

# Synthesis and Characterization of Tungsten Carbide nanoparticles

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## Abstract

The nano sized particles of tungsten carbide (WC) have been synthesized by aqueous sol-gel method using Tungstophosphoric acid as a source of tungsten and carbon soot as a source of carbon. Glycolato complex of tungsten was prepared in sol form to obtain gel by hydrolysis using acid/alkali. Solid state reaction between calcined precursor and carbon soot under argon at 1200 and 1500°C yielded WC nano powder. The powder was characterized using ray powder diffraction, HRTEM and DTA/TGA analysis. The size of the crystallites was observed to be  $25\pm 3$  nM.

## Introduction

Transition metal carbides in general and tungsten carbide (WC) in particular finds wide applications due to their high melting point, extreme hardness and other unique properties. WC has a melting point of 2870°C [1] and hardness of 9 to 9.5 on Mho's scale [2], with a Vickers number of approximately 2600 [2]. It has an ultimate tensile strength of 344 MPa [3], an ultimate compression strength of about 2.7 GPa and shear modulus of 274 GPa [4]. As compared to Young's modulus value of 200 GPa for steel, the tungsten carbide typically has a value between 500-700 GPa [5]. The thermal

conductivity of WC is reported to be 110 W/(M.K) and coefficient of linear thermal expansion value of about  $4.5 \times 10^{-6}$  to  $6.5 \times 10^{-6}$  for an added Co content of about 5.9 to 13.2% [6-8]. It is notable that for coating applications metallic cobalt or nickel are used as binders. Due to these favorable properties, tungsten carbide is widely used in cutting tools, mining tools, cement drills, saw blade tips, milling cutters and machine tools etc. Due to similarity in electronic structure of WC and Pt, tungsten carbide has also been used as catalytic material for replacement of noble metal Pt in fuel cells [9, 10].

Since the reduction in size to nano scale further increases the surface area, reactivity as well as hardness, it was considered worthwhile to develop tungsten carbide nano particles using low cost raw materials. The nano powder of WC was synthesized using Tungstophosphoric acid and carbon soot using sol-gel followed by solid state carbonation at temperatures of 1200 and 1500 °C in an inert environment.

## **2. Experimental details**

### **2.1 Chemicals**

Tungstophosphoric acid (BDH), potassium hydroxide (AR) Rankem, nitric acid (SDFCL), ethylene glycol (Pro Analysis), and ammonium nitrate (Pro Analysis) both of Merck, India make, were used as received.

### **2.2 Instruments**

Identification of the phases present in the synthesized material was carried out using X-ray diffraction spectrometer (Bruker – Model D-8) using Cu K $\alpha$  radiation ( $\lambda=1.54$  nm), operated at 40 kV and 40 mA at a scan rate of 1°2 $\theta$ /s in the range  $2\theta = 10 - 70^\circ$  and comparing the inter-planar distances and intensity values with those of the corresponding standard peaks using JCPDS files. The particle size and morphology was studied using

High Resolution Transmission Electron Microscope (JEOL 3010 operating at 300 keV). For HRTEM studies the synthesized samples were sonicated in acetone for 15 min followed by ambient drying and mounted on carbon coated copper grids. Thermal analysis (TGA) of the precursor material was carried out in flowing nitrogen with heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in the temperature range of  $50\text{-}1500^{\circ}\text{C}$  using Mettler Toledo (Model-TGA/DSC-1 STAR) system.

### **2.3 Method of synthesis**

WC nanoparticles were prepared by the reaction of  $\text{WO}_3$  and Carbon soot at  $1200\text{ }^{\circ}\text{C}$  and  $1500\text{ }^{\circ}\text{C}$ .  $\text{WO}_3$  was prepared by sol gel method where tungstophosphoric ( 3.6425 g) acid and potassium hydroxide ( 2.8055g) were mixed thoroughly using a magnetic stirrer to obtain white precipitate of potassium tungstate. For making sol, potassium tungstate and NaOH, corresponding to 0.5 M and 0.3 M respectively were taken in ethylene glycol (total volume 150 ml) and distilled for 2 hrs to get a clear sol of tungsten glycolato complex. The synthesized tungsten sol was hydrolyzed using (i) 25% ammonium nitrate or (ii) 3% nitric acid under constant stirring to obtain a thick gel. The hydrolyzed gel was filtered, made substantially free from alkali free following the procedure reported earlier [11], washed with distilled water and then dried at  $50^{\circ}\text{C}$  in a hot air oven. Both the dried gel were powdered using agate mortar and pestle and then calcined at  $500^{\circ}\text{C}$  for 2 hrs in an electric muffle furnace to obtain  $\text{WO}_3$  A - (prepared using 25% ammonium nitrate) and  $\text{WO}_3$  H - (prepared using 3% nitric acid). The above prepared  $\text{WO}_3$  samples (both A & H) were mixed with carbon soot and heated at  $1200$  and  $1500\text{ }^{\circ}\text{C}$  for 2 hrs in a tubular electric furnace under continuous flow of argon similar to the procedure followed in the

case of nano SiC [12] and nano TiC [13]. The prepared WC nanoparticles were characterized using different characterization techniques.

### **3. Result and discussion**

#### **3.1 X-ray diffraction studies**

##### **Tungsten carbide prepared from WO<sub>3</sub> – A Precursor**

The X-ray diffractograms of WC powder prepared by heat treating WO<sub>3</sub> – A precursor and carbon soot mixture for 2 hrs at 1200 and 1500 °C are shown in Fig. 1a and Fig. 1b respectively. Fig. 1a shows the presence of peaks with 'd' value 2.51, 2.85, 1.44 and 1.22 corresponding to tungsten carbide (WC) indicating that formation of tungsten carbide has started. Further the mixture when heat treated at 1500°C shows the major peaks with 'd' value 2.56 and 2.85 have increased in intensity and an additional peak with 'd' value of 1.32 corresponding to WC have appeared. In addition peaks with 'd' value 3.43 corresponding to WO<sub>2</sub> can also be seen. The lattice parameter calculated for two major peaks of hexagonal WC was observed to be a=2.8920 and c= 2.8012 corresponding to the standard value of a=2.906 c=2.836. Crystallite size of the particles, calculated from

the X-ray diffraction data using Scherer [14] equation was observed to be 23.7 nm.

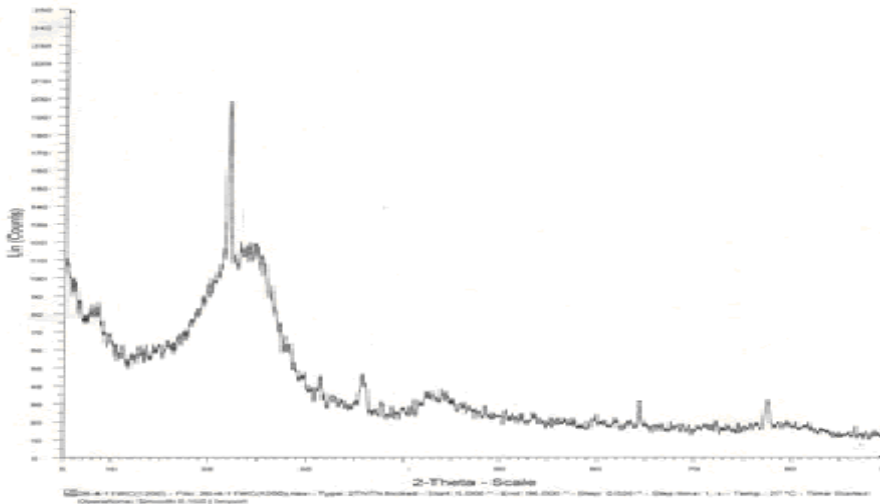


Fig. 1a – X-ray Diffractogram of Tungsten carbide sample prepared at 1200°C

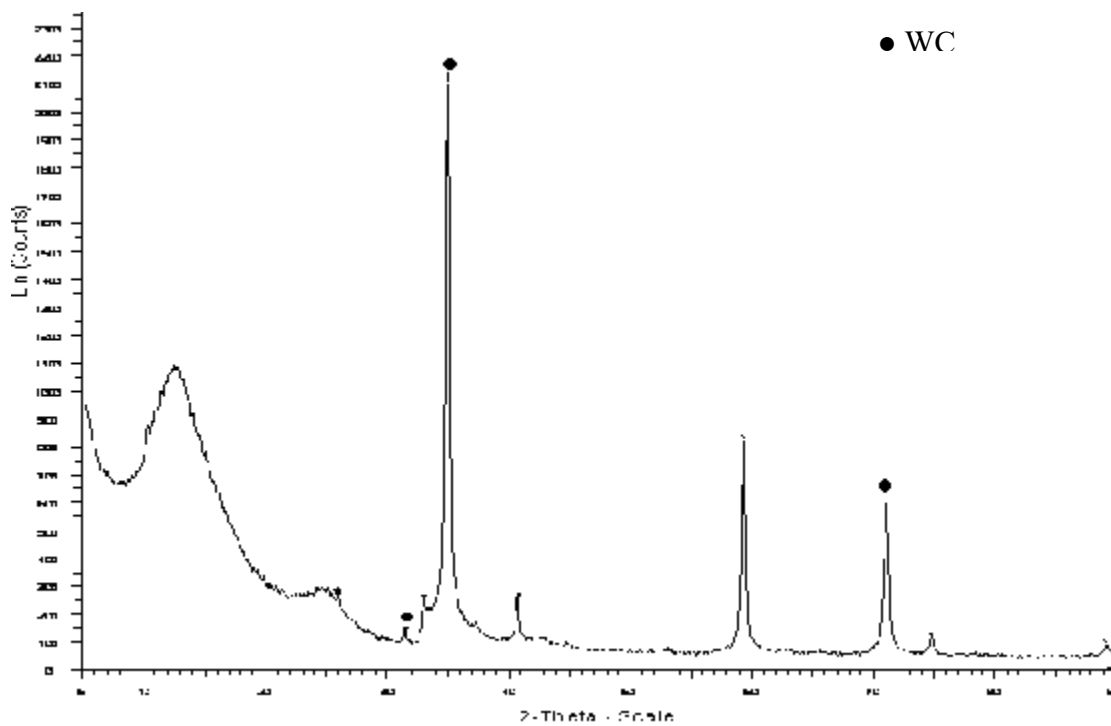


Fig. 1b X-ray Diffractogram of Tungsten carbide sample prepared at 1500°C using

WO<sub>3</sub>-A precursor

## Tungsten carbide prepared from WO<sub>3</sub> –H

The X-ray diffractogram of WC prepared by heat treating WO<sub>3</sub> – H precursor and carbon soot mixture for 2 hrs at 1500 °C under continuous flow of argon is shown in Fig. 2. It shows the presence of peaks with 'd' value 2.56, 1.85, 1.32 and 1.26 corresponding to WC. The lattice parameter calculated for two major peaks of hexagonal WC was observed to be a=2.881 and c= 2.815, corresponding to the standard value of a=2.906 c=2.836. The crystallite size of the particles was calculated from the X-ray diffraction data using Scherer equation and was observed to be 27.70 nm.

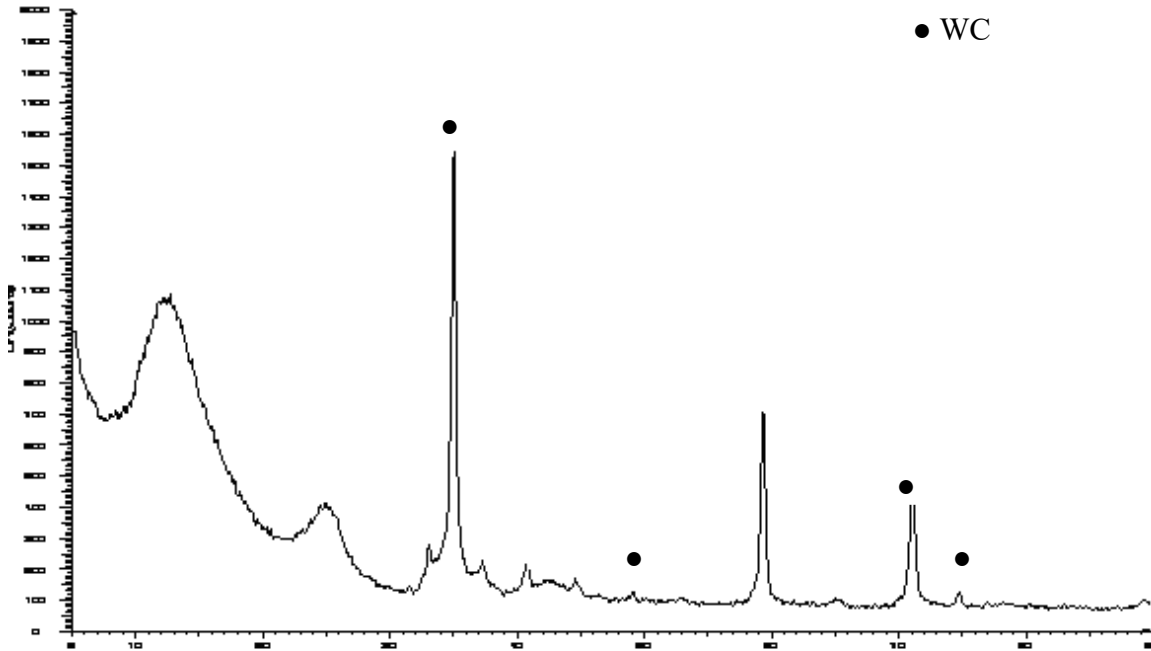


Fig. 2 X-ray diffractogram of tungsten carbide sample prepared at 1500°C using  
WO<sub>3</sub>-H precursor

### 3.2 HRTEM studies

The HRTEM micrographs recorded at two different magnifications for the WC sample (prepared from WO<sub>3</sub> – A) reacted for 2h under inert environment at 1200 °C is shown in Fig. 3 (a) while that at 1500 °C is shown in Fig 2 (b). Considerable agglomeration is observed in both the samples. The HRTEM recorded at higher magnification for the sample heat treated at 1500 °C is shown in Fig. 3 (c), where arrangement of atoms is clearly seen.

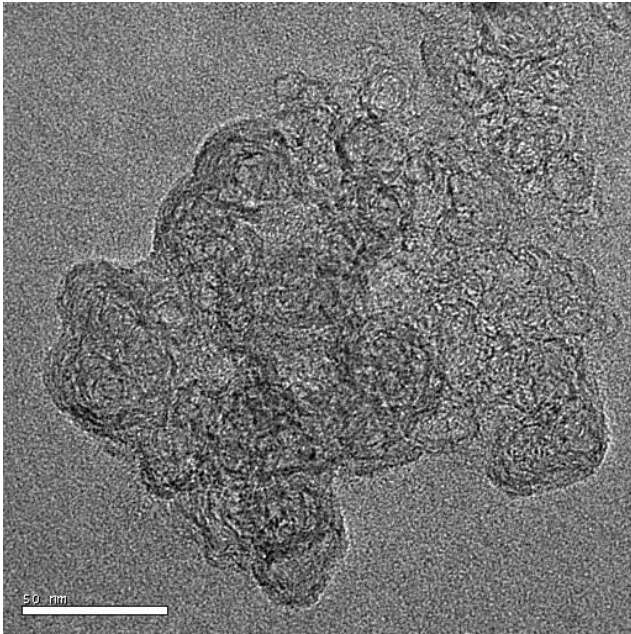


Fig 3(a) HRTEM image of tungsten carbide synthesized at 1200 °C



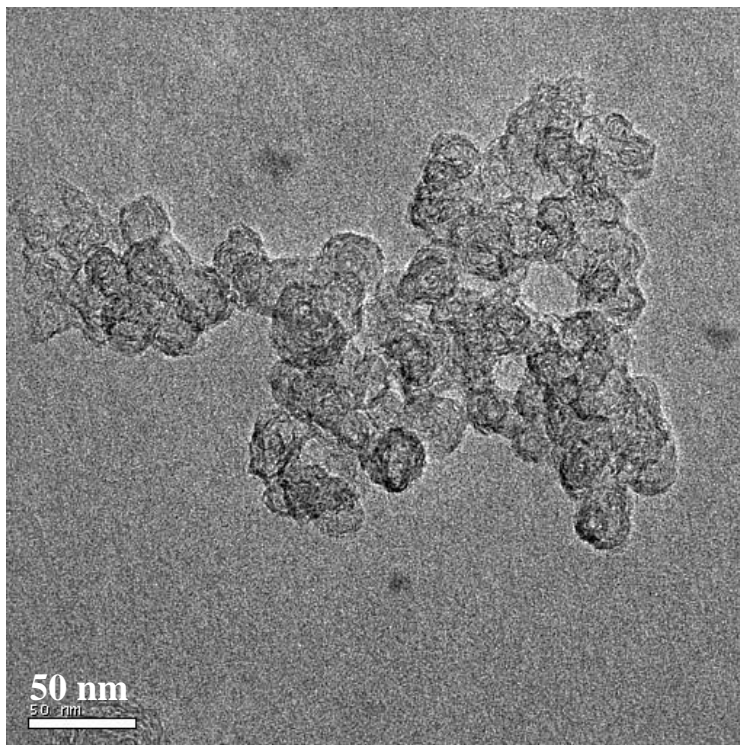


Fig 3(b) HRTEM of tungsten carbide synthesized at 1500 °C using  $\text{WO}_3\text{-A}$  precursor

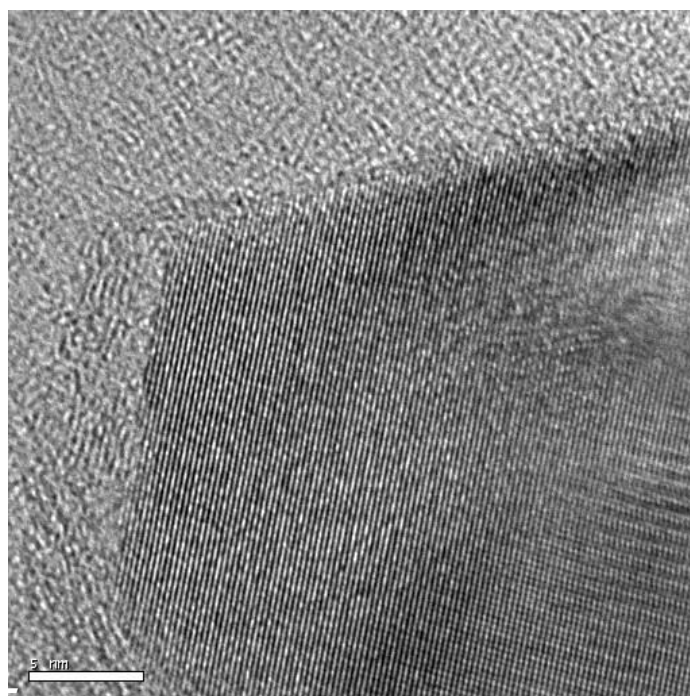


Fig 3(c) HRTEM image recorded at higher magnification of the tungsten carbide sample synthesized at 1500 °C using  $\text{WO}_3\text{-A}$  precursor



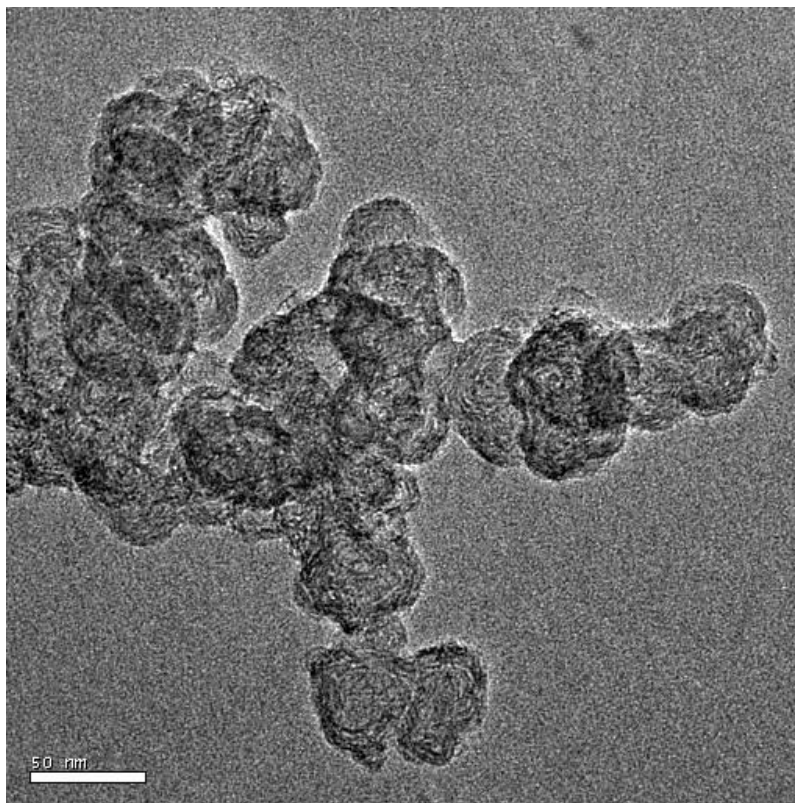
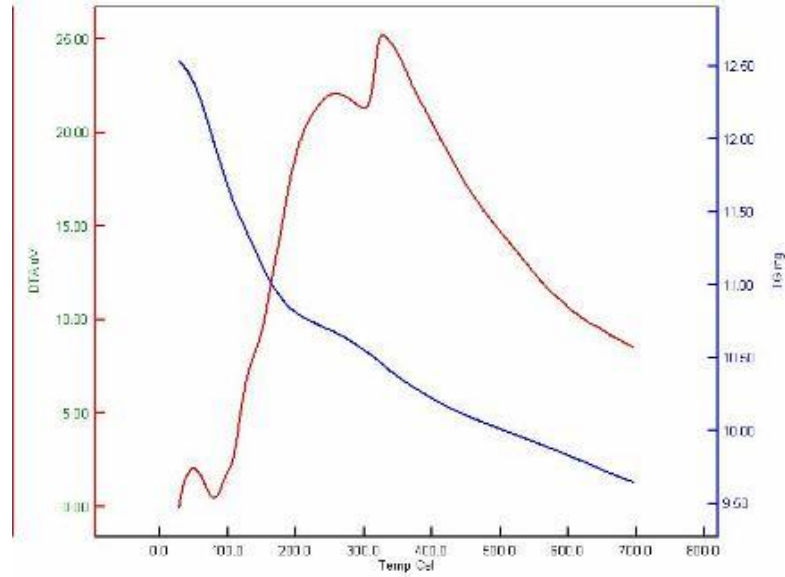


Fig 3(a) HRTEM of tungsten carbide synthesized at 1500 °C using  $\text{WO}_3\text{-H}$  precursor

### 3.2 TGA studies

Fig. 4 shows the TGA analysis of the WC precursor (mixture of  $\text{WO}_3\text{-A}$  and carbon soot) between 50 - 800°C. The TGA curve shows a total weight loss of 38 % in three stages. In the first stage between ambient and 220 °C, a weight loss of 14 % may be attributed to removal of water from the gel and the second weight loss beyond 200 °C, may be attributed to the formation of carbon mono/dioxide, which may be swept away with flowing nitrogen used during DTA/TGA studies.. The DTA curve shows two exothermic effects; the first with peak at about 250 °C attributable to reaction between nano carbon and oxygen available in  $\text{WO}_3$  to form carbon mono/di oxide and the second at about 350°C, which may be attributed to beginning of formation of WC.



#### 4. Conclusion

Very fine nanoparticulate crystals of Tungsten carbide can be synthesised carbonization of dried  $WO_3$  gel (obtained by sol – gel method) and Carbon soot . The crystallite size of the WC powder obtained by calcination at 1500 °C is observed to be  $\sim 25 \pm 3$ nm. The method described above provides a rapid procedure for synthesis of a well defined nanocrystalline WC powder.

#### References :

1. YuanZhang, Guoqi Tan, Da Jiao, Jian Zhang, Shaogang Wang, Feng Liu, Zengqian Liu, Longchao Zhuo, Zhefeng Zhang, Sylvain Deville, Robert O. Ritchie; J. Materials Science & Technology; Vol. 45 (2020), 187-197

2. Groover, Mikell P. (2010). *Fundamentals of Modern Manufacturing: Materials, Processes, and Systems*. John Wiley & Sons. p. 135. ISBN 978-0-470-46700-8.
3. Cardarelli, François (2008). *Materials Handbook: A Concise Desktop Reference*. Springer Science & Business Media. p. 640. ISBN 978-1-84628-669-8.
4. [https://en.wikipedia.org/wiki/Tungsten\\_carbide](https://en.wikipedia.org/wiki/Tungsten_carbide) down loaded on August 1<sup>st</sup>, 2020.
5. Matthew David Markko; *Lubricants* 2019, 7(2),14; <https://doi.org/10.3390/lubricants7020014>
6. K. Becker; *Z. Physik* 51, 481 (1928).
7. C. Agte; *Metal J. Wirtschaft* 9 (1), 401 (Jan.-June 1930).
8. Peter Hidnert; *Journal of Research of the National Bureau of Standards, Volume 18, January (1937) Paper No. RP960.*
9. WeiminZhu, AnnaIgnaszak, ChaojieSong, RyanBaker, RobHui, JiuJunZhang, FeihongNan, GianluigiBotton, SiyuYe and StephenCampbell; *Electrochimica Acta* 61(1) (2012), pp 198-206
10. Bisht A, Tyagi T, Rekha, Mehtab S, Masroor S, Zaidi M. WC (Tungsten Carbide) : A Novel Material for Electrochemical Energy Conservation and Storage. *Mat.Sci.Res.India*;15(2). Available from: <http://www.materialsciencejournal.org/?p=8190>
11. Amritphale, S.S., Chandra, N., Kroke, E., Riedel R.; German Patent No. 19952 337.
12. Meenakshi Sharma, Ravi Kant Upadhyay, S.S. Amritphale, Navin Chandra; *Materials Letters, Vol 65 (2011)2161-4.*
13. Navin Chandra, Meenakshi Sharma, Deepesh Kumar Singh, Navin Chandra; *Materials Letters, Vol. 63 (2009) 1051-3*
14. P. Scherrer, *Göttinger Nachrichten Gesell., Vol. 2, (1918), p 98.*