Journal of Alloys and Compounds 724 (2017) 586–596

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Spray drying of hydroxyapatite powders: The effect of spray drying parameters and heat treatment on the particle size and morphology

F.E. Bastan [a, *], G. Erdogan [b], T. Moskalewicz [c], F. Ustel [a, **]

[a] Sakarya University, Engineering Faculty, Department of Metallurgy and Materials Engineering, Thermal Spray Research and Development Laboratory, 54187, Esentepe, Sakarya, Turkey

[b] Celal Bayar University, Engineering Faculty, Department of Metallurgy and Materials Engineering, 45140, Muradiye, Manisa, Turkey

[c] AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Czarnowiejska 66, 30-054, Kraków, Poland

A R T I C L E I N F O

Article history:
Received 23 March 2017
Received in revised form
30 June 2017
Accepted 9 July 2017
Available online 10 July 2017

Keywords:
Ceramics
Coating materials
Nanostructured materials
Precipitation
Sintering

A B S T R A C T

The physical and chemical properties of spray dried hydroxyapatite (SD-HA) are significantly depended on precipitation and spray drying (SD) process parameters. This study presents the effects of precipitation pH, solid content, slurry feed rate, atomization pressure, hot air temperature and hot air flow rate on the particle size distribution of SD-HA. Moreover, the physical and chemical properties of SD-HAs and heat treated micro-granules depending on the precipitation pH were investigated. Taguchi Experimental Design (DoE) was employed to optimize the parameters and to determine the significant factors. The physical properties of SD-HA and heat treated micro-granules were analyzed via particle size analyzer, SEM and TEM. RAMAN and FTIR were carried out to examine the chemical properties. Increasing of the precipitation pH led to slightly increase of the median particle size and the high temperature stability of the SD-HA. DoE results demonstrated the most significant SD parameters as atomization pressure and slurry feed rate. The increases in heat treatment temperature decreased the specific surface area, pore volume and particle size of SD-HA, while increased the crystallinity and powder density. SD-HA were stable up to 1250 °C and decomposed at approximately 1450 °C.

1. Introduction

Hydroxyapatite (HA) is the main inorganic component of natural bone, which can be derived from natural resources [1] or synthesized chemically [2]. HA is generally used for biomedical applications owing to its bioactivity, osteoconductivity, and lower solubility [3–5]. The brittle nature and inferior mechanical properties of HA restricts its use under higher mechanical stresses [6]. Therefore, it is frequently deposited on metallic implants to accelerate bone formation and prevent the releasing of the metallic ions (Ni, Cr, Ti) into tissues [6–8]. Plasma spraying is one of the most prevalently used process for the deposition of HA [9] owing to the reliability and the long time survivability of the coating in vivo [10]. Plasma sprayed HA coatings used in the clinical applications should have dominant HA phase with minimum amount of other CaP and high adhesive bond strength to metallic substrates [6].

Besides thermal spraying parameters, the properties of starting HA particle such as morphology and particle size distribution (PSD) influence the micro-structure, phase, and mechanical properties of plasma sprayed coatings [11]. The unique advantages of the spray drying, such as controlling morphology and PSD, pave the way for granulating of plasma sprayable HA. Plasma sprayed coarse HA particles maintain the phase structure, yet non-molten particles adhere to substrate weakly. Finer particles are exposed to alteration of the phase structure due to the high temperature of plasma [12]. Spray drying (SD) is a simple and attractive route to granulate particles with controlled morphology, size and density. SD is capable to produce different particle morphologies such as hollow, donut and spherical shapes with high production yield. During SD process, a prepared slurry is atomized to droplets by a pressure or centrifugal force. Subsequently, the droplets are dried in a hot chamber and are collected in a jar. SD has the ability to produce particles with a narrow size distribution, spherical morphology and free flowing property which are the key parameters for thermal spraying feedstock [13–16].

SD-HA can not only be used for plasma spraying but also used in

* Corresponding author.
** Corresponding author.
E-mail addresses: febastan@sakarya.edu.tr (F.E. Bastan), ustel@sakarya.edu.tr (F. Ustel).

http://dx.doi.org/10.1016/j.jallcom.2017.07.116

electrophoretic deposition (EPD), high velocity oxy-fuel (HVOF), and hot pressing. HA with different morphologies can be produced by SD and can be used for drug delivery systems [17–20]. Moreover, it is possible to produce nano structured SD-HA with the feeding of calcium and phosphate source to a two-liquid nozzle and collecting the particles by electrostatic precipitator [21]. Julklang and Golman studied numerical simulation of spray drying of HA in order to design safe and efficient industrial scale spray dryer [22]. In recent years, fabrication of HA/polymer composite powders via spray drying has drawn attention in order to further functionalization of the properties of HA [23,24].

SD-HA particles with different properties have been used for various applications, although, there have been limited studies dealing with the effects of heat treatment [25–28] and process parameters [17,29,30] on the properties of the (SD-HA) particles until now. These limited studies suggested that increasing of the concentration and slurry feed rate of HA slurry and decreasing of the atomization pressure increase median particle size [29,30]. The crystallinity degree of SD-HA increases with increases in heat treatment temperature. However, the phase structure of SD-HA decomposes to other calcium phosphates (CaP) at approximately 1000 °C [25,26]. The specific surface area of SD-HA decreases gradually with increasing temperature [27,28] due to diffusional sintering of precipitates. Wang et al. [29] emphasized on the significance of controlling the HA slurry parameters to adjust the properties of the SD-HA. However, there are limited studies dealing with the effect of precipitation conditions on the characteristics of SD-HA.

The aim of this study is to analyze the effects of the slurry and SD parameters along with the heat treatment on the physical and chemical properties of SD-HA. In this study, nano structured HA micro-granules were produced from nano HA precipitates by SD under different conditions. This study provides an in-depth analysis and discussion on the effects of slurry and SD process parameters and heat treatment on the PSD, physical and chemical properties of SD-HA. The effects of slurry and SD parameters on the median particle size (d50) as well as d10 and d90 were analyzed according to DoE approach. The results could shed light not only producing SD-HA but also spray drying of other nano-structured advanced ceramics.

2. Experimental procedure

Experimental section of the study is divided into three sections, as presented in Fig. 1. Briefly, HA nano precipitates were produced and filtered initially. Afterwards, the slurries were prepared from nano HA and deionized water and were spray dried according to the selected parameters. Finally, SD-HAs were heat treated with gradual rise in temperature. The physical and chemical properties of the SD-HA particles were characterized via various techniques.

2.1. Preparation of the slurries

HA nano precipitates were synthesized by precipitation with the reaction of calcium nitrate tetra hydrate ($Ca(NO_3)_2 \cdot 4H_2O$, 98%, Merck) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 98%, Merck). In the first step, 1 M calcium and 0.5 M phosphate solutions (Ca/P molar ratio was fixed 1.67) were prepared and mixed individually. The solutions' pH was fixed via ammonia solution (NH_4OH, %29, Merck) ~12 and 10.2, respectively. Afterwards, the phosphate solution was poured into calcium solution with 0.6 l/min flow rate. In the final stage, the pH of HA suspensions was adjusted with the ammonia solution to 10.45 and 10.75 by using pH-meter. Approximately 600 ml NH_4OH solution was poured into the HA suspension in order to increase the pH from 10.45 to 10.75.

The HA suspensions were stirred strongly for 24 h, then precipitated for 24 h at room temperature. Next, the supernatant were separated from the precipitates via vacuum filtering and washed with deionized water. Ultimately, the filtered wet HA cake and deionized water were mixed to prepare the spray drying slurries. The solid content of slurries was adjusted by adding deionized water into the filtered HA wet cake. The slurries were mixed vigorously for 30 min, afterwards, the viscosity was measured via BROOKFIELD DV-II + Pro viscometer. In order to investigate the effect of precipitation pH, the viscosity of slurries 19 and 20 (Table 2) were measured with a constant shear rate (100 rpm) and with increasing shear rates (10, 20, 50, 100 rpm). Fig. 2 shows the results of viscosity measurements.

2.2. Spray drying

The HA slurries were mixed vigorously throughout the SD period to prevent early sedimentation and to maintain the required viscosity. They were fed by a peristaltic pump to a two-fluid external nozzle (1.5 mm dia.) and atomized to droplets with an adjustable air pressure. The high-pressure atomization gas disintegrates the slurry to droplets with high frictional force [31,32]. This type of nozzle allows independent control of the slurry and air pressure, and it has the ability to fabricate finer particles and to

Table 1
The selected factors and their levels for Design of Experiment.

Factor	1. level	2. level	3. level
Precipitation pH	10.45	10.75	–
Solid content (%)	12	13	14
Slurry feed rate (rpm)[a]	5	10	20
Atomization pressure (bar)	1	1.5	2
Inlet temperature of hot air (°C)	185	200	215
Hot air flow rate[a]	90	100	110

[a] The mass flow rates of the slurry: 20.1 ± 0.6, 38.3 ± 1, 55.7 ± 1.8 g/min for 5, 10, 20 rpm, respectively. The hot air flow rates: 6.18, 6.8, 7.5 m/s for 100, 110, 120, respectively.

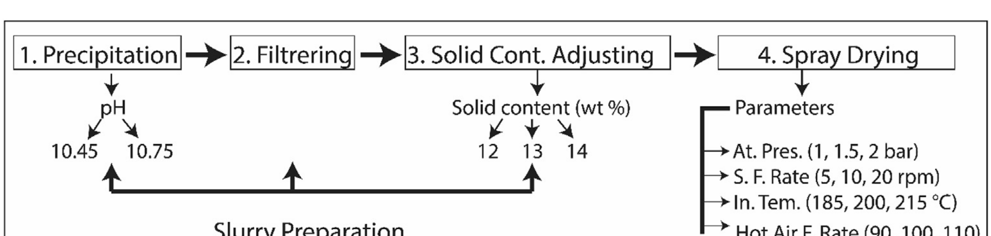

Fig. 1. Schematic illustration of the experiments.