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Ceramics International 34 (2008) 511–516

CERAMICS INTERNATIONAL

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Hydroxyapatite coatings by pulsed ultrasonic spray pyrolysis

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Received 9 October 2006; received in revised form 26 October 2006; accepted 24 November 2006

Abstract

Hydroxyapatite coatings on 316L stainless steel substrates were prepared using ultrasonic spray deposition with substrate temperature kept at 300 °C. Two spray patterns, continuous and pulsed (intermittent), were used coupled with precisely control of substrate movement. It was determined that the ability to form continuous and relatively dense, well bonded coatings, was related primarily to the control of the flowrate of precursor solution and temperature and movement of the substrate. The microstructure and bonding strength of the coatings were evaluated in relationship with continuous and pulsed (intermittent) spray routes. Coatings prepared by continuous spray contained relatively large cracks while coatings by pulse spray exhibited finer cracks and higher bonding strength.

Keywords: B. Surfaces; B. Microstructure-final; C. Strength; D. Apatite

1. Introduction

Ultrasonic spray pyrolysis (USP) of chemical solutions has been studied for preparing coatings of structural oxides [1–3], spinels [4], and high temperature superconductors [5,6]. USP offers simplicity of the apparatus and operation, good productivity on a large scale for industrial applications, and good control of thickness of the coatings [7]. In recent years, calcium phosphate bioactive coatings have also been prepared using USP [8–10]. Plasma spraying (PS) has been widely used to deposit calcium phosphate coatings on metallic implants [11–13]. However, there are two major drawbacks of PS, besides the complex and expensive processing. Firstly, control of stoichiometry and phase composition of the deposited calcium phosphate is poor because of the high deposition temperature (7000–12,000 K) [8,14]. Secondly, the coating deposited by plasma spray is relatively thick, typically in excess of 50 μm [15]. It is difficult to reproduce fine implant profile, e.g. for bone in-growth and interlocking, using PS. Calcium phosphate coatings with thickness varying between 5 and 70 μm have been prepared using spray pyrolysis [8–10]. Up to now, continuous spray has been used in all the reported spray pyrolysis deposition of calcium phosphate [8–10,15,16]. However, continuous coatings are difficult to obtain by USP unless sprayed 1.5 h [8]. This deposition time is relatively long and not practicable for industrial application. Besides, there is no control of coating thickness for such a long deposition time [8]. This work reports formation of relatively dense, smooth hydroxyapatite coatings on 316L stainless steel substrates by USP. In order to form continuous coatings within a relatively short time, the flowrate of precursor solution and the movement of substrates were precisely controlled in pulsed (intermittent) schedule. In this work, intermittent spray was also used to investigate the influence of spray patterns on the bonding strength between the coatings and the substrate.

2. Experimental procedures

An aqueous solution with a Ca/P ratio of 1.67, corresponding to the stoichiometric composition of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp), was prepared using calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, BDH Inc., Toronto, Canada), ammonium dihydrogen phosphate ($NH_4H_2PO_4$, Fisher Scientific) and nitric acid (HNO_3, Assay 68%, Fisher Scientific). 47.230 g of $Ca(NO_3)_2 \cdot 4H_2O$ and 13.804 g of $NH_4H_2PO_4$ were dissolved in 285.60 and 94.66 ml deionized water, respectively. Then $NH_4H_2PO_4$ solution was poured into $Ca(NO_3)_2 \cdot 4H_2O$ solution slowly under stirring. After mixing of the two solutions, 16.68 g of HNO_3 was added to the mixed solution.

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doi:10.1016/j.ceramint.2006.11.014

The obtained solution had concentrations of 0.5 M Ca^{2+} and 0.3 M of P^{5+} (the total water amount was 400 ml). Correspondingly, the solution would yield a concentration of 0.008 M in terms of the product hydroxyapatite, i.e. 1 l of the solution would generate 0.008 mol hydroxyapatite.

316L SS of 25 mm × 25 mm × 1 mm size samples were mechanically polished from 120 to 1000 grit SiC papers followed by polishing with 6 and 1 μm diamond suspensions to get a mirror finish. Then the substrates were washed with pure acetone and distilled water in an ultrasonic cleaner. USP was carried out using an ultrasonic nozzle (Sono-Tek AccuMist, Milton, USA) with a 120 MHz transducer. The 316L stainless steel substrate was attached to a hot plate (Wenesco Inc., Chicago, USA), which was seated on a precision movement (software-controlled) X–Y table under the nozzle. The flowrate of the precursor solution was also software-controlled by a syringe pump. The parameters for spray deposition are summarized in Table 1. Two spray patterns were used: (1) continuous spray and (2) pulsed-intermittently spraying (stopping for 30 s between two cycles of spray). After deposition, the coatings were left as deposited or subjected to additional heat treatments in air at temperatures of 600 °C for 5 h with a heating rate of 5 °C/min.

The phase composition of the coatings was determined using an X-ray diffractometer (XRD, Rigaku MultiFlex, Tokyo, Japan). The mean crystallite size of the major phase in the as-deposited coatings was calculated from X-ray diffraction broadening of the peak ($\bar{1}$ 1 2) of monetite ($CaPO_3(OH)$) using the Scherrer equation. The morphology of the coatings and cross-section of the coatings and substrates were observed by scanning electron microscopy (SEM, S3000N, Hitachi, Japan). Elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDS) connected with SEM. The bonding strength of the coatings was qualitatively estimated using a tape test [9,10]. A piece of Scotch tape (#810) was adhered to the coating on a substrate and then was removed from it. The bonding strength was considered ‘‘strong’’ or ‘‘weak’’ through observing whether the coating remained on the tape-side or not.

3. Results and discussion

Table 1
Parameters for pulsed USP of hydroxyapatite coatings

Substrate temperature	300 °C
Solution flowrate	0.2 ml/h
Nozzle-to-substrate distance	30 mm
Carrier gas pressure	1.5 psi
Generator powder	1.6 W
Path acceleration	150 mm/s^2
Path deceleration	150 mm/s^2
Path speed	10 mm/min
Area spacing	1.0 mm
Spray area	15 mm × 7 mm
Spray cycles	50 times

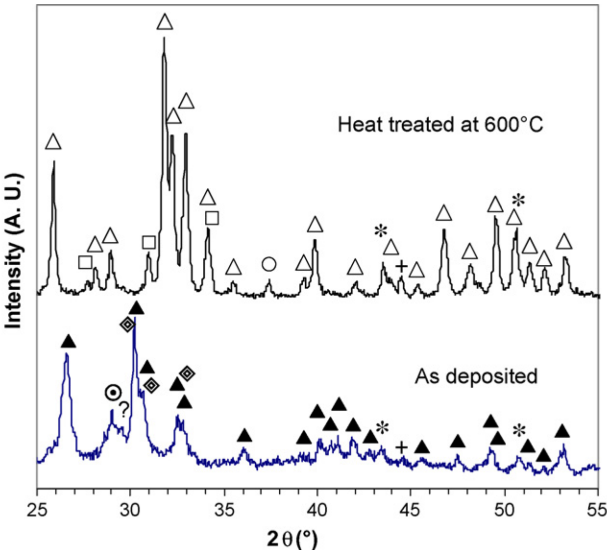

Fig. 1. Phases of the USP coatings as-deposited and after heat treatment at 600 °C for 5 h [(△) hydroxyapatite (JCPDS No. 09-0432); (□) $Ca_3(PO4)_2$ (JCPDS No. 09-0169); (▲) $CaPO_3(OH)/CaHPO_4$ (JCPDS No. 09-0080); (◉) Fe_3PO_7 (JCPDS No. 37-0061); (◈) $Fe_3(PO_4)_2$ (JCPDS No. 49-1087); (○) CaO (JCPDS No. 77-2010); (*) Cr–Ni–Fe–C austenite (JCPDS No. 31-0619); (+) Fe (JCPDS No. 06-0696)].

XRD results (Fig. 1) show that the as-deposited coating is composed of anhydrous calcium hydrogen phosphate $CaPO_3(OH)$ (JCPDS No. 09-0080); and ferrous phosphates (Fe_3PO_7, JCPDS No. 37-0061 and $Fe_3(PO_4)_2$, JCPDS No. 49-1087) were present. After heat treatment at 600 °C for 5 h, the major phase was HAp (JCPDS No. 09-0432), with a minor phase of tricalcium phosphate ($Ca_3(PO_4)_2$, TCP, JCPDS No. 09-0169). CaO was observed in the heat treated coating because formation of ferrous phosphates consumed PO_4 groups.

Fig. 2 shows that there were not much change in the coating morphology for the samples prepared with intermittent spray before and after the heat treatment at 600 °C. It is also seen that no significant cracking occurred in the coatings after the heat treatment. However, short and finer cracks (~10 μm long and ~0.05 μm wide) were more often observed in some areas of the coatings under higher magnification (see Figs. 2d and 3), attributed to the shrinkage and partial sintering of the coatings during the heat treatment. No obvious grain/particle shape could be distinguished in the coatings before heat treatment (Fig. 2b), suggesting that the crystallites in the coatings were very small. In fact, the average crystallite size of monetite calculated from XRD date was 56 nm. In contrast, the grains/particles of the heat treated coatings are visibly polygonal, indicating grain growth during the heat treatment.

Fig. 2 shows that the coating surface is continuous and relatively smooth. The cross-section configuration of the coatings (see Figs. 4a and 5a and b) also demonstrated that the coatings were continuous and smooth with a uniform thickness of roughly 7 μm, formed with pulsed spray on the substrate after 50 cycles of spray on an area of 15 mm × 7 mm. The total time for the spray deposition was 12 min. Formation of continuous USP coatings on the substrates in a relatively short time was due to the relatively low substrate temperature (300 °C), and good control of the precursor flow-rate and substrate movement. It was found previously that

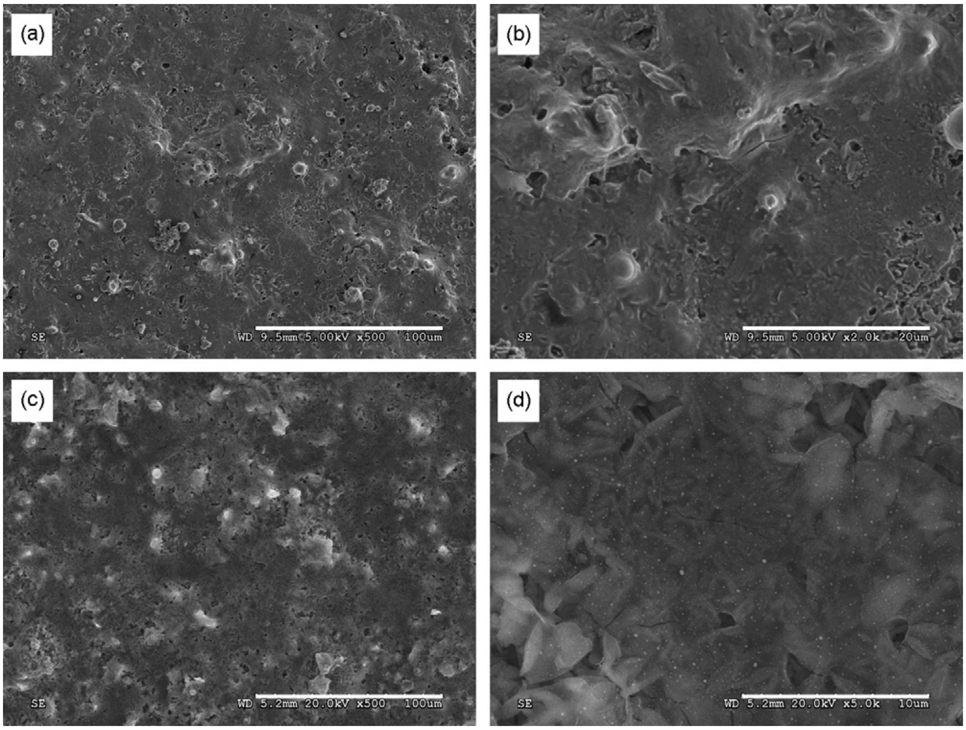

Fig. 2. Surface morphology of USP coatings prepared with pulsed spray before (a and b) and after (c and d) heat treatment at 600 °C for 5 h.

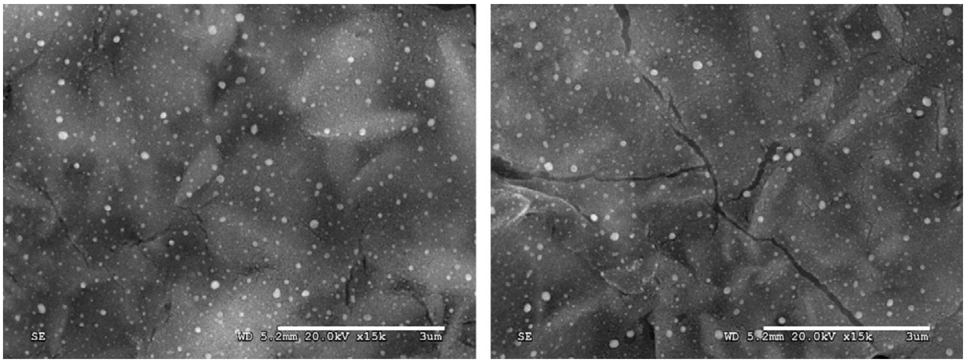

Fig. 3. Surface morphology of USP coating prepared with pulsed spray and after heat treatment at 600 °C for 5 h, showing fine cracks.

agglomerates of HAp particles formed when the substrate temperature was 600 °C [8] or the precursor solution was sprayed into a reactor tube with a temperature kept at 600 °C [10]. At higher deposition temperature (e.g. 600 °C), the solvent in the precursor droplets substantially evaporated before the droplets reached the substrates [17]. As a result, the droplets could not spread on the substrate, resulting in the porous coatings with poor bonding strength [8,10]. In contrast, the substrate temperature in this work was relatively low (300 °C), and the process of pyrolysis was partly de-coupled from the process of heat treatment/densification (600 °C). Thus, less solvent in the droplets evaporated during the flight and the droplets arrived at the substrate surface with the ability to spread and form a film [17]. As shown in Fig. 4a and b, the coatings integrated well with the substrates. The good bond between the coatings and substrates was qualitatively confirmed by the adhesive tape test. No coating material was observed on the tape after the tape was peeled off the coatings prepared with intermittent spray.

Figs. 4c and 5c and d show that the surface of the coatings was quite smooth and the thickness of the coatings before and after heat treatment was quite uniform in the range of 5–8 μm using continuous spray, indicating that continuous, flat and homogeneous HAp coatings could be formed using continuous spray when flowrate of precursor solution and movement of the substrates were precisely controlled as in this work. However, it is seen that network-like cracks formed in the coatings before and after the heat treatment (see Fig. 6a and c, respectively). Comparison of Fig. 6b and d reveals that the cracks widened due to the shrinkage of the coatings during the heat treatment. The coatings prepared with intermittent spray had no network-like cracks before and after the heat treatment (see Fig. 2). The densely distributed cracks in the coatings prepared with continuous spray (Fig. 6a and c) may be attributed to the

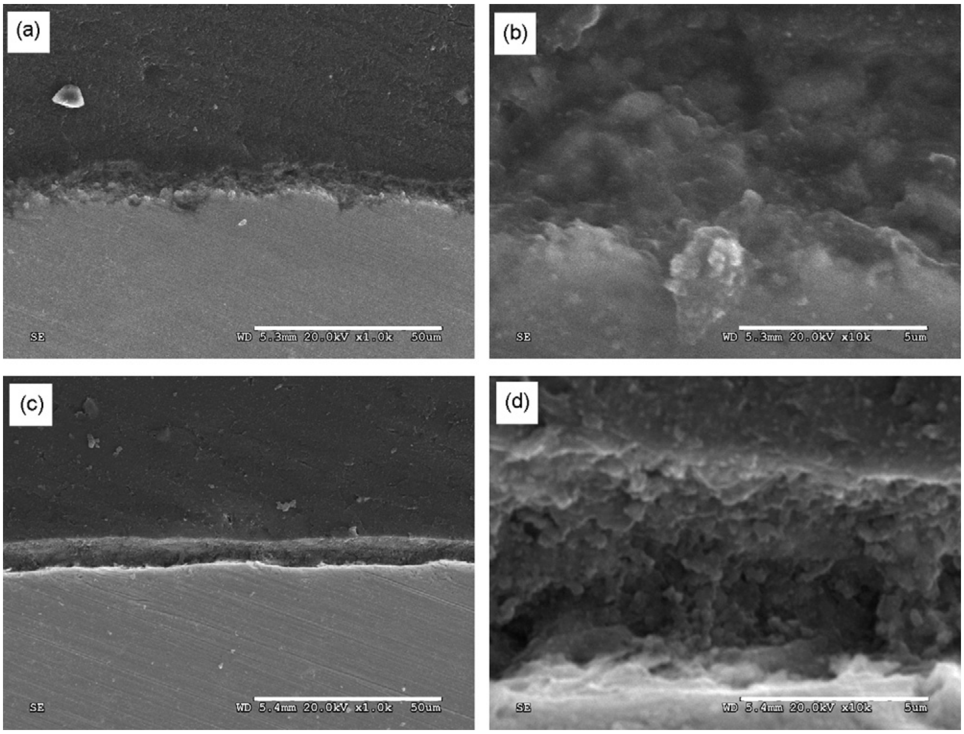

Fig. 4. Cross-section of USP coating prepared with (a) and (b) pulsed spray and (c) and (d) continuous spray and after heat treatment at 600 °C for 5 h.

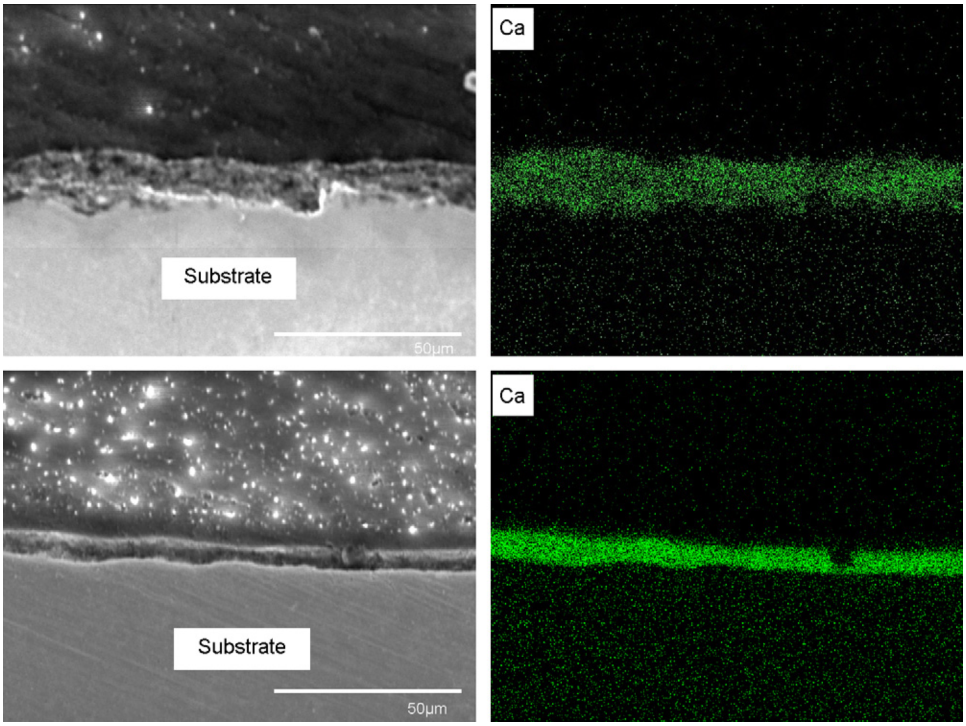

Fig. 5. EDS elements mapping for USP coating prepared with (a) and (b) pulsed spray and (c) and (d) continuous spray and after heat treatment at 600 °C for 5 h.

inadequate time for the solvent to evaporate from the precursor solution. That is, before a single layer formed in one cycle of spray was completely dried and decomposed, the second layer formed in the following cycle of spray during continuous spray, resulting in a wet state of the coatings during the whole continuous spray cycle. When the coatings were completely dried and decomposed after the spray processing, they shrank and consequently cracked. On the other hand, each layer of the coating deposited using the pulsed spray was completely dried and decomposed during the period of 30 s ‘‘rest’’ without spray.

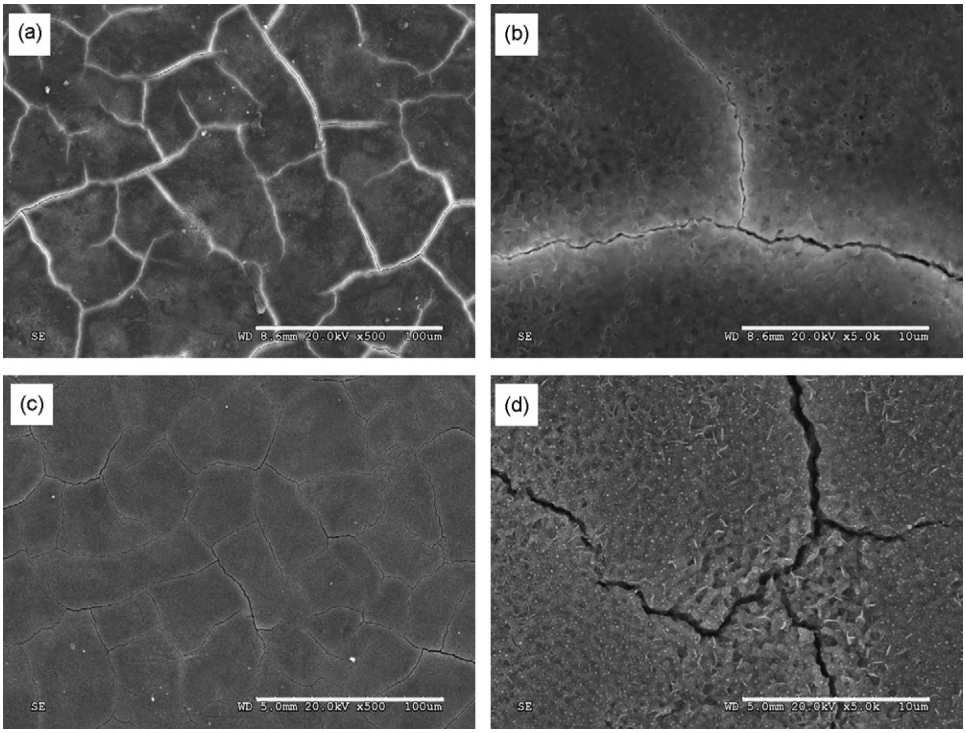

Fig. 6. Surface morphology of USP coatings prepared with continuous spray before (a and b) and after (c and d) heat treatment at 600 °C for 5 h.

Thus, each layer of coatings was in a dry state before the following cycle of spray and each layer of the coatings allowed relatively small shrinkage during further heating. As a result, the coatings prepared with pulsed spray had much fewer and smaller cracks than those prepared with continuous spray.

It is seen in Fig. 4c and d that the coatings prepared with continuous spray formed a groove in the cross section of the sample, indicating that the coating had relatively low integrity, and relatively low bonding strength with the substrate when compared the coatings prepared with pulsed spray (compare with Fig. 4a and b). In comparison with the coatings prepared with pulsed spray (see Figs. 2b and 4b), the coatings prepared in continuous spray mode is more porous (see Fig. 4d), which also contributed to their lower bonding strength.

4. Conclusions

Continuous, dense, flat and homogeneous HAp coatings were formed using pulsed ultrasonic spray pyrolysis (USP) deposition with precisely controlled flowrate of precursor solution and movement of the substrates. The relatively low substrate temperature of 300 °C allowed uniform spread of precursor droplets. Subsequent heat treatment at 600 °C allowed partial sintering of the coating, with increase of integrity and bond strength. Coating thickness of about 7 μm was produced for a spraying time of 12 min. Continuous spray generated coatings with relatively large cracks while pulsed spray yielded coatings with much fewer and finer cracks. The coatings prepared with pulsed spray had also higher bonding strength than those prepared with continuous coatings. It is hypothesized that the partial de-coupling of the pyrolysis heat treatment (at 300 °C) from the sintering heat treatment (at 600 °C) has significant influence on pulsed USP coating integrity and morphology.

Acknowledgements

The authors gratefully acknowledge the financial support for the project from the Natural Science and Engineering Council of Canada and MIV Therapeutics, Vancouver, BC.

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