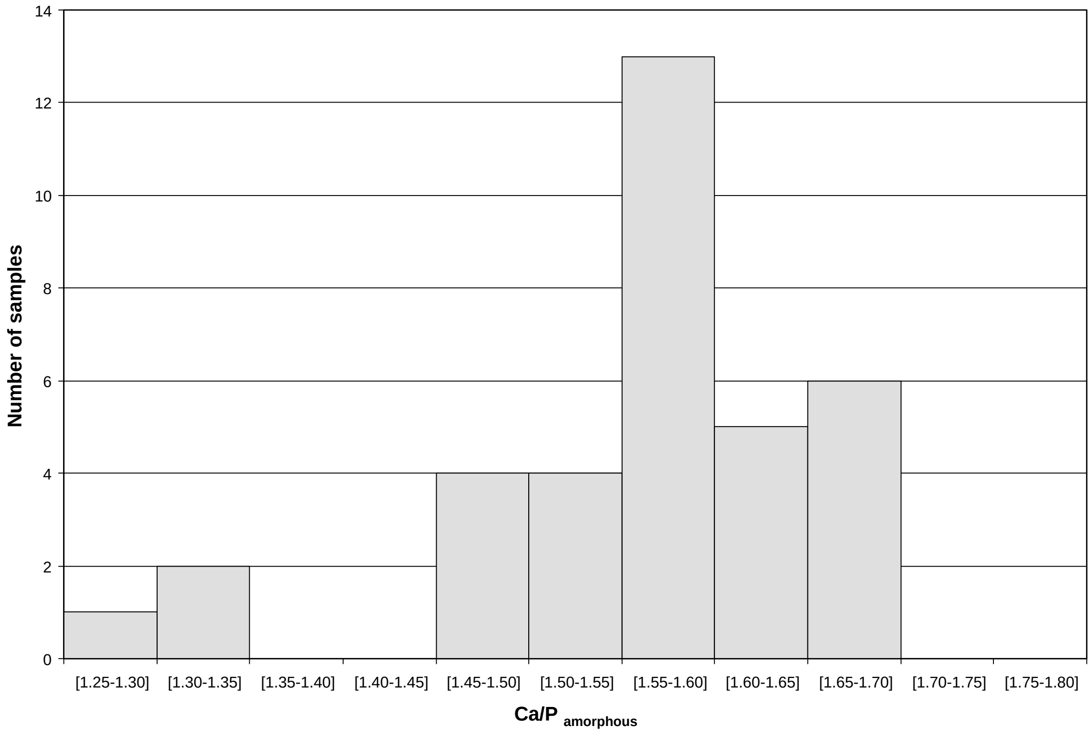


Fig. 11. Histogram of number of samples versus Ca/P atomic ratio of the amorphous phase.

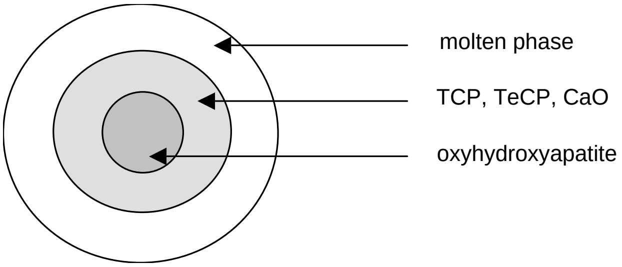


Fig. 12. Effect of the temperature gradient on a plasma-sprayed HAp particle.

Our observations suggest a modification of the molten phase Ca/P atomic ratio (noted Ca/P_{molten}) during the spraying of HAp. Examination of HAp decomposition–fusion and molten phase cooling-solidification stages allows a better understanding of the physical–chemical phenomena which govern the variations of the Ca/$P_{amorphous}$ ratio as well as the appearance of the mineral phases.

4.1. Decomposition-melting of the powder

When HAp is injected into the plasma jet, several phases can coexist under the effect of a temperature gradient occuring in the bulk of the particle (Fig. 12):

- a molten phase formed by surface melting of HAp particles, and which on solidifying gives the amorphous phase;
- phases resulting from the partial decomposition of the oxyhydroxyapatite (OxyHAp) such as TCP, TeCP, and CaO;
- an OxyHAp in the particle core.

A priori each whole system has a total Ca/P atomic ratio of 1.67. The liquid phase is formed by congruent melting of TCP and TeCP resulting from apatite decomposition following the reaction:

$$\text{oxyHAp} \rightarrow 2\text{TCP} + \text{TeCP}$$

in this way the Ca/P_{molten} ratio is fixed at 1.67. The Ca/P_{molten} ratio can vary if there is preferential solubilization of one of the phases (TCP, TeCP or CaO) in contact with the molten phase. Thus, it can tend towards values higher than 1.67 if CaO or TeCP is solubilized, or towards lower values if the melt is enriched in TCP. The quantity of TCP dissolved will be obviously limited by the degree of melting that occurs. Varying the Ca/P_{molten} ratio modifies the CaO/P_2O_5 ratio and consequently leads to the preferential crystallization of mineral phases according to the CaO–P_2O_5 phase diagram (Fig. 13).

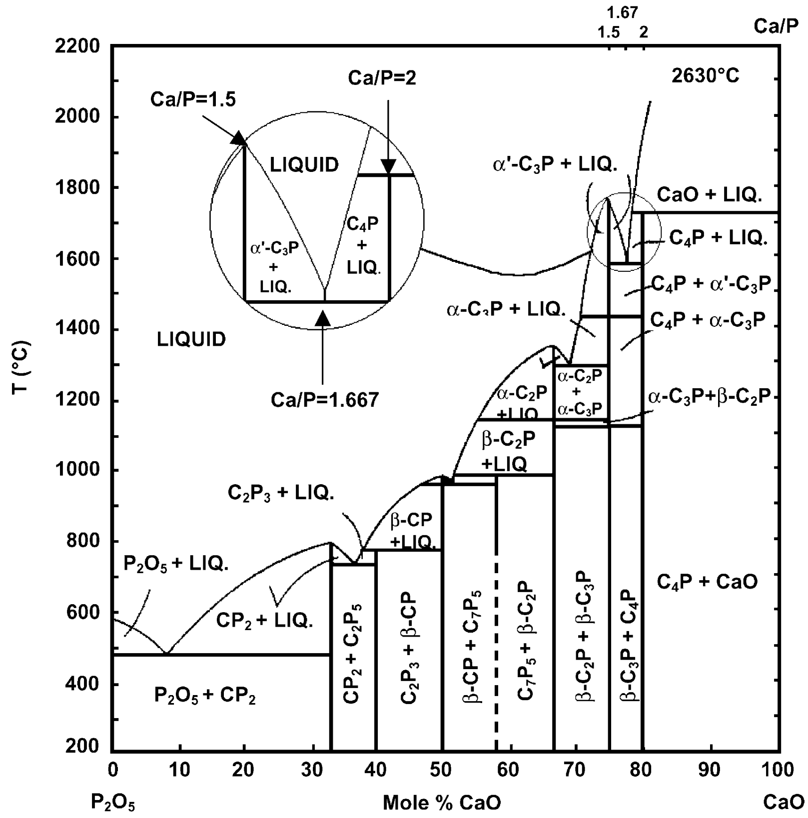


Fig. 13. Phase diagram of the system CaO–P_2O_5 (C = CaO, P = P_2O_5), (according to Kreidler and Hummel [11]).

4.2. Cooling and solidification of the molten phase

After deposition on the prosthesis, the TCP, TeCP and CaO phases resulting from HAp decomposition can either react together to form HAp, or remain as such, as residues. The OxyHAp can transform by hydrolysis to HAp. The OxyHAp often observed in the coatings is exclusively residual.

The molten phase always has a Ca/P ratio lower than 1.67, and similar to that of the amorphous phase. The molten phase can:

- either solidify immediately to form the amorphous phase which can in turn later crystallize to give TCP;
- or cool before solidifying and let TCP crystallize. In fact if one takes into account that the Ca/P_{molten} ratio is lower than 1.67 and if one considers the diagram of the CaO–P_2O_5 phases, TCP must crystallize. However the Ca/P_{molten} ratio remains lower than 1.67 because Ca/$P_{\text{amorphous}}$ is lower than 1.67.

But, whatever the behavior of the molten phase and according to the diagram of CaO–P_2O_5 phases (Fig. 13), there is undoubtedly crystallization of TCP because the Ca/$P_{\text{amorphous}}$ ratio is lower than 1.67. Thus, the congruent melting of TCP and TeCP resulting from HAp decomposition would lead to the formation of a melt with a Ca/P ratio of 1.67 on the particle surface. Then there would be dissolution of TCP produced by decomposition of HAp and, being directly in contact with the molten phase, the Ca/P_{molten} ratio becomes lower than 1.67. The value of the Ca/P_{molten} ratio is conditioned by the quantity of TCP dissolved in the melt. During cooling, certain phases can react between each other: the amorphous phase can crystallize TCP and TeCP without modifying the Ca/$P_{\text{amorphous}}$ ratio (the quantity of TCP and TeCP crystallized depends only on the value of the Ca/$P_{\text{amorphous}}$ ratio), then TeCP and TCP can combine together to form HAp.

The whole set of curves (Figs. 2–10) underlines the generalized simultaneous variation of the following parameters:

- increase of the levels of the TCP, TeCP, CaO and amorphous phase;
- decrease of the proportion of HAp and the Ca/$P_{\text{amorphous}}$ ratio.

For Ca/$P_{\text{amorphous}}$ ratios of 1.50, there are high levels of TCP, TeCP, CaO and amorphous phase, as well as low levels of HAp. If the HAp decomposition rate is high, the production of TCP, TeCP and amorphous phase is high. Part of the TeCP produced is decomposed into TCP and CaO. TCP is almost entirely dissolved to bring the Ca/P$_{\text{molten}}$ ratio towards values close to 1.50. During cooling, the phase that crystallizes from the amorphous phase will be primarily TCP. The amount of TCP formed will increase with the amount of amorphous phase. There cannot be recombination of TCP and TeCP to form HAp because the amorphous phase cannot crystallize TeCP. TeCP present in the coatings is exclusively residual.

For Ca/P$_{\text{amorphous}}$ ratios of 1.67, there are high levels of HAp, and low levels of TCP, TeCP and amorphous phase. CaO is not detected. When HAp decomposition is low, the production of TCP, TeCP and amorphous phase is not very high. TCP is dissolved but the quantities produced being low, the Ca/P$_{\text{molten}}$ ratio cannot be modified in any consequent way, so it remains close to 1.67. TCP can crystallize from the amorphous phase but so can TeCP. The quantities of TCP and TeCP produced remain low because the quantity of amorphous phase is relatively low.

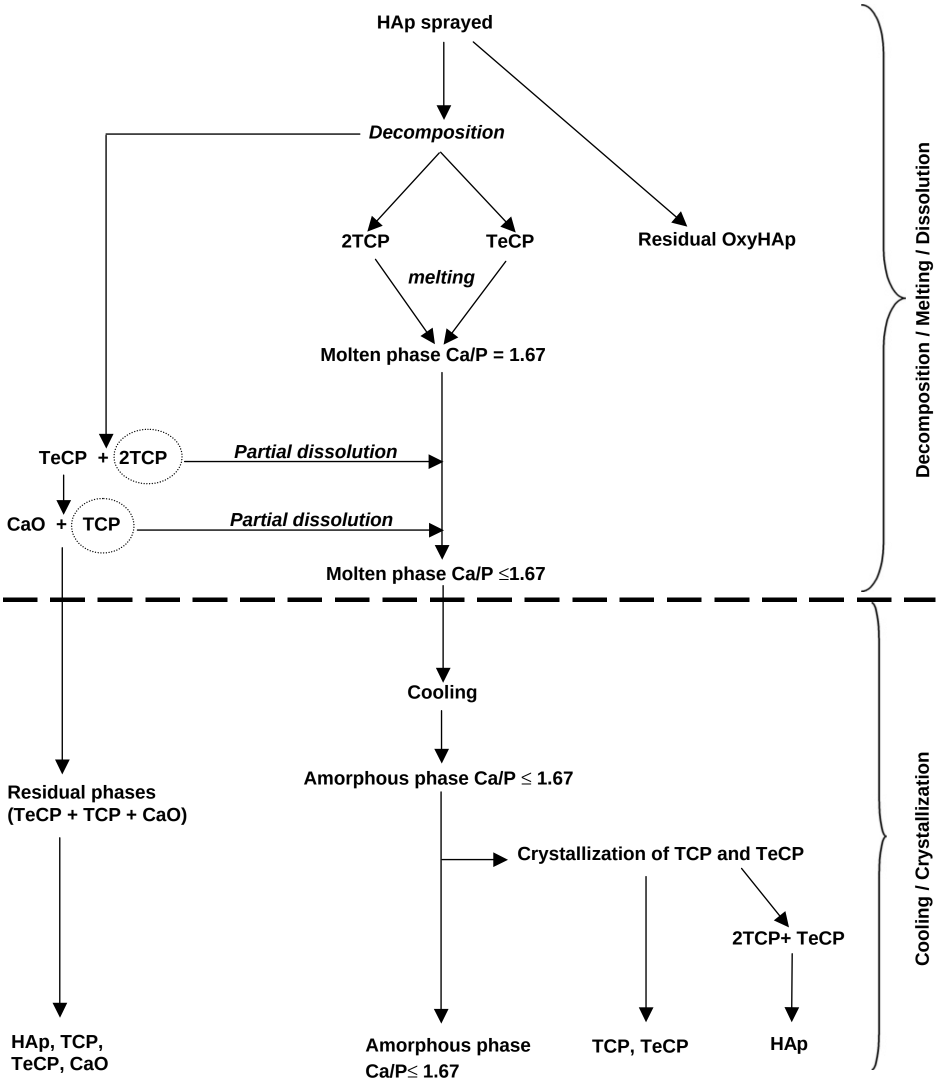
5. Conclusion

After plasma spraying of pure HAp powder, various phases can be observed in the deposit:

- the molten spray gives the amorphous phase;
- the amorphous phase provides part of the TCP, TeCP and HAp;
- HAp decomposes for the remainder of the TCP and TeCP;
- HAp decomposes for CaO and OxyHAp.

The Ca/P atomic ratio of the amorphous phase varies in the range 1.50–1.67 depending on the HAp decomposition rate and the cooling conditions.

The following diagram can be proposed:



Acknowledgments

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