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Electrochemical corrosion response of ZrN coated Nickel-Titanium alloy in 0.9% NaCl solution

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Abstract: The biomedical application as metallic body implants of Nickel-Titanium shape memory alloys are of high interest due to its unique property of pseudo elasticity. However, high content of nickel and its potential to release from the surface due to corrosion raises safety concerns about its allergic reactions, toxicity and carcinogenicity. Hence, it is necessary to produce proper passivity to prevent surface layer degradation. In this study, ZrN coating on Nickel-Titanium shape memory alloys was obtained by vacuum cathodic arc physical vapor deposition technique to improve electrochemical corrosion resistance. The electrochemical corrosion response was studied in 0.9% NaCl solution at 37^{0}C using Tafel extrapolation method. Surface morphology was studied using SEM/EDAX and XRD. ZrN coating increases corrosion stability and micro hardness.

Keywords: Shape memory alloy; pseudoelasticity; vacuum cathodic arc PVD; electrochemical corrosion; micro hardness.

I. INTRODUCTION

The unique combination of pseudoelasticity, shape memory effect and bio-compatibility makes Nickel-titanium alloy as a fascinating metallic implant bio-material [1-7]. Due to affinity of oxygen with titanium forms titanium oxide film on surface naturally which makes NiTi safe and bio-compatible. This oxide film is actually preventing NiTi from corrosion as well leaching-out of nickel from the surface [8-10]. But the possible mechanical damage of superficial oxide film in corrosive media causes leaching of nickel from the substrate surface [11, 12]. Nickel is known to induce hypersensitive reactions and tissue necrosis. The induction of cancer by nickel ions is suspected [13-15]. The toxicity of NiTi implant products noted *in vitro* [16] and increase of nickel in blood reported after implanted into animals [17]. Therefore, proper surface modification is needed to prevent surface layer degradation and ions release into body environment, which is considered crucial for its medical application as metallic implant.

The transition metal nitride coating is attractive and economical so widely used in biomedical materials in current decade. Zirconium nitride (ZrN) coating started to attract more attention for its excellent corrosion resistance. It has been reported that ZrN coating showed higher corrosion resistance compared to that of TiN coating [18, 19]. Stoichiometry of ZrN is the only stable phase with a gold-like colour due to its metallic band structure. This coating appears to have substantial potential in aero engine, industrial and biological application [20]. ZrN thin films can be synthesized by ion-beam assisted deposition [21], reactive sputtering [22], plasma nitridation [23], vacuum arc deposition [24], ion plating [25], ion implantation [26, 27], reactive direct current magnetron sputtering [28] and ultra-high vacuum sputtering [29].

Recently, the cathodic arc physical vapor deposition is the most promising and practically applicable coating technique having tremendous applications in various fields. It is reported the ZrN and TiN coating by optimising parameters using cathodic arc physical vapor deposition improves corrosion resistance [30, 31].

In present work, ZrN coating on NiTi-shape memory alloy is obtained by cathodic arc physical vapor deposition with different bias voltages and their corrosion responses in 0.9% NaCl (normal saline solution) is investigated.

II. MATERIAL AND METHODS

Samples in the sheet form of NiTi-shape memory alloy were used in the present study. Chemical composition of NiTi is shown in Table I.

TABLE I
CHEMICAL COMPOSITION (WT.%) OF NITI

Ni	Ti	C	O	Total All Others
55.74	44.24	≤ 0.05	≤ 0.05	≤ 0.20
All others are Al, Co, Cr, Cu, Fe, Mn, Mo, Nb, Si, and W				

The sheet was cut into 15 mm X 15 mm square samples each having thickness 0.5 mm. Samples were mechanically polished using polishing machine with silicon carbide paper in successive grades from 1000 to 2000 grit followed by a final mirror polish with a 0.5 µm grade diamond-lapping compound. Samples were ultrasonically cleaned with acetone before coating.

Cathodic arc physical vapor deposition technique was used to produce ZrN coating on samples with process condition of substrate bias voltage of -50 V, -200 V, -350 V, -500 V; nitrogen gas pressure 10 mtorr and deposition time 20 minutes. In this process, samples are immersed in the plasma produced by the vacuum cathodic arc technique and negative bias is applied to them. The energetic ions having energy equal to neV (where n is the charge state of the ions and V, the applied bias voltage) are extracted from the plasma and are bombarded on the samples at nearly perpendicular direction. As the sheath of plasma takes the shape of the samples, samples having any complicated geometry can be uniformly bombarded by these ions. Before deposition, coating chamber was first evacuated to base vacuum of 10^{-5} torr. To get good adhesion of ZrN film with the samples, the samples were prior to deposition first sputter cleaned with argon ions at the gas pressure of 10^{-4} torr and then heated to temperature 400^0C. The increase in surface temperature of samples helps in better bonding of film with the samples. This was done using radiant heater mounted in the chamber. The sample surface was also sputtered by zirconium bombardment for three minutes. For this bombardment the zirconium ions coming from arc source were accelerated towards the sample surface with the bias voltage of -1000 V. Because of this, zirconium ions clean the substrate as well as they get implanted in the sample surface. The projected length of these ions is of the order of few nm. These implanted ions help in the formation of good adherent film. Six zirconium cathodes with purity 99.95% were used. All coated samples were ultrasonically cleaned with acetone again before electrochemical test. Corrosion resistance of ZrN coated NiTi were investigated by Tafel extrapolation method. Tafel curves were obtained through Gamry-Potentiostat/Galvanostat (reference 3000). Icorr, Ecorr, β_a, β_c and corrosion rate were obtained by Tafel fit and DC corrosion software. The electrochemical measurements were performed at the scan rate of 1mV/s in a standard three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrochemical tests were carried out at 37^0 C in 0.9% NaCl solution.

TABLE III
Concentration of electrolytes in Normal Saline (NS-Sodium Chloride 0.9%)

Ions	Concentration of ions mmoles/L
Sodium	150
Chloride	150

Microhardness measurements were performed on six different places of a sample by means of a microhardness tester of indenter type Vickers, duration time 5 seconds and test load of 10g. Film surface morphology was studied using SEM/EDAX and XRD- which was carried out at low angle.

III.RESULTS AND DISCUSSION

The essential readings acquired from the electrochemical tests are summarized in Table III.

TABLE IIIII
Corrosion rate by Tafel extrapolation method in 0.9% NaCl solution

Sample code	Sample	Bias Voltage	Pressure	E_{corr} (mV)	I_{corr}	Corrosion Rate in mpy
A	NiTi	--	--	-512.7	1.563µA	0.82
B	Ti6Al4V	--	--	-763.0	1.603µA	1.00
C	316L SS	--	--	-419.4	1.128µA	0.51
D	NiTi	-50V	10mtorr	-356.6	32.05nA	$16.96\ e^{-3}$
E	NiTi	-200V	10mtorr	-200.1	11.54nA	$6.104\ e^{-3}$
F	NiTi	-350V	10mtorr	-341.4	13.20nA	$6.981e^{-3}$
G	NiTi	-500V	10mtorr	-343.4	17.06nA	$9.024e^{-3}$

Fig.1 shows the Tafel plots of NiTi, Ti6Al4V, 316LSS and Fig. 2 shows the Tafel plots of ZrN coated NiTi to investigate corrosion behaviour in 0.9% NaCl solution. The corrosion current density is an important parameter to evaluate the kinetics of corrosion reactions. The lower the value of i_{corr} gives lower value of corrosion rate. ZrN coated samples had high corrosion potential E_{corr} and low corrosion current density I_{corr} compared to the uncoated NiTi, Ti6Al4V and 316L stainless steel samples. This indicates that ZrN coating by cathodic arc physical vapor deposition method effectively improves the corrosion resistance property of NiTi alloy. Corrosion rate for sample-E (substrate bias voltage of -200 V, nitrogen gas pressure 10 mtorr) was found 6.104 e^{-3} mpy, which is less than all other ZrN coated samples under investigation.

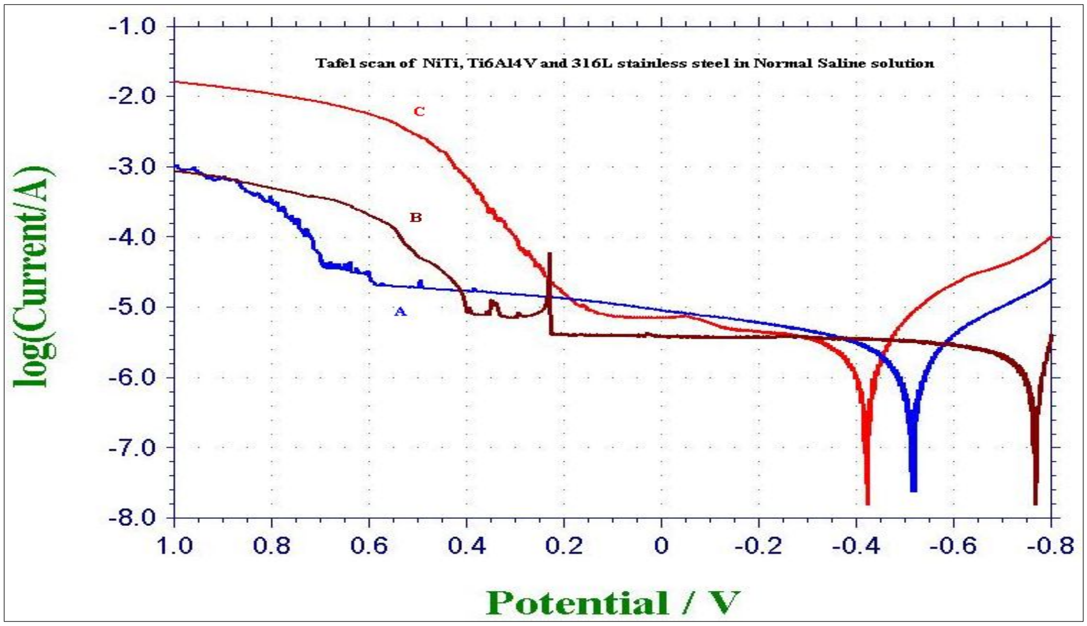

Fig.1. Tafel plots of bare NiTi, Ti6Al4V and 316L stainless steel in 0.9% NaCl solution.

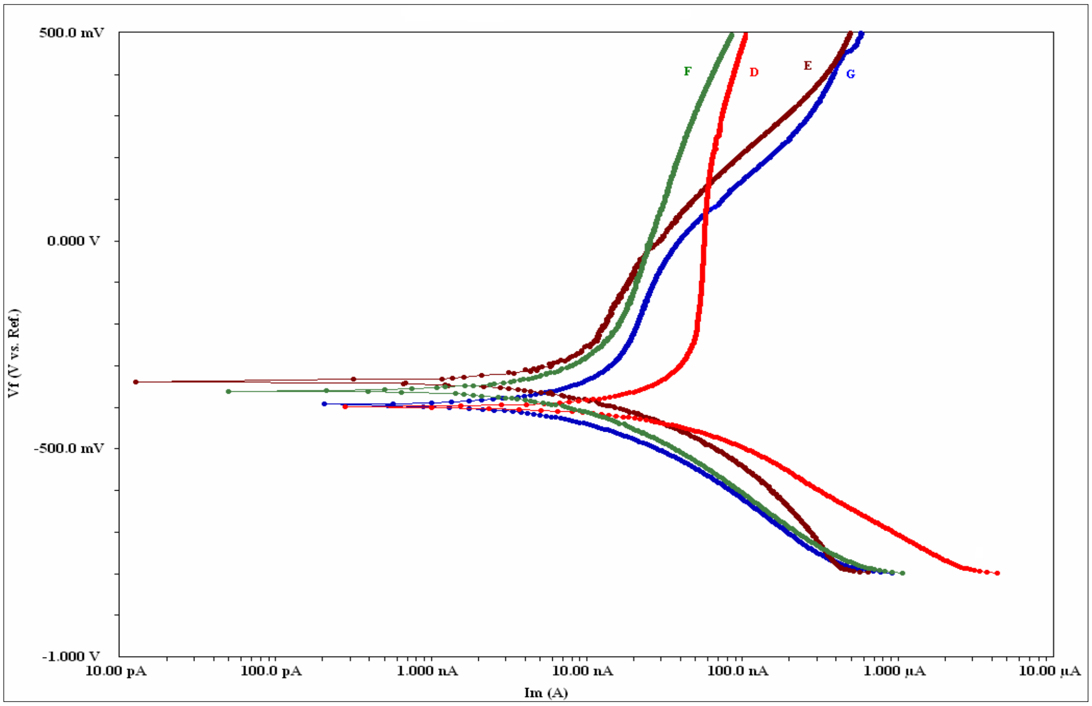

Fig.2. Tafel plots of ZrN coated NiTi in 0.9% NaCl solution.

The XRD study shows the different phases present in the film. For sample-D (-50 V), ZrN[200] peak is dominant indicating that the preferred orientation is ZrN[200]. For samples E (-200 V), F (-350 V), G (-500 V), ZrN[111] peak is dominant indicating that preferred orientation is ZrN[111]. When biasing voltage is changing from -50V to -200V, the preferred orientation changes from ZrN[200] to ZrN[111] and this changes may help in reduced corrosion rate at bias voltage -200V.

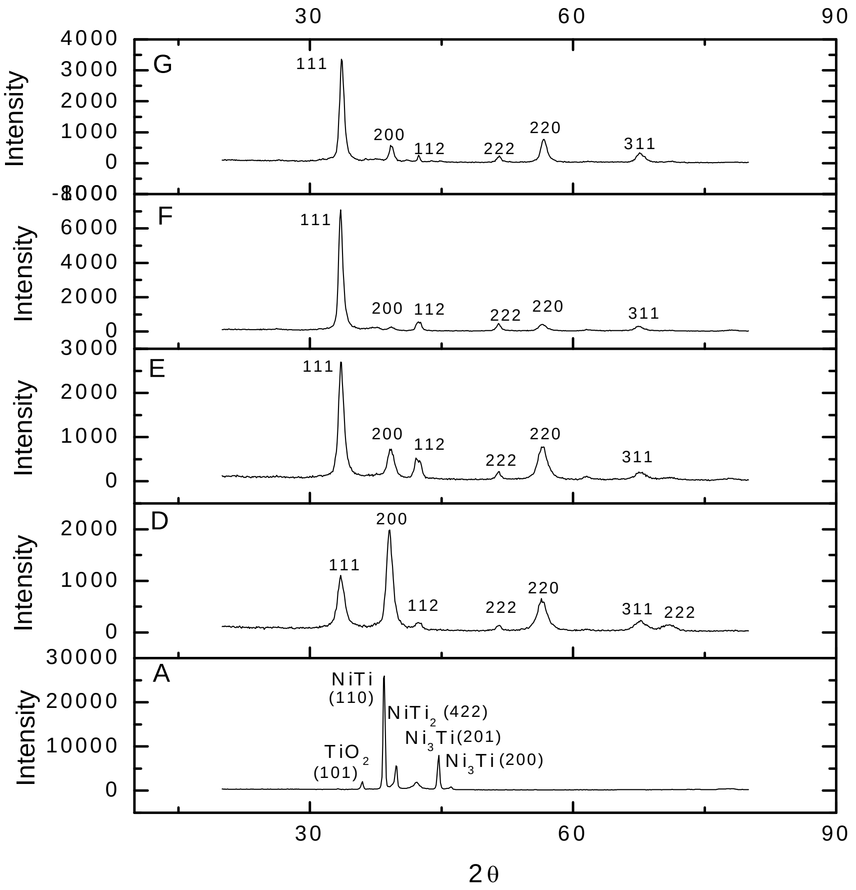

Fig.3. XRD pattern of ZrN coated NiTi

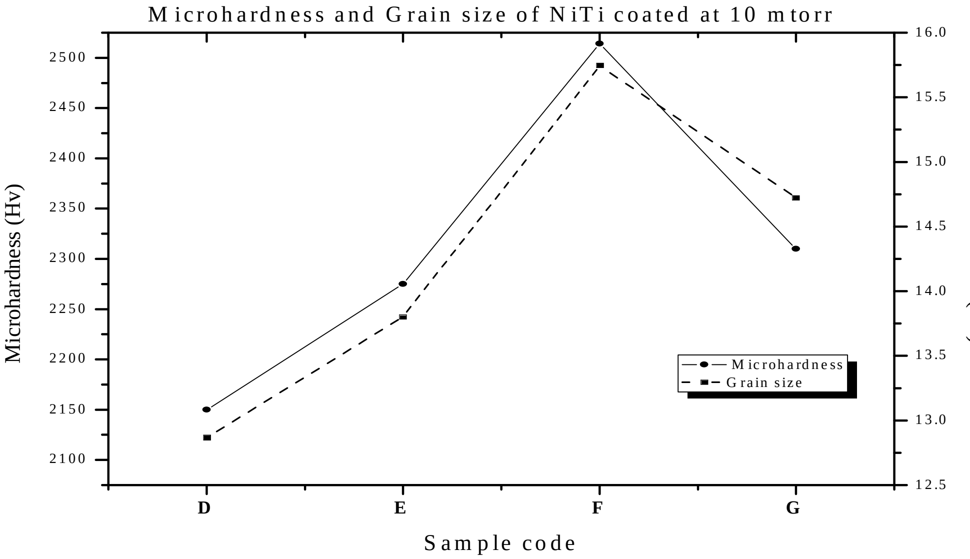

Fig. 4. Microhardness and grain size of ZrN coated NiTi

The average grain size were estimated from full-width at half-maximum (FWHM) of peaks in XRD patterns by Scherrer's formula, $t = k\lambda/\beta\cos\theta$, where λ (1.540600 A^0 in this case), θ and β are the X-ray wavelength, Bragg diffraction angle and FWHM in radians respectively. On increasing the substrate bias voltage in steps, -50 V, -200 V, -350 V respectively the average grain size increased but for -500V it decreased. It was found in between 11.8 nm to 15.9 nm. The increase in substrate bias voltage results in increase of Zr ion energy. At higher Zr ion energy, the surface adatoms obtains higher momentum transferred by Zr ions through elastic collision, which enhances surface mobility and therefore grain size increases. But for -500 V, the decrease in grain size is due to resputtering of Zr ion from surface.

The film average microhardness was found to be increased with substrate bias voltage as shown in Fig. 4, but -500 V, microhardness of the film reduces. This decrease in microhardness is due to the resputtering of Zr from the surface and increased energy of Zr causes the increase in entropy in film.

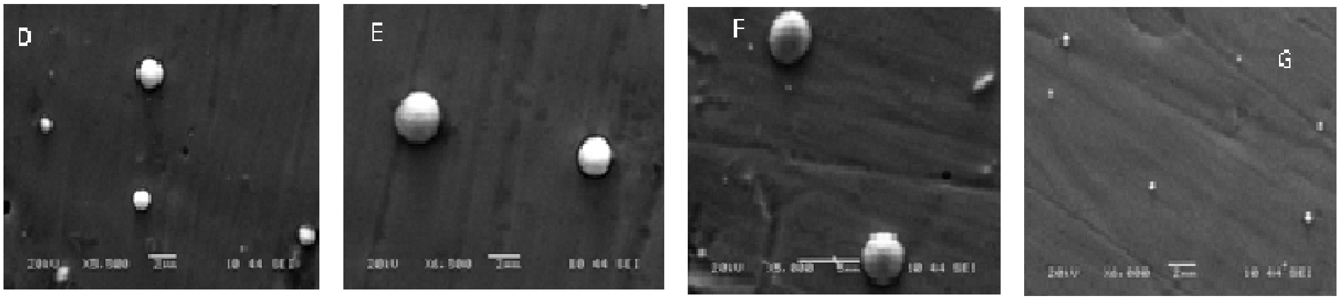

Fig.5. SEM of ZrN coated NiTi

SEM micrograph shows droplets like defects recognized as microparticles and black spot recognized as cavities or pinholes. Under the best deposition condition of bias voltage of -200 V superior corrosion resistance was observed for ZrN coating prepared on NiTi alloy by cathodic arc physical vapor deposition and also -200V bias voltage reduces the droplet like defects.

IV. CONCLUSIONS

The negative substrate bias voltage influences corrosion resistance, average grain size and micro hardness. Substrate bias voltage of -200 V with nitrogen gas pressure 10 mtorr gives minimum corrosion rate than the other biasing voltages in 0.9% NaCl solution. For the samples with substrate bias voltage of -50 V shows the preferred orientation ZrN[200] and for other samples with substrate bias voltages of -200 V, -350 V, -500 V the preferred orientation is ZrN[111]. The change in preferred orientation and reduced droplet like defects at substrate bias voltage of -200V increases the corrosion resistance.

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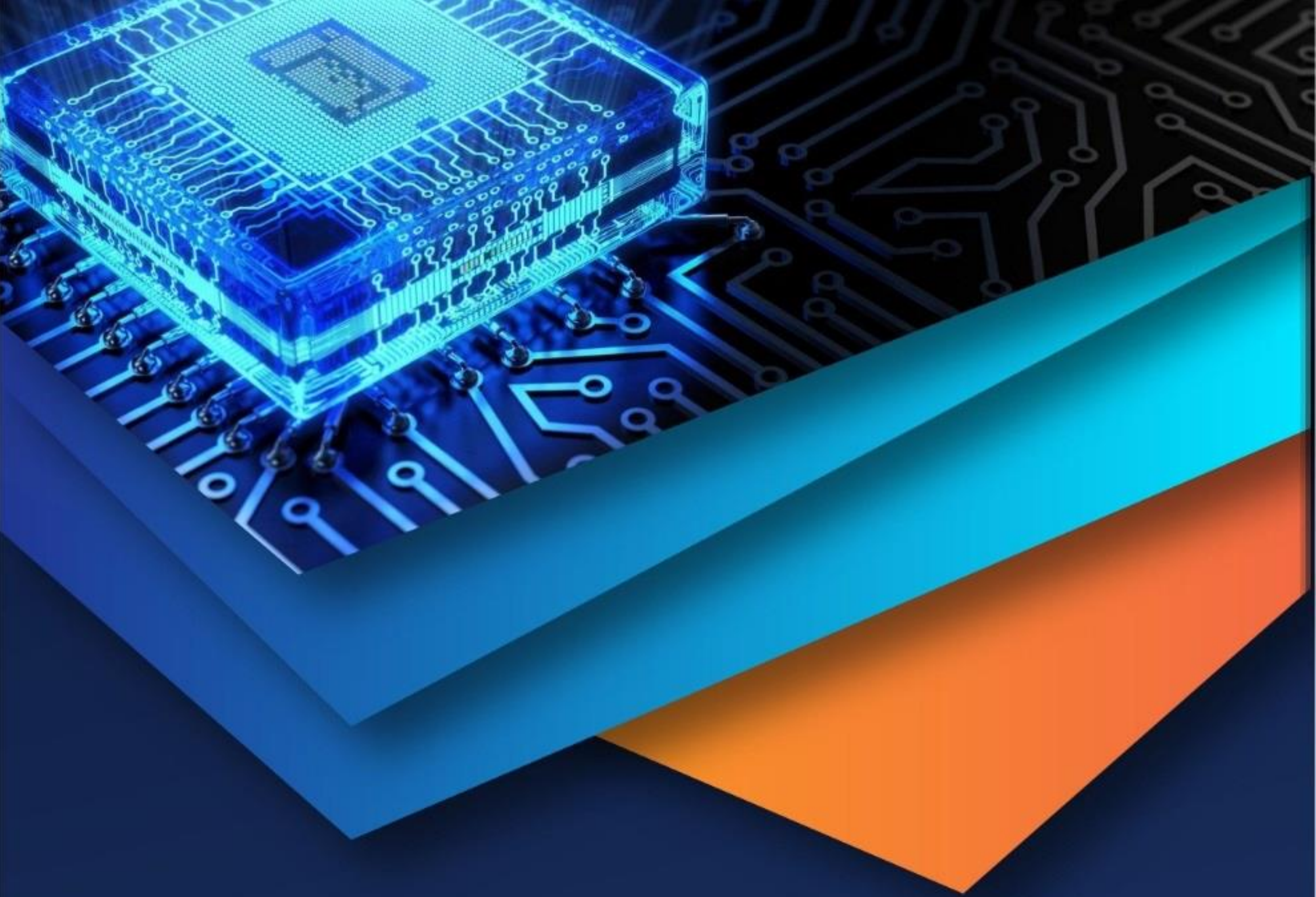

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