Effect of stand-off distance (SOD) on the properties of synthesized Hydroxyapatite (HA) Coatings deposited on Ti-alloy (Ti-6Al-4V) substrate by Flame spray Technique

M.Tech. Thesis

By

Aniruddha Ganesh Fapal

(2302103002)

DEPARTMENT OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY INDORE

June 2025

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A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

of

Master of Technology

by

ANIRUDDHA GANESH FAPAL

DEPARTMENT OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled " **Effect of stand-off distance (SOD) on the properties of synthesized Hydroxyapatite (HA) Coatings deposited on Ti-alloy (Ti-6Al-4V) substrate by Flame spray Technique** " in the partial fulfilment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF MECHANICAL ENGINEERING** , **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2024 to June 2025 under the supervision of **Prof. Kazi Sabiruddin ,** Discipline of Mechanical Engineering and Indian Institute of Technology (IIT) Indore .

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

17-06-2025

Aniruddha Ganesh Fapal

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge .

Prof. Kazi Sabiruddin

ANIRUDDHA GANESH FAPAL has successfully given his M. Tech. Oral Examination held on **26th May , 2025 .**

Signature of Supervisor of M. Tech. Thesis

Date : 17/06/2025

Signature of Convener DPGC

Date :18-06-2025

Acknowledgement

I would like to express my special thanks to my mentor **Prof. Kazi Sabiruddin** for his time and efforts he provided throughout. Your useful advice and suggestions were helpful to me during the project's completion. In this aspect, I am eternally grateful to you.

I would also like to convey my heartfelt gratitude to **Mr. Setu Suman** (Research Scholar) my senior , for his valuable advice and assistance in this project.

Aniruddha Fapal

(2302103002)

Abstract

In the present study , Ti-6Al-4V alloy is flame sprayed with HA-800 powder , with different stand off distances 50 mm , 80 mm , 100 mm , 120 mm , by keeping all other parameters same .

The mechanical characterization of these sample is done , with various tests including surface roughness , adhesion , reciprocating wear , Vicker's hardness and porosity test . FESEM analysis and XRD analysis of these sample is also done .

SBF solution (simulated body fluid) solution is prepared for further tests . Free standing coating samples of the

HA – 800 are prepared and dipped in SBF solution for different durations 7 days , 14 days and 21 days . FESEM analysis and XRD analysis of these SBF dipped samples is done .

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Acronyms

HA :	Hydroxyapatite
FESEM :	Field-Emission Scanning Electron Microscope
APS :	Atmospheric Plasma Spray
XRD :	X-ray Diffraction
Ra :	Average Surface Roughness

Chapter 1 . Introduction

1.1 Flame Spray and Plasma spray techniques

In the recent years , various methods have been adopted to deposit HA coatings on metal surfaces for biomedical applications.

Sol-gel, plasma spraying, flame spraying , electrochemical deposition, and micro-arc oxidation are the few examples of it .

These methods offer advantages in enhancing the biocompatibility and long-term stability of metal implants in the body. They can also help to prevent corrosion of the metal implant , which can lead to adverse reactions in the body.

Flame spray and plasma spray are the two major techniques used among

1] Flame Spray Technique 2] Plasma Spray Technique

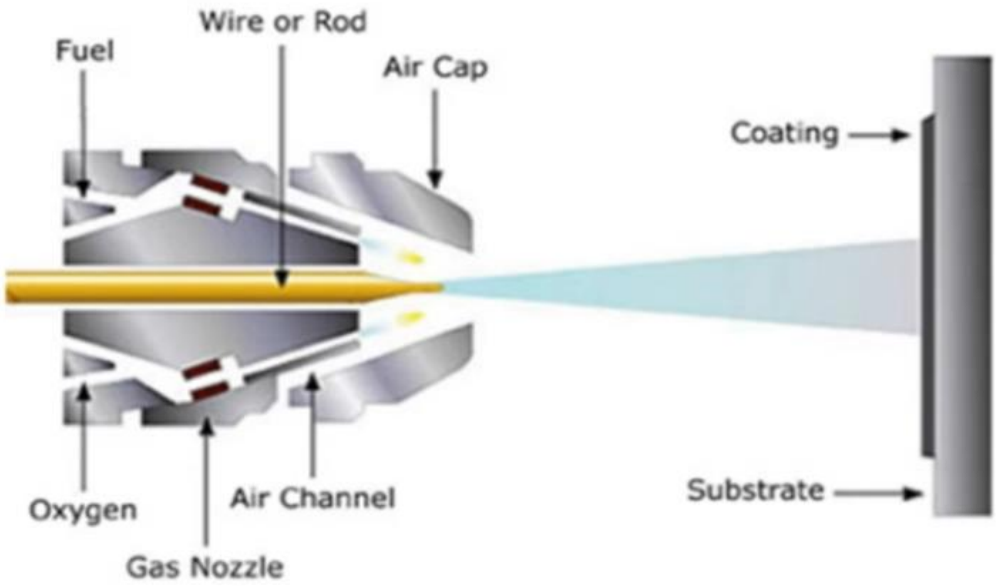


Fig. 1.1 : Flame Spray Technique Schematic

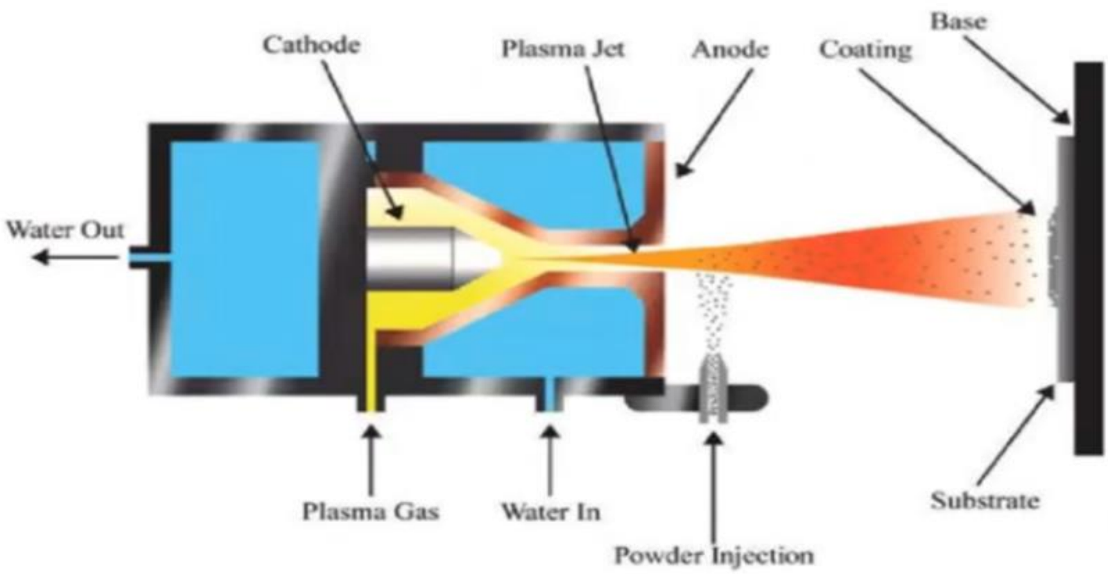


Fig. 1.2 : Plasma Spray Technique Schematic

Flame Spray	Plasma Spray
Flame spraying process is fueled by a heat source that is created by a chemical reaction between a fuel of combustion and oxygen to create a stream of gas .	In plasma a high-temperature plasma jet to rapidly heat and accelerate powder-form material to a high velocity. The plasma is created by an electric charge.

1.2 Hydroxyapatite (HA)

The properties of HA are fundamentally determined by its composition, phase, crystal size, particle size, morphology, and crystallinity, which in turn depend on synthesis precursors and processing methods .

Hydroxyapatite (HA) is treated as an excellent bioceramic material that is applied in biomedical areas, such as orthopedic, dental, and maxillofacial fields, due to its bioactivity, biocompatibility, and osteoconductive characteristics .

In this presentation we are going to do a comparative analysis of flame sprayed HA samples at different SODs and a plasma sprayed HA sample .

1.3 Literature Review

- Nattawit Yutimit (2024) Highly bioactive properties were due to high surface area from rough coating and porous structure, which is beneficial from the flame spray technique . [1]

- Shahid Hussain , Kazi Sabiruddin , Zuber Ali Shah and Anup Kumar Keshri (2022) Various hydroxyapatite (HA) powders synthesized at different temperatures are deposited on titanium alloy by using an atmospheric plasma spray process. The synthesized HA powders are spray-dried to obtain agglomerated powders suitable for spraying during the coating application . [2]

- Arjak Bhattacharjee, Amit Bandyopadhay, Susmita Bose (2022) this work indicates that the anti-bacterial and biological properties of HA can be enhanced with optimized Zn^{2+} and F^- co-doping . [3]

- Jheng-Yang Wang (2020) the Sr-HA and SrMg-HA coatings promoted cell growth and mineralization reactions . [4]

- R. Gadow, A. Killinger and N. Stiegler (2010) the pull-off performance of the HVSFS HA coatings strongly depends on the dispersive medium and the oxygen flow rate, for HVOF-HA coatings it is the spray distance and for the APS-HA coatings the electric arc current is the most influencing parameters . [5]

- S.W.K. Kweh , K.A. Khor , P. Cheang (1999) It was found that the microhardness and elastic moduli improved with the effects of increasing heat treatment temperature . [6]

- K. A. Khor , P. Cheang (1997) The present study shows that flame spheroidised HA powders can be used as powder feedstock for plasma spraying of bioceramic coatings . [7]

1.4 Identified Research Gap and Objectives

- The research works on APS-coated HA is widely available but works on flame-sprayed HA are limited. Seashell-derived HA has never been deposited using the flame spray technique .

- Also, the effect of the stand of distance on the properties of the flame-sprayed HA coating has never been tried before

- A comparison between HA coatings deposited by APS and flame spraying techniques are rarely observed

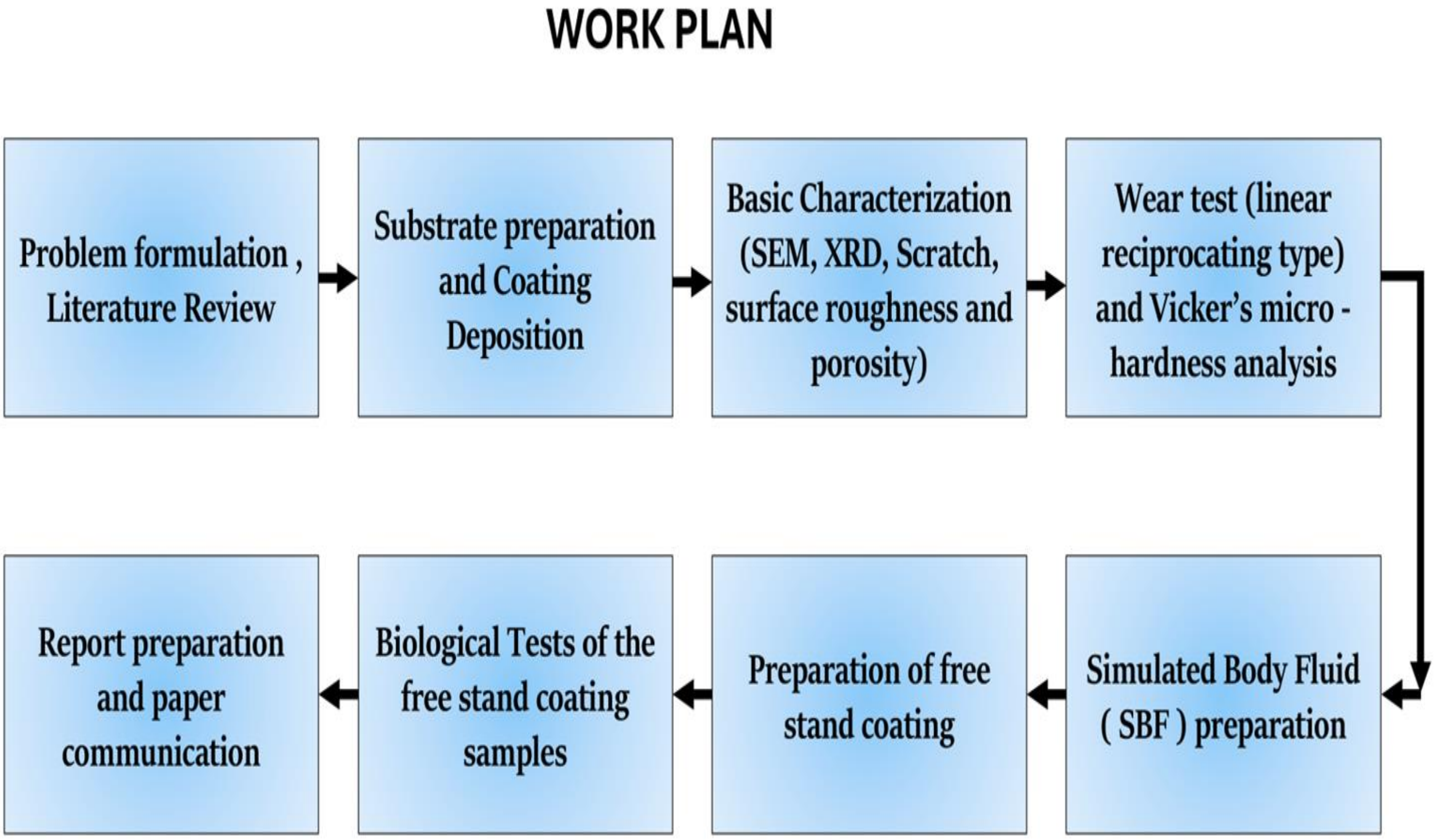
➢ The objectives of this research are as follows :

✓ To deposit seashell-derived HA coating by flame spraying technique with varying process parameters to find the suitable coating in terms of adhesion strength

✓ To deposit seashell-derived HA coating by APS technique

✓ Characterisation of both the coatings and carry out a comparative study

1.5 Work Plan


WORK PLAN
Problem formulation , Literature Review
Substrate preparation and Coating Deposition
Basic Characterization (SEM, XRD, Scratch, surface roughness and porosity)
Wear test (linear reciprocating type) and Vicker's micro - hardness analysis
Simulated Body Fluid (SBF) preparation
Preparation of free stand coating
Biological Tests of the free stand coating samples
Report preparation and paper communication

Chapter 2 : Experiment Procedure

2.1 Substrate Selection and Sample Preparation

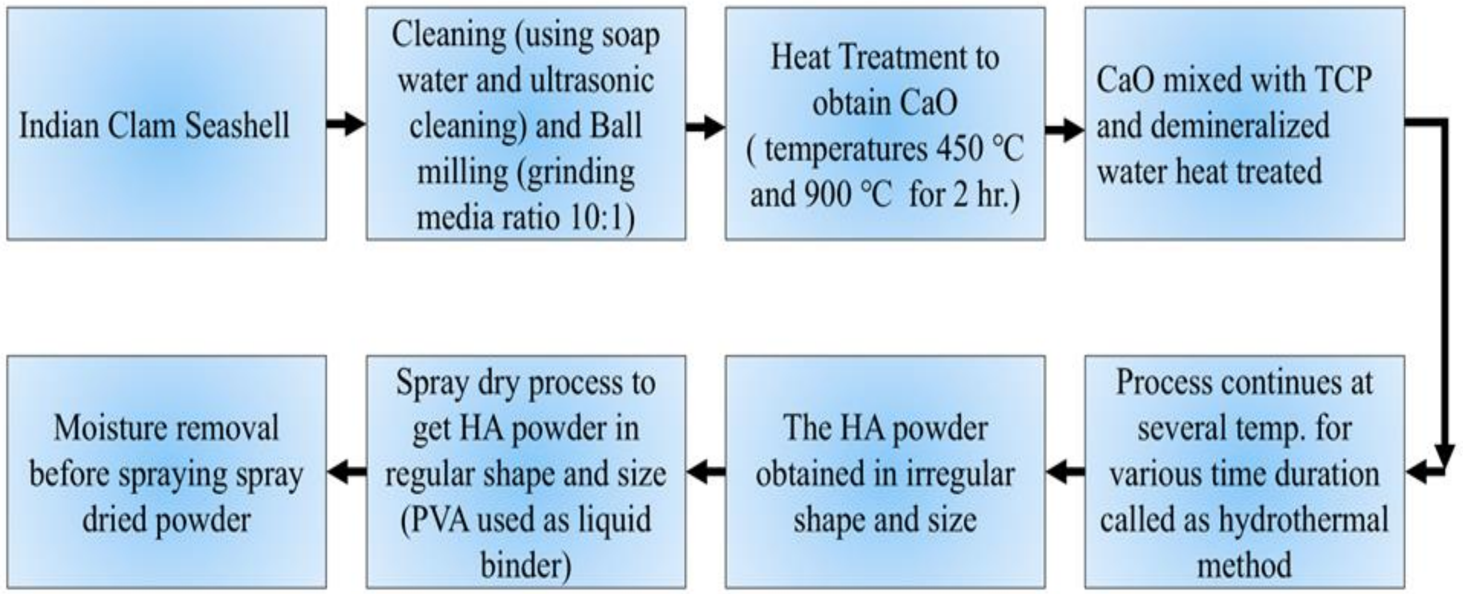
- ✓ For coating, Four samples of Titanium alloy (Ti-6Al-4V) has been prepared.
- ✓ TI-6Al-4V substrate Grit blasted by using Alumina grit 18-mesh after ultrasonic cleaning.

Table 2.1 Grit Blasting and substrate parameters

Sr. No.	Grit Blasting SOD (mm)	Shape of Substrate	Substrate thickness (mm)	Titanium Substrate roughness (Ra µm)
1	100	Circular (Dia. 22 mm)	5	5.08
2	100	Rectangular (10 mm * 15 mm)	5	5.92
3	100	Circular (Dia. 22 mm)	5	4.67
4	100	Rectangular (10 mm * 15 mm)	5	5.87

2.2 Powder / Feedstock Preparation

Flowchart of Powder Preparation



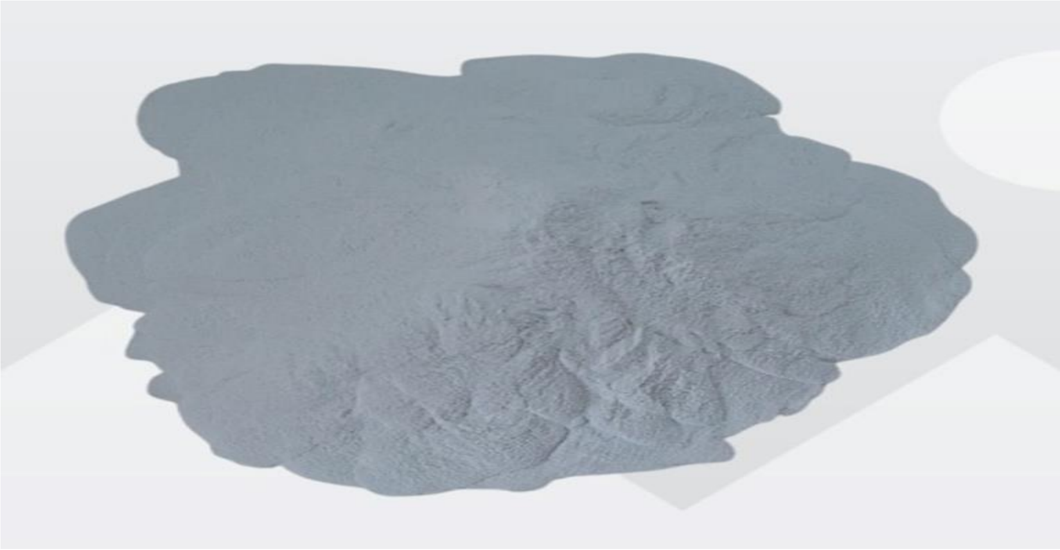


Fig. 2.1 : Synthesized Spray dried HA -800 Powder

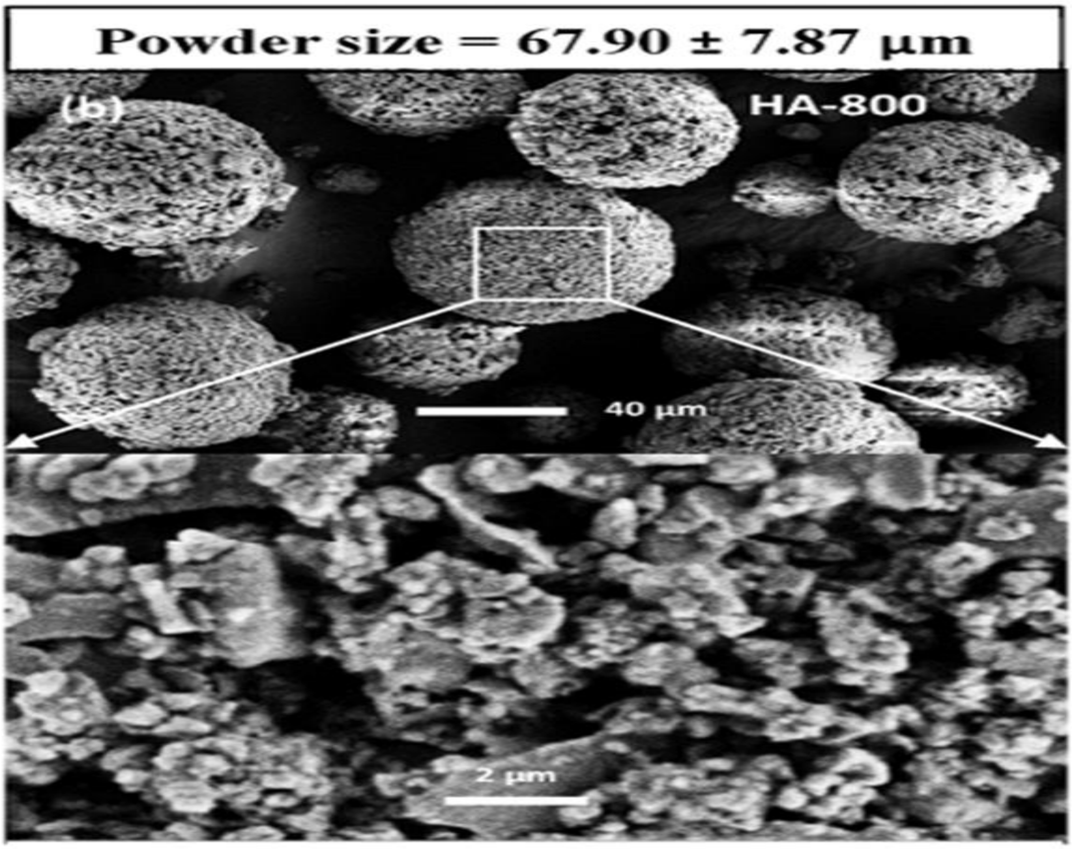


Fig. 2.2 : Low and high magnification FESEM micrographs of spray-dried HA powder [2]

2.3 Deposition Parameters

Table 2.2: Flame spray deposition parameters

Sr. No.	Parameters	Values
1	voltage (V)	220
2	Acetylene flow rate (SCFH)	48
3	Oxygen flow rate (SCFH)	73
4	Powder feed rate (g/min)	3
5	Stand of distance (mm)	50 , 80 , 100, 120

Table 2.3: Plasma spray deposition parameters

Sr. No.	Parameters	Values
1	voltage (V)	45
2	Primary gas (Ar) flow rate (SCFH)	65
3	Secondary gas (H2) flow rate (SCFH)	6
4	Powder feed rate (g/min)	10
5	Stand of distance (mm)	100

Table 2.4: Varying SOD with pre-heat temperature
Flame Spray samples

Sr. No.	SOD (mm)	Preheat Temperature (°C)
1	50	202
2	80	325
3	100	412
4	120	202

2.4 Substrate Selection and Sample Preparation for Wear and Hardness Test

- ✓ For this , 8 samples of Titanium alloy (Ti-6Al-4V) has been prepared.
- ✓ TI-6Al-4V substrate Grit blasted by using Alumina grit 18-mesh after ultrasonic cleaning.
- ✓ 4 samples for wear test and 4 samples for hardness test have been prepared at stand off distance 50, 80, 100, 120 mm.
- ✓ Wear samples are comparatively larger in dimensions as that of Hardness samples

Table 2.5: Grit Blasting and substrate parameters

[Wear samples]

Sr. No.	SOD (mm)	Titanium Substrate roughness (Ra μm)
1	50	5.1
2	80	5.34
3	100	5.94
4	120	6.18

Table 2.6 : Grit Blasting and substrate parameters [Hardness samples]

Sr. No.	SOD (mm)	Titanium Substrate roughness (Ra µm)
1	50	4.92
2	80	6.02
3	100	5.48
4	120	5.28

2.5 Preparation of SBF solution

- SBF solution has ion concentrations nearly equal to those of human blood plasma and is buffered at pH 7.40 with 50 mM tri-hydroxymethyl aminomethane and 45 mM hydrochloric acid at 36.5°C.

- ✓ Wash all the bottles and wares with 1N-HCl solution, neutral detergent, and ion - exchanged and distilled water, and then dry them.
- ✓ Put 500 ml of ion-exchanged and distilled water into one liter polyethylene bottle and cover the bottle with a watch glass.
- ✓ Stir the water in the bottle with a magnetic stirrer and dissolve the reagents one by one in the order as given in Table 1 (One after the former reagent was completely dissolved).
- ✓ Adjust the temperature of the solution in the bottle at 36.5°C with a water bath, and adjust pH of the solution at pH 7.40 by stirring the solution and titrating 1N-HCl solution (When the pH electrode is removed from the solution, add the water used for washing the electrode to the solution).
- ✓ Transfer the solution from the polyethylene bottle to a volumetric glass flask. Add the water used for washing the polyethylene bottle to thew solution in the flask.
- ✓ Adjust the total volume of the solution to one liter by adding ion-exchanged and distilled water and shaking the flask at 20°C.

- ✓ Transfer the solution from the flask to a polyethylene or polystyrene bottle, and store the bottle in a refrigerator at 5-10°C (If some substance is precipitated in the solution during the storage, do not use this solution as SBF and its container again).

Table 2.7 : Ion concentrations (mM) of SBF and human blood plasma

Ion	Simulate Body Fluid	Blood plasma
Na^{+}	142.0	142.0
K^{+}	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^{-}	148.8	103.0
HCO_3^{-}	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

Table 2.8 : Regents for preparing SBF (pH7.40, 1L)

Order	Reagent	Amount
1	$NaCl$	7.996 g
2	$NaHCO_3$	0.350 g
3	KCl	0.224 g
4	$K_2HPO_4 \cdot 3H_2O$	0.228 g
5	$MgCl_2 \cdot 6H_2O$	0.305 g
6	1M-HCl	40 mL
(About 90 % of total amount of HCl to be added)		
7	$CaCl_2$	0.278 g
8	Na_2SO_4	0.071 g
9	$(CH_2OH)_3CNH_2$	6.057 g

2.6 Preparation of free standing samples for SBF solution

- To prepare free-standing coating samples, grit blasting of the substrate has been avoided while keeping all other parameters same.
- The substrate is polished instead of grit blasting to avoid interlocking between the substrate and the coating.
- In this way free standing coating is prepared , (image shown for reference)

Fig. 2.3 : Coating as-sprayed

Fig. 2.4 : Free Standing Coating after delamination

2.7 List of Instruments used

Fig. 2.5 : Stylus Profilometer

Fig. 2.6 : Polishing Machine

Fig. 2.7 : Fretting Wear Tribometer

Fig. 2.8 : Grit Blasting

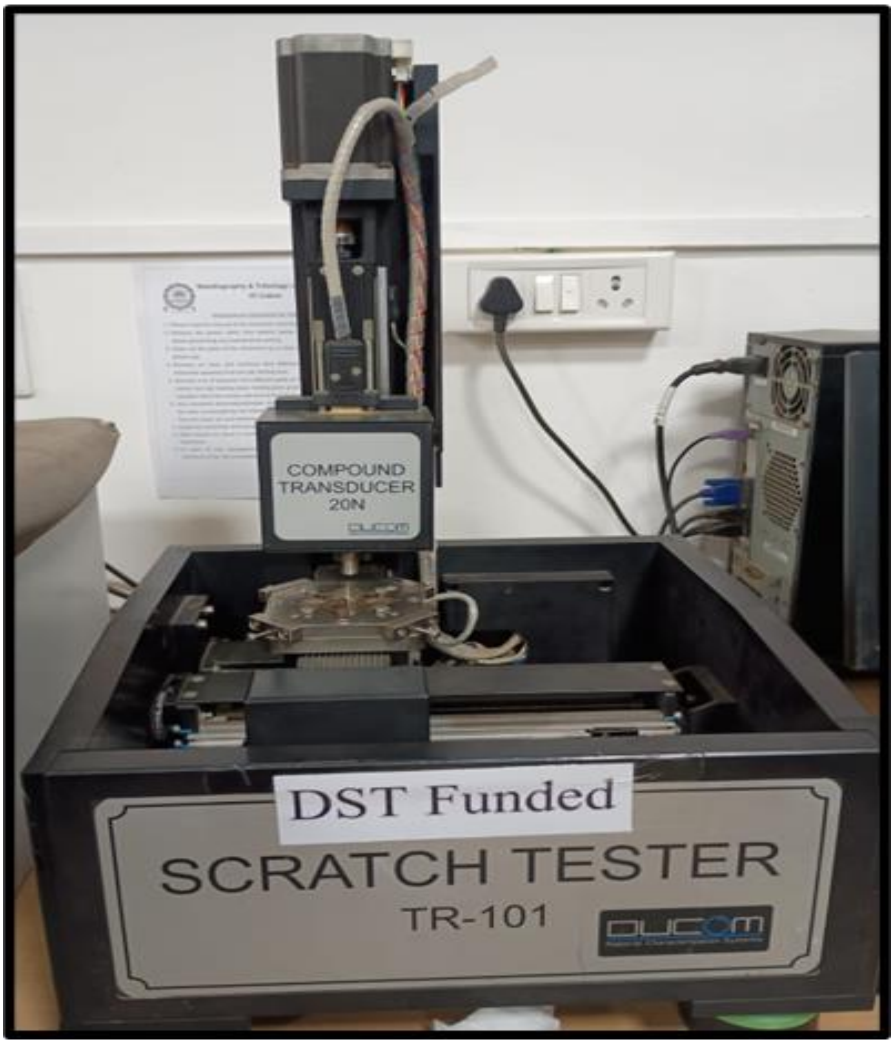


Fig. 2.9 : **Scratch Tester**

Chapter 3 : Result and Discussion

3.1 Average Surface Roughness measurement

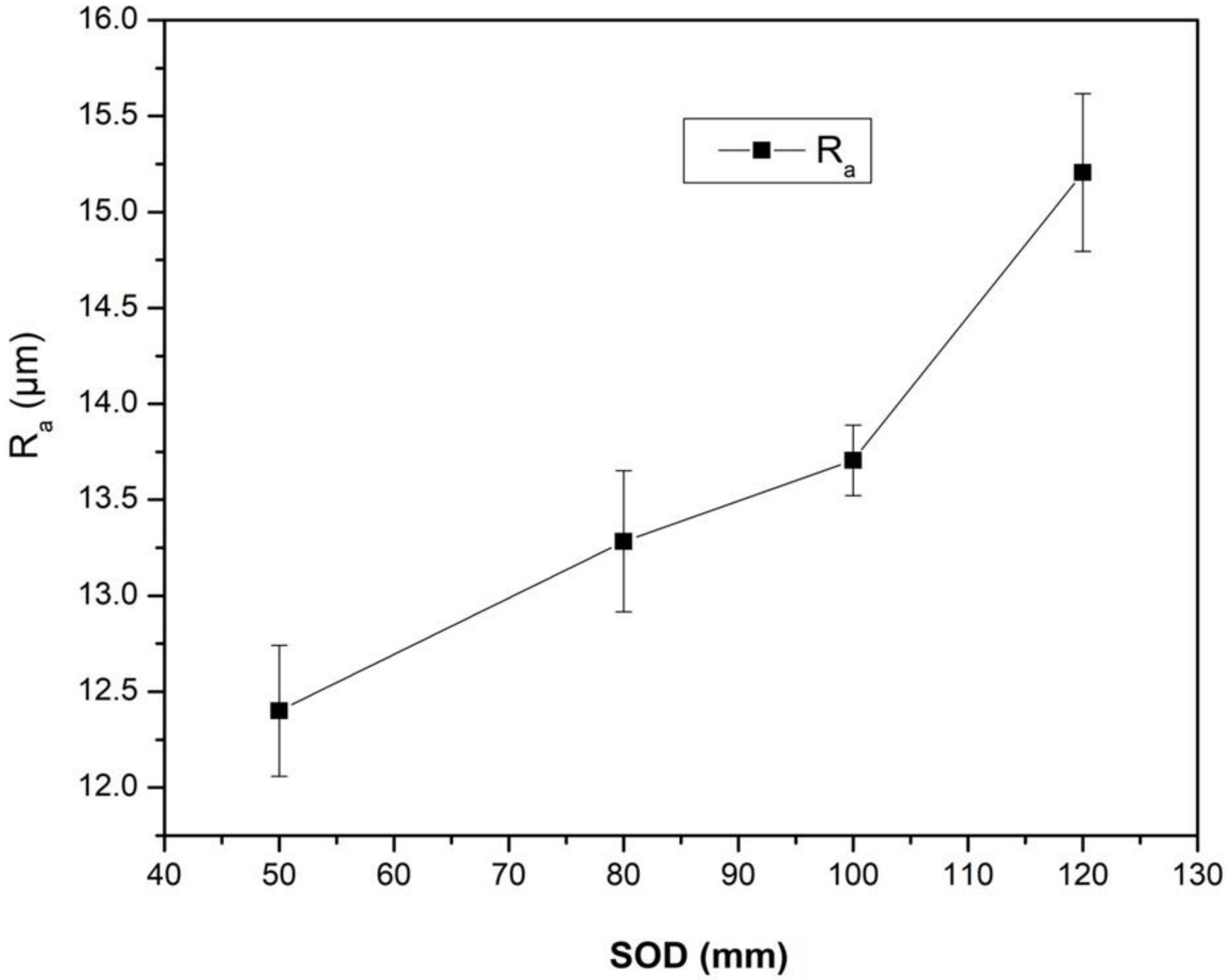


Fig. 3.1 : Variation of Surface roughness of as deposited HA coatings with SOD

3.2 Scratch Tests

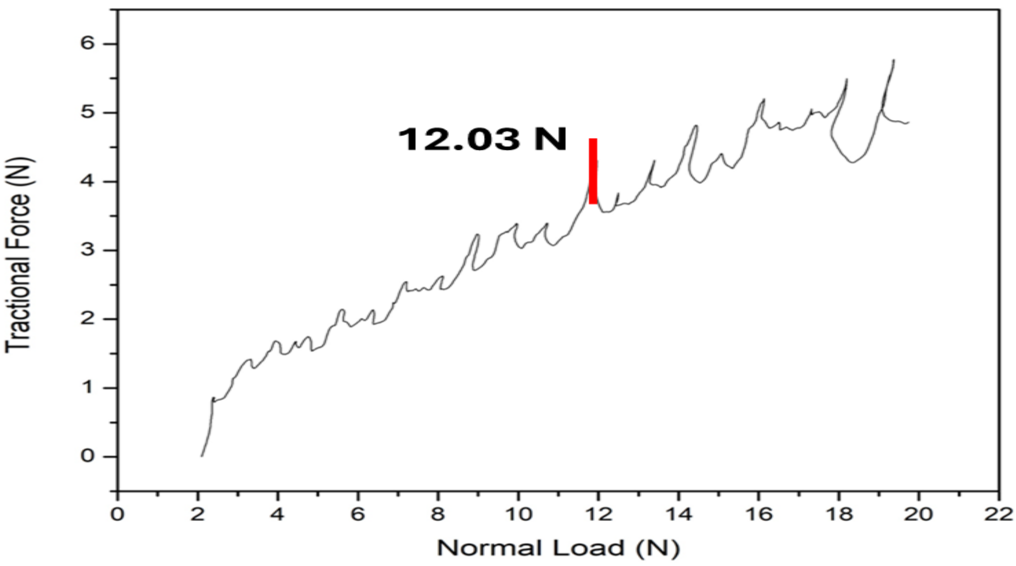


Fig. 3.2 : Variation of tractional force with normal load (Flame sprayed coating) SOD 50

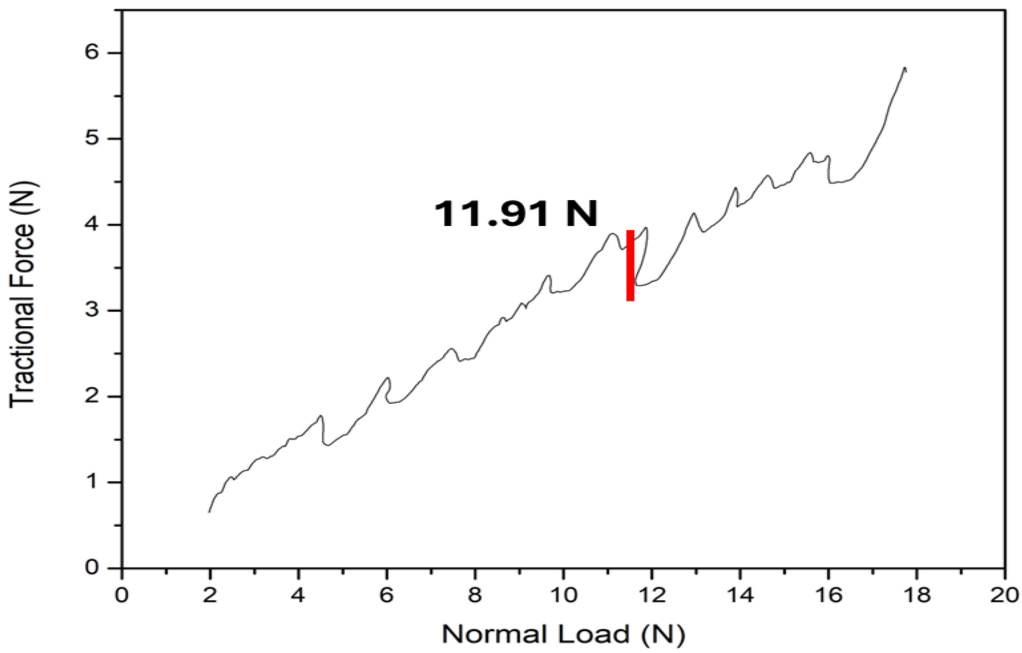


Fig. 3.3 : Variation of tractional force with normal load (Flame sprayed coating) SOD 80

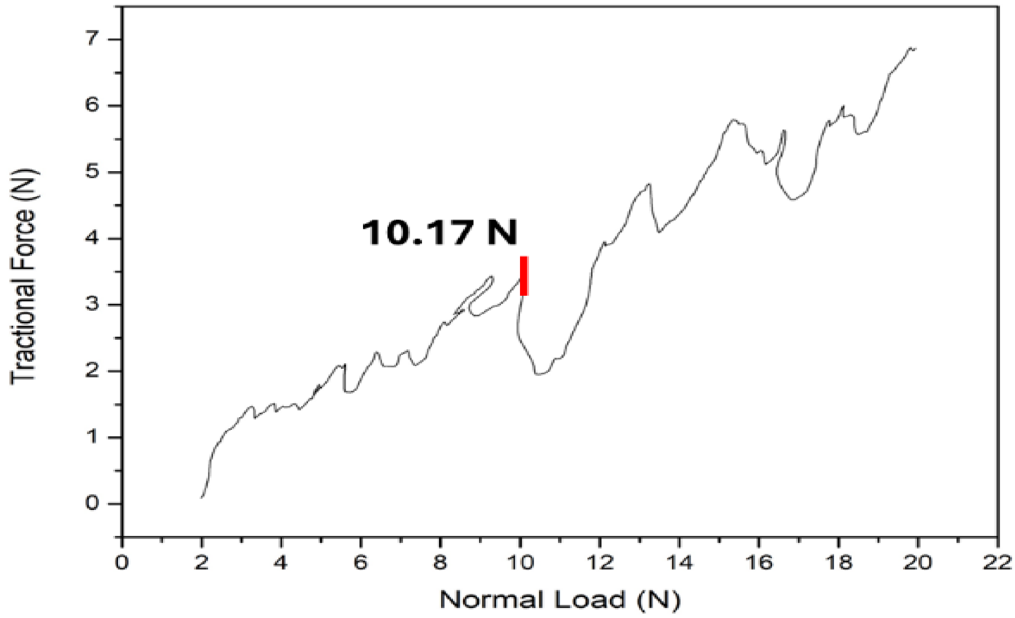


Fig. 3.4 Variation of tractional force with normal load (Flame sprayed coating) SOD 100

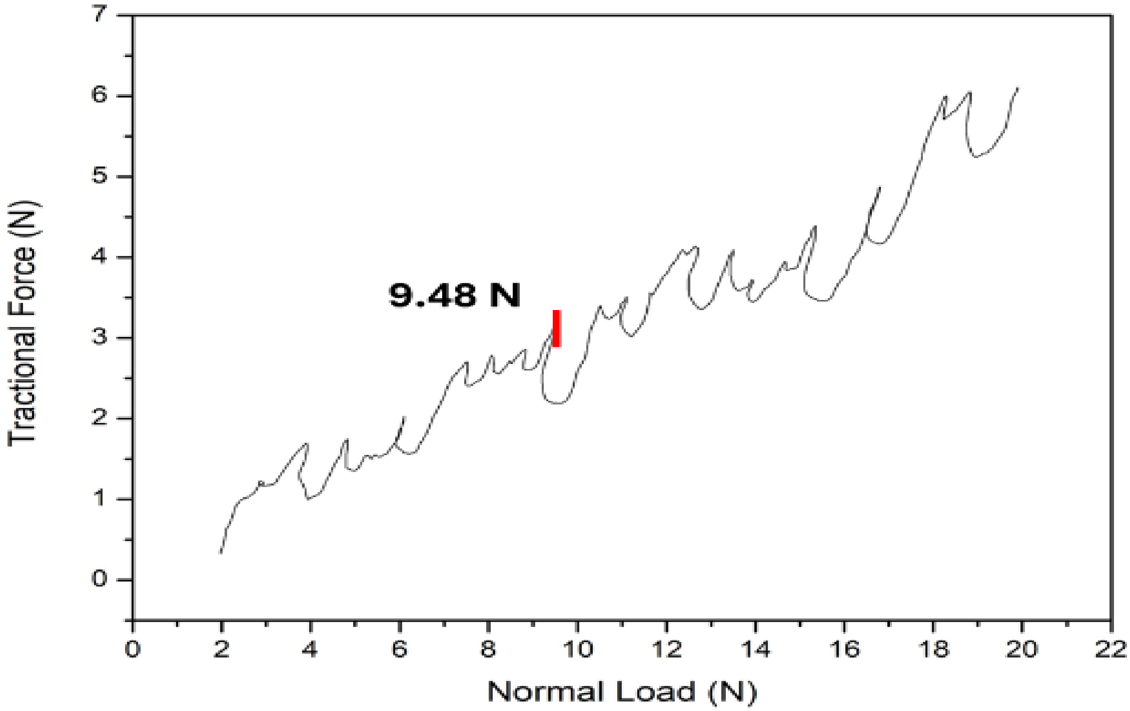


Fig. 3.5 : Variation of tractional force with normal load (Flame sprayed coating) SOD 120

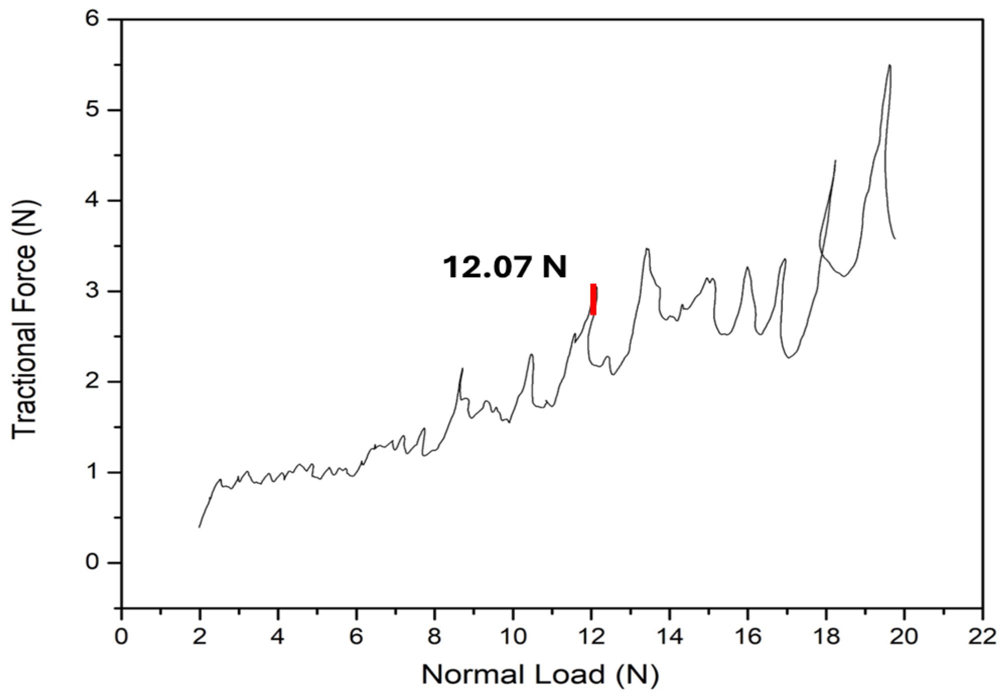


Fig. 3.6 : Variation of tractional force with normal load (Plasma sprayed coating) SOD 100

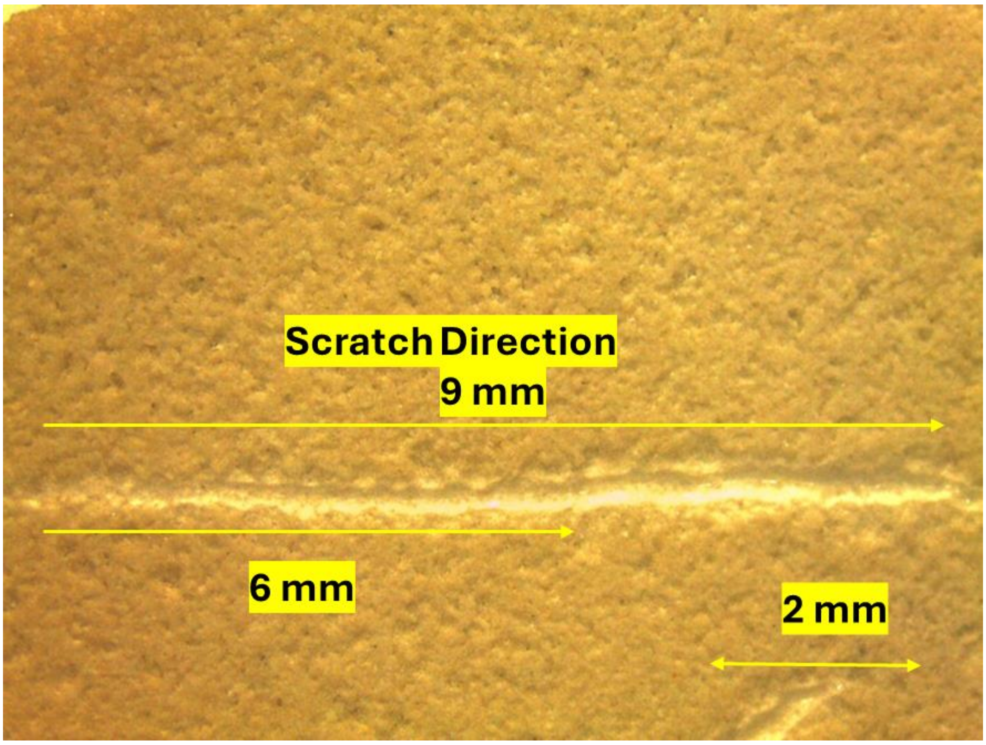


fig. 3.7 : Scratch track of HA coatings at SOD 50

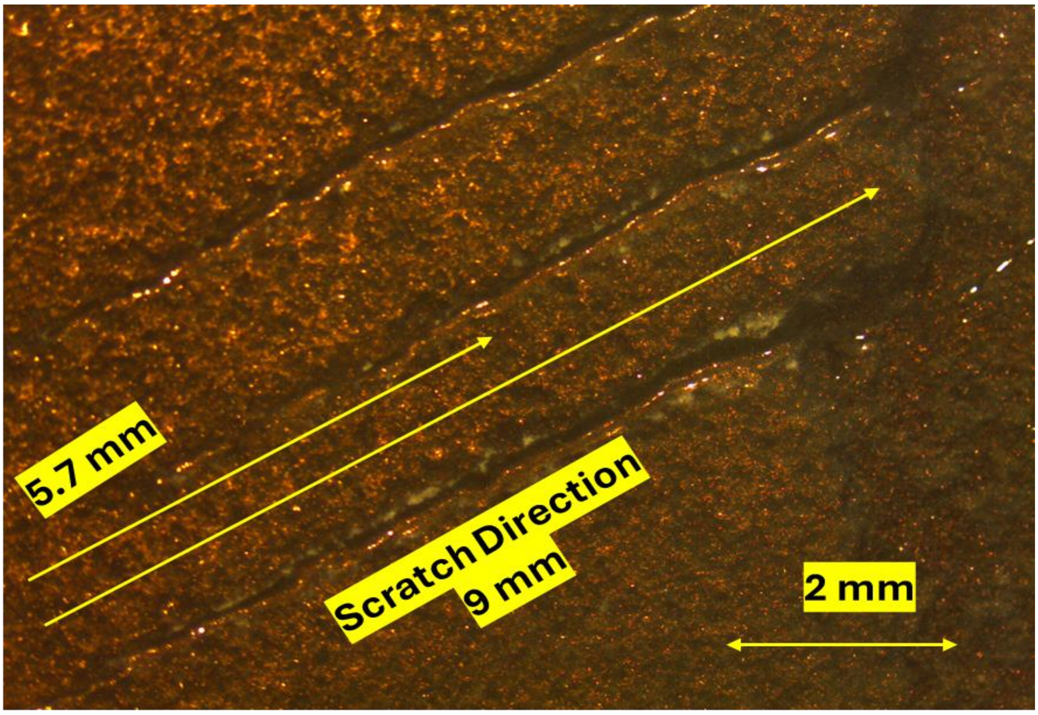


Fig. 3.8 : Scratch at HA coatings at SOD 80

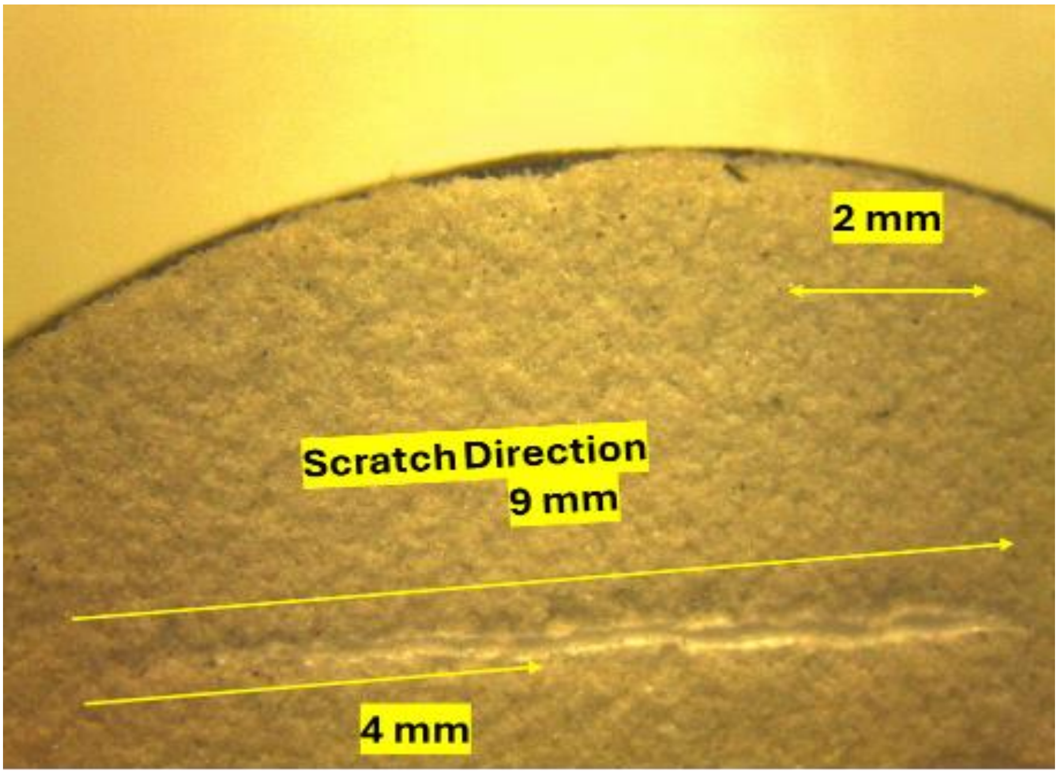


Fig. 3.9 : Scratch at HA coatings at SOD 100

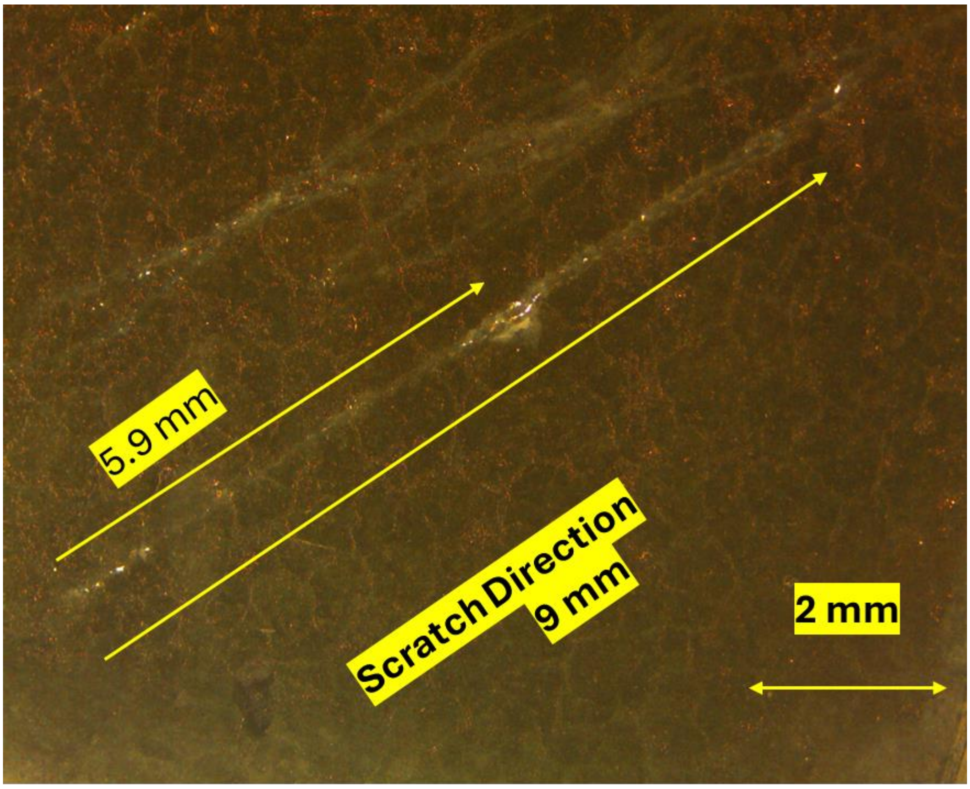


Fig. 3.10 : Scratch track of HA coatings at SOD 120

3.3 XRD Analysis

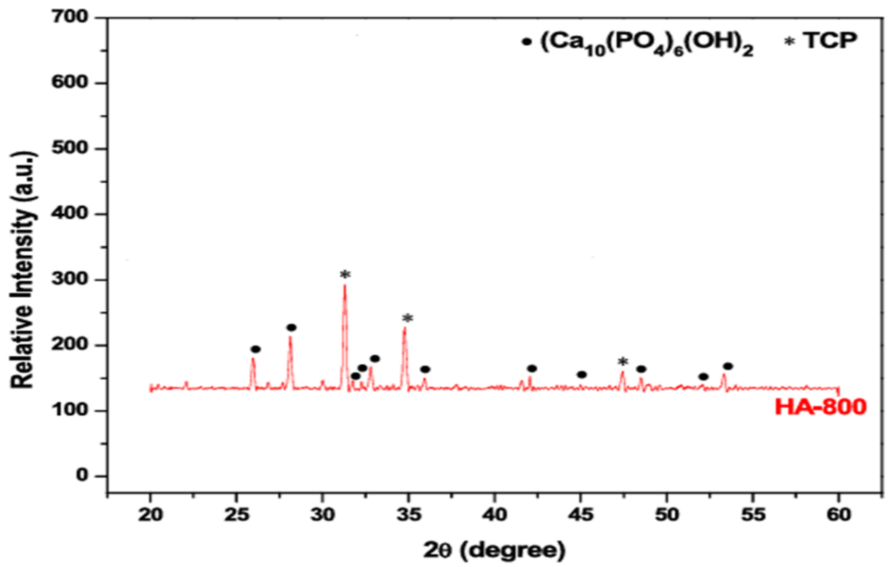


Fig. 3.11 : XRD pattern of synthesized Hydroxyapatite powder (HA-800) [2]

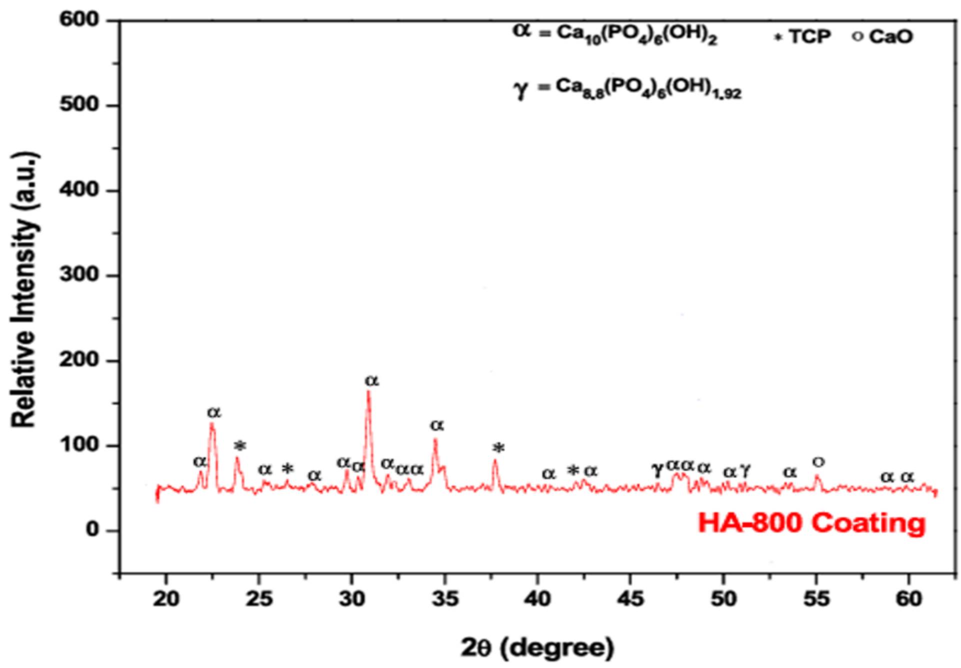


Fig. 3.12 : XRD pattern of plasma sprayed HA 800 coatings at 100 mm SOD [2]

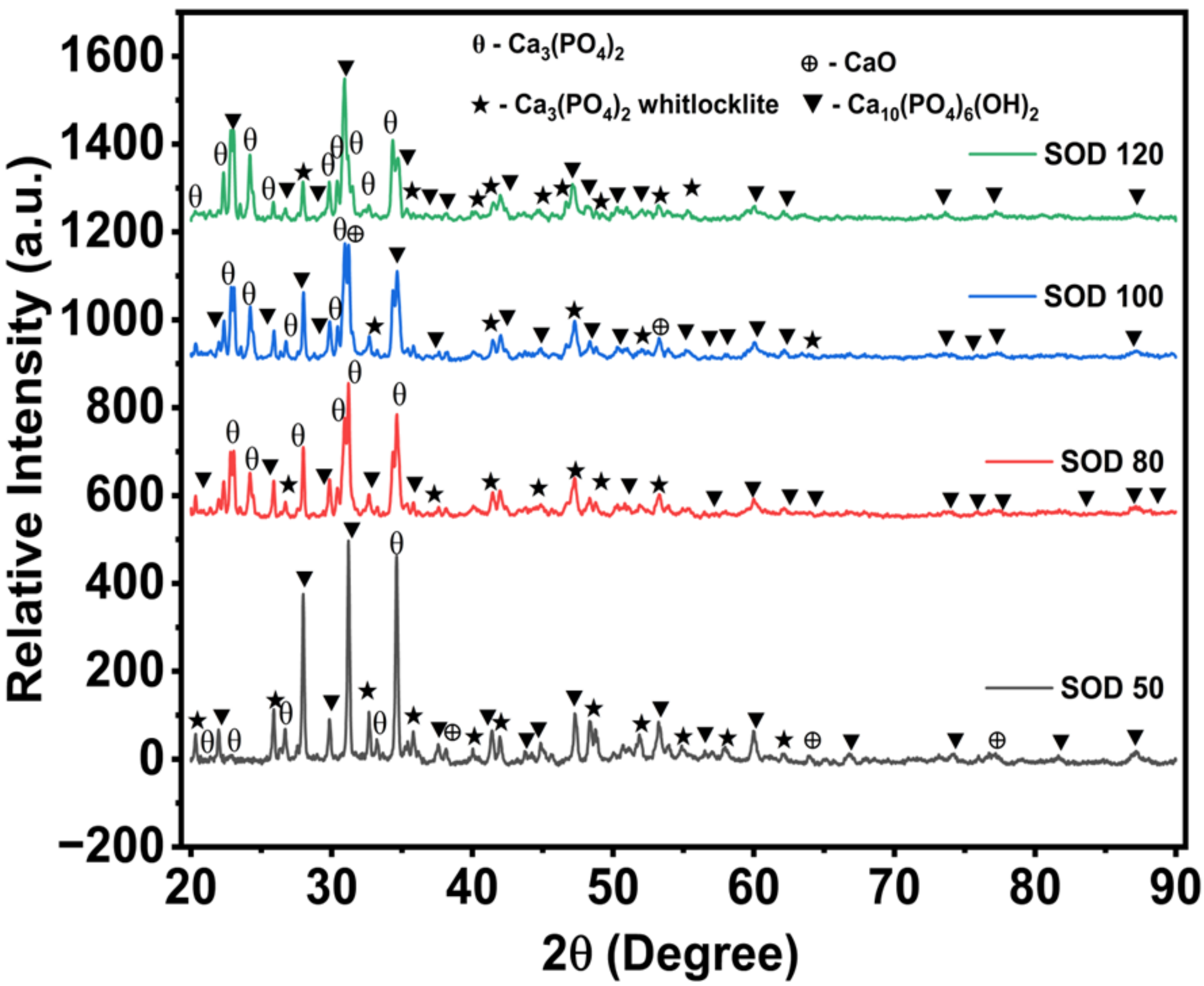


Fig. 3.13 : XRD pattern of flame sprayed HA 800 coatings with Varying SOD

3.4 FESEM Analysis (Top Surface)

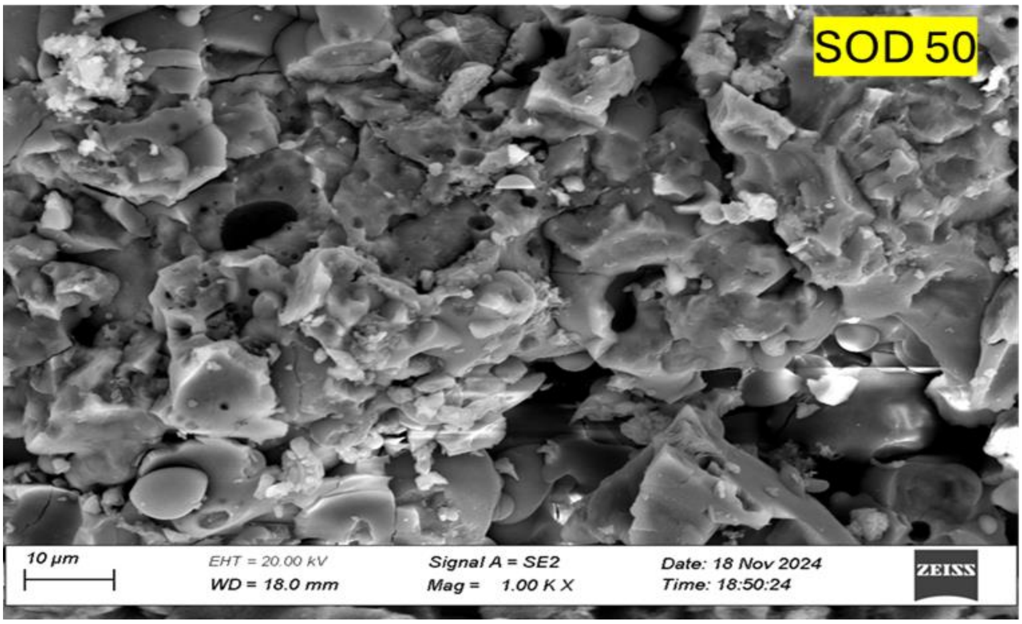


Fig. 3.14 : FESEM micrographs of Flame Sprayed HA coatings SOD 50

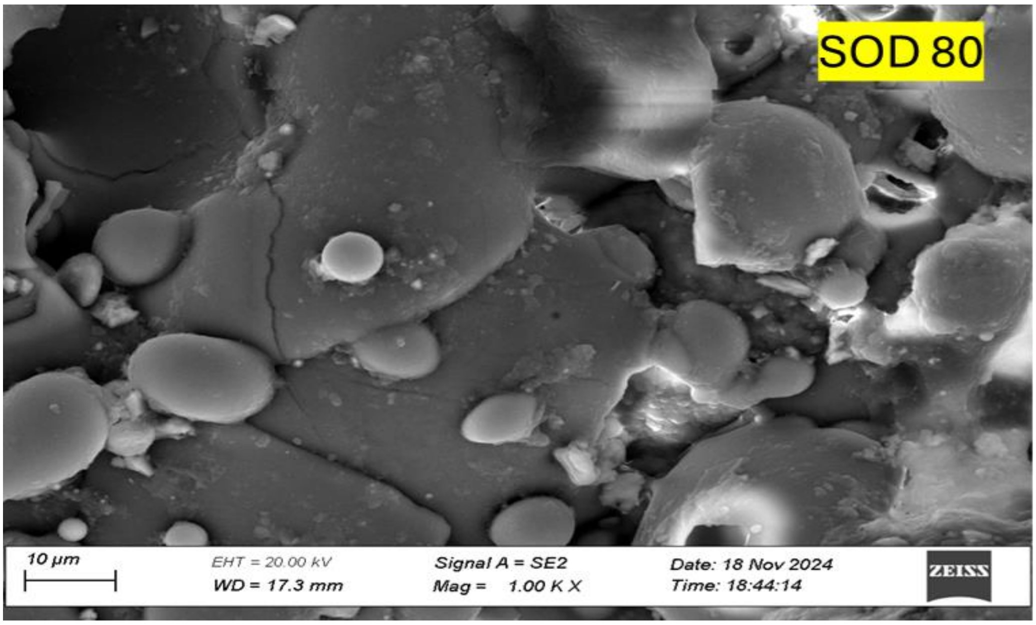


Fig. 3.15 : FESEM micrographs of Flame Sprayed HA coatings SOD 80

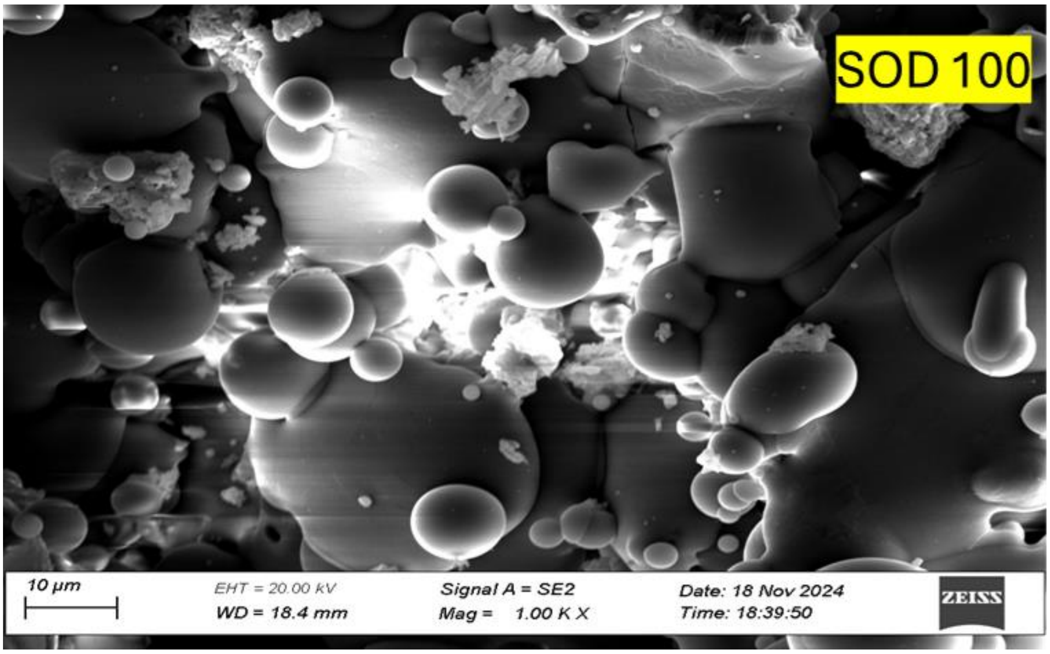


Fig. 3.16 : FESEM micrographs of Flame Sprayed HA coatings SOD 100

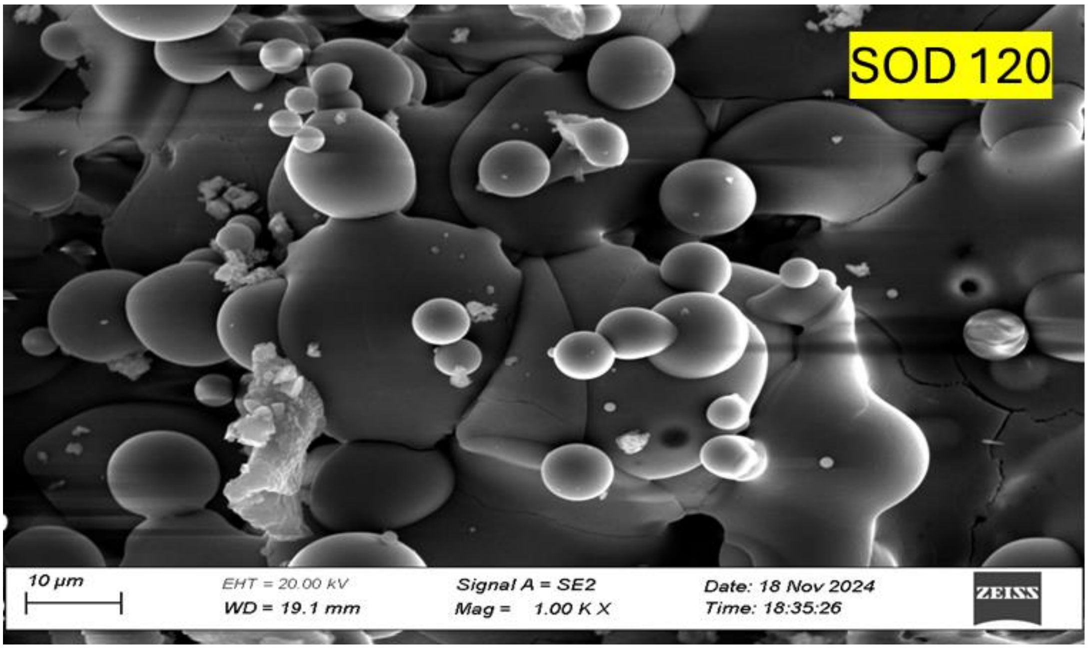


Fig. 3.17 : FESEM micrographs of Flame Sprayed HA coatings SOD 120

3.5 Porosity Analysis

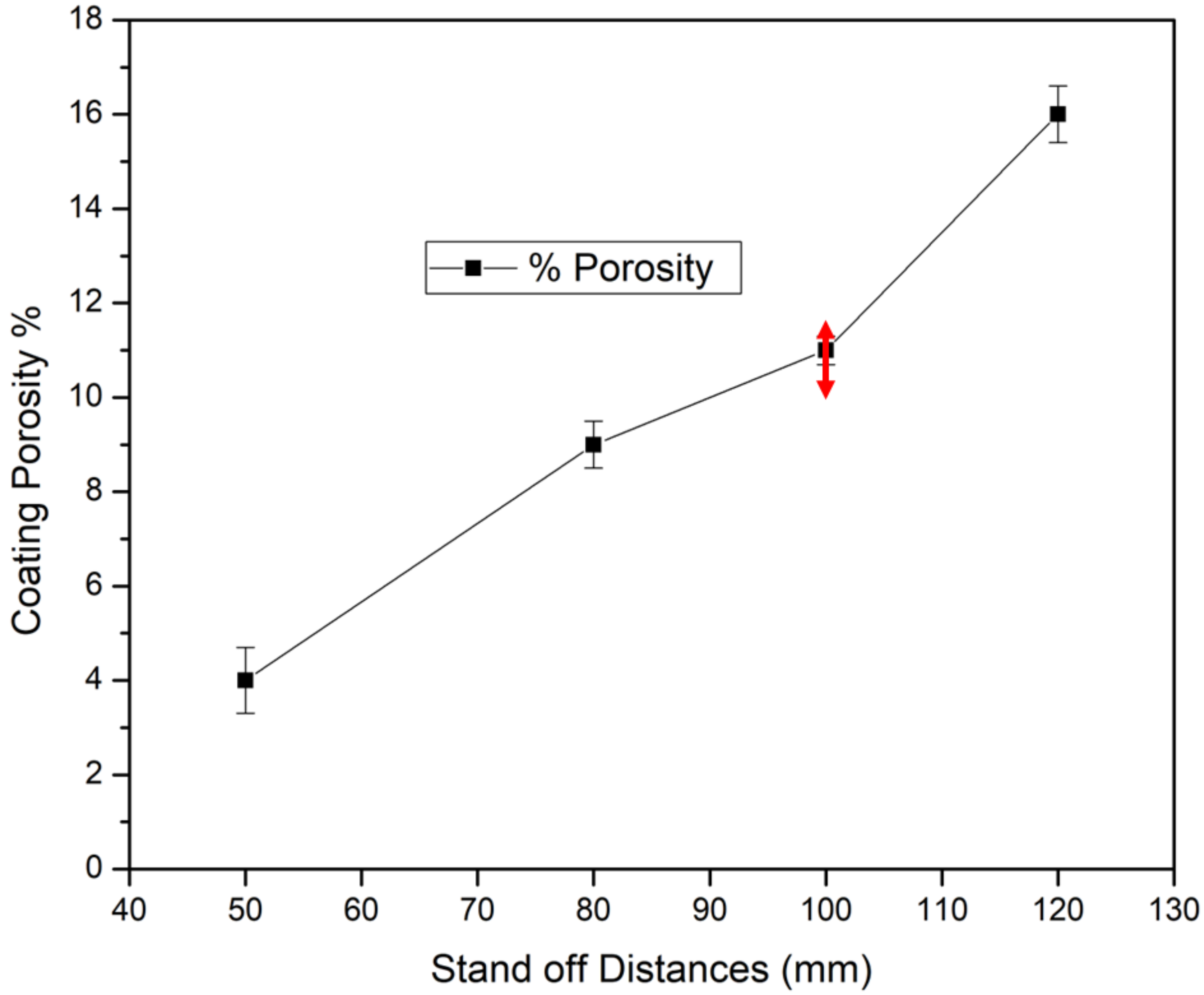


Fig. 3.18 : Coating Porosity of Flame Sprayed samples

For the same HA-800 with plasma spray method and SOD 100 the coating porosity lies between 9 – 11 % Red Segment indicates the Plasma sprayed samples coating [2]

3.6 Wear Test (Linear Reciprocating Type)

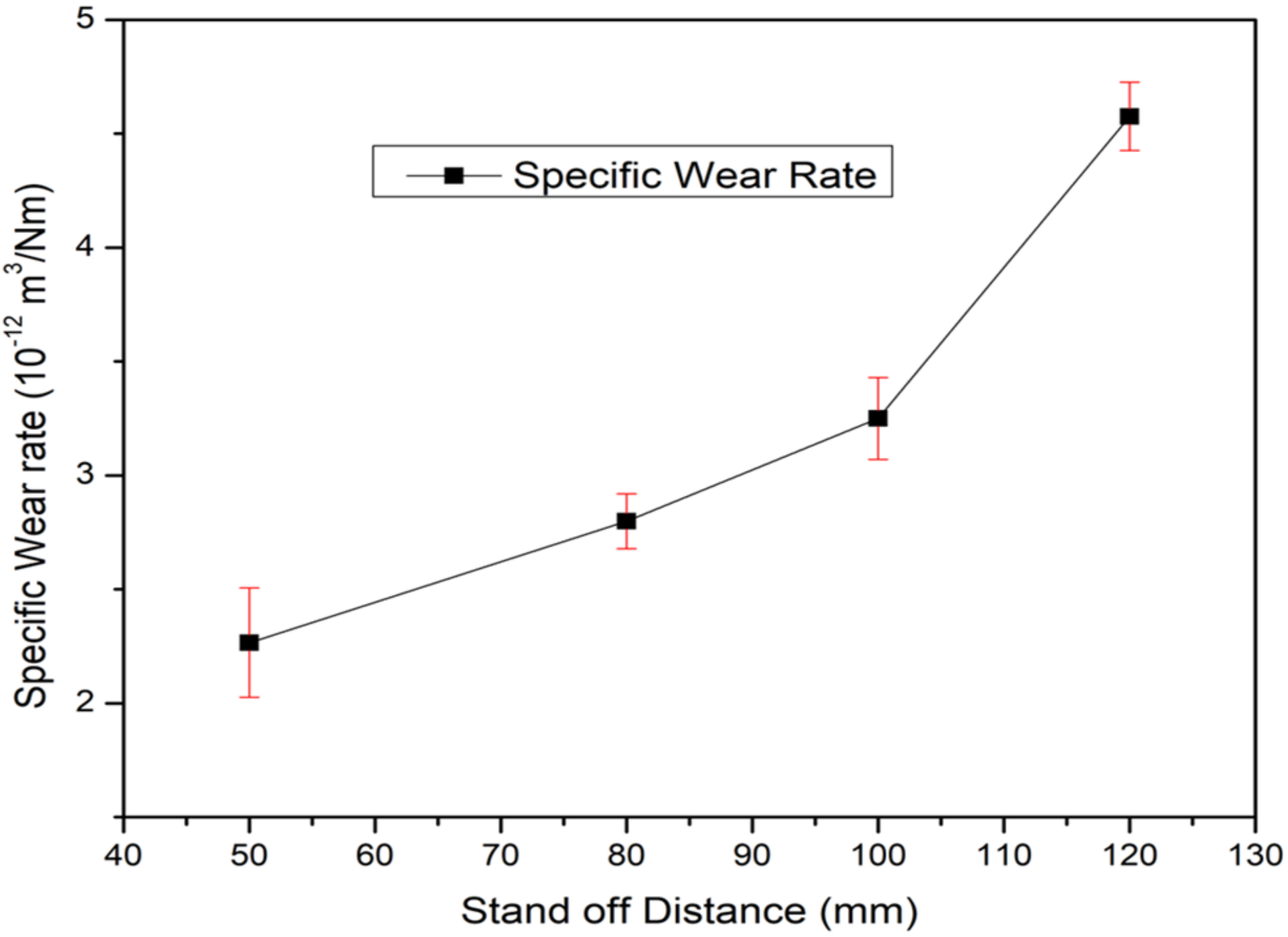


Fig. 3.19 : Specific Wear Rate of Flame Sprayed HA coatings

(Frequency - 12 Hz , Stroke Length / Amplitude - 3 mm , Test Duration - 15 min , Normal Load - 5 N)

3.7 Coefficient of Friction Vs Sliding Distance graph

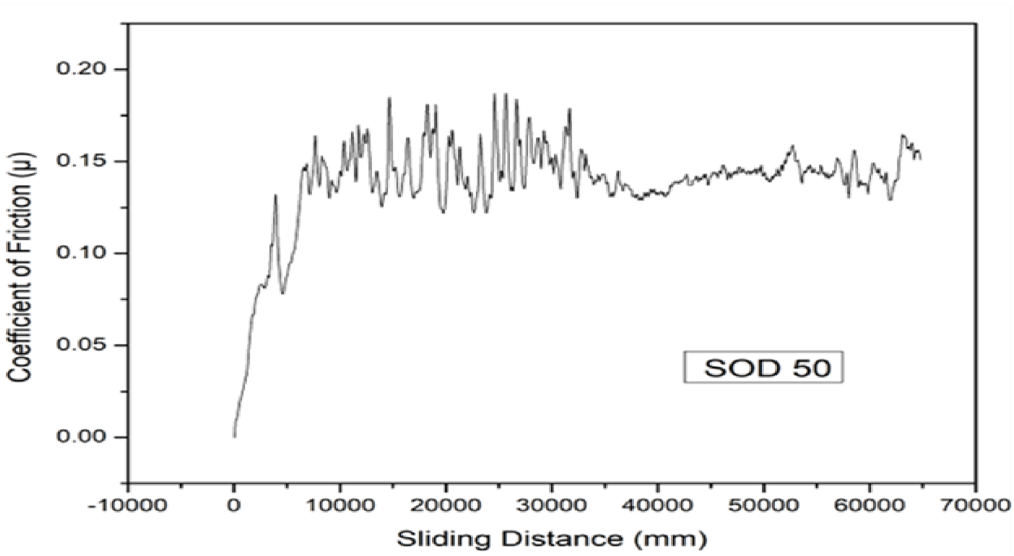


Fig. 3.20 : Coefficient of Friction Vs Sliding Distance graph SOD 50

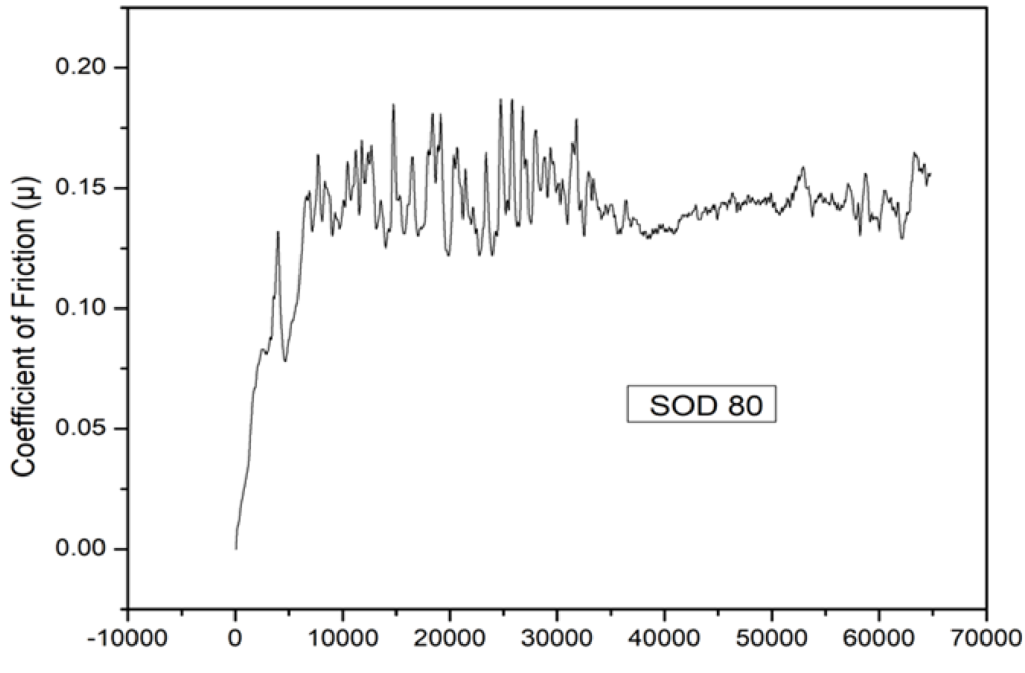


Fig. 3.21 : Coefficient of Friction Vs Sliding Distance graph SOD 80

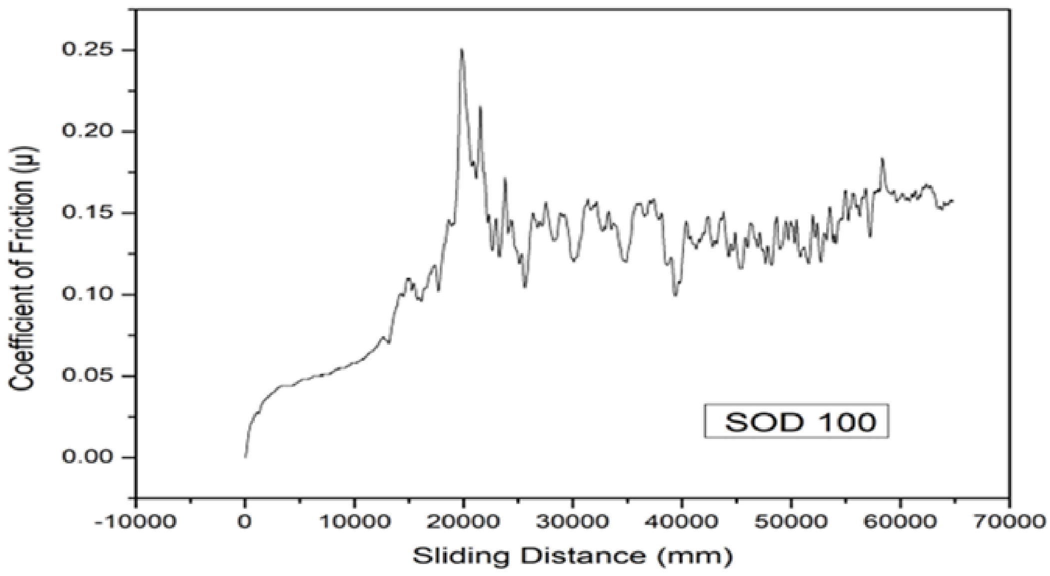


Fig. 3.22 : Coefficient of Friction Vs Sliding Distance graph SOD 100

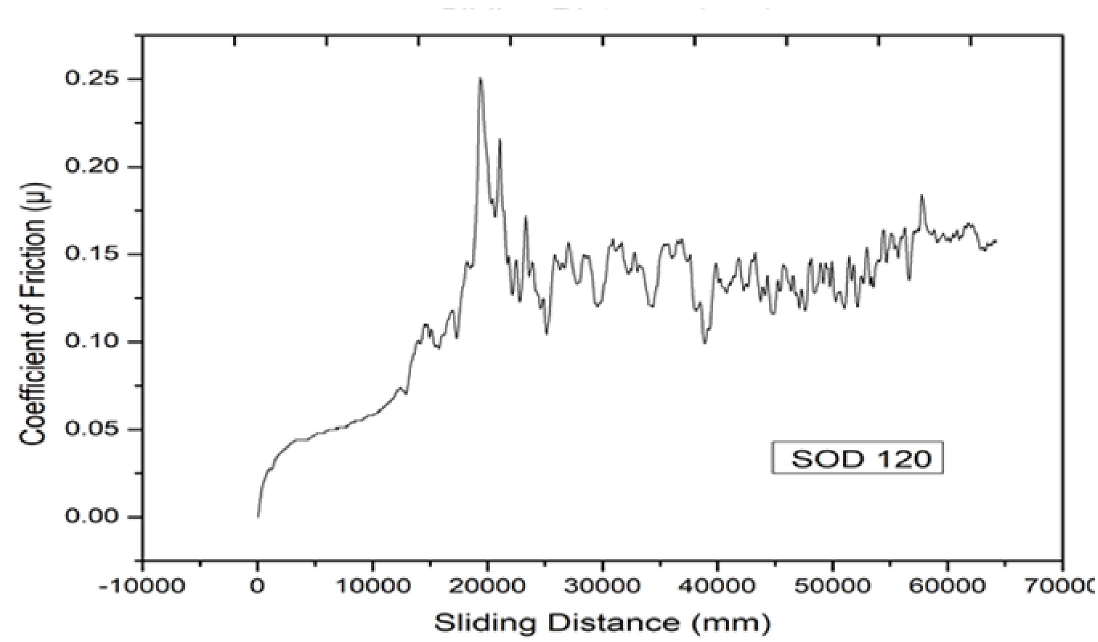
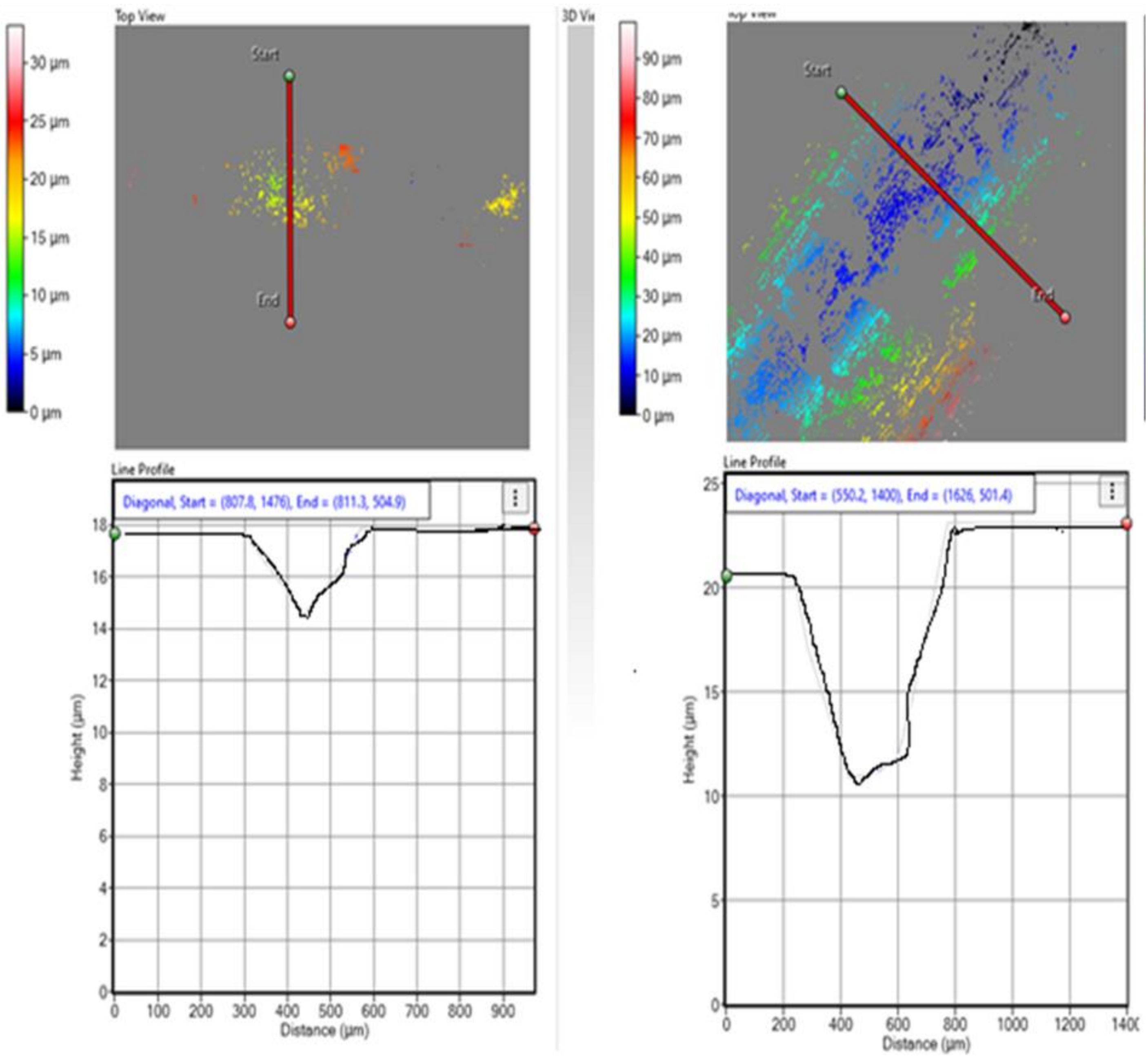


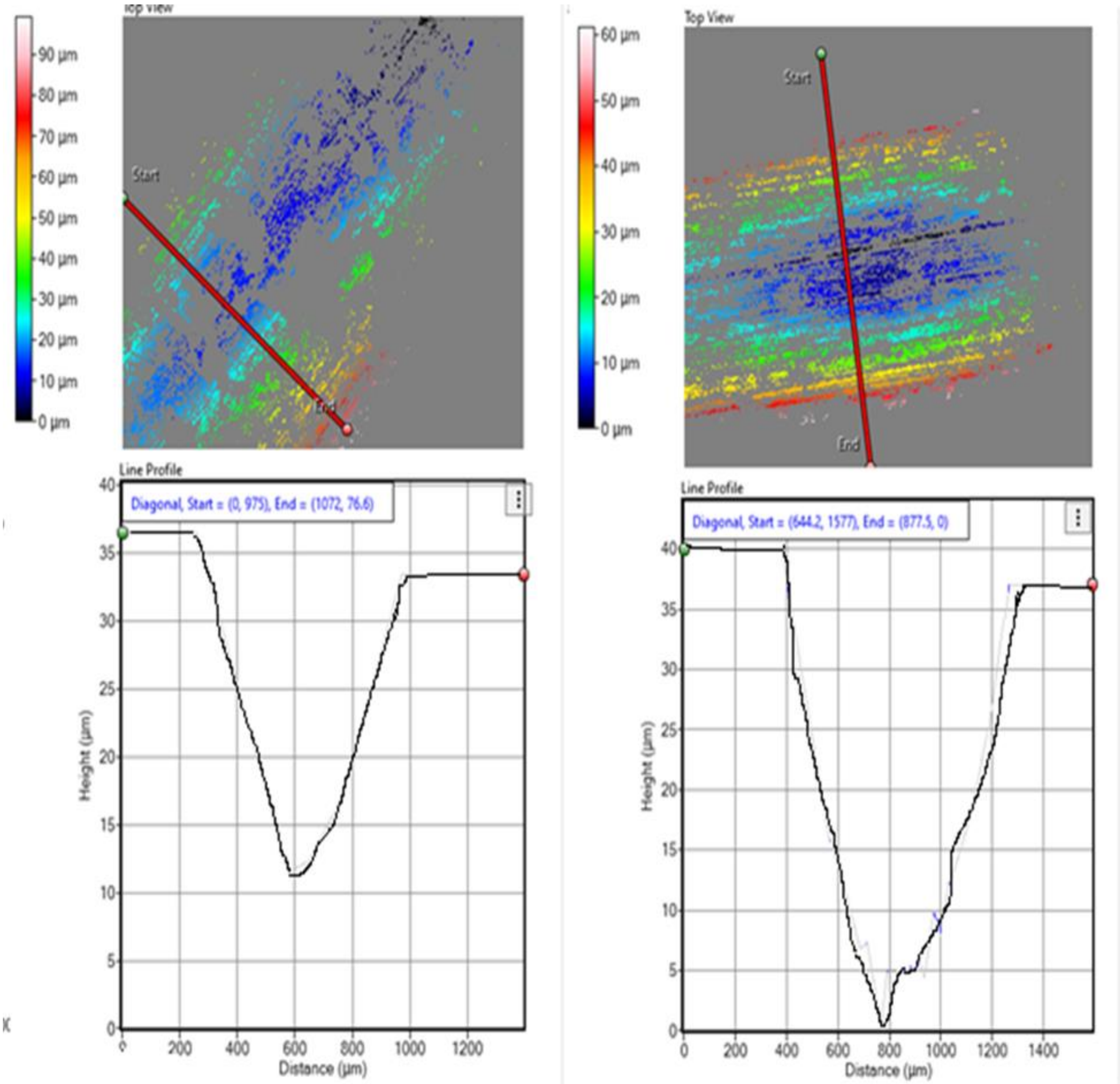
Fig. 3.23 : Coefficient of Friction Vs Sliding Distance graph SOD 120

3.8 Wear Track



SOD 50 **SOD 80**

Fig. 3.24 : Wear Track of Flame Sprayed Samples SOD 50 and SOD 80



SOD 100 **SOD 120**

Fig. 3.25 : Wear Track of Flame Sprayed Samples SOD 100 and SOD 120

3.9 Vickers Micro-hardness Analysis

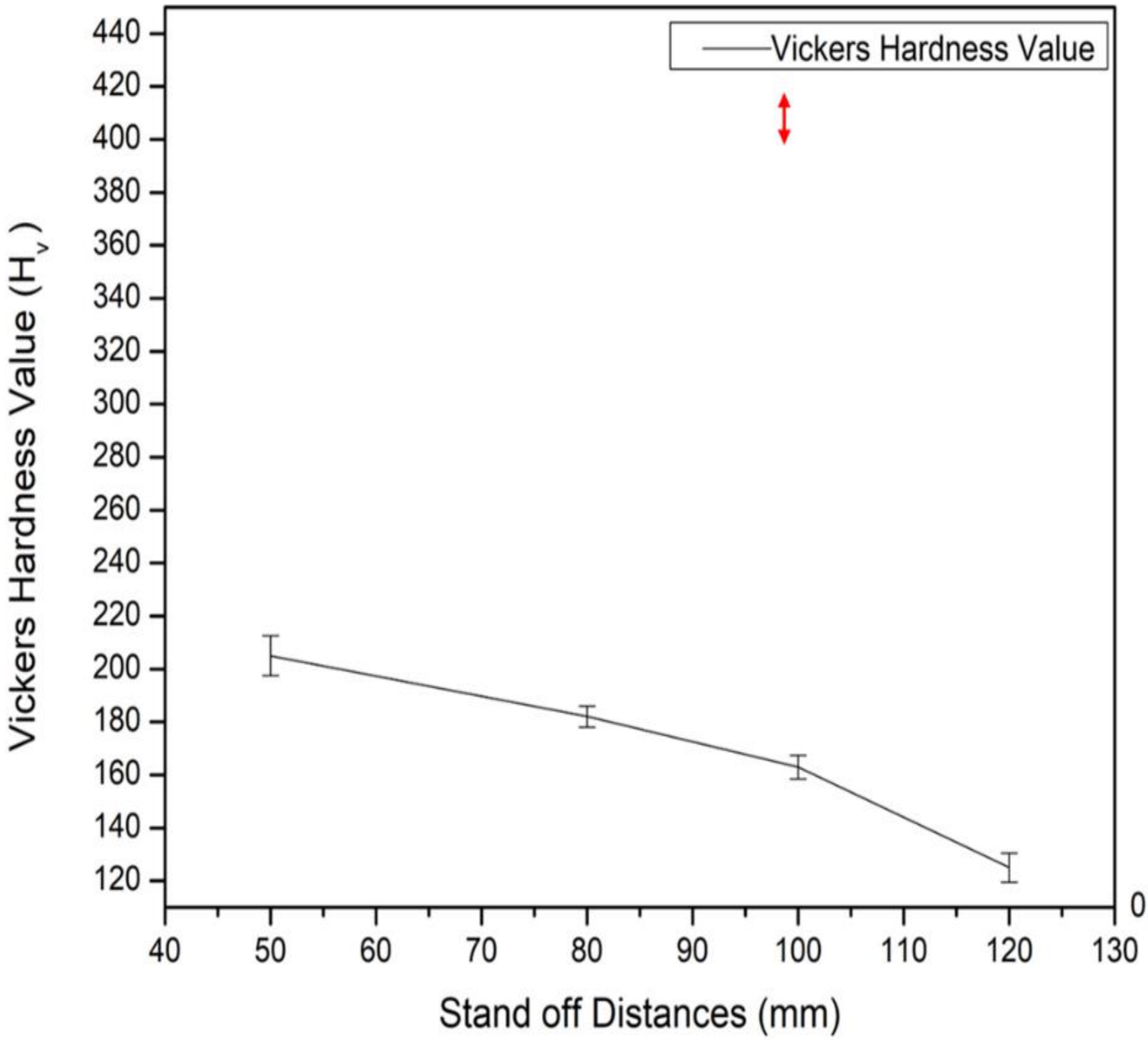


Fig. 3.26 : Hardness of Flame Sprayed Samples Red segment indicates APS sample

3.10 SEM Morphology of SBF samples

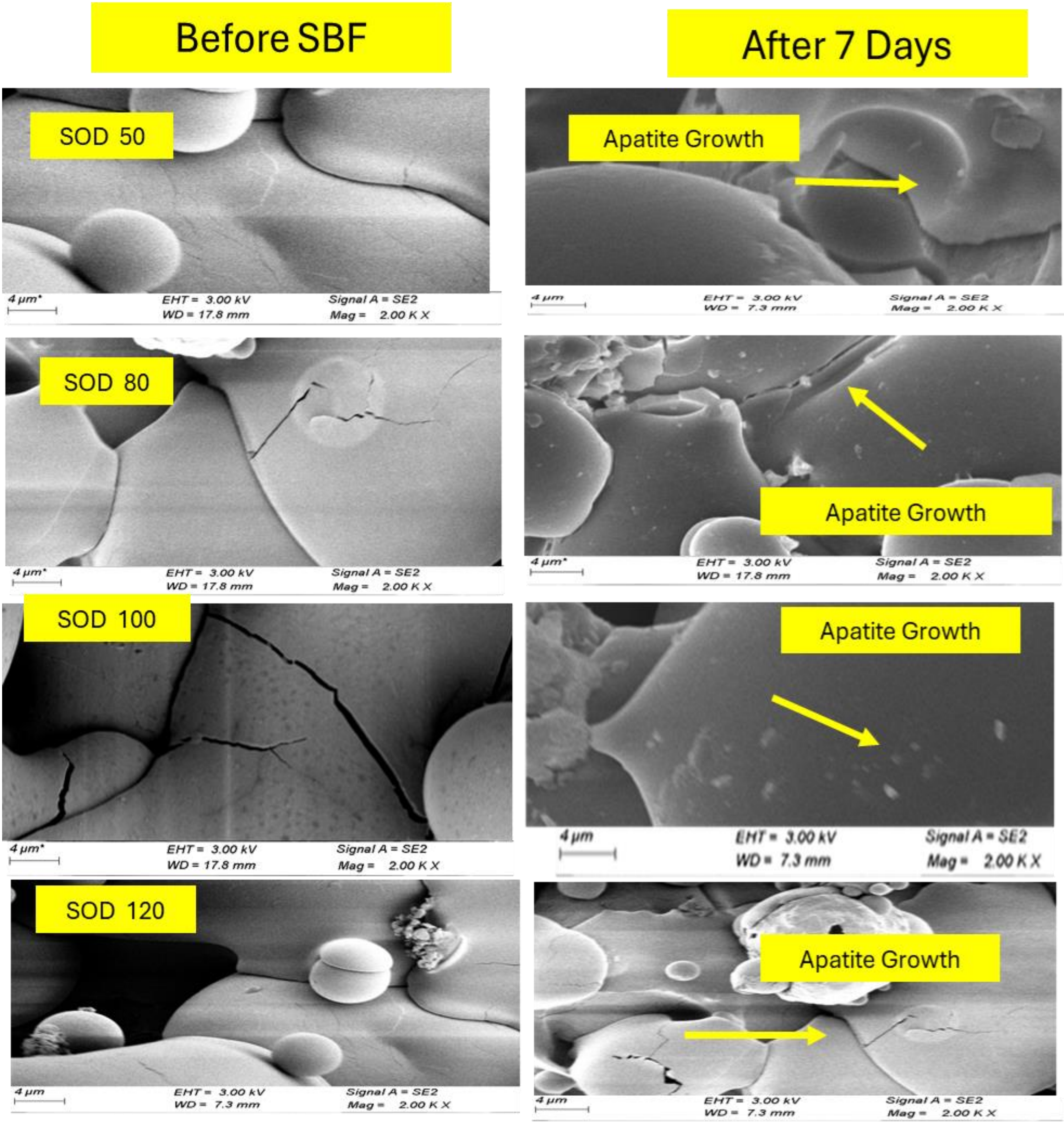


Fig. 3.27 : SEM Morphology of SBF samples

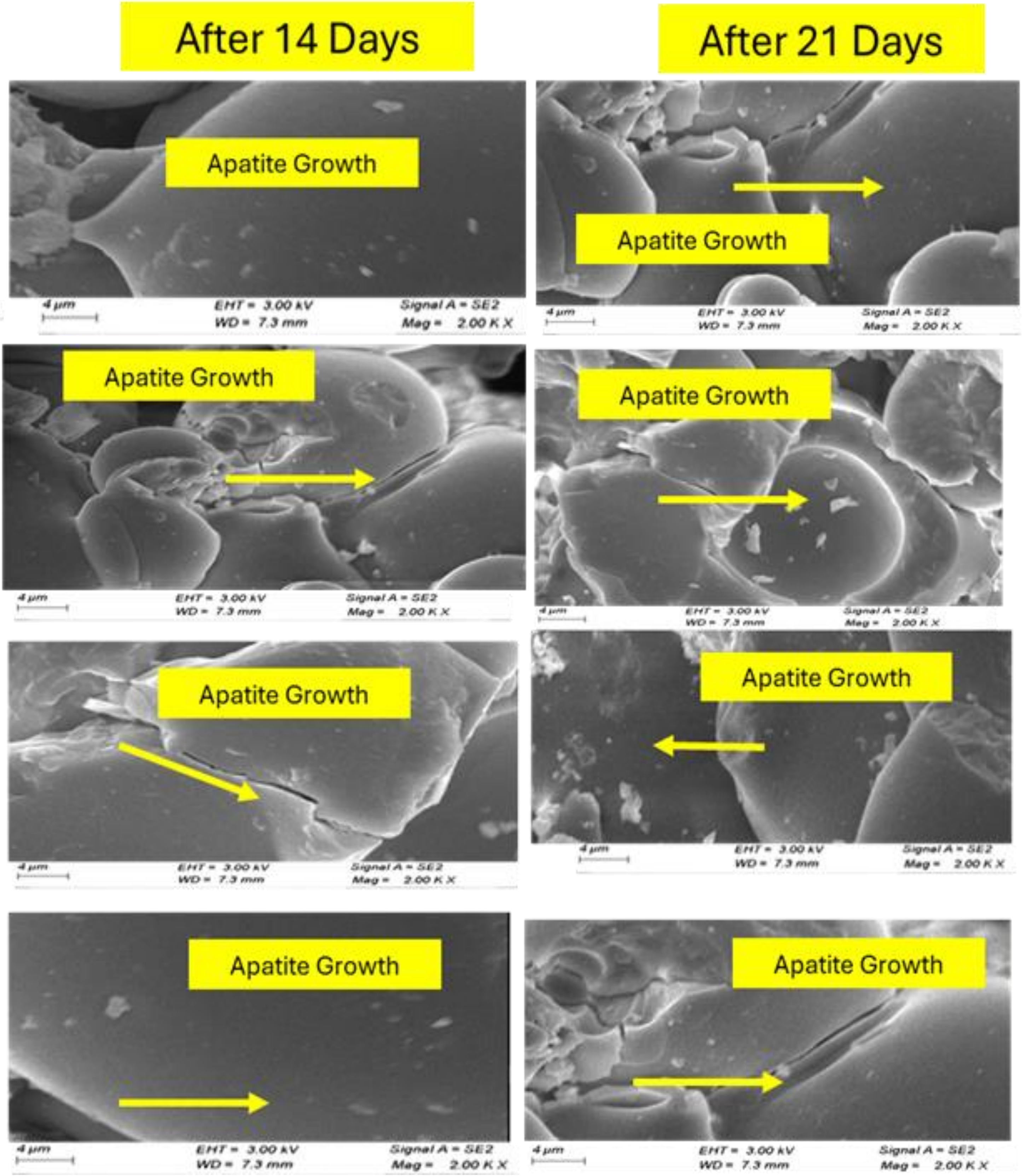


Fig. 3.28 : SEM Morphology of SBF samples

3.11 XRD Pattern of Free-standing Coatings SBF samples

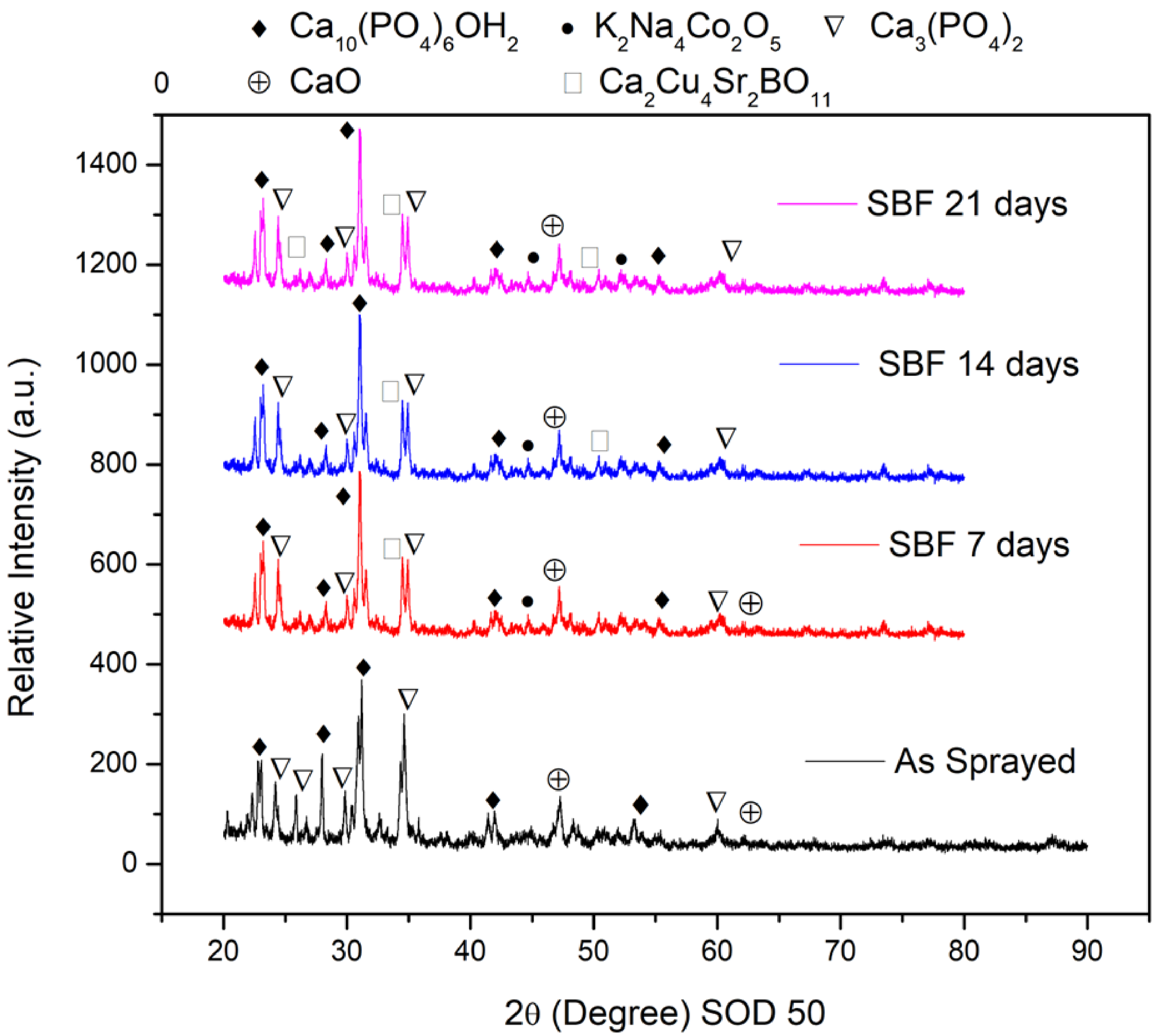


Fig. 3.29 : XRD pattern of flame sprayed HA 800 coatings with Varying SBF duration [SOD 50]

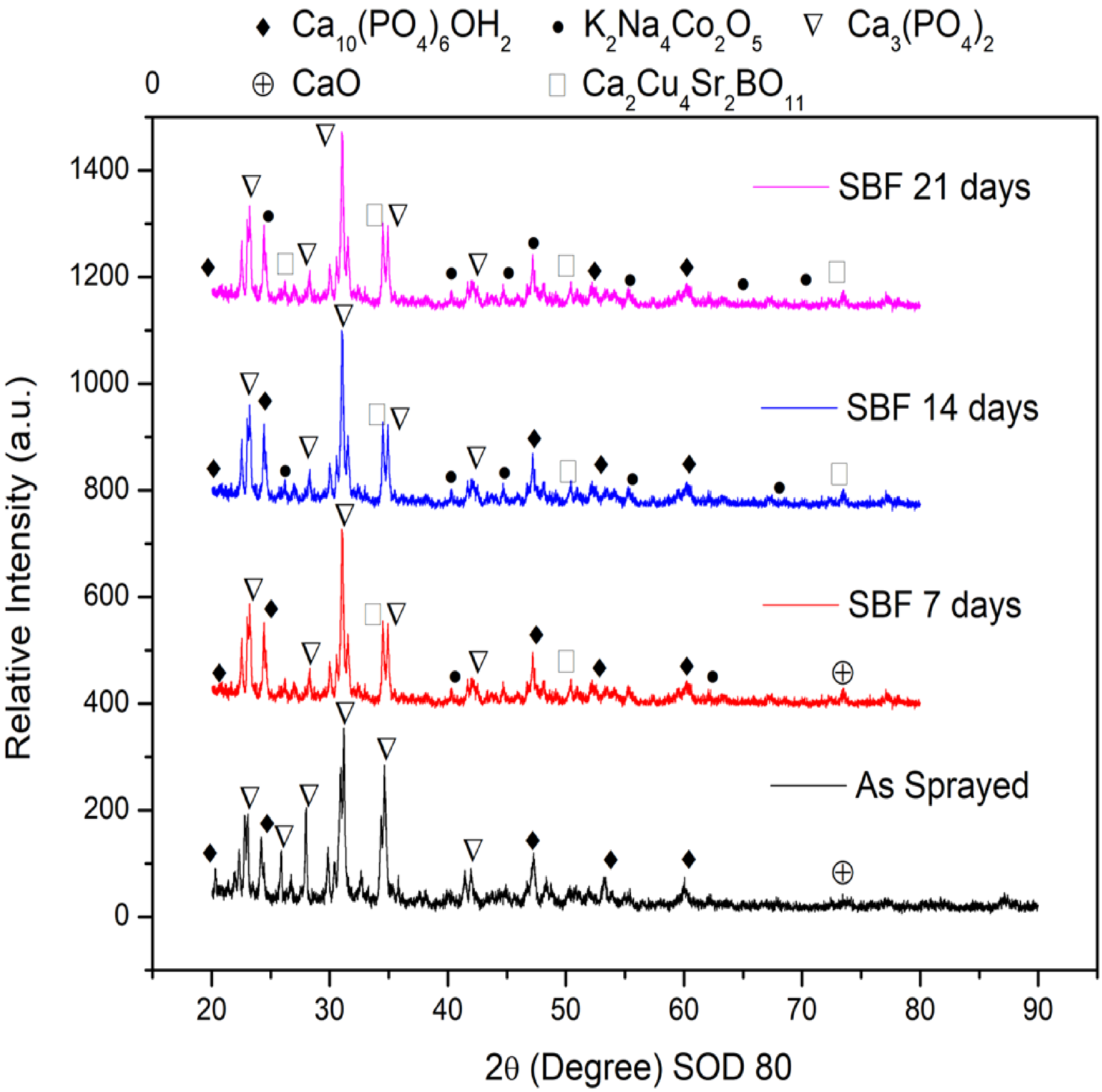


Fig. 3.30 : XRD pattern of flame sprayed HA 800 coatings with Varying SBF duration [SOD 80]

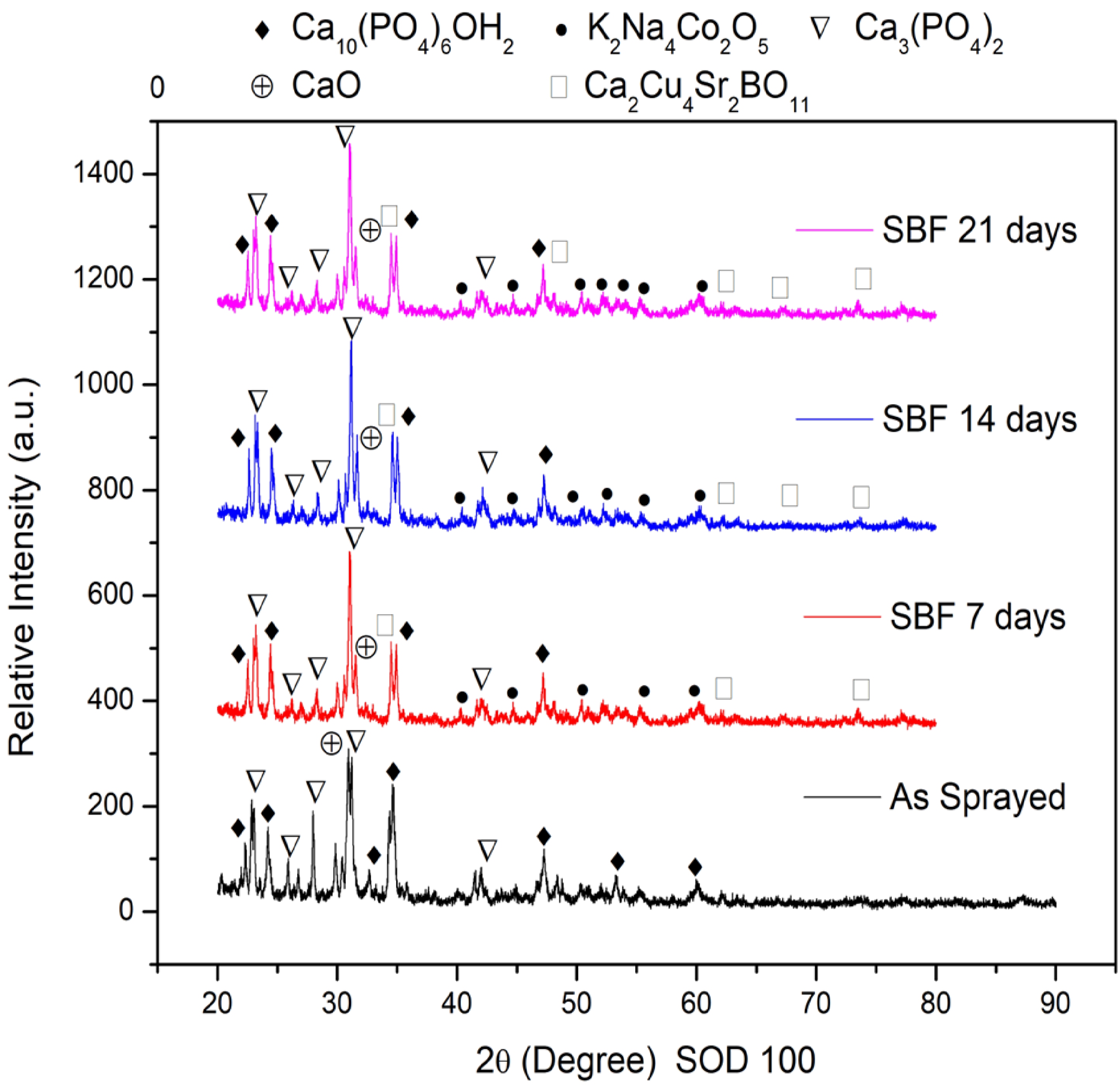


Fig. 3.31 : XRD pattern of flame sprayed HA 800 coatings with Varying SBF duration [SOD 100]

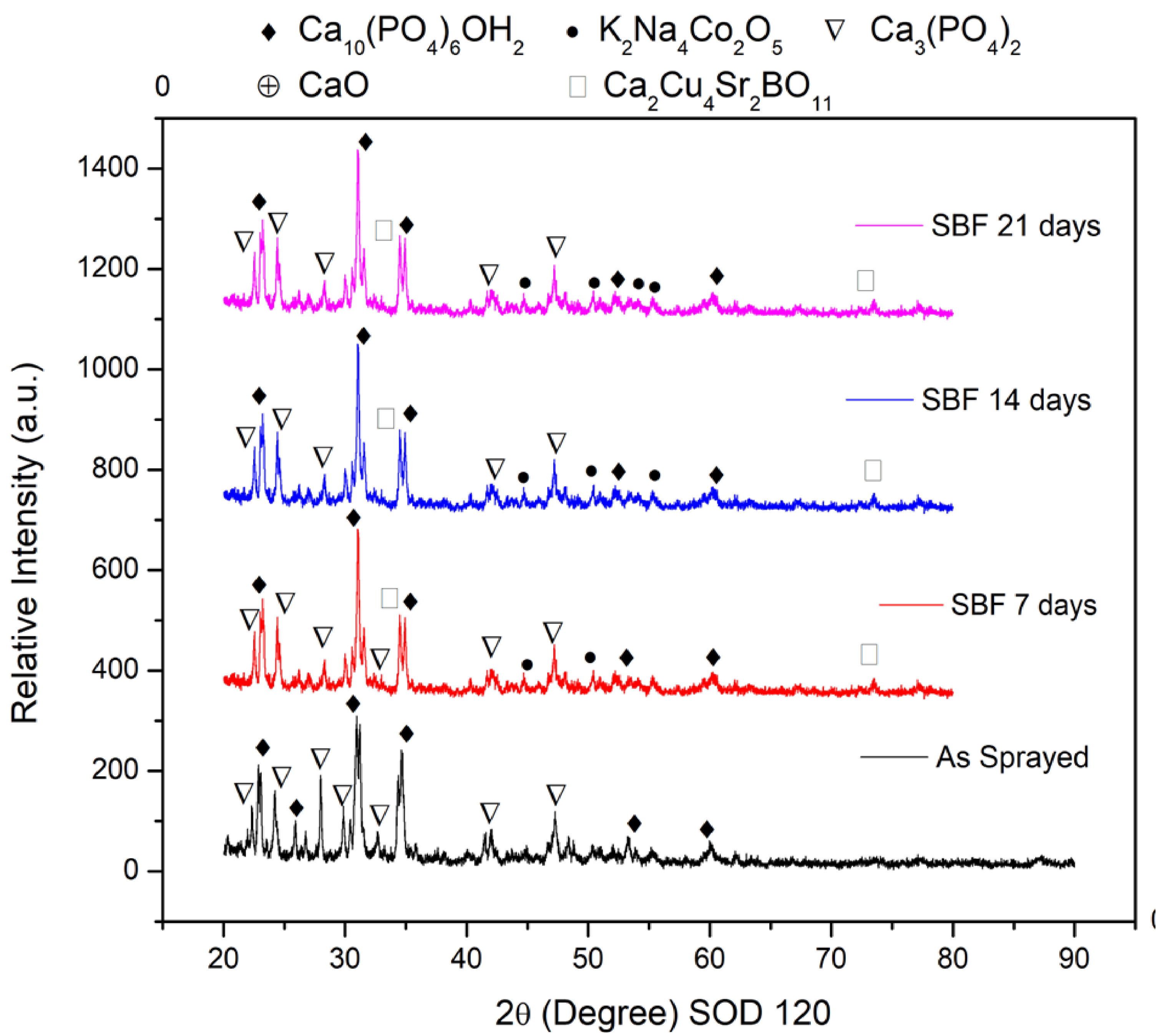


Fig. 3.32 XRD pattern of flame sprayed HA 800 coatings with Varying SBF duration [SOD 120]

Chapter 4 : Conclusions

1. Satisfactory coatings are obtained from all the selected SODs of flame spraying. Good melting and spreading of splats are observed in all the coatings.

2. The surface roughness of the flame sprayed HA coatings are increased with an increase in the stand of distance (SOD). It suggests good melting and spreading of splats at lower SOD. With higher SODs the molten volume dries up to a certain extent before reaching the substrate surface.

3. The adhesion strength of HA coating found to be the maximum at the SOD of 50, and further increase in SOD leads to a decrease in the same. With high spreading ability of the splats, the wetting of the surface has improved at lower SOD and hence the adhesion strength is found to be enhanced.

4. The stable Hydroxyapatite (HA) ,calcium phosphate and calcium oxide (CaO) phases are formed in all the flame sprayed HA coatings. On the other hand, less calcium phosphate phase is formed in APS coated HA. The low particle velocity in the oxyacetylene flame may have caused more decomposition of HA to form significant amount of secondary phases. It seems the chance of HA decomposition is lesser in case of APS coated HA due to a very high particle velocity in the plasma environment. However, the high solidification rate causes to form more metastable HA phases in APS .

5. The sharp and high intensity HA peaks obtained from 50 SOD suggests more HA phase formation and less decomposition compared to the same from the other SODs. Possibly, the low SOD has not allowed the HA to get sufficient time to decompose. Hence, a relatively lower amount of secondary phases are formed in such coating.

6. Porosity of HA coatings is increased with an increase in stand off distance (SOD) . At SOD 50 it is minimum

7. The bioactivity of the HA coating is found satisfactory when the SOD is kept around 80-100 mm . The high formation of TCP phase and moderately high porosity content may have helped them to improve the bioactivity in SBF solution .

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8. source: https://youtu.be/t5totwTeiRk?feature=shared