Jurnal Tribologi 46 (2025) 113-121

MYTRIBOS
Malaysian Tribology Society

Jurnal Tribologi

Website : jurnaltribologi.mytribos.org e-issn: 2289-7232

The role of nanotubes in enhancing plasma-sprayed hydroxyapatite coatings properties

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KEYWORDS

Plasma-spray technique
Crystallinity
Fracture toughness
XRD
Tribo-test

ABSTRACT

Hydroxyapatite (HA) coatings with low fracture toughness and crystallinity increment bioresorption, which comes about in poor attachment between the coating and substrate. This can be since HA coatings quickly lose bulk, which leads to destitute steadiness and inevitably extricating of inserts implant. In this manner, within the present work an endeavor is made to improve crystallinity and fracture toughness of HA coating reinforced with multiwalled carbon nanotubes (MCNT). Crystallinity and fracture durability of HA fortified with MCNT was observed to be better as compared to immaculate HA coat. These improvement attributed to mechanical and thermal properties offered by MCNT. The analytical tools were used to examine the phase and microstructure of the coatings in the present work.

1.0 INTRODUCTION

Hydroxyapatite (HA) is wordwide used in uncemented prosthesis (Lawton. K., et al.,2019; Benim, P. G., et al., 2019). HA is a bioactive substance that supports osseointegration and bone development that shares chemical similarities with human bones. Its work in orthopedic load-bearing applications is motivated by its unique ability to cooperate with living tissues and to stimulate tissue formation on the metallic embed surface (Kumar, A., et al., 2020). HA bioceramic powder is applied to these metal surfaces. In the medical field, metallic materials coated with HA are typically utilized for implants (Kumar, A., et al., 2013; Oladele, I. O., et al., 2022). Artificial implant-bone fractures early due to fast wear caused by brittleness and low fracture toughness of

Received 14 December 2024; received in revised form 1 January 2025; accepted 5 January 2025.
To cite this article: Renushe et al. (2025). The role of nanotubes in enhancing plasma-sprayed hydroxyapatite coatings properties. Jurnal Tribologi 46, pp.113-121.

HA. Numerous studies have established that lower tribological properties is the cause of the deterioration and eventual failure of orthopedic implants. After 10 to 12 years of use, knee and hip implants start to degrade (Phume, L., et al., 2018; Kumar, V., et al., 2024). Adverse oxyhydroxyapatite, TCP, TTCP, and CaO stages have too been detailed within the published writing to emerge in HA coating when utilizing the thermal spray technique (Singh, S., et al., 2020). Because these phases dissolve in body fluids, they may cause implant instability. By carefully choosing process settings and specific bioceramic reinforcement during the plasma spray HA coat method, the formation of these phases can be minimized. By doing this, the crystalline index structure of the HA coats is improved, these phases are eliminated, and residual stresses are decreased (Catauro, M., et al., 2017). Due to HA high melting point, high temperatures have been used in the majority of HA prosthesis fabrication processes. The challenge with these tactics is managing HA detachment from other phases. Throughout these processes, high temperatures are applied to HA powder. The low crystalline structure results from the thermal breakdown of HA at these high temperatures into new phases (Tan, C., et al., 2011; Ammarullah, M. I., 2023).

In an exertion to improve the mechanical characteristics of biometal substrates, various analysts have as of late tested with a assortment of HA fortifications. ZrO_2, CNTs, TiO_2, and Al_2O_3 are the distinctive bioceramic fortifications (Balani, K. et al., 2007). A few thinks about have uncovered that the break sturdiness of bioceramic HA coatings is within the run of 0.4-1.1 ($MPa.m^{0.5}$), though the comparing esteem of common dense bone is within extend of 1.9-6 ($MPa.m^{0.5}$) (Chai, G., Bao. et al., 2019). A few analysts worked on the half breed composites by strengthening changing % of aluminium oxide and carbon tubes with HA coated on metal samples. Advancement in break durability was watched within the sandwich coats (Ayu, H.M., et al., 2017; Khanal, S.P., et al., 2016) too investigated on the half breed composites utilizing functionalized carbon tubes and nylon in HA coating. The own ability of HA implant was identified to be made strides in this current research study.

According to a details examination of the relevant reported literature, there has been no systematized research of the manufacturing and characterization of HA-MCNT coating on titanium samples. The present paper describes the development of a HA-MCNT coats with improved fracture resistance and high crystallinity on titanium substrates utilizing a plasma technique. After an extensive review of the literature, the scope of the problem and the goal of this study were defined. To produce high-quality HA-MCNT coated titanium material bio-implants, thorough research is needed. The current study used plasma spray coating to coat titanium substrates with HA and HA fortify with 5% (by weight) MCNT) in separate batches. The most effective parameters were used to plasma spray both coatings onto the substrates. After that, the coated substrates underwent standard procedure tests to determine their wear characteristics and fracture toughness. For every coated substrate, SEM pictures were captured both before and after the wear test.

2.0 MATERIALS AND METHODS

Solid titanium metallic substrates were procured from Pradip Metal Ltd. located in Mumbai, India. Using laser technology, the 40 mm diameter and 6 mm thick samples produced. Metallic substrates were first polished, and then they were ultrasonically cleaned with acetone. The cleaned samples were dried for ten hours at 750^0C in an air-circulated oven. For sample preparation, the ASTM G99-95a standard was adhered to. The crushed and sintered HA powder with a Ca/P ratio of 1.66, crystallinity greater than 99%, and phase purity greater than 99% was utilized as the feedstock. HA satisfies the standards of ISO 13779-6, a global standard. ISO 13779-6 ensures the suitability of HA for biomedical applications, which is critical for implant success. The metallic samples were grit blasted at 3-5 bar blasting pressure prior to HA coating on metallic substrates in order to improve the binding between the metallic sample and the HA coating. To create a composite powder or powder precursor, 5% weight percent of MCNT (97% purity, 30-50 nm OD, 0.5-2.2 μm in length, density-1.9 g/cm^3, BARC, Mumbai) was combined with sintering HA powder (particle size 40–60 μm) in a ball mill. The industrials plasma spray gun was utilised to create HA and HA-MCNT coats on metal samples. Table 1 shows the input parameters for the plasma coat. Figure 1(a) and 1(b) show photographs of an HA and HA-MCNT coated specimen.

(a) (b)

Figure 1: (a) HA Coating; (b) HA-MCNT Coating.

The sprayed samples were analysed using FE-SEM for microstructure characterization of the coatings. XRD analytical tool used to assess the physical state of HA and plasma coatings on titanium. Equation 1 is then used to get the % crystallinity (Yang, Y. Li., et al., 2019).

$$\% \, Crystallinity = [\Sigma Ac/(\Sigma Ac + \Sigma Aa)] \, X100 \qquad (1)$$

Where ΣAc is the sum of HA crystalline peaks and ΣAa is the sum of amorphous peak.
The fracture toughness of coatings was determined by using the Anstis equation (Anstis, G. R., 1981) A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness].

$$k_{IC} = 0.016 \left(\frac{E}{H}\right)^{0.5} \frac{P}{C^{1.5}} \qquad (2)$$

Where k_{IC} – Fracture durability, E- Flexible modulus, H-coat hardness, P – Connected stack/weight and c- Spiral crack propagation.

To understand the context, Figure 1 presents the original configuration of the multi-pass dual-indenter scratch test (Xu, 2016).
The original test has 3 stages:
Creation of a pre-deformed surface local layer, similar to the layer presented during the abrasion testing, realized by pre-scratching with a large indenter (R = 100 μm);

Pre-scanning with small indenter (R = 5 μm), without load, of the central region profile of the wear scar generated by the large indenter, made by pre-scratching with the large indenter. Scratching with the small indenter (R = 5 μm), highlighting the local deterioration of the deformed surface layer and recording the evolution of damage by scratch.

3.0 RESULTS AND DISCUSSION

Figures 2(a, b, c) appear the XRD spectra of bio-ceramic HA powder, as well as a comparison of the XRD designs of HA powder, HA coating, and HA-MCNT coatings. Crystalline crests were distinguished concurring to JCPDS cards. The calculation of the crystallinity recorded from the XRD result.

In the thermal spray coating process, HA is experiencing a higher heat zone than its melting point (~1200°C). Due to this, XRD peak intensity for HA coating at different 2 theta values showed expand and shrink peaks compared to pure HA biocermic powder. This behaviour is ascribed to the formation of secondary phases in coatings like TTCP, TCP, and CaO. These secondary/amorphous phases are unsuitable for implant coating in orthopaedic applications. The formation of secondary/amorphous phases leads to the degradation and loosening of the implant in the in-vivo environment when it comes into contact with in-vivo body fluid. This causes implant failure.

By reinforcing the 5% MCNT in HA powder results demonstrated similar peak intensity traces like HA powder. This might be due to the thermal disintegration properties of MCNT. In heat zones of plasma spray, when mixed powders are exposed to high flume, the maximum heat is carried or absorbed by the MCNT powder instead of the HA powder due to its inherent conductivity and heat capacity. These properties and behaviors of MCNT avoid the formation of an unfavorable secondary/amorphous phases in the HA-MCNT coating. Higher the formation secondary phases weaker the coating-substrate interface. Weaker the coating-substrate interface lesser the crystallinity index of artificial implant (Kumar, A., et al., 2020).

The crystallinity index of HA-coated substrates ranged between ~78%, while that of HA-MCNT coated substrates ranged between ~ 93%. The percentage index was calculated with the help of data generated in the Excel sheet during the XRD analysis with the help of a spectrometer. Ten measurements were taken for each coating sample and average index value was recorded for each crystalline index. The improved index in the HA-MCNT coating is attributed to maintaining a strategic distance from the arrangement of troublesome secondary or amorphous stages within the coating due to MCNT powder. As already shown, a diminish in crystallinity quickens the debasement of the HA coating in vivo. In vivo dissolving is undesirable since it leads in a weaker coating that's incapable to secure the embed over time, coming about in embed disappointment. Figure 3 comparative % crystallinity index of HA and HA-MCNT coatings, highlighting the improvement in crystallinity with MCNT addition.

Table 1: Process parameters.

Sr. No	Process input	Value
1	DC power	25 - 28 KW
2	Primary and secondary gas	Argon
3	Flow rate	08 - 10g/min
4	SOD	230 mm
5	Traverse velocity	38 - 46 mm/s

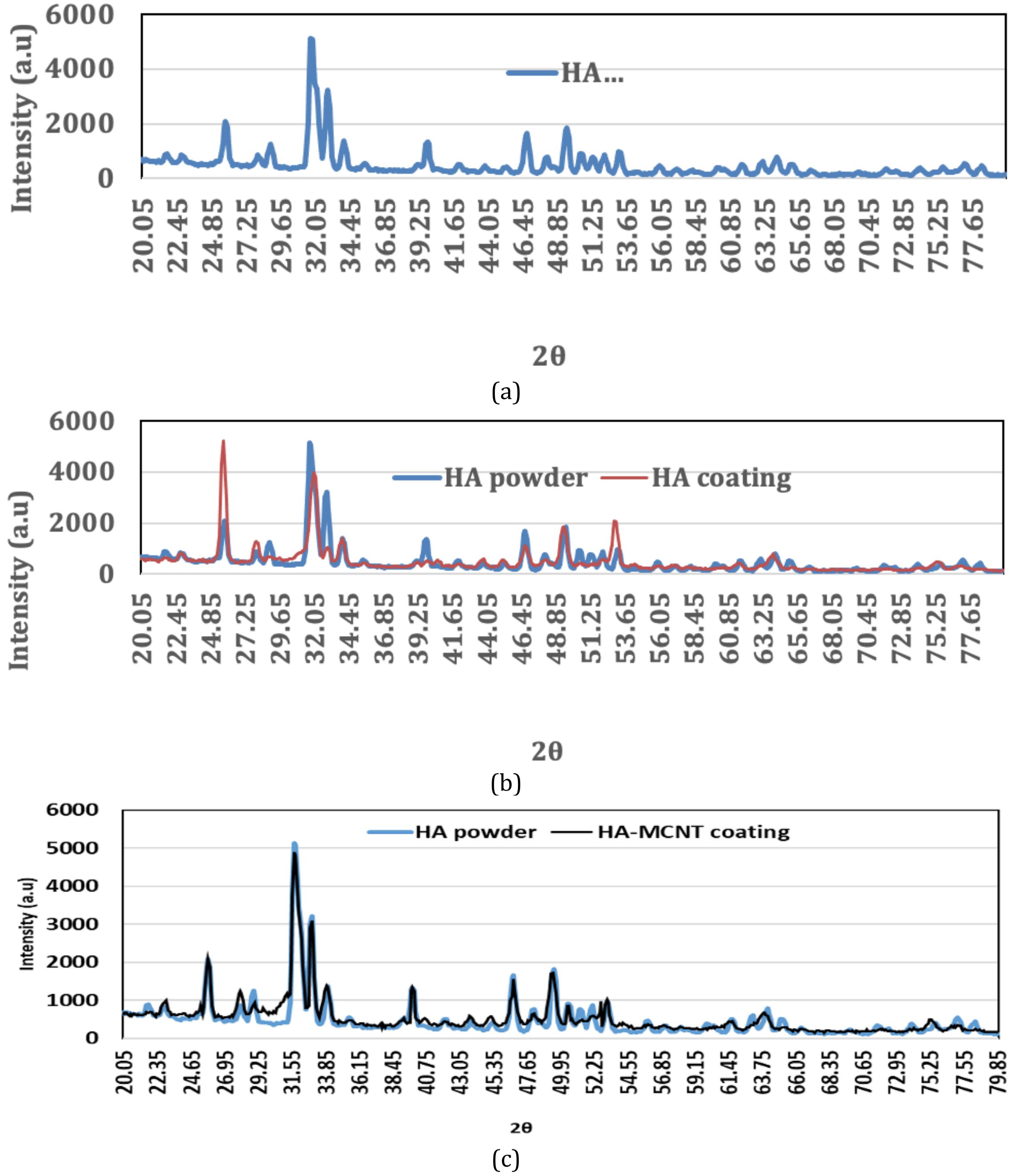


Figure 2: XRD (a) HA powder; (b) HA powder and HA coat; (c) HA powder and HA-MCNT coat.

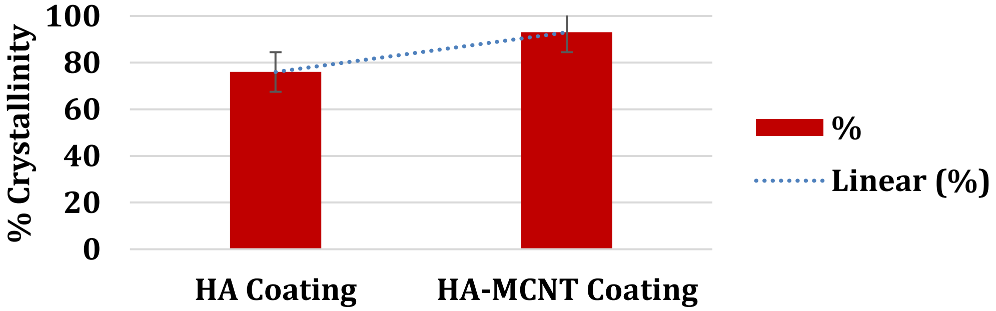
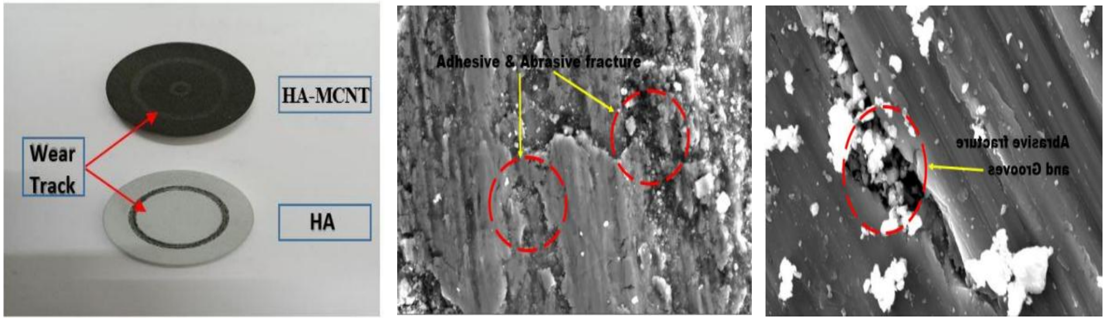


Figure 3: Comparative % crystallinity index of HA and HA-MCNT coatings.

The occurrence of radial cracks and wear tracks in HA coat was observe to be greater in comparison to those in HA-MCNT coatings. There was a significant betterment in coating cracking performance as a result of the decrease in average radial crack propogation and enhance wear strength.The high aspect ratio quality of MCNT introduced the crack deflection and self-stretch power mechanisms in the HA-MCNT coating (Chen, Y., et al., 2007). These two toughen mechanisms aid in enhancing the cracking resistance of HA-MCNT coats.

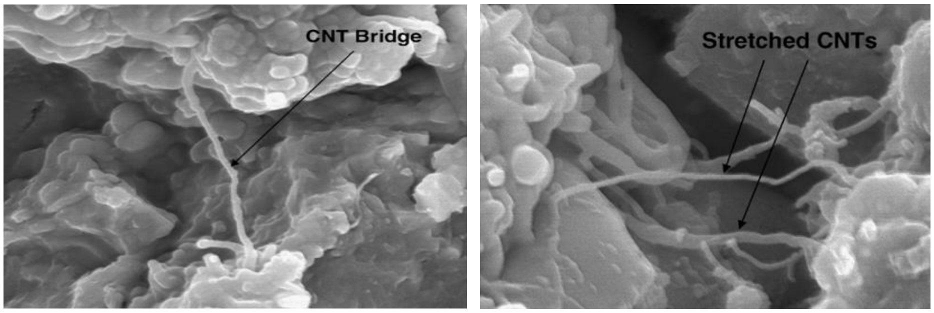
From SEM Figure 5, it is observed that by reinforcing the MCNT in HA powder, the MCNT acts as a connector to hold the HA splats. In some places of coatings, it's like a bridge between HA splats. These types of roles of MCNT in the coating avoid and prevent the separation of HA splats from each other. This mechanism improves the wear resistance of the coatings. The micrographs of different coatings after the wear test are shown in Figure 4 below.



(a) (b) (c)

Figure 4: Wear track (a) HA and HA-MCNT coat (b) HA coat (c) HA-MCNT coat.

The fracture toughness of HA-coated implant samples reported in the literature typically ranges from 0.6 to 1.2 MPa.m$^{0.5}$. However, these values can vary depending on factors such as the coating method, substrate material, and any additives or reinforcements used. In this study, the fracture toughness of the hydroxyapatite-coated implant sample was observed to be 1.1 MPa.m$^{0.5}$, which is within the typical range reported in the literature (Solanke, S., et al., 2023; Shinde, S. M., et al., 2023). For HA-MCNT coat samples, the average fracture toughness was determined to be ~3.38 MPa.m$^{0.5}$. These obtained values fall within the normal range for cortical bone seen in nature. The MCNT reinforcements, which serve as connector/splat bridges and prevent neighboring splats from separating, are responsible for the decreased wear rate and increased crack toughness of the plasma sprayed HA-MCNT coat. Researchers have shown that CNTs offer lubricating conditions during intense abrasion (Chen, Y., et al., 2007; Singh, L., et al., 2022; Khan F.S.A., et al. 2021). The improved performance of HA-MCNT coatings suggests their potential to extend the lifespan and reliability of orthopedic implants, particularly in load-bearing applications such as hip and knee replacements. By mitigating in vivo degradation and ensuring stronger bonding with the substrate, HA-MCNT coatings could contribute to reducing implant failure rates and improving patient outcomes. Further studies could explore long-term in vivo performance and biocompatibility to support clinical adoption.



(a) (b)

Figure 5: (a);(b) HA-MCNT coating reflects MCNT connector between splats.

CONCLUSIONS

XRD analysis revealed that HA-MCNT coating had a more crystalline structure than HA coating. The incorporation of MCNT into HA powder enhanced its crystallinity by 20%, which is critical for improving the material's mechanical strength and biocompatibility. This improvement makes it a promising candidate for use in medical implants, where superior structural properties are essential for performance and longevity.

The addition of 5% (by weight) MCNT in substrates resulted in a threefold improvement in the fracture toughness of HA coatings. Additionally, the average wear loss and resistance increased when MCNT was incorporated into HA coatings. Microstructural studies of HA-MCNT produced coatings show that MCNT reinforcement has the potential to improve tribo-mechanical properties of HA. As a result, Therefore, MCNT has arisen as a likely support for HA to settle difficulties of crack sturdiness and wear opposition.

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