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**DEVELOPMENT AND MICROSTRUCTURAL
CHARACTERIZATION OF HARD COATINGS FOR
DAMPING APPLICATIONS IN AEROSPACE SYSTEMS**

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FINAL REPORT

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1.0 EXECUTIVE SUMMARY

The main goal of this research was to improve the vibration damping performance of the Titanium (Ti) substrates by surface modification of the substrates with Titanium nitride (TiN) thin film coatings. TiN thin films were deposited on Ti substrates by pulsed laser deposition (PLD) and radio frequency (RF) magnetron sputtering. Damping ratios of the TiN-coated beams were 1-2 orders of magnitude greater than uncoated beams. Additionally, the damping amplitudes of the TiN coated beams have been observed to return to zero position faster than the uncoated beam. The energy dissipation due to internal friction at the beam-coating interface and inter-lamellae interface within TiN coatings are the mechanisms responsible for reducing vibration amplitudes of TiN-coated beams. Corrosion properties of TiN thin films were investigated. Electrochemical results indicated that TiN films bring about a significant improvement in the corrosion resistance of the Ti disks in phosphate buffer saline (PBS) solution.

2.0. BACKGROUND OF THE PROPOSED RESEARCH

Vibration fatigue failure remains a primary problem in the aerospace industry. High cycle fatigue (HCF) is the principal cause of the failure arising from the vibrations. The high-frequency vibratory loading that is characteristic of HCF can cause unpredictable and catastrophic failure. Currently, researchers are focusing on surface modification with the aid of hard coating materials as one of the potential means to reduce this fatigue-failure in aircraft engine components. Hard coatings can reduce vibration amplitudes by absorbing or dissipating energy, reducing mechanical loads and increasing the fatigue life. The energy absorption/dissipation process originates at internal defects, intergranular and substrate-coating interfaces, and locations with active dislocation motion. Popular viscoelastic damping materials perform well but have temperature limitations and low stability in harsh environments. To extend damping to these extremes, thermally stable hard coatings are used. Some popular hard coating materials are 8 wt% yttria stabilized zirconia (YSZ), polycrystalline alumina, NiCrAlY, FeCrAlY and magnesium aluminate spinel ($MgO+Al_2O_3$). Torvik et al. have compared the damping performance of magnetoelastic materials and plasma sprayed ceramic with a viscoelastic infiltrate [1]. Tassini et al. compared damping and stiffness properties of 8 wt% yttria-stabilized zirconia ceramic coating deposited by arc plasma spraying and electron beam-physical vapor deposition [2]. Du G. Y. et al. evaluated better damping performance of ZrTiN on TC4 titanium alloy [3].

Interestingly, transition metal nitrides such as TiN, ZrN, and TiZrN are emerging as attractive coating materials to mitigate damping due to their high hardness, high thermal and chemical stability, and low electrical resistivity. Aerospace requirements of high strength, excellent corrosion resistance, and high operating temperature have made titanium and its alloys more attractive over steel and aluminum. The density of titanium alloys ($\sim 4.5 \text{ g.cm}^{-3}$) is about half of Ni-based superalloys ($\sim 8.9 \text{ g.cm}^{-3}$). With an excellent strength-to-weight ratio and exceptional corrosion resistance, the use of titanium alloys in the aerospace sector is frequent in airframe, engine, and space applications, with greater use in military applications over commercial. TiN films exhibit excellent mechanical properties such as high hardness, wear resistance, high thermal stability, and high chemical stability. Additionally, TiN thin films are used in many industrial sectors due to its high abrasion resistance, low friction coefficient. TiN coatings are also widely used to enhance functional properties such as lubricity, biocompatibility, and antimicrobial characteristics for medical devices and surgical tools. Previous studies have explored many different titanium based hard coatings for damping treatments, but the feasibility of TiN as a suitable damping material remains to be sufficiently demonstrated. Given the attractive corrosion resistance of a TiN damping coating, the aerospace industry has keen interest in development of this technology. The primary objective of this work was to demonstrate the unique capability of TiN thin-film coatings to

favorably affect two important mechanisms for enhancing the lifecycle of engine components: (a) decrease corrosion and (b) suppress fatigue-failure due to vibration.

3.0. PROPOSED METHODOLOGY

Historically, two physical vapor deposition-based methods have been employed for depositing TiN thin film coatings on the Ti beam substrates: pulsed laser deposition (PLD) and radio frequency (RF) magnetron sputtering. As RF magnetron sputtering builds thicker films in shorter times than PLD, all coatings for vibration damping specimens were deposited by RF magnetron sputtering. Our methods for structural and surface morphology characterizations included x-ray diffraction (XRD) and scanning electron microscopy (SEM). The methods for mechanical and corrosion tests included nanoindentation, adhesion, potentiodynamic polarization, and electrochemical impedance spectroscopy. Lastly, the vibration damping performance was analyzed using a dynamic ring down approach.

4.0. RESEARCH ACCOMPLISHMENTS

The XRD patterns indicate that the TiN thin films are polycrystalline with mixed (hkl) planes such as (111), (200), (311), and (222) as seen in Figure 1. The d-values of these planes correspond to the face-centered rock salt type crystal structures of the TiN, which are in agreement with JCP2.2CA:00-038-1420 (TiN) from the International Centre for Diffraction Data (ICDD) card. The pattern indicates that (200) is the preferred orientation for samples deposited in at room temperature and 600°C. At 750°C, the preferred orientation is (111).

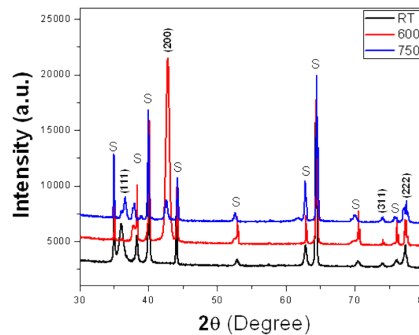


Figure 1: XRD Pattern for TiN Grown on Titanium Disks at Different Temperatures

The adhesion test of thin-film coatings on the substrate is of paramount importance in many diverse technologies and industries. The adhesion strength of TiN coatings on Ti substrate was performed according to the standard of American Society for Testing Materials (ASTM) standard D3359-17. A total of 17 tape tests were used to evaluate the adhesion of TiN coatings using cross-cut patterns through the coating. Optical images of the patterns were taken using a high-resolution microscope camera (AxioCam MRc5, Carl Zeiss). The results obtained using the tape test are shown in Figure 2. As seen in the optical images, the entire coating remains intact after the removal of the tape from the sample. This indicates that the TiN coating has strong adhesion to the Ti beam substrate.

The potentiodynamic polarization measurements of uncoated Ti substrates and TiN coated Ti substrates are shown in Figure 3. The corrosion current densities (I_{corr}) and corrosion potentials (E_{corr}) of all samples were determined from the respective abscissa and ordinate values at the intersection point of anodic and cathodic curve extrapolation, as demonstrated in the inset of Figure 3a. It is clear from these results that TiN coatings

exhibit better corrosion resistance than bare Ti disks in terms of lower current densities and lower negative corrosion potentials. The corrosion properties of TiN coating has the best corrosion potential when the TiN deposition is carried out in the presence of 100 mTorr nitrogen at 600 °C (Figure 3b), though its corrosion current density is marginally greater than room temperature coated TiN sample.

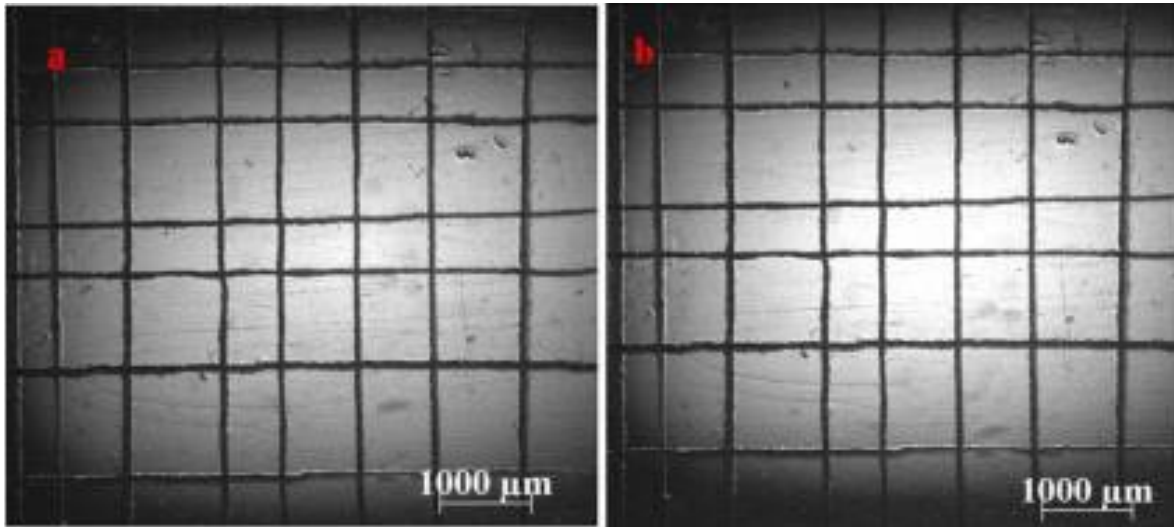


Figure 2: Optical Images of the TiN Coating Deposited at 750° C in Vacuum (a) Before and (b) After the Adhesion Test

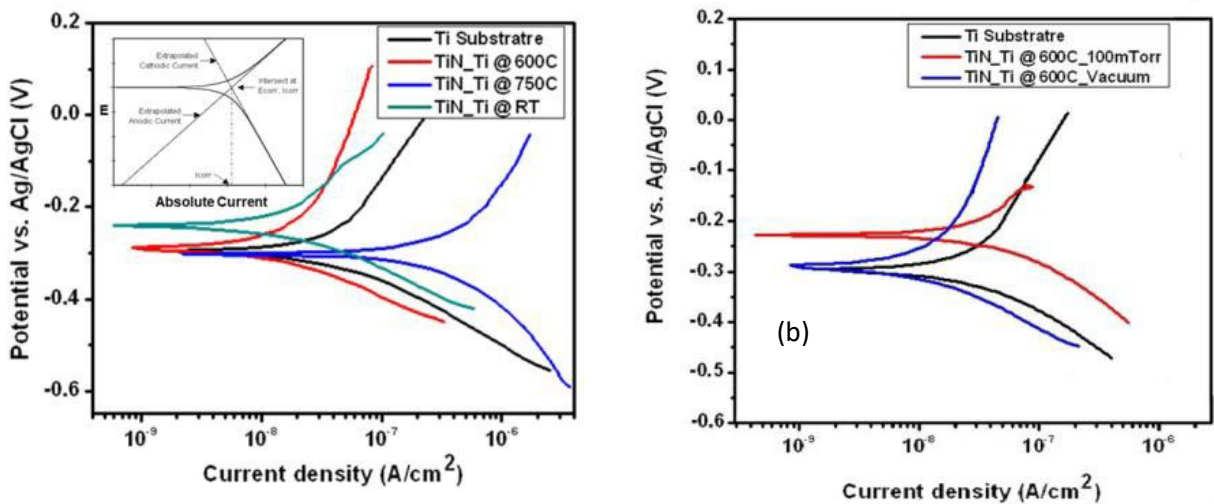


Figure 3: (a) Potentiodynamic Polarization Curves for TiN Coatings at Different Temperatures on Titanium Substrates and Uncoated Titanium Substrates Simulated in PBS; (b) Potentiodynamic Polarization Curves for TiN Coatings Deposited at 600 °C in a Vacuum, 600 °C in 100 mTorr of Nitrogen and Uncoated Titanium Substrates

The anti-corrosion properties of TiN coating are attributed primarily to its oxidation resistance behavior, which in turn, arises from its stable electronic structure brought about by strong interactions between Ti 3d and N 2p electron orbitals. The corrosion protective nature of TiN coatings was further analyzed by the electrochemical impedance spectroscopy (EIS) study. The EIS study was performed in the frequency range of 0.1-10⁴ Hz under 10 mV amplitude of the perturbation signal. The EIS technique gives information about the corrosion resistance of coatings to be obtained by measuring the impedance. Figure 4 shows Nyquist and Bode plots of the uncoated Ti substrate and Ti substrate coated with TiN thin films at an applied potential corresponding to the value of the open-circuit potential. Nyquist plots in Figure 4 (a) show that TiN coated Ti substrates have arcs with a larger radius of the curvature in comparison to the uncoated Ti substrate. Both the real impedance (Z_{real}) and imaginary impedance (Z_{imag}) for TiN coating at room temperature are greatest. The greater impedance of TiN coating at room temperature prevents the diffusion of the electrons and ions from the solution to the Ti substrate and thus improves its corrosion resistance. The observed EIS results are in a good correlation with the results obtained using the potentiodynamic polarization study. The greatest corrosion resistance of TiN at room temperature is also confirmed by the greatest value of $|Z|$ in the Bode plot in Figure 4 (b).

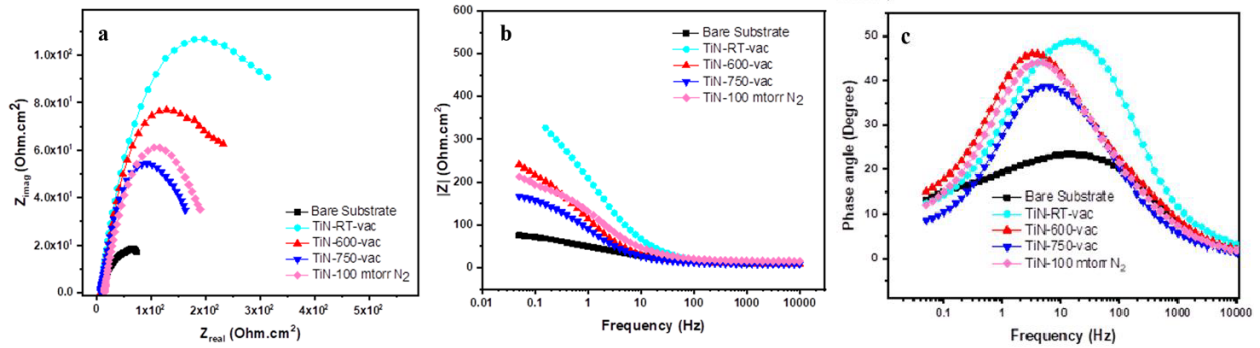


Figure 4: Nyquist Plot (a), $|Z|$ vs $\log f$ (b), and Phase Angle vs $\log f$ Plots (Bode plots) (c) for Different TiN Coatings on Ti Substrates

Damping performance of TiN films was investigated by analyzing the decay in wave amplitude of vibrations generated on both uncoated- and TiN-coated Ti beams. The vibrational behaviors of uncoated and TiN-coated Ti beams are shown in Figure 5 as a function of time. The decay (δ) parameter of each sample was calculated using Equation (1):

$$\delta = \frac{1}{n} \ln \left(\frac{X(t)}{X(t+nT)} \right) \quad (1)$$

where n is an integer number of successive (positive) peaks, T is the period of oscillation, $X(t)$ is an amplitude at the time t , and $X(t + nT)$ is an amplitude at the time $t + nT$. From this decay parameter, the damping ratio (ζ) of each sample was calculated using Equation (2). The results obtained are plotted in Figure 6. For this calculation, amplitudes of 4th and 15th peak as $X(t)$ and $X(t+15T)$, respectively.

$$\zeta = \frac{\delta}{\sqrt{4\pi^2 + \delta^2}} \quad (2)$$

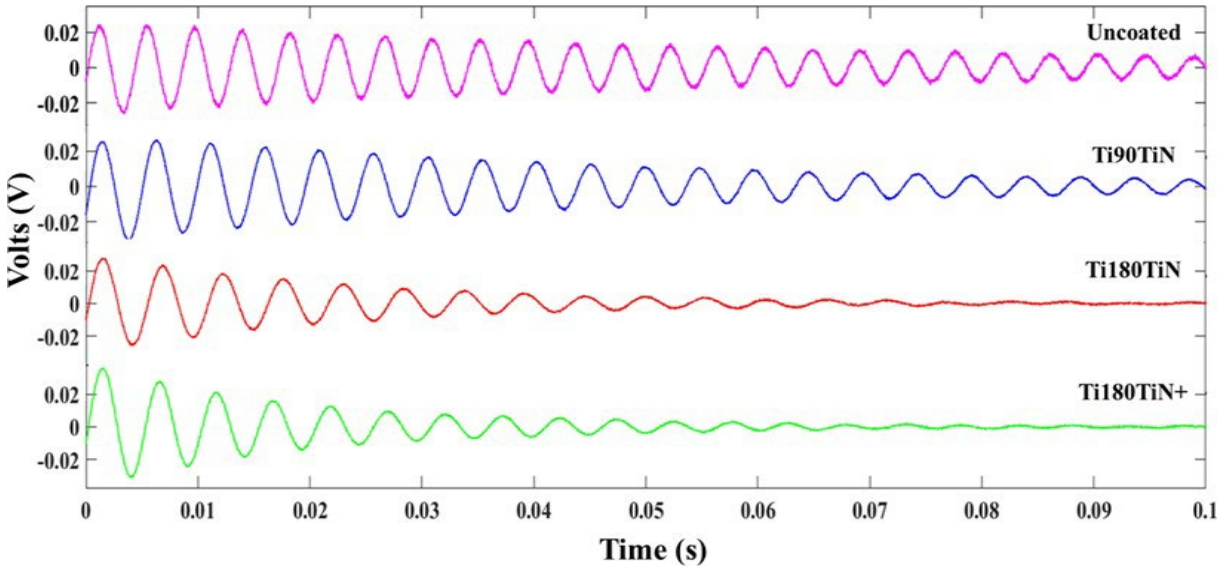


Figure 5: Damping Performance Comparison of the Average Amplitude Responses in Coated and Uncoated Beams, namely, Uncoated, 1.5 hour-coated TiN (Ti90TiN), 3 hour-coated TiN (Ti180TiN), and 3 hour-coated TiN + 10min Ti layer (Ti180TiN+), respectively

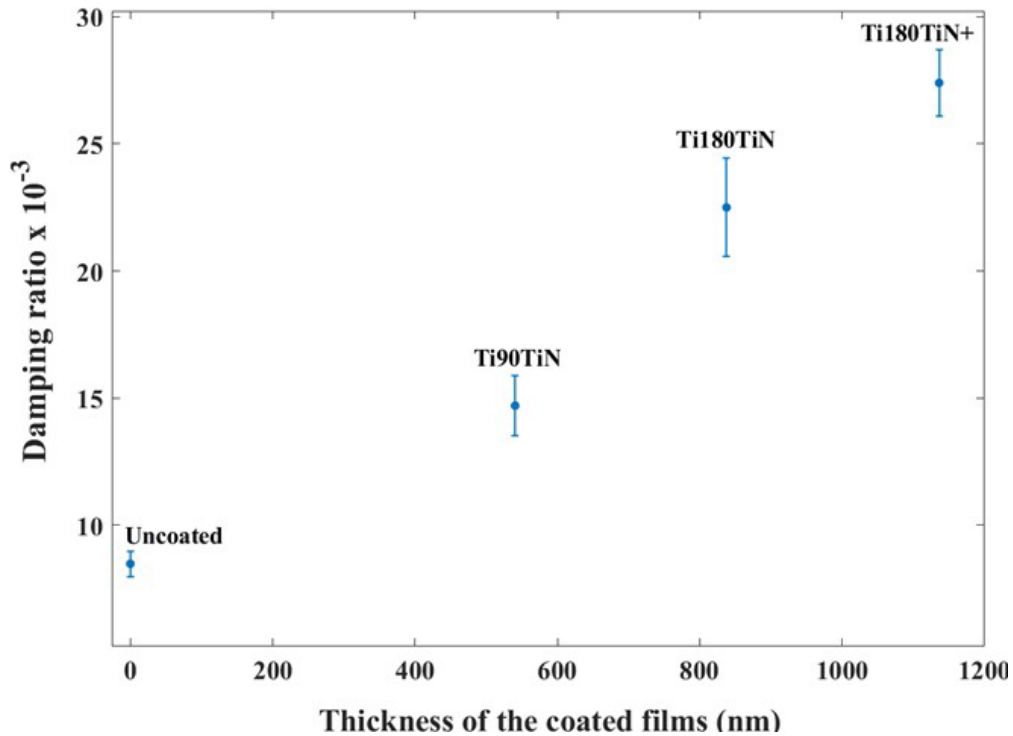


Figure 6: Relation between Average Damping Ratio and Thickness of the Coatings, namely, Uncoated, 1.5 hour-coated TiN (Ti90TiN), 3 hour-coated TiN (Ti180TiN), and 3 hour-coated TiN + 10min Ti layer (Ti180TiN+), respectively

The damping measurements were repeated five times for each sample. The average damping ratio for Ti beams coated with a TiN layer deposited for 180 minutes (named as Ti180TiN+) was found to be the greatest (0.0274) among all the samples studied. The oscillation of this sample (Ti180TiN+) was found to decay most rapidly. This sample had an intermediate coating of a thin layer of pure Ti which was performed to increase the TiN coating adhesion to Ti beams. The decay of vibration amplitude in the samples that were prepared by depositing TiN for 180 minutes and 90 minutes, Ti180TiN and Ti90TiN respectively, were slower with respect to Ti180TiN+, but faster with respect to the uncoated Ti beam. Figure 6 shows that the average damping ratio value of the Ti180TiN+ coated sample (0.0274) is greater with respect to the uncoated Ti beam which had an average damping ratio of 0.00848. For the 3-hour TiN-coated (Ti180TiN), the average damping ratio was 0.0225, and the 1.5-hour TiN-coated (Ti90TiN) specimens had an average damping ratio of 0.0147, damping improvements of 165% and 73% respectively when compared to uncoated beams.

The quality factor (Q), with the relation $Q=1/2\xi$, and the loss factor (η), with the relation $\eta = 1/Q$ [1], were used to further assess the damping behavior. The loss factor reflects the energy dissipated in a unit volume of material during one complete cycle of oscillation at a particular combination of temperature and amplitude oscillatory strain. Thus, a good damping material should dissipate more energy i.e., the material should have higher η and lower Q values. It is clear from these results that TiN-coated beams dissipate more energy than the bare Ti beam as their ξ values are larger and Q values are smaller in comparison to those in the uncoated sample. The amount of energy dissipated during beams' vibration was determined quantitatively by finding the area under vibrational amplitude decay curves as a function of time. These curves were generated by plotting the maximum height of each peak in Figure 5 as a function of time. The results are presented in Figure 7. The curves were then fitted to an exponential decay of the first order. The integrated area for bare Ti-beam and TiN coated Ti-beam (Ti180TiN+) were 0.00139 V.s and 0.000742 V.s, respectively. The integrated area of our TiN-coated beam shows a high effective decrease in the integrated area by 47% for the best case compared to the uncoated beam.

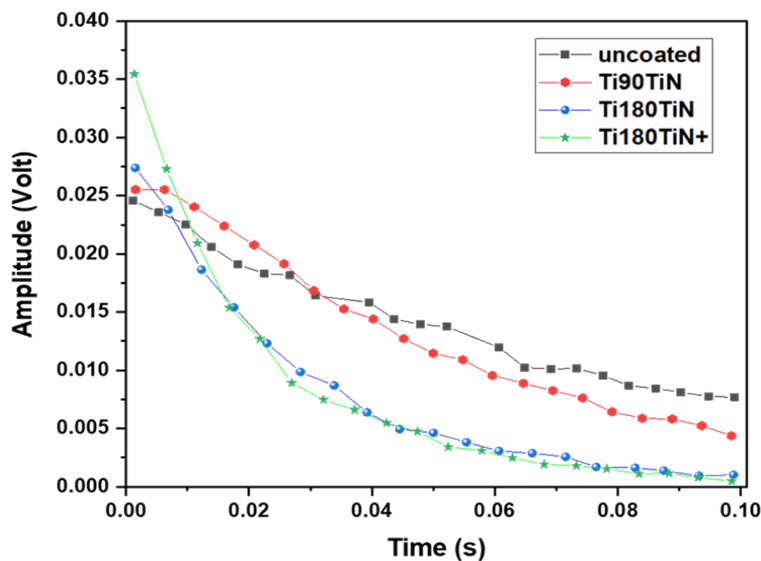


Figure 7: Average Amplitude Values of the Output Vibration Signals in each Sample, namely, Uncoated, 1.5 hour-coated TiN (Ti90TiN), 3 hour-coated TiN (Ti180TiN), and 3 hour-coated TiN + 10min Ti layer (Ti180TiN+), Demonstrating their Decay as a Function of Time

5.0. CONCLUSIONS

Uniform and hard TiN thin film coatings were applied to Ti substrates by a commonly used physical vapor deposition method. The effect of this TiN coating on Ti substrates in terms of corrosion resistance and vibration damping was investigated. The coatings were found to be favorably effective as corrosion protection and demonstrated measurable vibration damping performance. Potentiodynamic polarization data showed that the corrosion current densities of TiN coated Ti beams were up to 87% lower with respect to uncoated Ti beams. Electrochemical impedance spectroscopy indicated that TiN coating at room temperature was the most corrosion resistive among other coatings studies in this research. Tape tests revealed that TiN coating had strong adhesion to Ti substrates. The damping performance of the Ti beams was found to be enhanced significantly by TiN film coatings. The damping ratio values of the coated beams were greater than those of the uncoated leading to the future use of TiN coatings in vibration critical applications. An intermediate layer of Ti film between Ti beam and TiN coating further improved the damping performance. The energy dissipation at the Ti beam-TiN coatings interface and inter-lamellae interface within TiN coatings was believed to be the mechanism responsible for reducing vibration amplitudes of TiN-coated beams.

6.0. PUBLICATIONS AND PRESENTATIONS

1. Kaushik Sarkar, Panupong Jaipan, Jonghyun Choi, Talisha Haywood, Duy Tran, Nikhil Reddy Mucha, Sergey Yarmolenko, Onome Scott-Emuakpor, Mannur Sundaresan, Ram K. Gupta, Dhananjay Kumar, Enhancement in corrosion resistance and vibration damping performance in titanium by titanium nitride coating, SN Applied Sciences, 2020, <https://link.springer.com/article/10.1007/s42452-020-2777-1>
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8.0. LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

ASTM	American Society for Testing Materials
EIS	Electrochemical Impedance Spectroscopy
FeCrAlY	Iron-Chromium-Aluminum-Yttrium
HCF	High Cycle Fatigue
ICDD	International Centre for Diffraction Data
NiCrAlY	Nickel-Chromium-Aluminum-Yttrium
PBS	Phosphate Buffer Saline
PLD	Pulsed Laser Deposition
RF	Radio Frequency
SEM	Scanning Electron Microscopy
Ti	Titanium
TiN	Titanium Nitride
XRD	X-ray Diffraction
YSZ	Yttria stabilized zirconia