

A COMPARATIVE STUDY OF THE EFFECTS OF FERRIC CHLORIDE AND FERRIC NITRATE AS ETCHANTS FOR PHOTOCHEMICAL MACHINING OF MOLYBDENUM

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ABSTRACT

This study was carried out with the aim of finding an effective etchant for photochemical machining of molybdenum. Two etchants- ferric chloride and ferric nitrate at various concentrations and temperatures were used to etch molybdenum in a beaker. The etch rates were determined based on the weights of molybdenum sample before and after etching. The study observed that the etch rates of ferric nitrate are generally higher than those of ferric chloride. It was also observed that etch rate of ferric chloride increases with increase in temperature and with a decrease in the concentration hence higher values of etch rate were obtained at low concentrations. However, in the case of ferric nitrate, higher etch rates were observed at high concentrations while lower etch rates were observed at low concentrations. The surface roughness at high concentration was higher and it reduced with dilution until a concentration of 34°Bé (1.83M) was reached. Any further dilution increased the surface roughness. The increase in surface roughness depended also on the temperature of the etchant. The study, among other things, recommended the use of ferric nitrate as etchant for photochemical machining of molybdenum based on its high etch rate.

KEYWORDS: Photochemical, Machining, Etchant, Concentration, Molybdenum.

INTRODUCTION

Molybdenum is characterised by high melting point, high strength, stiffness and excellent thermal and electrical characteristics. Molybdenum is also resistant to several of the common chemical reagents including most caustic solutions and hydrochloric, sulphuric and hydrofluoric acids under many conditions of temperature and concentration. All these properties make molybdenum a very important metal. However, the difficulty of machining molybdenum and the subsequent high cost of tooling meant it was used mostly in powder metallurgy and then sintered. Its use is limited especially when intricate shapes, small and close tolerances are required which precision stamping can not achieve (Wickes, 1966).

Photochemical machining (PCM) is a relatively new method of producing complex, high precision parts from conventionally difficult to machine metals such as molybdenum, although all the commonly used metals and alloys are suitable for PCM. Photochemical machining is used for the manufacture of precision parts such as colour television shadow masks, integrated circuit lead frames, light choppers and encoder discs and decorative objects such as costume jewellery (Allen, 1986). Photochemical machining involves etching metals and plastics and it is mostly limited to thin materials of 0.003 to 1.5mm thick (Allen, 1986 and Albert, 1990). This is achieved by coating a cleaned metal with a photoresist thus sensitising the metal.

The photoresist is a photopolymer that can be used to coat metal with an acid resistant coating and can be selectively removed through the action of ultraviolet radiation by masked phototooling. In some cases the resist is negative-working, when the exposed areas are insolubilised and in others, it is a positive-working resist, when the exposed areas are solubilised. However, in both cases the soluble areas are removed by development leaving the required maskant pattern on the surface ready for selective etching (Allen, 1986).

One of the most important aspects of PCM is the etching of metal stage with a suitable etchants. Although potassium ferrocyanide gives a high etch rate, the PCM industry favours ferric chloride solution as a standard etchant due to its cheapness, low toxicity and ability to etch a wide variety of metals and alloys (Maynard, Moscony & Saunders, 1984a). However, due to the small etch rate of ferric chloride on molybdenum other suitable etchants have to be formulated, with the most effective ones usually found to be hazardous to operators. Such hazardous solution which yielded etch rate of 50µm in 6 to 7mins was made up of 200g of potassium ferrocyanide per litre, 25g of sodium hydroxide per litre and 3.5g of sodium oxalate per litre and by raising the temperature to 50°C an etch rate of 8µm min⁻¹ was achieved (Allen, Beristain & Gillbank, 1986). Some other less hazardous etchants yielded relatively very low etch rate.

One other etchant that has been used for molybdenum is ferric nitrate with which Allen *et al* (1986) achieved etch rate of 6.5µm min⁻¹ at a temperature of 50°C and concentration of 40°Bé. They observed that adding HNO₃ or H₂SO₄ significantly increased the etch rate however with unfortunate rise in temperature and evolution of fumes.

The main aim of this study is to find a suitable relatively cost effective and safe etchants for molybdenum which can have a good etch rate. Specifically, the study was conducted to, among other things, determine the relationship between etch rate on one hand and etchant temperature and concentration on the other hand for the selected etchants.

MATERIALS AND METHODS

The materials for the study are stock solution of ferric chloride (40% w/w ferric chloride), molybdenum sheet (300 x 300 x 0.25mm³), ferric nitrate crystal and "MICRO" liquid cleaner. The equipment include Talysurf 4 Measuring Instrument, hot plate, magnetic stirrer, Vickers M41 Photo-plan Microscope and weighing scale Oxford Series-S, hydrometer and 250ml beakers.

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Samples of 36mm x 52mm x 0.25mm size from 99.99% pure molybdenum sheet were used for this study. The samples were cleaned using a proprietary "MICRO" liquid cleaner. Etching was carried out in a 250ml beaker containing 200ml of the required etchant at various concentrations and temperatures. The 250ml beaker was placed in a larger beaker containing water and the whole assembly placed on a hot plate. A thermometer held in a retort stand was inserted into the 250ml beaker.

An etchant with known concentration in the beaker was allowed to rise to the required temperature and this temperature was controlled to vary only between $\pm 1^\circ\text{C}$ of the desired temperature by means of the water jacket. When the temperature reached its equilibrium, a weighed sample piece was held by means of nylon forceps and then immersed into the etchant. The retort stand was used to hold both the thermometer and the nylon forceps. The etchant was stirred with a magnetic stirrer at a constant speed throughout the study. The temperatures at which the experiments were conducted were 40-80°C. The etching duration was 6mins for temperatures of 40-60°C and 5mins and 4mins for temperatures of 70 and 80°C, respectively.

After etching, the sample was washed and rinsed in water and then dried using compressed filtered air and weighed again. The etch rate was calculated using equation 1 (Mu-Lin Li, 1987).

$$\text{Etch rate} = \frac{(w_1 - w_2) \times 10^4}{2A \times t \times \rho_{mo}}, \quad \mu\text{m} \cdot \text{min}^{-1} \quad \dots\dots\dots 1$$

Where

- w_1, w_2 - Weight of molybdenum sample before and after etching respectively, g
- 2A - Areas covered by etchant, cm^2
- ρ_{mo} - Density of molybdenum, $\rho_{mo} = 10.2\text{g cm}^{-3}$
- t - Time taken to etch the surface, mins.

The surface roughness of the etched sample of molybdenum was determined using a Rank Taylor Hobson Talysurf 4 measuring instrument.

RESULTS AND DISCUSSION

The curves of etch rates are shown in Figs. 1 and 2 for various temperatures of 40-80°C under varying concentration.

The surfaces of the samples etched in FeCl_3 were covered with black smut and the surfaces were therefore cleaned. However, the surfaces after cleaning remained dull. Generally, the etch rate at low concentration is higher than that at high concentration for the FeCl_3 etchant. There was an increase in etch rate with increase in concentration up to certain optimum concentration and further increase led to a decrease in the etch rate. This reduction in etch rate with increase in concentration (Baumé) agrees with the results of Maynard *et al* (1984a) and can be explained by the presence of both $\text{FeCl}_2(\text{H}_2\text{O})_4^+$ and $\text{FeCl}_3(\text{H}_2\text{O})_3$ in ferric chloride at low concentration. With increase in concentration, $\text{FeCl}_3(\text{H}_2\text{O})_3$ becomes the predominant specie with $\text{FeCl}_2(\text{H}_2\text{O})_4^+$ becoming less and at the same time FeCl_4^- appears at high concentration.

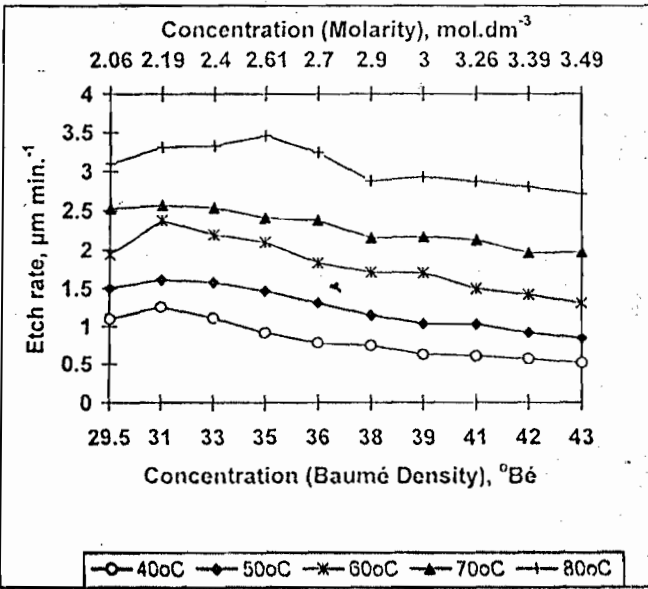


Fig. 1: The Effects of Temperature and Concentration of FeCl_3 on its Etch Rate

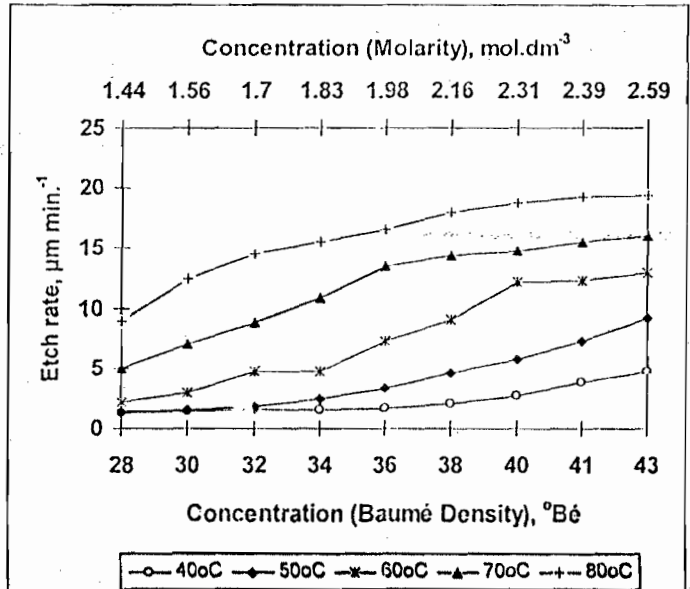


Fig. 2: The Effects of Temperature and Concentration of $\text{Fe}(\text{NO}_3)_3$ on its Etch Rate

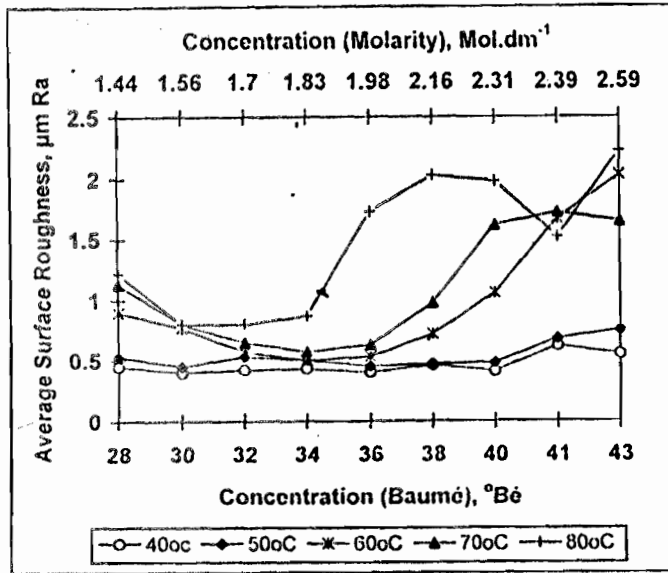
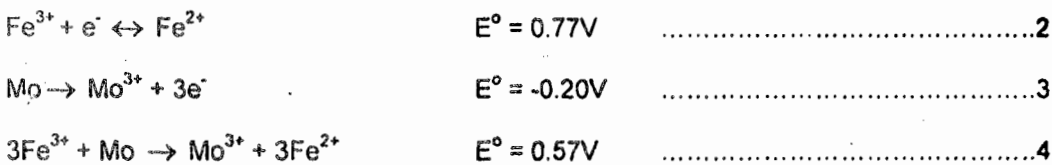


Fig. 3: The Effects of Temperature and Concentration of Fe(NO₃)₃ on the Average Surface Roughness of the Etched Sample

It was observed that in all cases, the etch rate achieved in Fe(NO₃)₃ was higher than that in FeCl₃ etchant. For Fe(NO₃)₃ etchant, the curves (Fig. 2) do not resemble those produced from etching of molybdenum in FeCl₃. This is due to the fact that those factors described above for FeCl₃ are not experienced when using Fe(NO₃)₃ and subsequently the etch rate increases with increase in etchant concentration. Unfortunately, the increase in the etch rate with increase in concentration was accompanied by increase in roughness of the etched surface as shown in Fig. 3.

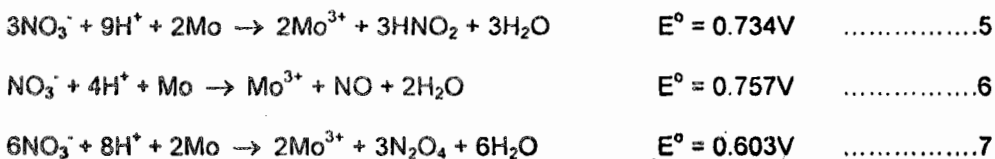
However, the roughness achieved with Fe(NO₃)₃ of 32-36 °Bé at 60°C was comparable to those achieved for Fe(NO₃)₃ of 28-40 °Bé at temperatures of 40-50°C, although the roughness of the former was better than that for the latter. Therefore, Fe(NO₃)₃ of the concentration of 32-36 °Bé at 60°C should be used for parts requiring surface finish of grade N5-N6 (low values of Ra) while those requiring lower surface finish of grade N7 and above (higher values of Ra) may be etched with Fe(NO₃)₃ etchant of higher concentration and temperature.



The reaction of ferric chloride with Mo was slower. The chloride ions (Cl⁻) only formed complexes and this, coupled with the slow reaction in equation 3 could be said to be the contributory factor of the black smut observed on the surface of the sample.

Equations 5-7 show the effective chemical reaction of nitrates with molybdenum. The equations showed that they were reactive and thus contributed to the reaction in equation 4 unlike the chloride ions. This phenomenon could be the reason why faster etch rates were observed during this investigation.

During the etching process of molybdenum in ferric nitrate, bubbles were noted and these bubbles increased with each increase in temperature. At temperatures of 70°C-80°C, the bubbles on the surface of the sample became so vigorous at high concentrations. It was thought that the surface roughness observed at high concentrations might have been caused by the vigorous bubbles on the surface of the etchant. The same observation was also noticed by Maynard *et al* (1984b) when etching low carbon (1008 rimmed) steel in ferric perchlorate - perchloric acid solution. The bubbles were thought to emerge from equations 6 and 7. The bubbles could equally be a means of forming cavities on the surface of the sample.

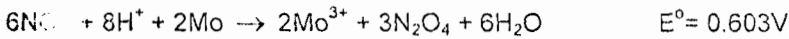
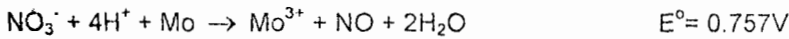


CONCLUSIONS AND RECOMMENDATIONS

The study was conducted to determine an effective etchant to be used on molybdenum and the following conclusions

were made.

1. Ferric chloride has low etch rates on molybdenum.
2. Ferric chloride has high etch rates at low concentrations and low etch rates at high concentrations and etch rates increased significantly with increase in temperature.
3. Observations from the experimental plates revealed that rough surfaces were obtained at low concentrations while smooth surfaces were achieved at high concentrations and temperatures.
4. Ferric nitrate has higher etch rates on molybdenum than ferric chloride. Higher etch rates were observed at higher concentrations and the surface roughness at high concentration was poorer.
5. During the experiments conducted on etching of molybdenum in ferric nitrate, bubbles were evolved particularly at high temperatures and concentration. The bubbles were thought to emerge from the following equations:



The study, based on the findings, made the following recommendations:

1. The study of practical component production using ferric nitrate and studying the parameters of the component to be produced should be carried out. Such parameters should include undercut, etch factor and the behaviour of photoresists to be used. This is important since ferric nitrate was found to etch molybdenum faster than ferric chloride and there is a potential benefit from using this etchant commercially.
2. An investigation into the effect of metal by-product on etch rate and surface roughness on molybdenum should be conducted too. This would give an understanding of the type of metals that could be processed in the same etchant with molybdenum without much problem.
3. The study suggested the use of ferric nitrate of 32-36°Be at 60°C for parts requiring smooth surface finish of grade N5 and N6 while those requiring rougher surfaces of grade N7 and above could be etched in ferric nitrate of higher concentrations and temperatures.

REFERENCES

- Albert, B. D., 1990. Photochemical Machining of Molybdenum with Ferric Nitrate. Unpublished M.Sc Thesis, College of Manufacturing, Cranfield Institute of Technology, 62pp.
- Allen, D. M., 1986. The Principles and Practice of Photochemical Machining and Photoetching. Adam Hilger, Bristol (UK), 190pp.
- Allen, D. M., Beristain, L.S. and Gillbanks, P.J., 1986. Photochemical Machining of Molybdenum. *Annals of the CIRP*, 35(1):129-132.
- Maynard, R. B., Moscony, J.J. and Saunders, M.H., 1984a. Ferric Chloride Etching of Low Carbon Steels. *RCA Review*, 45(March): 73-89.
- Maynard, R. B., Moscony, J. J. and Saunders, M. H., 1984b. A Study of the Etching Kinetics of Low Carbon Steel Using the Ferric Perchlorate-Perchloric Acid System as a Model. *RCA Review*, 45(March):58-72.
- Mu-Lin Li., 1987. The Photochemical Machining of AISI 316 Stainless Steel. Unpublished M.Sc Thesis, Cranfield Institute of Technology, 73pp.
- Wicks, W.C., 1966. *Patent T2, 900, 283*, June 27.