

**Manoj Mittal\*, S.K. Nath, Satya Prakash**

Indian Institute of Technology Roorkee, Department of Metallurgical and Materials Engineering,  
Civil Lines, Roorkee, Uttarakhand, India, Email: [manojmittal74@yahoo.com](mailto:manojmittal74@yahoo.com)

## **SPLAT FORMATION AND DEGRADATION OF HYDROXYAPATITE DURING PLASMA SPRAYING PROCESS**

### **ABSTRACT**

Plasma spraying is most used thermal spray process for coating of bioceramic and bioinert materials. It is line of sight technique, easy to use and inexpensive as compared to other processes used for coatings. The main disadvantage of this technique for coating hydroxyapatite (HA) is that due to high temperature of plasma (of the order of 16000°C) HA tends to degrade into amorphous calcium phosphates. These amorphous phases are not desirable and have a tendency to dissolve in body environment. In this article an attempt has been made to understand the plasma spraying process for coating of hydroxyapatite.

**Keywords:** *plasma spraying, thermal behavior, coating, hydroxyapatite.*

### **PLASMA ARC FORMATION**

Plasma is a complicated phenomenon. It is often referred to as the ‘Fourth State of Matter’, as it differs from solid, liquid and gaseous state and does not obey the classical physical and thermodynamic laws [1]. Plasma are used in many different techniques e.g. for modification activation of surfaces. There is currently much research being carried out into understanding them and controlling them. The actual processes involved in plasma formation are complicated. All gases at a nonzero absolute temperature contain some charged particles, electrons and ions, along with some neutral gas atoms. The charged particles only substantially affect the properties of the gas at concentrations where the space charge found by the particles is large enough to restrict their motion. Dissociation and ionization of the gas leads to free electric charge carriers. As the charge concentration increases, the restriction on particle motion becomes more and more stringent and at sufficiently high concentrations, the interaction of positively and negatively charged particles results in persistent neutrality within the whole gas. Any disturbance of neutrality induces strong electric field, which quickly restore it. The gas is thus termed as quasi-neutral, which means the total density of electrons and negative ions will be equal to density of positively charged ions [1]. An ionized gas at such concentration is called plasma, as coined by American physicist Langmuir, [2].

Due to the nature of plasma, it is necessary to choose the gases that are easily ionized and dissociated. It is also necessary to protect the electrode from oxidation. The argon, helium, hydrogen and nitrogen are the four main gases used for plasma. Both argon and helium are the

monatomic gases while hydrogen and nitrogen are diatomic gases. Diatomic gases must first be dissociated and thus need a larger energy to enter the plasma state, resulting in plasma with higher thermal conductivity than monatomic plasma flame, which needs only to be ionized to enter the plasma [3]. Addition of small quantity of diatomic gas to monatomic gas especially argon leads to enthalpy of plasma, which increases the rate of heat transfer from plasma to powder particles and promotes the melting of powder particles. High enthalpy-containing plasma, by adding hydrogen into air, induces more impurity phases and amorphous contents in as-sprayed coating. The crystallinity of the coating is related to particle size of pristine powder and enthalpy of plasma gas [4].

A re-circulated cooling system prevents the gun components from overheating during spraying and thus increases life of components. The plasma flame is produced by passing a plasma gas through an arc formed between the tip of the cathode and the wall of the anode. The arc frequently fluctuates in length and position due to drag forces of gas flowing and magneto-hydrodynamic forces. Very high velocity and a temperature up to 16600°C can be attained with plasma flame (Sulzer Metco). Particle velocity as high as 2300 m/s has been reported by. The velocity of plasma creates vortex rings that unite and results in large scale eddies which entrain cold surrounding gas [5].

## FORMATION OF COATING

The powder particles are fed into the plasma flame by the carrier gas. During their travel within the flame, being propelled towards the substrate, a high temperature causes them to melt. The degree of particle melt depends upon the amount of heat to which they are exposed, which further depends on heat content of plasma, location of particles in the plasma, velocity and size of particles. As the particles strike the substrate they may be solid un-molten, semi-molten or fully molten and thus within the flame they may be solid, liquid, vapor or a combination of these phases. The possible state (solid, liquid or vapor) of particles as they pass through the plasma are represented in Fig.1.

It can be seen from Fig. 1 that when the outer layer is in molten state, if the flame temperature is less than the particle temperature during the flight of particle in plasma, the outer layer will begin to solidify again (III) and if flame temperature is more than surface temperature of particle, evaporation of liquid will occur, causing dimensions of particle to decrease (V). The HA particles in the plasma exhibit many of these states, particle may melt to greater or lesser extent depending on their individual size, shape and density. The greater the variation in particles in the plasma flame, the greater the degree of variability in their melting. Depending on the flame temperature in plasma spraying, HA may be transform into various phases. The phases that are present in stage V in Fig. 1 are represented in Fig. 2.

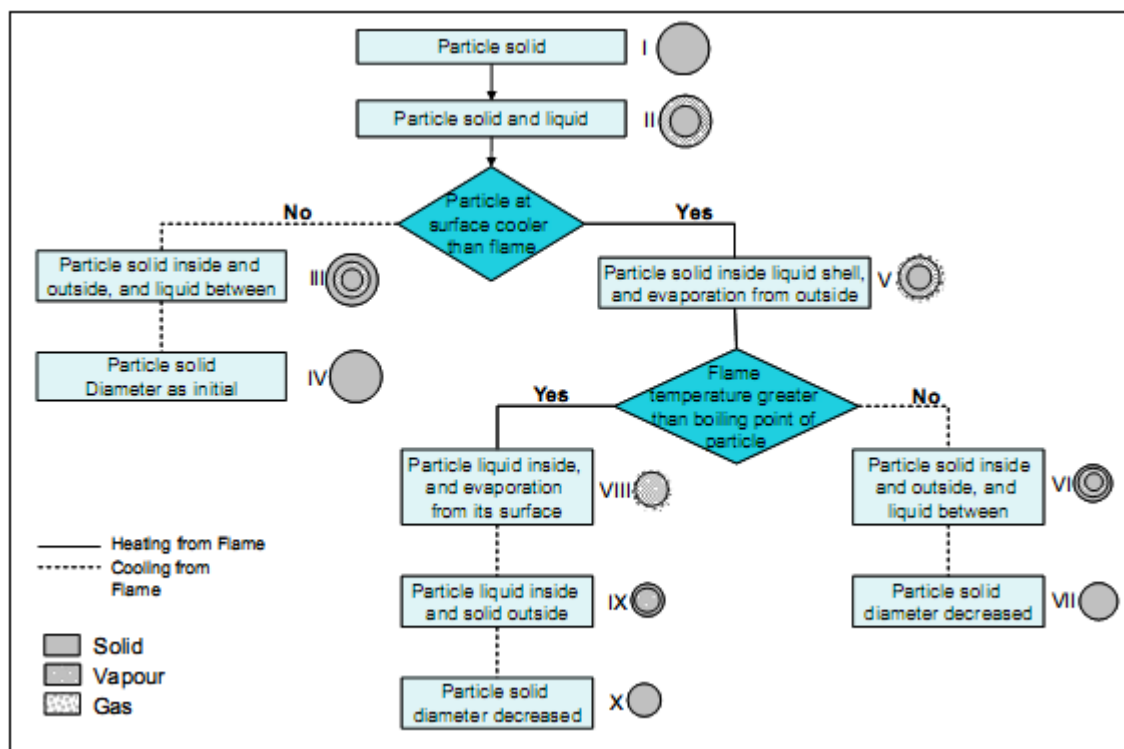


Fig. 1. State of the particles passing through plasma flame [6]

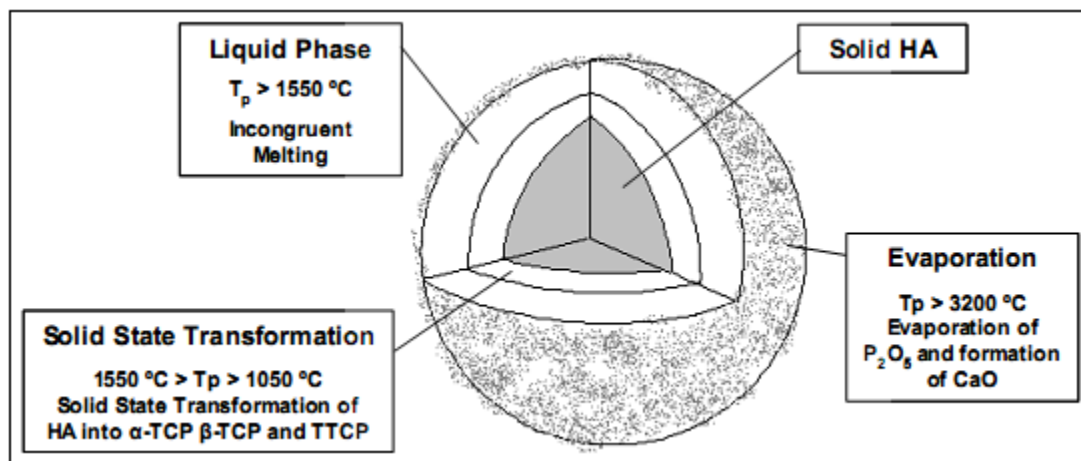


Fig. 2. Transformation inside HA particle in the plasma flame before impact,  $T_p$ : temperature [7]

## MICROSTRUCTURE AND LAMELLA MORPHOLOGY OF COATING

The partially or fully molten particles when come in contact with substrate solidify rapidly due to temperature difference between HA particles and the substrate. Deformation and solidification of partially molten particle occur when it come in contact with the substrate. Due to pressure generated when the particles impinges on the substrate, deformation is first process to occur.

Firstly the particle begins to deform from spherical to cylindrical shape, the time of deformation from sphere to cylinder was estimated as  $10^{-10} - 10^{-9}$ s. The cylinder then expands in radial direction. The degree of deformation and thus the shape of particle depend on a number of properties, such as viscosity and wettability and cooling condition of particles, the powder granularity and surface morphology of substrate. Solidification begins after deformation is completed at the particle substrate interface (or previously deposited layer), as this interface acts as heat sink.

The solidified particles on substrate are called lamella or splat. The solidification time for HA particles has been suggested to be as short as  $10^{-7} - 10^{-6}$ s [8], which further depends on the thermal conductivity of material of substrate and the thickness of any previously deposited lamella on which they impact. The temperature of substrate is affected by heat transfer from both the plasma flame and droplets impacting on it, which can be in excess of  $1000^{\circ}\text{C}$  depending on the spray parameters used [9]. The particles flatten, cool down and solidify so rapidly that the next impinging particulate hit already solidified lamella [10]. Successive impacting particles cause lamella to built-up to form the coating. One pass of plasma gun generally produces a coating layer of about 10 – 15 lamellae thick. Between the depositions, reaction between the surface of deposited lamella and surrounding environment may occur, such as absorption of water or oxidation. The number of lamellae deposited depends on the requirements of the thickness of coating.

Particle size, velocity and temperature have been recognized as plasma spray conditions that have a greatest influence on lamella formation [11]. The properties of substrate or previously deposited layer also effect the lamella formation. The lamella may exhibit one of the two principle morphologies: pancake or flower as represented in Fig. 3.

The effect of plasma gas flow rate, percentage of secondary gas, velocity and temperature of plasma and particle on splat characteristics was investigated by Yankee and Pletka [11]. The results showed that the splat size was inversely proportional to the plasma velocity, with smaller droplets being formed at high plasma velocity. This was thought to be due to shorter residence time of the HA particles in the flame leading to less superheating of droplets. Relatively low plasma velocity was observed to produce large lamellae.

Hotter plasma conditions produced lamellae of ‘pancake’ while less hot plasma conditions produced ‘flower’ morphology. The formation of arms of the ‘flower’ lamellae depend on the viscosity of molten particles. The appearance of the ‘flower’ splat shows that solidification occurred after the effect of surface tension became dominant over viscous flow forces. The size and the mass of the particles were also seen to influence the splat characteristics, larger particles being more likely to create ‘flower’ morphology. A variety of lamellae can be obtained in one spraying operation, because the particles due to their different size and injection velocity distribution, experience different trajectories and thus different thermal and momentum histories [10].

he structure of the coating at grain level is termed as ultrastructure. Examination of the ultrastructure of a coating looks at the crystals that are formed during recrystallization. The size and structure of crystals formed depend on the phenomenon that occurs inside each newly generated coating layer. The microstructural features such as pores, cracks and splat boundaries influence the coating quality. During the solidification crystals generally grows in on preferential direction within the splat. Two types of lamellae generally forms during recrystallization, either columnar or fine grained equiaxed also referred as brick wall [6]. Fine grained equiaxed crystals grow parallel to the surface. Both types of ultrastructures are represented in Fig. 4. The dimensions of crystal in thermal spray coating are of nanometer range.

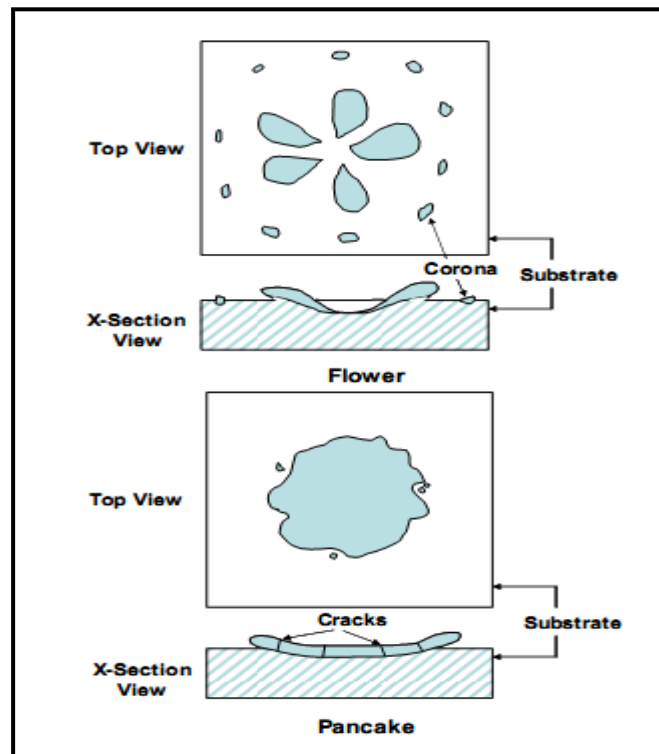
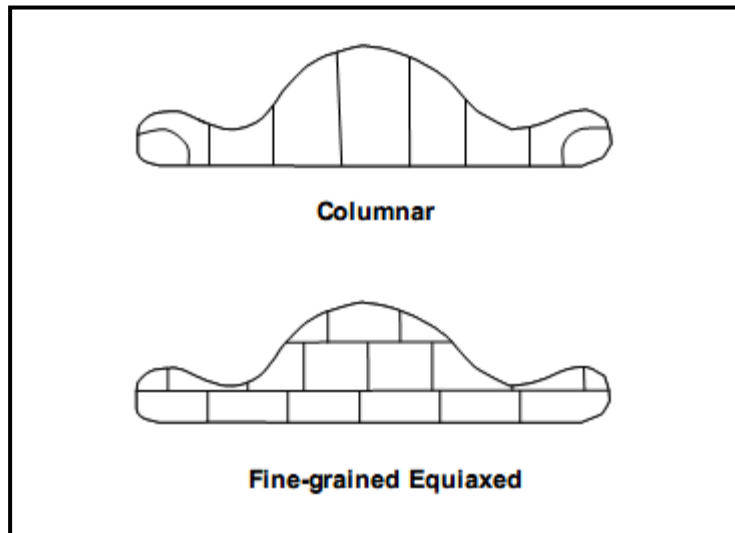


Fig. 3. Splat morphologies of particle by plasma spray process [6]

The rapid cooling and solidification generally results in columnar ultrastructure, while the slow heat removal rate at interface results in fine-grained equiaxed microstructure [6]. If the cooling rate is very high, the coating may solidify before any crystals can be formed which leads to higher contents of amorphous phases in the coating [12]. The variation of grain size and phase stability of HA coating as a function of coating thickness is reported by Yankee and Pletka, [11]. Crystal size of the initial layers is very small as rapid cooling and rapid solidification at substrate restrict crystal growth. The size of the crystal increases from interface towards coating surface due to smaller cooling rates [13-14].

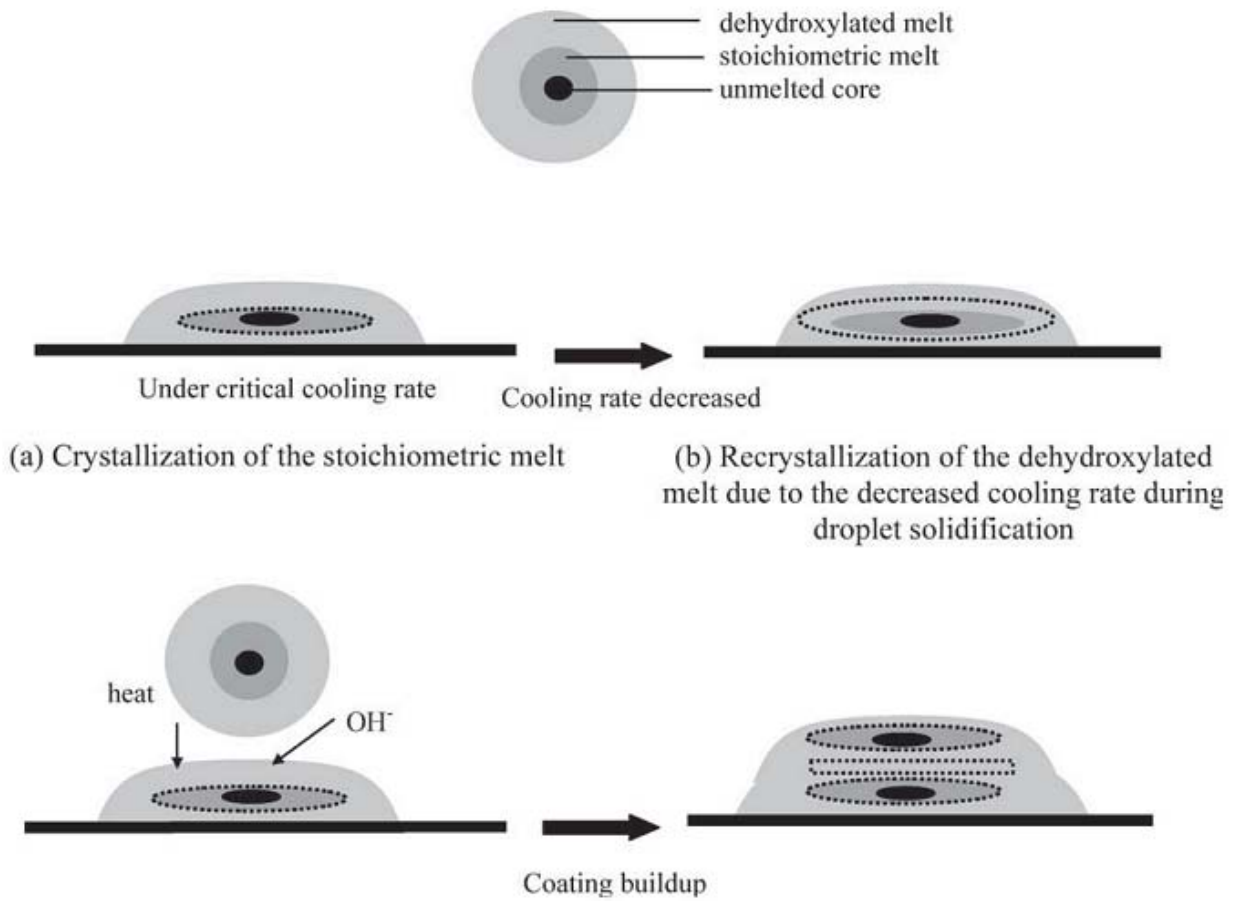


**Fig. 4.** Ultrastructure of lamellae resulting after recrystallization [6]

The solidified splat is affected by the heat content of incoming molten splat. The amorphous phases in the already solidified splats can be recrystallized by heat of incoming molten splat, heat content of plasma and re-hydroxylation process. The detailed process of the mechanism is explained in Fig. 5.

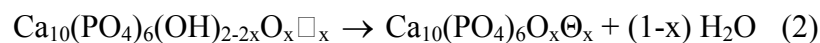
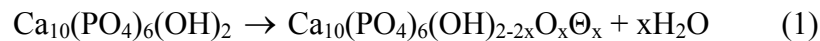
### **THERMAL BEHAVIOR OF HA**

The plasma spray process involves high temperatures; the plasma flame temperature can be as high as 16600°C depending upon the application involved. Thermal decomposition and change of phase occur when HA particles come in contact with high temperature. This leads to HA coating with significantly different crystal structure, phase composition and morphology than starting powder. Three processes occur by heating HA: evaporation of water, dehydroxylation and decomposition.



**Fig. 5.** Recrystallization of amorphous phase in prior formed splat due heat from incoming molten splat and plasma flame and re-hydroxylation during coating built-up [15]

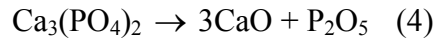
HA easily absorbs water which is present both on the surface and trapped in the pores [16]. Low temperature heating of HA results in evaporation of absorbed water and this is recommended before the powder is fed into the hopper of plasma spray system. At high temperature, dehydroxylation occurs where HA gradually loses its hydroxyl (OH<sup>-</sup>) group. Following reactions represent the dehydroxylation process.



Where  $\Theta$  is vacancy and  $x < 1$

Equation 1 involves the formation of hydroxyl ion deficient product, known as oxy-hydroxyapatite (OHA). The OHA has a large number of vacancies in its structure, a bivalent oxygen ion and a vacancy substitute for two monovalent OH<sup>-</sup> ions of HA [17]. Further dehydroxylation leads to the formation of oxy-apatite. Oxy-hydroxyapatite and oxy-apatite rapidly retransform into HA in presence of water [18].

Below a certain critical point of temperature, HA retains its crystal structure, however, once the critical point exceeded, complete and irreversible dehydroxylation results. This process is called decomposition, which leads to formation of other calcium phosphate phases, such as  $\beta$ -tricalcium phosphate and tetracalcium phosphate. The following reaction shows the formation of various phases of HA:



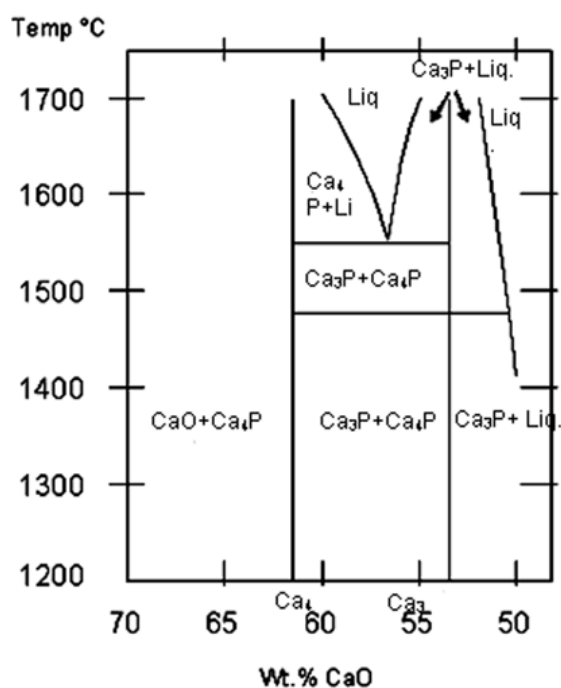
The stoichiometry of HA powder and partial pressure of water in surrounding atmosphere have the greatest effect on the phase formation when HA is heated. The consequences of changing these have been investigated by many researchers [17, 19, 20]. Fang et al. [19] from experiments in which HA powders with Ca/P ratio of 1.52 – 1.68 were heated to 1100°C showed the effect of stoichiometry on the thermal stability of HA. The results showed that the powder with Ca/P ratio of 1.57 fully decomposed to TCP, the powder with Ca/P ratio of 1.67 partially decomposed to TCP, while no change was observed to the powder with Ca/P ratio of 1.68. Tampieri et al. [21] reported that stoichiometric HA endures thermal treatment at significant higher temperature in respect to non-stoichiometric HA.

The thermal behavior of CaO-P<sub>2</sub>O<sub>5</sub> system at high temperature without presence of water vapor is shown in Fig. 6, while Fig. 7 represents the thermal behavior of CaO-P<sub>2</sub>O<sub>5</sub> system at high temperature in presence of water vapors. It can be seen from Fig. 6 that HA is not stable under these conditions and various calcium phosphates including TTCP (Ca<sub>4</sub>P), TCP (Ca<sub>3</sub>P), monetite (Ca<sub>2</sub>P) and mixture of calcium oxide (CaO) and Ca<sub>4</sub>P.

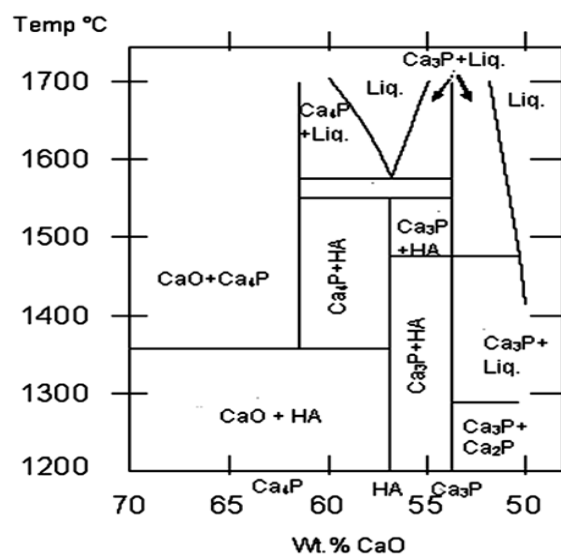
Figure 7 shows the CaO-P<sub>2</sub>O<sub>5</sub> system at a partial water pressure of 500 mm of Hg. Under these conditions HA is found to be stable up to a maximum temperature of 1550°C. The Ca/P ratio is generally not exactly equal to 10/6, hence other calcium phosphates such as CaO or TTCP are also stable at this temperature. It can be concluded that in order to avoid dehydroxylation and decomposition of HA during thermal spraying a highly crystalline, stoichiometric HA powder should be used.

Although there is agreement between researchers about the processes that occurs during thermal decomposition of HA, it is difficult to predict the exact temperature at which these reactions take place. This is because of the reason that reaction does not occur instantly but take place over a wide range of temperature. Researchers have used several techniques to determine the effect of temperature on HA, such as Thermogravimetric Analysis (TGA) [21–22], Differential Thermal Analysis (DTA) [20, 23], X-ray Diffraction (XRD) and Fourier Infrared Spectroscopy (FTIR) [16].





**Fig. 6.** Phase equilibrium diagram of calcium phosphates ( $\text{CaO-P}_2\text{O}_5$ ) at high temperature [24]



**Fig. 7.** Phase equilibrium diagram of calcium phosphates ( $\text{CaO-P}_2\text{O}_5$ ) at high temperature in water atmosphere [2]

The evaporation of water from hydroxyapatite has been reported to occur in a wide range of temperature ( $25^\circ\text{C} - 600^\circ\text{C}$ ) [17, 20-22]. The total weight loss of absorbed water is reported to be as high as 6.5 wt% [22]. The ranges of temperature in which reactions occur as HA is heated from room temperature to  $1730^\circ\text{C}$  are summarized in Table 1.

**Table 1.** Thermal Effects of Hydroxyapatite

Temperature	Reaction
25 – 600°C	Evaporation of absorbed water
600 – 800°C	Decarbonation
800 – 900°C	Dehydroxylation of HA forming partially dehydrated (OHA) or completely dehydroxylated oxy-apatite
1050 – 1400°C	HA decomposes to form $\beta$ – TCP and TTCP
<1120°C	$\beta$ – TCP is stable
1120 – 1490°C	$\beta$ – TCP is converted to $\alpha$ – TCP
1550°C	Melting temperature of HA
1630°C	Melting temperature of TTCP, leaving behind CaO
1730°C	Melting of TCP

## CONCLUSIONS

Following conclusion may be drawn from this review article.

1. Melt fraction of HA particles in plasma spraying depends upon temperature of plasma, particle size, particle velocity and time for which it has been exposed to plasma.
2. The shape of splat depends upon the temperature of plasma.
3. The recrystallization of amorphous phases of solidified splats depends upon heat content of incoming molten splat and plasma absorption of water from atmosphere during spraying (dehydroxylation).
4. HA degrades to amorphous phases such as tricalcium phosphate, tetracalcium phosphate, CaO and other hydroxyl deficient compounds.

## REFERENCES

1. Rossnagel S. M. Cuomo J. J. Westwood W. D.: Handbook of plasma processing technology: fundamentals, etching, deposition and surface interaction, Noyes Publication, Park Ridge, N.J 1990.
2. Golant V. E. Zhilinsky A. P. Sakharov I. E. Brown S. C.: Fundamental of plasma physics, Wiley, New York 1980.
3. Leung K. Heberlein J. Pfender E.: Particle trajectory control with the use of different carrier gases, Proc. of 8<sup>th</sup> National Thermal Spray Conference on Thermal Spray Science and Technology, (ed.) Berndt C. C. Sampath S., Houston, Texas, 1995.
4. Wolke J. G. C. Klein C. P. A. T. de Groot K.: Bioceramics for maxillofacial applications, bioceramic and the human body, (ed.) Ravaglioli A. Krajewski A. Elsevier, Amsterdam, 1991
5. Fauchais P.: Understanding plasma spraying, J. Physics: Applied Physics, 37 (2004), R86
6. Pawlowski L.: the science and engineering of thermal spray coatings, Wiley, New York 1995.
7. Dyshlovenko S. Pateyron B, Pawlowski L. Murano D.: Numerical simulation of hydroxyapatite powder behavior in plasma jet, Surf. Coat. Technol., 179 (2004), 110-117.

8. Tong W. Yang Z. Zhang X. Yang A. Feng J. Cao Y. Chen J.: Studies of diffusion maximum in x-ray diffraction pattern of plasma-sprayed hydroxyapatite coatings, *J. Biomed. Mater. Res.*, 40 (1998), 407-413.
9. Oosterbos C. J. M. Rahmy A. I. A. Tonino A. J. Witpered W.: High survival rate of hydroxyapatite-coated hip prostheses 100 consecutive hips followed for 10 years, *Acta Orthop. Scand.*, 75 (2004), 127-133.
10. Fantassi S. Vardelle M. Fauchais P. Moreau.: Investigation of the splat formation versus different particulate temperature and velocities prior to impact, *Proc. Thermal Spray: International Advances in Coatings Technology*, (ed.) Berndt. C. C., 13<sup>th</sup> International Thermal Spray, Orlando, Florida 1992
11. Yankee S. J. Pletka B. J.: Microstructural analysis of impacted hydroxyapatite droplets, *Proc. Thermal Spray: International Advances in Coatings Technology*, (ed.) Berndt C. C. 13<sup>th</sup> International Thermal Spray, Orlando, Florida, 1992
12. Tong W. Yang Z. Zhang X. Yang A. Feng J. Cao Y. Chen J.: Studies on diffusion in x-ray diffraction patterns of plasma sprayed hydroxyapatite coatings, *J. Biomed. Mater. Res. Vol.* 40 (1998), 407-413.
13. Le Geros R. Z. Le Geros, J. P.: *Dense Hydroxyapatite, An introduction to bioceramics*, (ed.), Hench L. L. Wilson J. World Scientific, London, 1993, 139-180
14. Ji H. Pinton C. B. Marquis P. M.: Microstructural characterization of hydroxyapatite coatings on titanium, *J. Mater. Sci.-Mater. Med.*, 3, (1992), 283
15. Sun L. Christopher Bernd, C.C. Grey C.P.: Phase, structural and microstructural investigations of plasma spray hydroxyapatite coatings, *Mater. Sci. Eng. A*, 36 (2003), 40-84.
16. Liao C. Lin F. Chen K. Sun J.: Thermal decomposition and reconstitution of hydroxyapatite in air atmosphere, *Biomaterials*, 20 (1999), 1807-1813.
17. Sridhar T. M. Kamachi Mudali U. Subbaiyan M.: Sintering atmosphere and temperature effect on hydroxyapatite coated type 316l stainless steel, *Corros. Sci.*, 45 (2003) 2337-2359.
18. Heimann R. B.: Thermal spraying of biomaterials", *Surf. Coat. Technol.*, 201 (2006), 2012-2019.
19. Fang Y. Agrawal D. K. Roy D. M.: Thermal stability of hydroxyapatite, hydroxyapatite and related material, (ed.) Brown P. W. and Constantz B. CRC Press, London, 1994
20. Park E. Condrate Sr. R. A. Lee D. Kociba K. Gallagher P. K.: Characterization of hydroxyapatite: before and after plasma spraying, *J. Mater. Sci. Mater. Med.*, 13 (2002), 211-218.
21. Tampieri A. Celotti G. Sprio S. Mingazzini C.: Characterization of synthatic hydroxyapatite and attempt to improve their thermal stability, *Mater. Chem. Phys.*, 64 (2000), 54-61.
22. Lazic S. Zee S. Miljevic N. Milonjic S.: The effect of temperature on the properties of hydroxyapatite precipitated from calcium hydroxide and phosphoric acid, *Thermochim. Acta*, 374 (2001), 13-22.
23. Deram V. Minichiello R. Le Maguer A. Pawlowski L. Murano D.: Microstructural characterization of plasma sprayed hydroxyapatite coatings, *Surf. Coat. Technol.*, 166 (2003), 153-159.
24. Klein C. P. A. T. Wolke J. G. C. de Groot K.: Stability of calcium phosphate ceramics and plasma spary coating, 'In' *An Introduction to Bioceramic*, (ed.) Hench L. L. Wilson J. World Scientific, London, 192-221, 1993