Electro-Discharge Machining of *Ti-6Al-4V* Alloy Using *Cu-TaC* Compact Electrode with Urea Dielectric: Reactions and their Effects on the Machined Surface

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***Abstract*—This paper presents the investigation of compounds / phases formed during the Electrical Discharge Machining (EDM) of titanium alloy (*Ti-6Al-4V*) with *Cu-TaC* compact electrode using urea dielectric fluid. It is proposed that the materials involved in the machining are likely to react and form new compounds on the EDMed surface. The outcomes of the reactions were predicted. The EDMed surfaces were subjected to energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analysis to determine the changes in the surface composition. Results of EDX analysis indicate the presence of additional elements (*Cu*, *Ta*, *O* and *C*) on the surface of the parent alloy. XRD results also confirm the main compounds formed on the surface to include metallic oxides, carbides and nitrides (*TaC, TiC, Ti_2N, TiO*) of tantalum and titanium. It is concluded that the surface was reinforced during the EDM with hardened ceramic layers which are capable of enhancing its wear properties.**

Keywords-EDM; Ti-6Al-4V alloy; Cu-TaC compact electrode; Urea dielectric fluid

I. INTRODUCTION

Electrical discharge machining (EDM) is among the most versatile non-conventional machining techniques whose mechanism converts electrical energy to thermal energy by a series of successive electric discharges between the cutting tool and the workpiece in presence of dielectric fluid. The discharges occurring between the pair of electrodes create collision process that transforms the kinetic energy of the atomic particles in form of heat and pressure. The amount of heat generated in the inter-electrode gap during this process can be as high as 10^{17} W/m^2 [1] at temperature which ranges between 8,000 – 12,000 °C or even up to 20,000 °C [2]. The process ultimately results in localized melting and partial vaporization of material from the workpiece. The dielectric fluid is also partially ionized and pyrolysis takes place with this intensive sparks during the period [3]. This process is liable to cause decomposition of the base compounds in the heat affected zones. Changes in average chemical compositions and the phases would be experienced on solidification of the melts [4].

Studies have shown that both electrode and dielectric materials do migrate to the workpiece surface during the process to change its state after machining. Investigations on the composition of EDMed surfaces found that hydrocarbon based dielectric fluids enriches the base materials with higher carbon contents. Lahiri et al [5] reported the occurrence of pyrolysis of hydrocarbon dielectric fluid during EDM, and also that increase in pulse duration reduces the carbon yield. Bleys et al [6] observed increased carbon content on the surface of a steel workpiece. In powder-mixed dielectric fluids, pyrolysis of organic components also leads to transfer materials onto the workpiece. Khan et al. [7] and Zain et al. [8] working with Al_2O_3, TiC and TaC powders in kerosene dielectric confirmed material transfer between the dielectric and the mild and stainless steel workpieces respectively enhances their hardness.

Electrode materials can also migrate onto the workpiece material during EDM. Mohri et al [9] reported tungsten deposition on AISI 1049 steel workpiece in an accretion process using Ti powder compact electrodes. In a recent investigation with WC/Cu green compact electrode, Patowari et al. [10] obtained improved micro-hardness on C-40 steel grade. They suggested that the presence of WC and Cu in the morphology of EDMed surface contributed immensely to the attainment of micro-hardness to about 1632 Hv.

From these and many other literatures, it is established that elemental exchanges take place between the materials involved in machining during the EDM. Such exchanges must have being in form of reactions, since the compounds that were found on the various EDMed surfaces were normally different from the parent materials. This paper investigates the compounds that can be formed during the EDM of *Ti-6Al-4V* alloy with urea dielectric fluid using *Cu-TaC* compact electrode through reactions. The *Cu-TaC* electrode has earlier been used to machine the alloy with distilled water [11]. In these investigations however, the mode of reactions during machining with either the distilled water or urea dielectric fluid is yet to be determined. In this paper therefore, the reactions between the materials involved in machining which lead to formation of various compounds are proposed. Analysis of the EDMed surface for elemental composition and phase changes was conducted to determine its state and to confirm the compounds precipitated. This final analysis determines if the compounds are those that can enhance the surface wear properties of the alloy. The effects of the new state of the material's surface on functional applications have been proffered.

II. EXPERIMENTAL METHODS AND MATERIALS

The materials that make-up the machining system are: the electrode (*Cu-TaC*), urea dielectric fluid (NH_2CONH_2) and the titanium alloy (*Ti-6Al-4V*) as workpiece. The *Cu-TaC* composite electrode was prepared from copper and tantalum carbide powders with 50/50% composition and compacted at a pressure of 27.56 MPa. It has a low density of about 6.00 g/cm^3. Urea is a white solid crystal material belonging to amid group. It used to be a major animal waste with up to 46% nitrogen content [12]. A solution of 10.00 g/l of it in distilled water was prepared for use as dielectric fluid.

Machining was conducted on the alloy with the electrode under the urea dielectric and other EDM electrical pulse conditions. These conditions are the peak current, I_p (3.5, 5.5A) and pulse duration t_{on} (3.3, 5.3µs). The system which combines the reacting materials is represented in Fig 1. Scanning electron microscopy (SEM) / energy dispersive X-ray (EDX) analysis of the machined surfaces was conducted to examine the surface composition, whereas the X-ray diffraction (XRD) analysis was used to determine the compounds on the EDMed surface.

Under the illustration of Fig 1, the possibilities assumed for the reactions during machining are:

1. Reactions may take place between the electrode and the dielectric fluid and result in formation of different compound on the EDMed alloy surface.
2. Both the electrode and the topmost part of the alloy which is subjected to machining may also react in the dielectric fluid medium.

The new possible compounds that would result from these reactions during machining are presented in the following subsections.

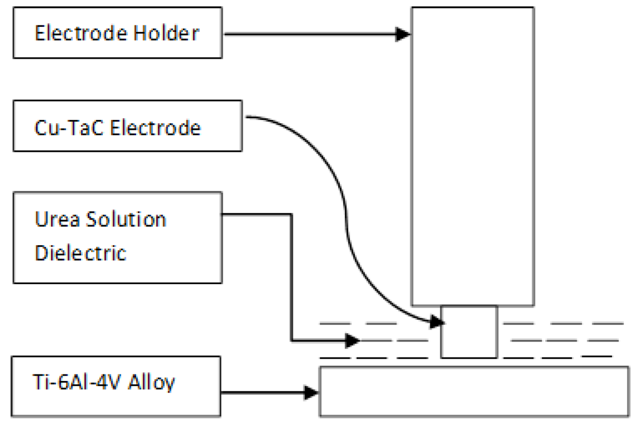

Figure 1. Schematic diagram of EDM with the materials under reaction

III. EXPECTED REACTIONS

A. Dielectric Fluid with Ti-6Al-4V Alloy

Urea is highly soluble in water and it decomposes on heating with the tendency to provide elements that are reactive to varying degrees. During reactions, the electrons shift in such a way so as to form chemical bonds in order to attain the structure of stable octets [13]. Table 1 presents the possible elements of pyrolysis of NH_2CONH_2 solution with their electron configurations and the valence energy level electrons.

TABLE I. ELECTRON CONFIGURATIONS OF THE MAJOR REACTING ELEMENTS

Compound	Element	Electron Configuration	Electrons in Valence Energy Level
NH_2CONH_2 and H_2O	$_6C$	$1s^2\ 2s^2\ 2p^2$	4
	$_7N$	$1s^2\ 2s^2\ 2p^3$	5
	$_8O$	$1s^2\ 2s^2\ 2p^4$	6
	$_1H$	$1s^1$	1
Ti-6Al-4V	$_{22}Ti$	$[Ar]3d^2\ 4s^2$	4
Cu-TaC	$_{73}Ta$	$[Xe]\ 4f^{14}\ 5d^3\ 6s^2$	5

The *Ti-6Al-4V* alloy has the high affinity for gases like oxygen and nitrogen [14]. Considering that *Ti* as the major element from the alloy to undergo reaction and is also a transition element. Since it exhibits variable oxidation numbers with electrons from 3d sublevel [13], the formations of the compounds in (1–3) are possible with *Ti* using +2, +3 and +4 oxidation numbers.

$$Ti + C \rightarrow TiC \quad (1)$$
$$2Ti + N_2 \rightarrow 2TiN \quad (2)$$
$$2Ti + O_2 \rightarrow 2TiO \quad (3)$$

From Table I, it is observed that the 3d sublevel of *Ti* electron configuration is filled with two electrons. With possible oxidation numbers of +2, +3 and +4 for *Ti*, a variety of bonds with the three elements (*C*, *N* and *O*) of period 3 can be formed as in (1-3).

B. Dielectric Fluid with Electrode

Considering that the electrode material (*Cu-TaC*) is of low density (about 6.00 g/m^3) [15, 16], it is likely to decompose into *Cu, Ta,* Ta_2C and *C* or other intermediate compounds. However, some of the *TaC* may not decompose due to its extreme hardness and high chemical stability [17].

The *Ta* being a group 5 element in row 6 of the periodic table is also a transition metal with the valence energy level electrons of 5 and variable oxidation states of +4 and +5. Various compounds involving *Ta* or *TaC* may be synthesize with the products of decomposition of urea (*C, N, O* and NH_3). With these variable oxidation numbers, the carbides, nitrides and oxides of *Ta* can be formed in different phases. The possible general reactions of *Ta* with the non-metallic anions (N_2, O_2 and *C*) can then be summarized in (4-7).

$$Ta + C \rightarrow TaC \quad (4)$$

$$2Ta + N_2 \rightarrow 2TaN \quad (5)$$

$$4Ta + N_2 \rightarrow 2Ta_2N \quad (6)$$

$$2Ta + O_2 \rightarrow 2TaO \quad (7)$$

Intermediate phases like Ta_2C and Ta_2O_5 can be formed during the reactions. However, they would be suppressed if the pyrolysis of NH_2CONH_2 is able to provide sufficient carbon atoms in the reacting medium [18]. Hence, all or most of them would be converted to *TaC* as represented by the reactions in (8-9).

$$Ta_2C + C \rightarrow 2TaC \quad (8)$$

$$Ta_2O_5 + 7C \rightarrow 2TaC + 5CO \quad (9)$$

C. Electrode with Ti-6Al-4V Alloy

The elements of the electrode and workpiece can react in presence of dielectric fluid (NH_2CONH_2 solution) to form bimetallic-mixed alloys of their carbides and nitrides [14]. In this situation, monocarbide or mononitride of the two metals (*Ta* and *Ti*) may be synthesized as complex structures during the EDM. The most possible stable bimetallic mixed alloys of these materials are *TaC-TiC* and *TaN-TiN* [14]. In addition, the synthesis of mixed carbo-nitrides of *Ta* (*TaC-TaN* or *TaCN*) can also occur during the reactions [19].

IV. Results and Discussion

The results of the surface analysis conducted after machining are presented and discussed in this section. This includes the presentation and discussion of the elements and the compounds precipitated on the EDMed surface through the reactions that occurred during the machining. The effects of such precipitates on the alloy surface are also discussed.

A. Elemental Analysis

The results of SEM/EDX spectra analysis of the parent *Ti-6Al-4V* alloy presented in Fig 2 shows peaks from *Ti, Al* and *V*. The quantitative analysis of the alloy's peaks gives the relative presence of the elements as Ti=89.04 wt%, Al=6.53 wt% and V=4.43 wt%. This give a very close approximation in percentages to the stoichiometric ratio of the alloy (Ti=90%, Al=6%, and V=4%). Table II shows the summary of EDX elemental analysis of EDMed surfaces. It can be observed from the table that *Ta, Cu, O* and *C* are slightly higher in percentages at higher machining conditions (I_p-5.5A, t_{on}-5.3μs). This implies that more materials migration of those elements might have occurred at such conditions from both electrode and dielectric fluid onto the EDMed surface. Thus, higher I_p and t_{on} give room for high heat intensity which facilitates elemental disintegration from the two materials.

In the results of EDX analyses presented in Figs 3 and 4, elements from the electrode, workpiece and the dielectric fluid can be seen indicated on the spectra graphs. The elements whose peaks were detected are *Cu, Ta, Ti, C* and *O*. The additional ones (*Cu, Ta, O* and *C*) must have resulted from the electrode and dielectric fluid materials since they are not found in the spectra graph of the parent material (*Ti-6Al-4*V) shown in Fig 2. Though, there are variations in the counts for the two different machining conditions (thus, I_p and t_{on}), the presence of *C* and *O* suggest that carbides and oxides of the transition elements can be precipitated on the EDMed surface during machining. However, these are subject to confirmation by XRD analysis which is presented in the section IV B.

Through scanning electron microscopy (SEM), the surface topography of the post-EDM material is presented in Fig 5. The surface indicates a few mild micro-cracks, appearing smooth with small craters. The reaction between the *Cu-TaC* electrode and the urea dielectric is expected to have influenced the creation of these cracks/craters [20].

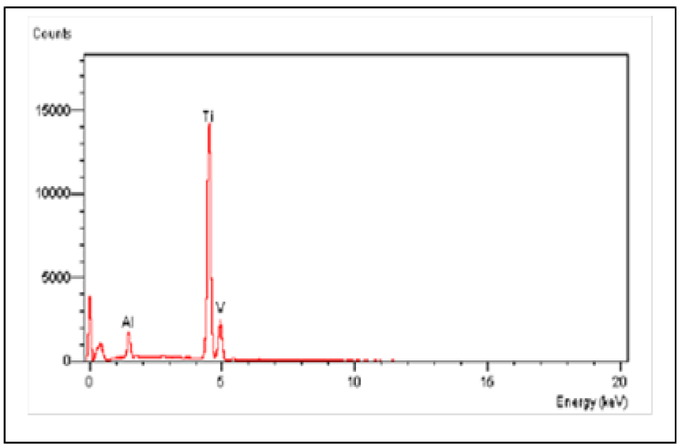

Figure 2. EDX spectra of *Ti-6Al-4V* alloy before EDM

TABLE II. COMPOSITION OF THE MACHINED SURFACE

Element (%)	Machining Settings	
	I_p-3.5A, t_{on}-3.3μs	I_p-5.5A, t_{on}-5.3μs
C	17.26	21.35
O	33.27	35.12
Ti	20.50	10.97

Element (%)	Machining Settings	
	I_p-3.5A, t_{on}-3.3µs	I_p-5.5A, t_{on}-5.3µs
Cu	10.93	13.12
Ta	18.05	19.44

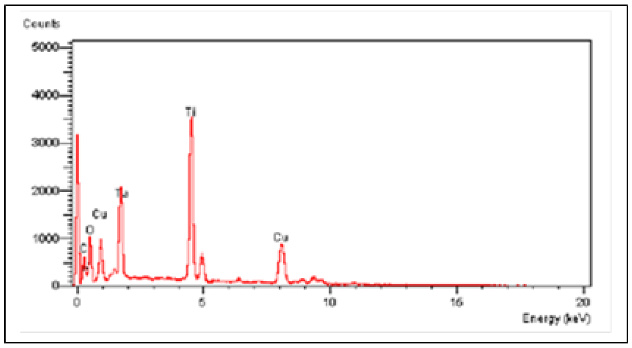

Figure 3. EDX Spectra of the alloy machined with I_p=3.5 A and t_{on}= 3.3 µs

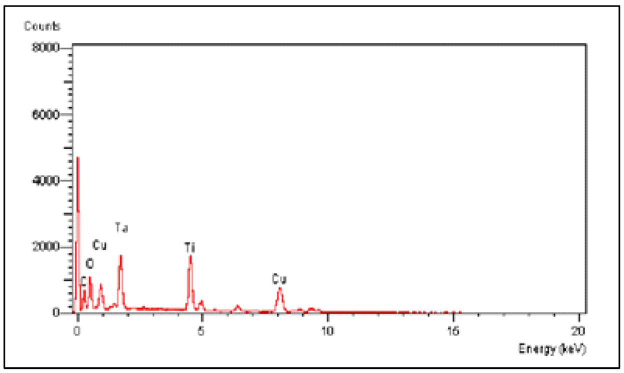

Figure 4. EDX Spectra of the alloy machined with I_p=5.5 A and t_{on}= 5.3 µs

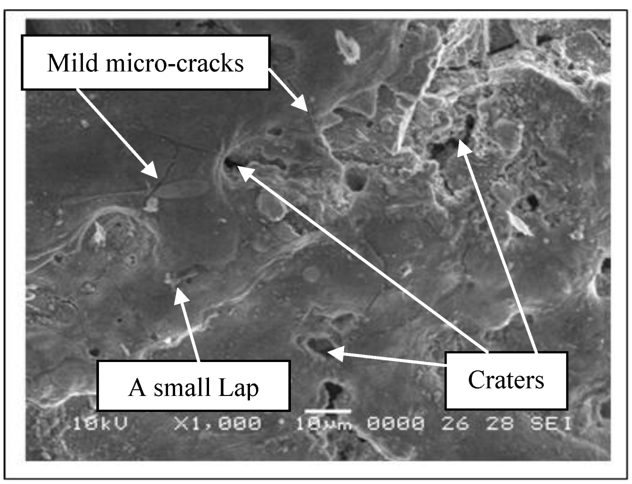

Figure 5. SEM micrograph of the EDMed surface using *Cu-TaC/* urea dielectric

B. Compounds/Precipitates Formed

In Figs 6 and 7, XRD analysis shows the formation of the predicted compounds in different forms. These phases (compounds) which include amongst others, Ta_2N, TaC, TiC, Ti_2N, TiO and C_3N_4 resulted from the reaction of the electrode material, urea dielectric fluid and the workpiece during machining. In Fig 6, a mixture of carbides and nitrides of the two metals are formed on the EDMed surface. The bimetallic mixed carbide (*TaTiC*) is also found to have been formed under the machining condition. The XRD result of Fig 7 equally suggests the existence of carbon nitride (C_3N_4) precipitates on the surface. The possibility of formation of this compound from simple pyrolysis of urea has been confirmed by Liu et al. [21], when they produced graphitic carbon nitride (g-C_3N_4) from it.

It can therefore be concluded that the compounds synthesized during the EDM through reactions of the electrode and dielectric fluid on the workpiece surface are mainly the stable metallic oxides, carbides and nitrides of tantalum and titanium in individual or mixed forms as observed in Figs 6 and 7. Thus, most of the reactions suggested in (1–9) resulted in the products predicted to be formed on the EDMed surface during machining.

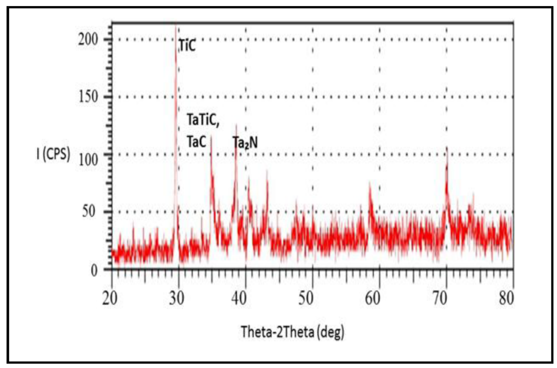

Figure 6. XRD of the compounds on the EDMed surface at I_p=5.5A, t_{on}=3.3µs [23]

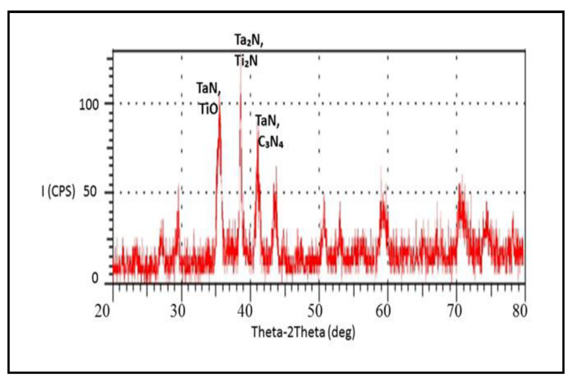

Figure 7. XRD of the EDMed surface with the compounds at I_p=3.5A, t_{on}=5.3µs [23]

C. Effects of the Precipitates on EDMed Surface

The reactions between the electrode material and the dielectric fluid on the surface of the *Ti-6Al-4V* alloy during machining have led to the synthesis of hardened ceramic layers on the EDMed material. The confirmed compounds which include carbides (*TaC, TiC*, *TaTiC*) and nitrides (*TaN*,

Ti_2N, Ta_2N) are capable of reinforcing or strengthening the alloy's surface properties after machining [22]. It is not unusual to have the machined zone of a parent material strengthen in terms of its hardness after machining. This is an important property which gives a measure of material's surface resistance to the application of an indentation load [23]. For instance, micro-hardness of die steel was significantly increased due migrations and carbide formation on it during EDM with different powders in dielectric fluid [24]. With the formation of these carbides as obtained in Figures 5 and 6, the surface of *Ti-6Al-4V* alloy can also have enhanced micro-hardness. Also, the presence of *TaC* and *TaN* among the reaction products on the surface of a material would not only improve the alloy's chemical inertness and thermal hardness, but it would also reduce its surface wear rate [14]. The high hardness of the nitrides of *Ta* and *Ti* made them suitable in inducing abrasive surface resistance on the alloy.

Researchers have found the major shortcomings of the *Ti-6Al-4V* alloy in applications to be its *poor shear strength and surface wear properties* [22,25]. It is also noteworthy that in ion implantation with the alloy, the normal conventional anti-wear treatments used are oxidizing and nitriding of the material [26]. Therefore, the possibility of alleviating these shortcomings through the nitrides, oxides and carbides derived from the combination of *Cu-TaC* electrode and NH_2CONH_2 solution dielectric fluid during the EDM can be explored to enhance the alloy's surface wear properties.

V. CONCLUSION AND RECOMMENDATION

The reactions between materials involved in electrical discharge machining of *Ti-6Al-4V* alloy were studied. The *Cu-TaC* composite electrode produced through *PM* technique and the urea solution dielectric fluid were used to machine the alloy. Thermo-chemical decomposition of the reacting materials (NH_2CONH_2 and *Cu-TaC*), which lead to formation of different phases of new compounds during EDM were predicted. The possibility of formation of carbides, nitrides, oxides of *Ti* and *Ta*, and their metallic mixed alloys were determined.

SEM/EDX and XRD analyses confirmed the additional elements and formation of such compounds like Ta_2N, *TiC*, Ti_2N, *TiO* on the EDMed surface. With these confirmations, the possibility of using EDM with *Cu-TaC* PM electrode and urea solution dielectric fluid to form hard ceramic compounds on the surface of *Ti-6Al-4V* alloy is established.

Finally, since the effects of these compounds on a given substrate such as *Ti-6Al-4V* alloy include enhancement of its thermal hardness, wear resistance and compressive strength, this machining technique which involves the combination of urea dielectric fluid and *Cu-TaC* composite electrode can be used to achieve these goals for the alloy. Further studies can be conducted to assess these post-EDM wear properties of the alloy.

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REFERENCES

[1] H. El-Hofy,"Fundamentals of Machining Processes: conventional and non conventional processes",London: Taylor & Francis Group, 2007.

[2] K. Ho, K.and S. Newman, "State of the art electrical discharge machining" Int J Mach Tools Manu, 2003, 43(13), pp. 1287-1300.

[3] P.N. Rao, Manufacturing Technology, vol 2: metal cutting and machine tools 2nd ed., New Delhi: Tata McGraw Hill Publishing Company Limited, 2009.

[4] M. Gostimirovic, P. Kovac, M. Sekulic, and B. Skoric, "Influence of discharge energy on machining characteristics in EDM," J Mech Sci Technol, 2012, 26, pp. 173-179.

[5] B.Lahiri, S. Mukherjee and B. Mullick, "Loss of energy in pyrolysis of dielectric in EDM process," J Inst Engrs , 1981, 62, pp. 66-69.

[6] P. Bleys, J.P. Kruth, B. Lauwers, B. Schacht, V. Balasubramanian, L. Froyen, et al., "Surface and Sub - Surface Quality of Steel after EDM," Adv Eng Mater, 2006, 8(1-2), pp. 15-25

[7] A.A. Khan, M.B. Ndaliman, Z.M. Zain, M.F. Jamaludin, and U. Patthi, "Surface modification using electric discharge machining with powder addition," Appl Mech Mater 2012, 110, pp. 725-733.

[8] M.Z. Zain, M.B. Ndaliman, A.A. Khan and M.Y. Ali, Improving micro-hardness of stainless steel through powder-mixed electrical discharge machining, Proc IMechE Part C: J Mechanical Engineering Science, 2014, Vol. 228(18) 3374–3380.

[9] N. Mohri, Y. Fukusima, Y. Fukuzawa, T. Tani, and N. Saito, "Layer generation process on work-piece in electrical discharge machining," CIRP Annals-Manuf Technol, 2003, 52(1), pp. 157-160.

[10] P.K. Patowari, U.K. Mishra, P. Saha, and P.K. Mishra, "Surface modification of C40 steel using WC-Cu P/M green compact electrodes in EDM," Int J Manuf Technol Managt, 2010, 21, pp83-98.

[11] M.B. Ndaliman, A.A. Khan, and M.Y. Ali, "Surface modification of titanium alloy through electrical discharge machining (EDM)," Int J Mech Mater Eng, 2011, 6, pp. 380-384.

[12] R.J. Gillespie, D.R. Eaton,D.A. Humphrey and E.A. Robinson, Atoms, Molecules and Reactions: An introduction to chemistry, New Jersey: Prentice–Hall International, Inc. Englewood Cliffs, 1994.

[13] J.A. Mascetta, Chemistry: the easy way, 4th ed., New York: Barron's Easy Way Series, 2003.

[14] D.J. Ham, and J.S. Lee, "Transition metal carbides and nitrides as electrode materials for low temperature fuel cells," Energies, 2009, 2, pp. 873-899.

[15] M.B. Ndaliman, M. Hazza, A.A. Khan, and M.Y. Ali, "Development of a new model for predicting EDM properties of Cu-TaC compact electrodes based on artificial neural network method, Aust J Basic Appl Sci, 2012, 6(13), pp. 192-199.

[16] M.B. Ndaliman, A.A. Khan, and Z.M. Zain, "Performance of PM Compacted Cu-TaC Electrodes during EDM," Proc. 2nd Int Conf Mech Manuf Eng (ICME 2011), P.I.C.C., Malaysia, June 6-8, 2011.

[17] Y. Ohshita, A. Ogura, A. Hoshino, S. Hiiro, and H. Machida, "Low-pressure chemical vapor deposition of TaCN films by pyrolysis of ethylamido-tantalum," J Crystal Growth, 2000, 220(4), pp. 604-609.

[18] S.R. Bakshi, V. Musaramthota, D.A. Virzi, A.K. Keshri, D. Lahiri, V. Singh, et al., "Spark plasma sintered tantalum carbide–carbon nanotube composite: Effect of pressure, carbon nanotube length and dispersion technique on microstructure and mechanical properties," Mater Sci Eng: A, 2011, 528(6), pp. 2538-2547.

[19] O.Y. Khyzhun, and V. Kolyagin, "X-Ray photoelectron and emission spectra of cubic and rhombohedral tantalum carbonitrides," J Alloys Compds, 2004, 363(1), pp. 32-39.

[20] M.B. Ndaliman, A.A. Khan, and M. Y. Ali, "Influence of dielectric fluids on surface properties of electrical discharge machined titanium alloy," Proc IMechE Part B: J Engineering Manufacture, 227(9) pp. 1310–1316

[21] J. Liu, T. Zhang, Z. Wang, G. Dowson, and W. Chen, “Simple pyrolysis of urea into graphite carbon nitride with recyclable adsorption and photocatalytic activity,” J Mater Chem, 2011, 21, pp. 14398-14401.

[22] M.B. Ndaliman, A.A. Khan, and M.Y. Ali, “Formation of Nitrides and Carbides on Titanium Alloy Surface through EDM,” Adv Mater Res, 2012, 576, pp. 7-10.

[23] A.K. Adiyodi, X. Joseph, P.V. Jyothy, G. Jose, N.V. Unnikrishnan, “Dielectric and microhardness studies of methylene blue doped PMMA matrix,” Materials Science-Poland, 2009, 27, pp. 297-305.

[24] A. Bhattacharya, A. Batish, and N. Kumar, “Surface characterization and material migration during surface modification of die steels with silicon, graphite and tungsten powder in EDM process,” J Mech Sci Technol, 2013, 27, pp. 133-140.

[25] M.B. Ndaliman, K.C. Bala, A.A. Khan, M.Y. Ali, U. Abdullahi, and A.A. Abdulmumin, “The effects of Sliding Parameters on Dry Wear Characteristics of Ti-6Al-4V Alloy,” Adv Mater Res, 2015, 1115, pp. 213-216.

[26] R. Martinella, S. Giovanardi, G. Chevallard, and M. Villani, “Wear behaviour of nitrogen-implanted and nitrided Ti-6Al-4V alloy,” Mater Sci Technol, 1985, 69, pp. 247-252.