

## **EFFECT OF HF ACID ON THE FORMATION OF NEW 2D Ti<sub>3</sub>C<sub>2</sub> MXENE FROM Ti<sub>3</sub>SiC<sub>2</sub>**

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### **Abstract**

With the developing technology, our need for renewable energy also increases. Limited energy sources brought along our need for alternative energy sources. When layer A in MAX phases is scraped to highlight the similarity to graphene called MXene a new 2D material type is created. Studies on 2D materials are carried out by researchers in many areas from energy to health. Converted to rechargeable materials to meet energy needs Mxene has become a new energy storage material with its layered structure. With the etching of Ti<sub>3</sub>SiC<sub>2</sub> powder in MAX phase with Hydrofluoric Acid (HF), it becomes an accordion-like two-dimensional Ti<sub>3</sub>C<sub>2</sub> Mxene structure. Hydrofluoric Acid etching is the most used method in converting MAX phase to Mxene structure. Like conductivity properties of 2D materials determining and changing many features surface terminations such as -O, -OH, -F group on Mxene were effective. The Mxene structure is an extraordinary combination of electrical and mechanical properties that combine the properties of metals and ceramics. In this article, the effect of etching time with hydrofluoric acid is investigated. Mxene phase Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> powder subjected to hydrofluoric acid (HF) at room temperature for 2, 8, 16, 32, and 48 hours, X-ray diffraction (XRD) was analyzed by scanning electron microscopy (SEM & FESEM) and Brunauer-Emmett-Teller (BET) Theory.

**Keywords:** MAX phase, Mxene, Ti<sub>3</sub>SiC<sub>2</sub>, Hydrofluoric Acid, 2D Material

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## HF ASİDİNİN $Ti_3SiC_2$ 'DEN YENİ 2D $Ti_3C_2$ MXENE OLUŞUMU ÜZERİNDEKİ ETKİSİ

### Özet

Gelişen teknoloji ile birlikte yenilenebilir enerji ihtiyacımız da artıyor. Sınırlı enerji kaynakları, alternatif enerji kaynaklarına olan ihtiyacımızı da beraberinde getirdi. MAX fazındaki A katmanlı, MXene adı verilen grafene benzerliği vurgulamak için kazındığında yeni bir 2D malzeme türü oluşturulur. 2D malzemelerle ilgili çalışmalar, enerjiden sağlığa pek çok alanda araştırmacılar tarafından yürütülmektedir. Enerji ihtiyacını karşılamak için şarj edilebilir malzemelere dönüştürülen MXene, katmanlı yapısı ile yeni bir enerji depolama malzemesi haline geldi. Hidroflorik Asit (HF) ile  $Ti_3SiC_2$  tozunun MAX fazında aşındırılmasıyla akordeon benzeri iki boyutlu  $Ti_3C_2$  MXene yapısı haline gelir. Hidroflorik Asit aşındırma, MAX fazını MXene yapısına dönüştürmede en çok kullanılan yöntemdir. MXene üzerinde -O, -OH, -F grubu gibi birçok özellik yüzey sonlandırmalarını belirleyen ve değiştiren 2D malzemelerin iletkenlik özellikleri gibi etkili oldu. MXene yapısı, metallerin ve seramiğin özelliklerini birleştiren olağanüstü bir elektriksel ve mekanik özellik kombinasyonudur. Bu yazıda hidroflorik asit ile aşındırma süresinin etkisi araştırılmıştır. 2, 8, 16, 32 ve 48 saat boyunca oda sıcaklığında hidroflorik aside (HF) tabi tutulan MXene faz  $Ti_3C_2Tx$  tozu, X-ışını kırınımı (XRD) taramalı elektron mikroskobu (SEM & FESEM) ve Brunauer-Emmett-Teller (BET) Teorisi ile analiz edildi.

**Anahtar Kelimeler:** MAX faz, MXene,  $Ti_3SiC_2$ , Hidroflorik Asit, 2D Malzeme

### 1. Introduction

The need for energy increases with the developing technology. Renewable energy sources have been developed to facilitate use in many devices used today. With the development of energy resources energy storage also gained importance. Researchers have worked on new generation materials to improve the performance of energy storage devices [1]-[12]. After the discovery of  $Ti_3C_2$  in 2011, two-dimensional (2D) materials called Mxene developed rapidly. Mxene's were first synthesized in 2011 from layered MAX phases. Mxene, the shining star of two-dimensional (2D) materials, layered structure, exceptional electrical conductivity, it perfectly displays the adjustable active

surface and mechanical strength. The combination of the properties of both metals and ceramics is the main advantage of these compounds and are called ductile ceramics accordingly. These phases, called Mxene, have the chemical stability of ceramics and metals, processability, shock resistance, like good electrical and thermal conductivity it combines its outstanding features [13]-[28]. MAX phases are triple-layer carbides generally known by the general formula of  $M_{n+1}AX_n$  ( $n = 1, 2, 3$ ). In this formula, M is an early transition metal, A is the group A element and X is carbon or nitrogen. MAX phases are atomically layered, triple carbides or nitrides [1]-[16]. In the MAX structure, X atoms fill the octahedral regions between the M layers, and the M and X layers are compacted together with pure A layers. This type of layered structure removed the A-element layers, causing MAX phases to be distributed to the Mxene. The A-atoms that bind the MX stacks remove the layer of atoms and form an accordion-like structure where a large number of coverslips are stacked close together. Mxene is a new nanomaterial class of two-dimensional (2D) transition metal carbide and nitrides with the chemical formula  $M_{n+1}X_nT_x$  [16]-[25]. M transition metal atom, X, C and / or N, ( $n = 1, 2$  or 3) and  $T_x$  represents surface groups. Mxene is a large family of 2D materials containing layered, hexagonal, early-pass metal carbides and / or nitrides.  $T_x$  means surface terminations (eg hydroxyl, oxygen or fluorine) [29]-[39].

Hydrofluoric acid (HF) is one of the common selective etching acids used to etch element [1]-[5],[7]-[13]. HF decomposition begins with the adsorption of H and F at the edges on the Ti atoms. The method based on HF treatment leads to different surface terminations with the O, OH and / or F terminal groups. While the synthesis of mxene refers to the etching process with acids, its surface is saturated with hydroxyl, oxygen and fluorine-based functional groups or combinations of these [17]-[20],[24]. The surface terminations such as the -O, -OH, -F group on the Mxene widely affect its properties. Number of Mxene and Mxene layers, The desired properties can be largely adjusted by controlling the interlayer spacing [29]-[38]. These initial surface terminations (-H and -F) increase the intermediate layer distance, which facilitates HF induction in the MAX phase structure. The Mxene have quickly become a new class of 2D materials that combine the metallic conductivity of the transition metal carbides with the hydrophilic nature of the hydroxyl or oxygen-terminated surfaces. The electronic properties of Mxene are also related to "X" atoms. In carbonitride and nitride, Mxene has stronger metallic

properties than carbide Mxene because N has more electrons [20], [26]. There are MAX known in more than 80 different compositions and their number is increasing day by day. According to theoretical calculations, there are more than 70 Mxene phases [1],[4],[9],[12],[15],[17]. Despite the presence of terminal surface groups, especially the most intensively studied Mxene is titanium carbide ( $Ti_3C_2T_x$ ) [20],[27],[33]-[35]. Experimentally, Mxene's transparent conductors [14], [17], [24] [29], [31], field effect transistors [13], [26], [30], super capacitor [4], [13], [15], [18], [20], [30],[42], sensor [1], [4], [6], [10], [14] [25], [31], batteries [13], [19], [24], [29], [34], [41] electromagnetic interface screensavers [1], [4], [11], [16], [20] [29]-[31],[38], in polymeric composites [7],[15], [25],[29] water treatment [3],[4],[8],[11], electrodes [4], [15], [25], [31], suitable substrate for paints [3], [29], catalyst [3], [4], [14], [29] and also for cancer treatment it has various uses, including ceramic biomaterials with high photothermal conversion efficiency [29]. Theoretically, many applications have been proposed for Mxene in electronic, biomedicine, magnetic, optical, thermoelectric, and sensing devices, as well as new potential materials for hydrogen, catalytic and photocatalytic reactions [1], [2], [4], [29],[41]. Among the electrochemical energy storage solutions, the redox-free super capacitors exhibit the highest power densities and the best cycle life and can easily reach over a million cycles. Despite these features, Li-ion batteries are preferred in most applications [13],[34],[41], especially in electric vehicle applications. This is because, it is low energy density compared to the second one. However, super capacitor technology continues to complement batteries in many ways. Excellent conversion performance for non-redox super capacitors is directly due to high recycled charge storage mechanisms [41].

## **2. Experimental Procedures**

MAX phase starting powder was purchased from Forsman Scientific (Beijing) Co., Ltd. Company. MAX phase  $Ti_3SiC_2$  powder is 98% purity (<2% TiC) and 200 mesh size. 1 gram of  $Ti_3SiC_2$  powder in the plastic beaker was slowly added to 10 ml of acid solutions in the beaker. While preparing the acid solution, 50% deionized water was used as a 50% Hydrofluoric Acid (HF) solution [7],[23],[25],[28]. The generated solution was mixed under a fume hoods with a magnetic stirrer set at 750 rpm for 2, 8, 16, 32 and 48

hours. The codes of the powders are expressed by the acid and mixing times used (Table 1).

Table 1: The code of HF treated powders.

Sample	Code
HF treated for 2 h	HF-2
HF treated for 8 h	HF-8
HF treated for 16 h	HF-16
HF treated for 32 h	HF-32
HF treated for 48 h	HF-48

Teflon Magnetic Fish (PTFE) was placed into the beaker for mixing. After mixing the solution and powder, it was taken from the beaker into the centrifuge tube. After mixing, the powders will settle to the bottom of the beaker. The solution remaining on the top is greenish in color. The residue remaining in the beaker is poured into the centrifuge tubes. The NF 200 Model was subjected to 5-minute processes at a speed of 3500 rpm in the centrifuge. The supernatant remaining in the upper part after centrifugation was poured into separate containers. Before the centrifuge tube was emptied, pH measurements of the supernatant were made with Mettler Toledo pH meter. Centrifugation was continued at 5 minutes until the pH value was between 5-6. After the pH reaches a value between 5-6, the supernatant in the centrifuge tube is discharged. The residue remaining under the centrifuge tube was placed in a glass beaker. The residues in the centrifuge tubes were cleaned with ethanol and poured into the glass beaker. 40 ml of ethanol was added to the glass beaker. It was left for 48 hours for the ethanol in the beaker to be removed and the powders to settle to the bottom. The remaining ethanol was then drained with the Eppendorf pipette. 5 ml of ethanol was added again and left for 24 hours. Later, the clay (mud) in which the dust was found collapsed to the bottom of the beaker. Vacuum filtering was carried out for 1 hour to filter the clay (clay) powder and separate it from the liquid. After the vacuum filtering process, the drying process was carried out by keeping it in the oven for 4 hours in order to easily remove the dust remaining from the filter paper. Summary of the Mxene production phase is shown in Figure 1.

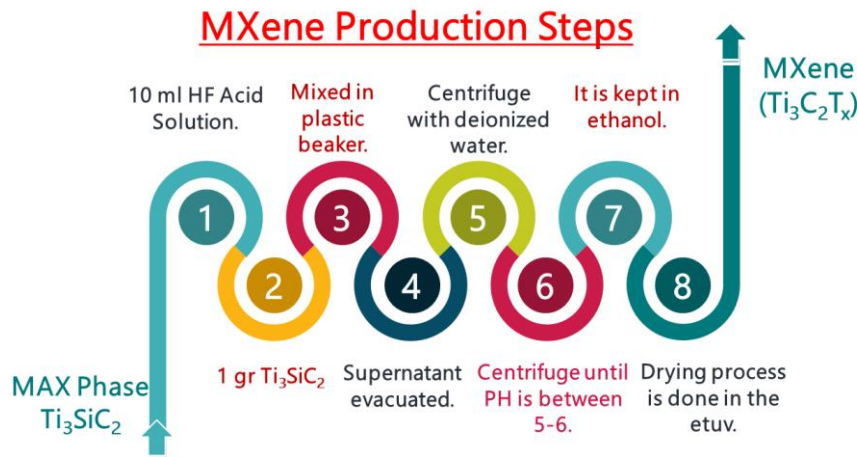


Figure 1: Production Phases from MAX Phase to Mxene.

Si atoms in the MAX phase are exfoliated to form  $Ti_3C_2$ . The exposed Ti atoms are highly reactive and the reaction medium easily reacts with water or HF to form compounds with -OH or -F (Table 2) [1],[4],[8],[32],[34]. Note that etching is an exothermic reaction and produces hydrogen, so the reaction vessel should be well ventilated [10].

Table 2: Termination equations in 2 steps with -OH and -F [1,4,8,10,32,34]

Finishing	Step 1	Step 2
-F	$Ti_3SiC_2 + 3HF = Ti_3C_2 + SiF_3 + 3/2H_2$	$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2$
-OH	$Ti_3SiC_2 + 3HF = Ti_3C_2 + SiF_3 + 3/2H_2$	$Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2$

RIGAKU D-MAX-2200 model X-Ray Diffraction, FEI Quanta FEG 450 model Field Emission Scanning Electron microscope (FESEM) and Micromeritics ASAP2020 model Brunauer-Emmett-Teller (BET) theory were analyzed. ZEISS-supra 40 vp/gemini Scanning Electron Microscope (SEM) was used for micro and nano size analyzes. Prior to SEM, the dust was coated with 80% Gold and 20% Palladium with the Quorum Q150R ES brand coating device.

### 3. Results and Discussion

Bonds in the MAX phase are too strong to break. In MAX phase structures, there is a mixture of ionic, metallic and covalent bonds between M and X elements, the M element is through the metallic bond, which is weaker than the bond between M and X,

binds to the element layer A [2]-[5],[9],[16],[20],[22]. It cannot easily separate from MAX phases directly by dispersion or mechanically [3],[7]. However, M-A bonds are more chemically active than strong M-X bonds that enable selective wear of the A-element layers, and M-A bonds are weaker compared to the M-X bond [4],[16],[30]. Due to the different properties and forces between the M-X and M-A bonds, a relatively high reactivity layer A can selectively break bonds using suitable chemicals or chemicals [3],[35]. The great difference in M-X and M-A bond strength allows M-A bonds to break and metal A to be removed from the 3D MAX phase form [5],[16]. This results in expanded layers separated by  $M_{n+1}X_nT_x$  called 2D MXenes. Ti-Si bond is weaker in  $Ti_3SiC_2$  MAX phase than Ti-C bond. Ti-Si bond is removed with HF and Silicon is removed from the environment [32],[33],[35]. Safety precautions should be carefully studied when working with HF, the strong acid [30].

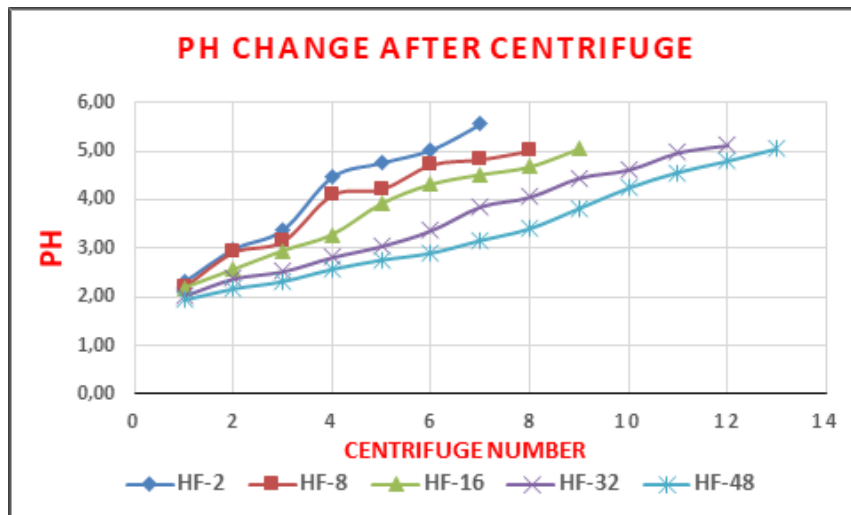


Figure 2: pH value change over time after centrifugation.

pH change of MXene phase  $Ti_3C_2T_x$  powder after centrifugation increases logarithmically. There is a linear proportion between the mixing time and the time taken for the centrifuge. As the mixing time increases, the time it takes for the pH value to reach a value between 5-6 is also increasing (Figure 2). FE-SEM and SEM images of MAX phase starting powder ( $Ti_3SiC_2$ ) can be seen before mixing with acids (Figure 3). It is understood from the analysis that the powder undergoes physical and chemical changes after mixing with acids for different periods of time.

SEM images of powders obtained by mechanical peeling of MAX Phase  $Ti_3SiC_2$  starting powder with Hydrofluoric Acid (HF) for 2, 16 and 48 hours are shown in Figure 4. As the mixing time increases, the effects of physical and chemical changes can be

easily seen. The starting powder is transformed into a layered structure by showing physical and chemical changes [7],[30],[38]. Si-Ti bonds are very weak and covalent Ti-C bonds are much stronger.  $Ti_3SiC_2$  exhibits unusual mechanical properties and chemical stability at high temperatures [28]. In the analysis of the layered structure in the transformation, the silicon difference between the layers can be easily seen. After mixing with acids, the silicone reacts and is expected to move away or decrease from the environment. It is understood that the amount of silicon decreases from SEM / EDS analysis to MXene when the HF process is performed (Figure 5). A small amount of  $Ti_3O$  and  $TiO$  phases were also found in the MAX Phase  $Ti_3SiC_2$  powder XRD image (Figure 6).

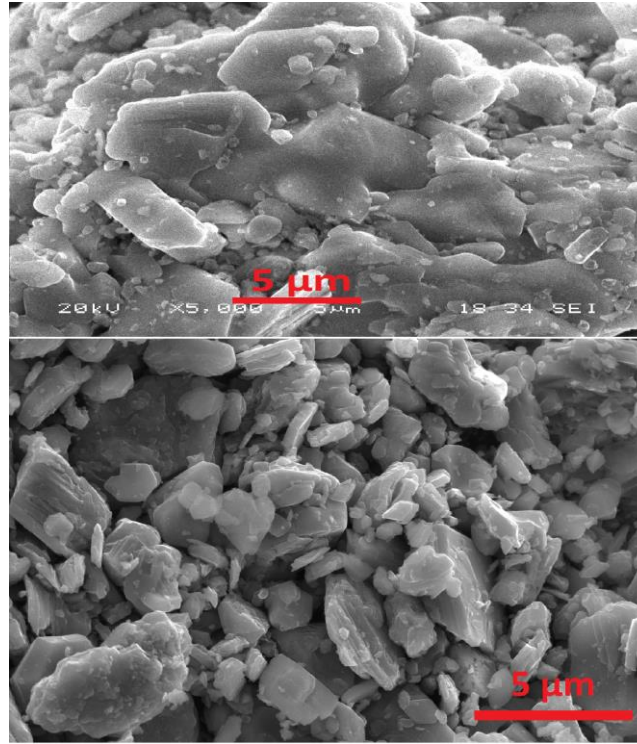


Figure 3: MAX Phase  $Ti_3SiC_2$  Powder a) SEM images, b) FE-SEM images.

XRD images of powders obtained by mechanical peeling of the MAX phase  $Ti_3SiC_2$  starting powder with HF for 2, 16 and 48 hours are shown in Figure 7. After mixing with hydrofluoric acid, the peaks on the XRD chart shift to the left. In HF, after processing, the layer spacing of the starting powders and lattice parameter increases and MXene refers to the change in structure. After the silicon is etched, stratification occurs and the layer gap increases. From XRD analysis, it is seen that d distances increase with increasing HF processing time. Peaks with shifting to higher angles for HF-16 and HF-



48, it can be connected to the diffusion of the Si atoms in the solution to the structure of the resulting TiC. In fact, the atomic radius of Si is lower than Ti [2],[5],[11].

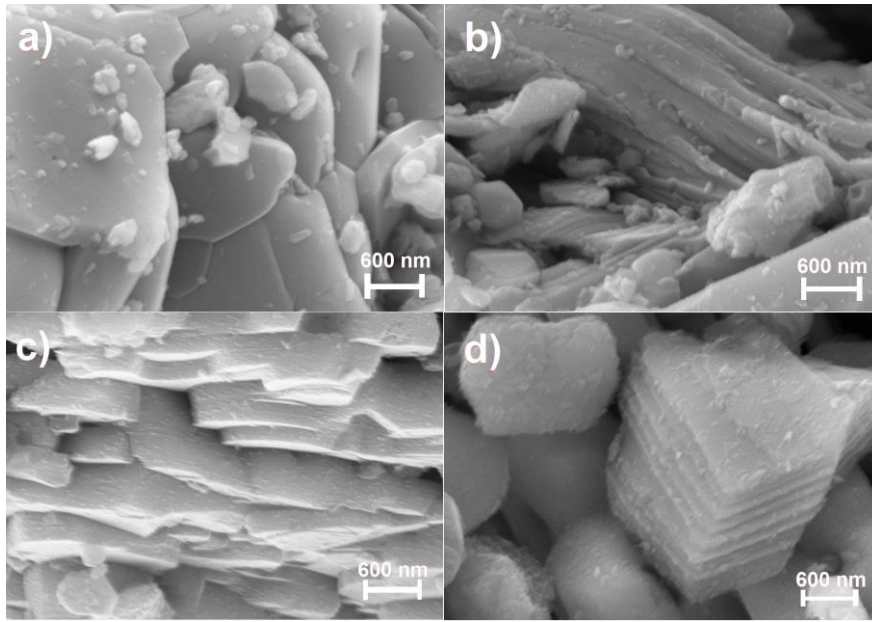


Figure 4: Starting powder of MAX Phase  $Ti_3SiC_2$  Powder (a), 2 hours (b), 16 hours (c) and 48 hours (d) SEM images of the powder obtained by mechanical peeling of Hydrofluoric Acid (HF).

$Ti_3SiC_2$  forms layers by treating the starting powder with HF solution and can be seen from XRD patterns that some layer spacing also increases. The chemical composition of HF-48 powder is analyzed by EDS (Figure 5). According to the XRD pattern and EDS analysis, it is seen that the 48-hour HF operation caused a decrease in Si amount. According to the XRD template of  $Ti_3SiC_2$  powder treated with HF, TiC is the most important impurity of the prepared  $Ti_3SiC_2$ .

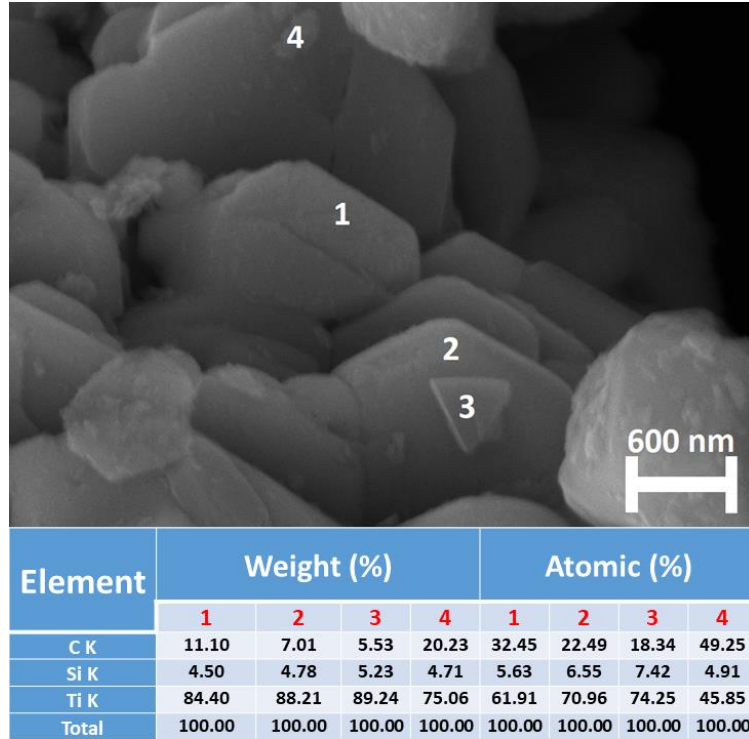


Figure 5: SEM/EDS Analysis of powder obtained by mechanical peeling of MAX Phase  $Ti_3SiC_2$  Powder for 48 hours Hydrofluoric Acid (HF).

In this context, it can be thought that the thermal expansion coefficient of TiC is lower than  $Ti_3SiC_2$  and the prepared powder has residual tension. The presence of residual stresses accelerates chemical activity and separation of the Si layer [2],[5],[11]. From a crystallographic point of view, successful etching is marked by weakening or even complete disappearance of the X-ray diffraction (XRD) peaks of the previous MAX phase. On the other hand, if no XRD peaks are detected and the etching reaction is not completed, the MAX phase peaks are combined with the new MXene peaks.

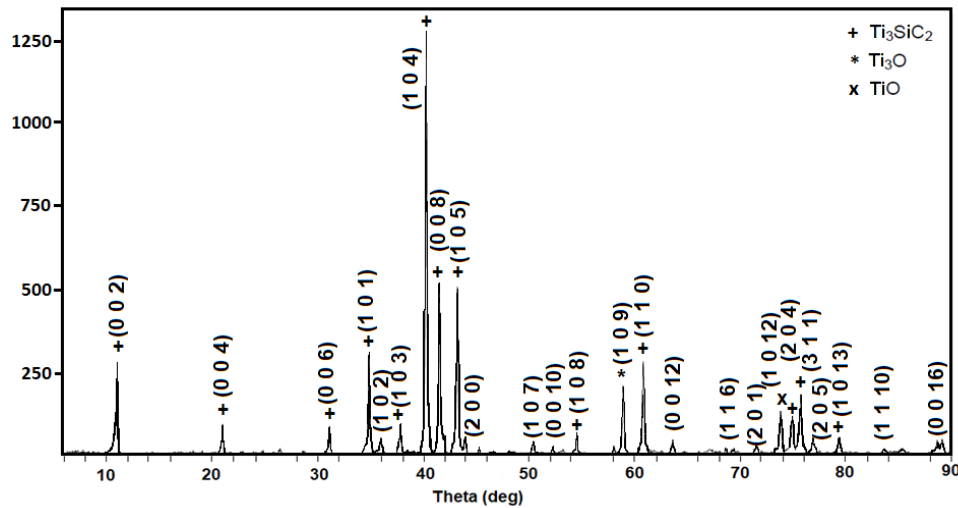


Figure 6: MAX Phase  $Ti_3SiC_2$  Powder XRD images.

Therefore, the MXene chemistry is  $M_{n+1}X_nT_x$ , which represents -O, -OH or -F atoms. Transformation to the MXene may cause the peaks to weaken or disappear in X-ray diffraction patterns [10], [11], [13], [14], [40]. There are more than ten MAX systems discovered. Classification is made as 3D MAX system  $M_2AX$  (211),  $M_3AX_2$  (312) and  $M_4AX_3$  (413). As the second classification, n values in phases vary from 1 to 3, with selective removal of A layers, 2D MXene has three possible mesh structures:  $M_2X$ ,  $M_3X_2$ ,  $M_4X_3$  [1], [2], [7], [13], [15], [27], [32] [33], [35],[39],[42].

HF reveals that the d distance of the planes increases with increasing processing time. After acid treatment with HF, (3 1 1) peak turned into (1 1 8) peak, (1 1 13) peak (2 0 6) peak. The peaks (2 0 0), (0 0 6) and (1 1 2) in the starting powder disappeared. A new peak (1 0 11) was formed after HF treatment. This plane expresses the MXene phase. Figure 5 shows the SEM microstructure of HF-48 powder. It is clear that by immersing the powder in the HF solution,  $Ti_3SiC_2$  breaks and layered structures are formed. Also, the chemical composition of the HF-48 powder is analyzed by EDS.

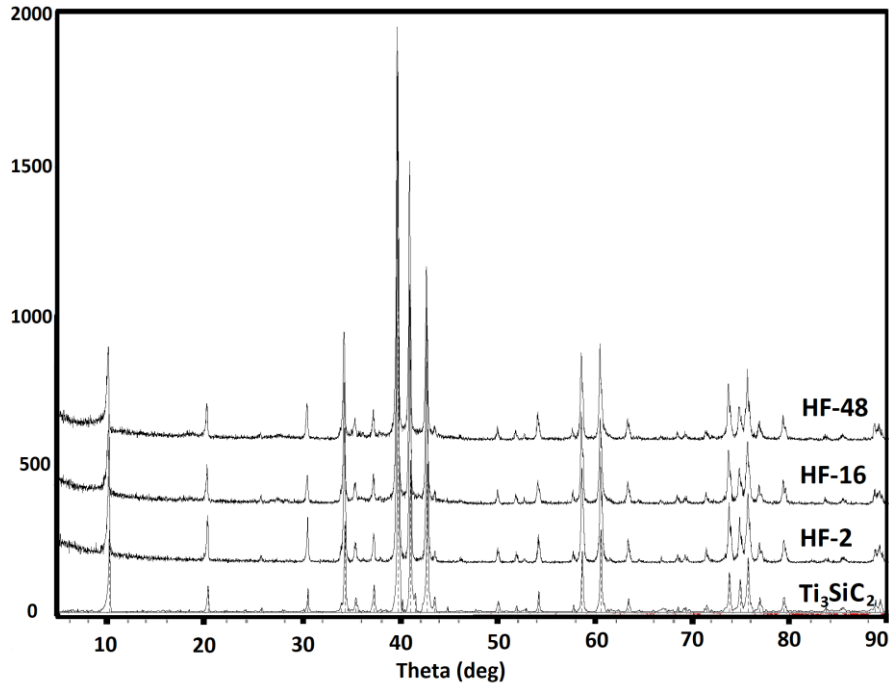


Figure 7: MAX Phase  $Ti_3SiC_2$  Powder, With Hydrofluoric Acid (HF) XRD image of powders formed by mixing for 2, 16 and 48 hours.

In accordance with the XRD pattern, the 48-hour HF treatment appears to lead to a reduction in the amount of Si (Figure 5). In other words, the layered structure of  $Ti_3SiC_2$  turns into thinner layers. The SEM images reveal that particles obtained at higher magnifications tend to become regular shapes (polyhedron) due to HF processing. As mentioned earlier, Ti-Si bonds are much weaker than Ti-C bonds and hence can be deduced from EDS and XRD results, where the HF process leads to the removal of Si layers. Observed peaks from the starting powder shifting to higher angles for HF-48 can be attributed to the diffusion of the Si atoms present in the solution into the structure of the resulting TiC [5]-[6].

Table 3: Brunauer - Emmett - Wires (BET) analysis of powders formed by mixing with MAX Phase  $Ti_3SiC_2$  Powder and Hydrofluoric Acid (HF) for 48 hours.

	Single point surface area at $p/p^\circ$ ( $m^2/g$ )	BET Surface Area ( $m^2/g$ )	Langmuir Surface Area ( $m^2/g$ )	t-Plot Micropore Area ( $m^2/g$ )	t-Plot External Surface Area ( $m^2/g$ )
$Ti_3SiC_2$	0,8957	0,9337	1,2978	0,1307	0,8031
HF-48	2,4581	2,5694	3,5748	0,1792	2,3902

The surface area was determined by multi-point analysis by the Brunauer-Emmett-Teller (BET) method and the total pore volume (porosity) was calculated from the volume of nitrogen adsorbed at relative pressure ( $P/P_0$ ). It was carried out using a Micromeritics ASAP 2020 device at 77 K after exporting  $N_2$  for 48 hours under vacuum at 200 °C.  $Ti_3SiC_2$  and HF-48 powders were compared with the Brunauer-Emmett-Teller (BET) theory by the multi-point analysis method (Table 3). Total pore volumes were calculated as  $0.8957 \text{ m}^2\text{g}^{-1}$   $P/P_0 = Ti_3SiC_2$  Powder,  $2.4581 \text{ m}^2\text{g}^{-1}$  in HF-48. Pore size distributions were obtained using the Barrette Joynere Halenda (BJH) model. It is seen that the desorption-adsorption ratio between MAX phase  $Ti_3SiC_2$  and MXene phase  $Ti_3C_2T_x$  is higher in HF-48 (Figure 8).

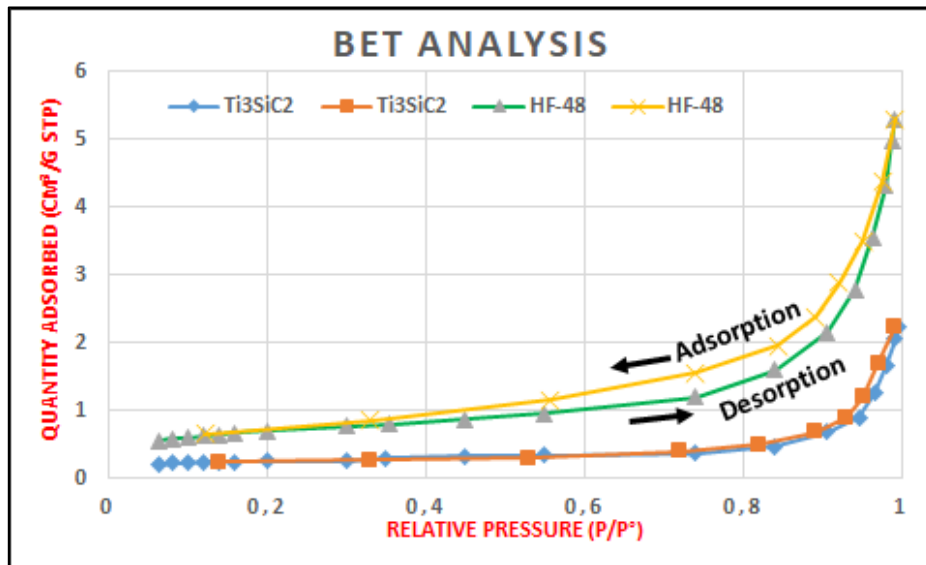


Figure 8: Comparison of desorption-adsorption data between MAX phase  $Ti_3SiC_2$  and HF-48 treated MXene phase  $Ti_3C_2T_x$ .

#### 4. Conclusions

In this study, changing phase and morphological structure of MAX phase  $Ti_3SiC_2$  powder after immersion in HF solution was investigated. The Hydrofluoric Acid (HF) used changes the physical and chemical structure of  $Ti_3SiC_2$  powder. A new structure is formed by breaking the weak bonds between Ti-Si and removing the silicon from the environment. There is a ratio between the mixing time with acids and the pH measured in the centrifuge process. As the mixing time increases, the number of centrifuges

increases to reach the desired pH value. It was seen that the best solution was obtained after mixing with HF-48 in conversion of MAX phase  $Ti_3SiC_2$  powder into layered  $Ti_3C_2T_x$  structure in MXene structure. It is seen in XRD and EDS analysis that mixing  $Ti_3SiC_2$  powder with HF for 48 hours is more effective in transforming it into graphene-like MXene structure. The MXene structure changes as a result of different terminations of MAX phase powders, mixing at different times and at different temperatures. For new researchers, MAX and MXene structures have a wide range of work and research opportunities.

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