

# Thermodynamic Calculation for Laser Synthesizing Hydroxyapatite Composite Coating

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**Abstract**—Thermodynamic calculation for main reactions happening in the process of fabricating hydroxyapatite(HA) composite coating by laser cladding using the mixture of the calcium carbonate ( $\text{CaCO}_3$ ) and calcium hydrogen phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) is carried out to obtain a high content of HA in coating. The experiments are conducted to verify the thermodynamic analysis and find ways to optimize process parameters. It indicates that HA can be obtained when the temperature is below 1500K, and the  $\text{CaTiO}_3$  is easier to form when the temperature exceeds 1300K.

**Keywords**—thermodynamic calculation; bioceramic composite coating; hydroxyapatite; laser cladding

## I. INTRODUCTION

The bio-ceramic coating of HA on metal substrate is an ideal implant for replacing natural bones, which combines the superior mechanical properties of metal and the excellent bioactivity and biocompatibility of HA. At present, various deposition techniques, such as plasma spraying, pulsed laser deposition, ion-beam sputtering and electrophoresis deposition, have been applied to fabricate thin HA coatings on metal substrate. Plasma spraying is the major method commercially available for coating implant devices with HA due to its high deposition rate and the ability to coat large areas [1]. However, the common disadvantage of these methods is the weak adhesive strength of coating which restricts its application and service life. Therefore, there is indeed a need for the development of new alternative techniques to produce better coating. Researchers proposed laser cladding which is a well-known technique in the metallurgical field. This method enhances the bond strength between coating and substrate, moreover, it can apply coatings onto three-dimensional surfaces and ensure precise treatment of the pieces. There are two raw materials fabricating HA coating on titanium substrate by laser cladding: the raw HA and the mixture of the calcium carbonate ( $\text{CaCO}_3$ ) and calcium hydrogen phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). The former one requires high quality of HA which increases coats. Additional, HA is easy to decompose and react with Ti substrate under high temperature. So this paper focuses on the later. However, the coating fabricated by this way would

appear the matter  $\text{CaTiO}_3$  which is produced by unintended reactions.

The purpose of this work is to evaluate the feasibility to fabricate HA on titanium substrate by laser cladding using  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  through the calculation of the Gibbs free energy for key reaction producing HA and comparison with the Gibbs free energy for reactions which can produce  $\text{CaTiO}_3$ . Furthermore, the experiment of laser synthesizing HA coating on TC4 substrate by  $\text{CO}_2$  laser is conducted to prove the thermodynamic analysis.

## II. EXPERIMENTAL

The mixture of  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  whose molar ratio of Ca/P is about 1.5 and pure Ti powders are used as the materials of coating. The all powders mixed together with polyvinyl alcohol (PVA) are manually preplaced on the thin plate of TC4. The laser cladding process is carried out using a 5kW  $\text{CO}_2$  laser equipped with X-Y table. The laser processing parameters are shown in Table I. Argon is used as the shielding gas. The phases of coating are analyzed by X-Ray diffraction (XRD), and the XRD pattern is recorded using Cu target  $\text{K}_\alpha$  radiation.

TABLE I. LASER CLADDING PARAMETER

No.	Ca/P ratio	Power (kW)	Travel speed (mm/min)	Spot size ( $\text{mm}^2$ )
1	1.5	1.8	120	12X1
2	1.5	1.8	240	12X1

## III. THERMODYNAMIC CALCULATION

### A. Thermodynamic Principle

According to the thermodynamic law, the direction of spontaneous and equilibrium state of reaction process are decided by the state function of free enthalpy (G or F) or entropy (S). Due to the actual reaction process can be regarded as an isobaric process, the state functions of the Gibbs free

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energy  $G$  is selected as the criterion that determine whether process happens spontaneously, which is:

$$\Delta G = \Delta H - T \cdot \Delta S \quad (1)$$

where  $\Delta H$  is the enthalpy change of process,  $\Delta S$  is the entropy change of process and  $T$  is the Kelvin temperature.

The result  $\Delta G < 0$  means that the process can happen spontaneously. But when  $\Delta G = 0$ , it indicates the process reaches equilibrium state.

Based on the Kirchhoff's law, matter B changes from 298K to  $T$  under standard state, the molar enthalpy  $H(T)$  is:

$$H(T) = \Delta_f H^0 + \int_{298}^T C_p dT + \sum \Delta H' \quad (2)$$

where  $\Delta_f H^0$  is the standard heat of formation for matter B,  $\Delta H'$  is the molar phase transition heat for B,  $C_p$  is the isobaric heat capacity. It is a function that depends on temperature  $T$ , which is:

$$C_p = a + b \times 10^{-3} T + c \times 10^{-5} T^{-2} + d \times 10^{-6} T^2 \quad (3)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are the heat capacity temperature coefficients.

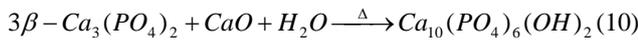
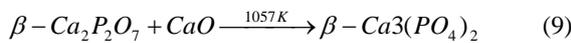
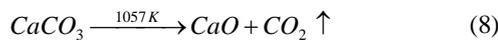
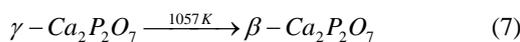
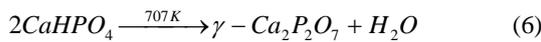
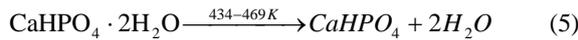
The enthalpies, entropies and heat capacity temperature coefficients of the reactants and product can be obtained by going through thermodynamic data sheet [2].

### B. Thermodynamic Calculation for HA

The overall chemical reaction of laser synthesizing HA coating by  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  can be represented as:

$$4\text{CaCO}_3 + 6\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 4\text{CO}_2 + 14\text{H}_2\text{O} \quad (4)$$

However, the mixture of  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  would experience complicated reactions[3], including:



During heating process,  $\text{CaO}$  and  $\text{Ca}_3(\text{PO}_4)_2$  are all easy to form, so (10) is the crucial reaction to synthesize HA. Therefore, the thermodynamic analysis of the reaction (10) is conducted to estimate whether HA can be synthesized by laser cladding using the mixture.

According to Hess's law, the enthalpy change for any chemical or physical process is independent of the pathway or number of steps required to complete the process provided that

the final and initial reaction conditions are the same. In order to calculate the Gibbs free energy change of (10), the reaction process is assumed to be divided to three steps: isotonic cooling down process of reactants, reacting process in standard state and isotonic warming up process of products, which is shown in Fig. 1[4]. And the total enthalpy (entropy) of (10) is the sum of the enthalpy (entropy) of three processes.

$$\Delta H_m(T) = \Delta H_1 + \Delta H_2 + \Delta H_m(298) \quad (11)$$

$$\Delta S_m(T) = \Delta S_1 + \Delta S_2 + \Delta S_m(298) \quad (12)$$

where  $\Delta H_1$  and  $\Delta S_1$  are the variables of the enthalpy and entropy of reactants during isotonic cooling down process,  $\Delta H_2$  and  $\Delta S_2$  are the variables of the enthalpy and entropy of products during isotonic warming up process,  $\Delta H_m(298)$  and  $\Delta S_m(298)$  are the standard molar reaction enthalpy and entropy of (10) at 298K.

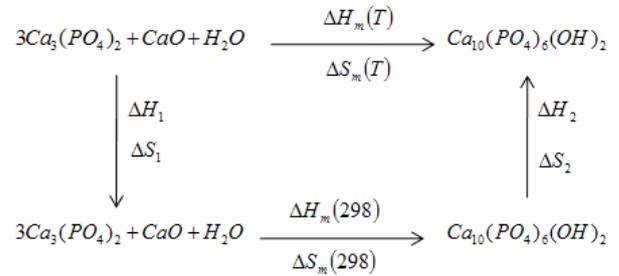


Figure 1. Schematic illustration of reaction process with different routes

Due to the difference of heat capacity temperature coefficients in different temperature range and the phase transition of matters, the temperature range of process is divided into 298K-800K, 800K-1373K and 1373K-1500K.

The thermodynamic calculation from 298K to 800K can be represented as follows:

$$\Delta H_1 = \int_T^{298} (3C_p(\text{Ca}_3(\text{PO}_4)_2) + C_p(\text{CaO}) + C_p(\text{H}_2\text{O})) dT \quad (13)$$

$$\Delta S_1 = \int_T^{298} \frac{(3C_p(\text{Ca}_3(\text{PO}_4)_2) + C_p(\text{CaO}) + C_p(\text{H}_2\text{O}))}{T} dT \quad (14)$$

$$\Delta H_m(298) = \sum_B \nu_B \Delta_f H_B^0 \quad (15)$$

$$\Delta S_m(298) = \sum_B \nu_B \Delta_f S_B^0 \quad (16)$$

$$\Delta H_2 = \int_{298}^T C_p(\text{HA}) dT \quad (17)$$

$$\Delta S_2 = \int_{298}^T \frac{C_p(\text{HA})}{T} dT \quad (18)$$

According to Hess's law, the enthalpy change and the entropy change for (10) can be obtained by plugging aforementioned formulas into (11) and (12). And then, the Gibbs free energy can be described as:

$$\Delta G = \Delta H_m(T) - T \cdot \Delta S_m(T) \quad (19)$$

Putting thermodynamic data into aforementioned formulas and applying the symbolic operation module of the software Matlab,  $\Delta G$  could simplify further to:

$$\Delta G = -2.91 \times 10^5 + 2177T - 322.7T \ln T + 0.242T^2 - 1.502 \times 10^{-5}T^3 + 7.383 \times 10^{-4}T^{-1} \quad (20)$$

It is a function depending on temperature T.

When the process temperature belongs to 800K-1373K, due to the difference of heat capacity about HA, the enthalpy change and the entropy change of product HA during isotonic warming up process should be written as:

$$\Delta H_2 = \int_{298}^{800} C_p(HA)dT + \int_{800}^T C'_p(HA)dT \quad (21)$$

$$\Delta S_2 = \int_{298}^{800} \frac{C_p(HA)}{T} dT + \int_{800}^T \frac{C'_p(HA)}{T} dT \quad (22)$$

Nevertheless, the heat capacity coefficients of reactants remain constant, the enthalpy change formulas and entropy change formulas of reactants are same as the 298K-800K. After calculating, the Gibbs free energy is:

$$\Delta G = -2.613 \times 10^5 + 1653T - 242.4T \ln T + 0.1678T^2 - 1.923 \times 10^{-6}T^3 + 4.061 \times 10^{-4}T^{-1} \quad (23)$$

When it reaches 1373K, owing to the phase transition and heat capacity coefficients of  $Ca_3(PO_4)_2$  change, the thermodynamic variables (13) and (14) should alter to:

$$\Delta H_1 = \int_{1373}^{298} (3C_p(Ca_3(PO_4)_2) + C_p(CaO) + C_p(H_2O))dT + \int_T^{1373} (3C'_p(Ca_3(PO_4)_2) + C_p(CaO) + C_p(H_2O))dT + \sum \Delta H' \quad (24)$$

$$\Delta S_1 = \int_{1373}^{298} \frac{(3C_p(Ca_3(PO_4)_2) + C_p(CaO) + C_p(H_2O))}{T} dT + \int_T^{1373} \frac{(3C'_p(Ca_3(PO_4)_2) + C_p(CaO) + C_p(H_2O))}{T} dT + \sum \Delta S' \quad (25)$$

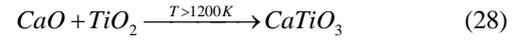
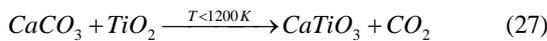
After calculating, the Gibbs free energy is given by:

$$\Delta G = -1.542 \times 10^5 + 872.5T + 8.127 \times 10^{-2}T^2 - 143.7T \ln T - 1.923 \times 10^{-6}T^3 + 7.199 \times 10^{-4}T^{-1} \quad (26)$$

Equation (20), (23) and (26) show the relation between Gibbs free energy  $\Delta G$  and temperature T at different temperature.

### C. Thermodynamic Calculation for $CaTiO_3$

Ti which is from the cladding mixed powders or TC4 substrate is easy to form  $TiO_2$  through reacting with  $O_2$  or other oxides, and  $TiO_2$  would further react with  $CaCO_3$  or  $CaO$  which is decomposed from  $CaCO_3$  when the temperature reaches 1200K. The reactions [5] should be:



Similarly, it is assumed that the processes of reaction (27) and reaction (28) consist of isotonic cooling down process of reactants, reacting process in standard state and isotonic warming up process of products. On basis of the thermodynamic data the temperature range of thermodynamic calculation is divided into 298K-1200K, 1200K-1530K and 1530K-2243K. The calculation of Gibbs free energy for  $CaTiO_3$  is similar to HA's. By plugging thermodynamic data into formulas and simplifying, the Gibbs free energy  $\Delta G$  in different temperature ranges can be represented as follows:

$$\Delta G = 9.893 \times 10^4 - 146.1T + 9.278 \times 10^{-3}T^2 - 4.255T \ln T + 3.135 \times 10^{-6}T^{-1} \quad (29)$$

$$\Delta G = -8.352 \times 10^4 + 93.83T + 5.094 \times 10^{-3}T^2 - 15.01T \ln T + 5.544 \times 10^{-5}T^{-1} \quad (30)$$

$$\Delta G = -8.458 \times 10^4 + 138T + 7.939 \times 10^{-3}T^2 - 21.54T \ln T + 8.451 \times 10^{-5}T^{-1} \quad (31)$$

### III. RESULTS AND DISCUSSION

In order to compare and analyze the Gibbs free energy for HA and  $CaTiO_3$ , the curve of the Gibbs free energy as a function depending on the temperature during 298K-2000K is plotted in Fig. 2, which is obtained by using software Matlab.

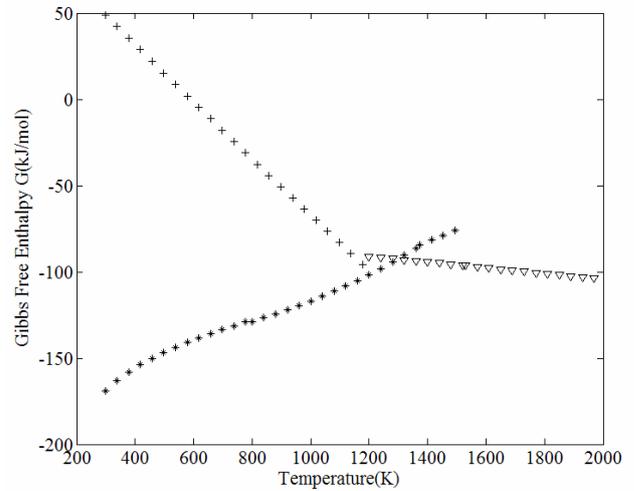


Figure 2. Variation of the Gibbs free energy for different reactions: (\*) reaction 10, (+) reaction and ( $\nabla$ ) reaction.

When the temperature is under 1500K, the  $\Delta G$  for HA is less than zero, which indicates that the reaction (10) satisfies the thermodynamic condition. However, the curve rises up with the temperature increasing in all field, and the rate increases when the temperature exceeds 1000K, it means that the reaction would become more difficult to conduct with the temperature rising up. Indeed, due to the complexity of actual reactions and matter phase transition under high temperature during laser cladding, the final obtained coating would contain

other matters, such as  $\beta$ -TCP,  $\text{CaTiO}_3$ ,  $\alpha$ -TCP and so on. The relation between the Gibbs free energy for reactions producing  $\text{CaTiO}_3$  and temperature  $T$  is approximate linear in the temperature range of 298K-1200K and 1200K-2243K respectively. Furthermore, the slope is negative, when  $T=590\text{K}$ ,  $\Delta G=0$ . It indicates that if the temperature reaches 590K, the reaction (27) satisfies the thermodynamic condition. Due to the temperature of laser cladding process exceeds 590K,  $\text{CaTiO}_3$  can produce through reaction (27). Additional, when the temperature  $T>1200\text{K}$ , (28) becomes the major reaction because of the decomposition of  $\text{CaCO}_3$ . The Gibbs free energy sustainable decrease, but the trend becomes gentle. Additional, when the temperature  $T$  exceeds 1300K, the  $\Delta G$  for reaction (28) would be above the  $\Delta G$  for reaction (10), it means that  $\text{CaTiO}_3$  would be easier to form than HA in this temperature range.

The XRD results for the coatings are shown in Fig. 3 and Fig. 4. It reveals that the main composition of coating 1 is  $\text{CaTiO}_3$ , but the coating 2 is mainly composed of  $\text{CaTiO}_3$ , HA,  $\alpha$ -TCP and  $\beta$ -TCP. The main reason is the different travel speed during laser cladding, which means the coating 1 experiences higher temperature than 2. It indicates that during laser cladding of coating 1 the main reaction is (27) and (28). And the HA synthesized by reaction (10) is easy to decompose into other matters when the temperature exceeds 1500K. The XRD analysis of coating 2 also declares that the reactions producing  $\text{CaTiO}_3$  play a major role during laser cladding. In any case, the HA can be obtained through laser synthesis. Moreover, the comparison between two coating XRD analysis indicates that the alteration of laser cladding parameters which influences the process temperature directly can change the content of HA in coating.

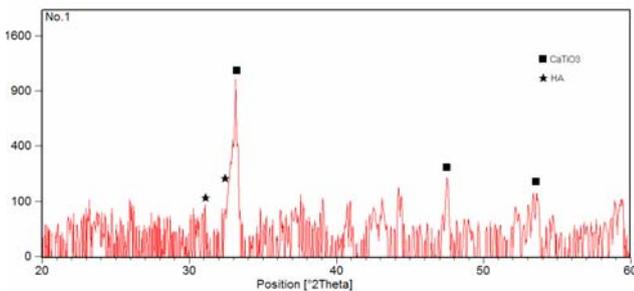


Figure 3. XRD analysis for the No.1 coating

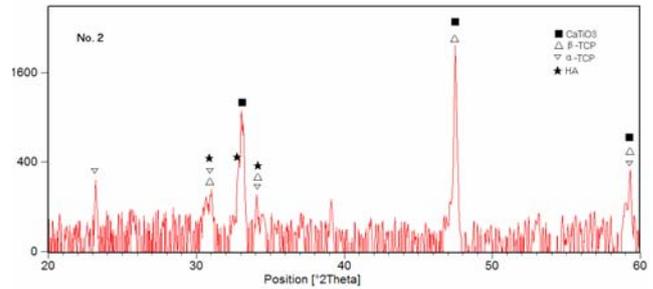


Figure 4. XRD analysis for the No.2 coating

#### IV. CONCLUSIONS

This study has performed the thermodynamic calculation of the main reactions during laser synthesizing HA coating using the mixture of  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  by  $\text{CO}_2$  laser and the experimental study. The results support the following major conclusions:

- (1) The major reaction of synthesizing HA satisfies the thermodynamic condition when the temperature is below 1500K, which means that the way of synthesizing HA by laser cladding using  $\text{CaCO}_3$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is feasible.
- (2) The Gibbs free energy for the reactions producing  $\text{CaTiO}_3$  is below zero when the temperature exceeds 590K, which means the reactions can happen. Moreover, it is less than the  $\Delta G$  for HA when the temperature reaches 1300K, it indicates that  $\text{CaTiO}_3$  is easier to form than HA in this temperature range.
- (3) The parameters of laser cladding would influence the content of HA in coating, it should be selected strictly to reduce  $\text{CaTiO}_3$  and improve the quality of coating.

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