Roszak, J.A. and Rosochowski, A. and Rosochowska, M. (2017) Chemical etching as a method of combatting adhesive tool wear during severe plastic deformation of commercially-pure titanium. In: Advances in Transdisciplinary Engineering. IOS Press, Amsterdam, pp. 15-20. ISBN 978-1-61499-791-7 , http://dx.doi.org/10.3233/978-1-61499-792-4-15

Chemical Etching as a Method of Combatting Adhesive Tool Wear During Severe Plastic Deformation of Commercially-Pure Titanium

J. A. ROSZAK[a,1], A. ROSOCHOWSKI[a], and M. ROSOCHOWSKA[b]
[a] *University of Strathclyde, Glasgow, UK*
[b] *Advanced Forming Research Centre, Inchinnan, UK*

Abstract. This paper investigates chemical etching as a potential temporary solution to severe adhesive wear experienced during forming of commercially-pure titanium. The aim was to identify contributing factors and experimentally quantify their effects on the etching of CP-Ti and Vanadis 23 tool steel.
A comprehensive literature review identified a promising etchant solution, containing 6.5% hydrofluoric acid, 2% formic acid and 2% triethanolamine. A full factorial experiment was designed to test the effects of three factors – hydrofluoric acid concentration, temperature, and time – with statistical analysis to interpret and validate the results.
The results confirmed that increasing any of the factors tested leads to a significant increase in titanium dissolution, while only temperature and concentration increases led to a significant increase in steel dissolution. Therefore, a 20 °C solution of 3.5% hydrofluoric acid and an etching duration of 35 minutes is recommended for removing adhered titanium without significantly affecting the steel.

Keywords. Etching, Pure Titanium, Severe Adhesive Wear, Galling, Hydrofluoric Acid, Vanadis 23, Tool Maintenance

1. Introduction

Severe plastic deformation (SPD) processes are capable of producing, through significant grain refinement, high strength metals such as ultrafine grain (UFG) commercially pure titanium (CP-Ti), with potential applications in the manufacturing of orthopaedic implants for the biomedical industry [1].

One common cause of tool failure during SPD of titanium, and many other titanium forming processes, is severe adhesive wear, also known as galling [2]. This is a phenomenon which occurs at the interface of two materials in high pressure contact, and is characterised by one material, such as a billet being processed, becoming attached to the other, such as the tool, through gradual adhesive wear mechanisms. The material which has become attached to the surface of the tool in turn leads to the presence of defects such as scratches on the product being processed [3]. A high susceptibility to

[1] Corresponding author, Department of Design, Manufacturing and Engineering Management, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom; E-mail: jacob.roszak@strath.ac.uk

galling therefore prevents a process from becoming industrially viable due to the frequent need to halt the process and service the tools in order to remove the galled material. By decreasing the likelihood of severe adhesive wear, metal forming processes can be made more practical in terms of improved tool life, thereby decreasing maintenance requirements and increasing cost-effectiveness.

Galling may occur despite preventative measures such as lubrication. In such cases, a simple yet effective method of quickly servicing the tool would be of great interest. One potential method may be to etch the surface of the tool. Traditionally, etching involves immersing a material into a powerful acid in order to remove a thin layer of material from the surface and achieve a higher quality surface finish. Available literature suggests that hydrofluoric acid (HF) possesses the greatest capability for etching titanium in terms of material removal rate [4]. Solutions containing as little as 20 ppm of fluoride ions can potentially attack titanium if the solution pH is below 6 [5]. Patents can be found for solutions and processes capable of dissolving titanium and yet leaving tool steel unaffected [6]. This would allow for relatively simple removal of titanium adhered to the surface of a die – a process which can otherwise involve days of manual polishing. The experiment documented in this report investigates the suitability of such a solution resolving galling issues between titanium billets and steel tools, with a focus on improving SPD processes.

The primary aim of the study was to experimentally quantify the effects of etching of tool steel and CP-Ti samples as a potential temporary solution when galling occurs, and to determine which factors have a statistically significant effect on etching results.

2. Materials and Methods

The experiment involved 27 samples of Grade 2 CP-Ti, with approximate dimensions 20 mm x 17 mm x 2 mm and surface area 820 mm^2, as well as 27 samples of Vanadis 23 tool steel (AISI M3:2/W.-Nr 1.3344), with approximate dimensions 20 mm x 10 mm x 7 mm and surface area 810 mm^2. All samples were individually measured in terms of mass. The compositions of the titanium and tool steel are provided in Tables 1 and 2, respectively.

Table 1. Typical composition (including impurities) of Grade 2 CP-Ti

Composition	C	H	O	N	Fe	Ti
Analysis (%)	≤ 0.08	≤ 0.015	≤ 0.25	≤ 0.03	≤ 0.30	Balance

Table 2. Typical composition of Vanadis 23 tool steel

Composition	C	Cr	Mo	W	V	Fe
Analysis (%)	1.28	4.2	5.0	6.4	3.1	Balance

A full factorial experiment, based on the design of experiments methodology laid out by Grove and Davies [7], was designed in order to investigate every possible combination of factor levels, thereby resulting in the most complete set of information and allowing for full analysis of the effects of each factor and any possible interaction between them.

The etching experiment was designed to study the effect of three specific factors over which the operator has complete control – the concentration of hydrofluoric acid

(HF), the temperature of the solution, and the etching time, which is the time for which each sample is immersed in the etchant solution. Each of these three factors was allocated three equally spaced levels, coded as (-), (0) and (+) for simplicity. The primary benefit of performing a three-level experiment is the ability to measure curvature in the effects of varying factors, whereas more straightforward two-level experiments only allow for linear effects and predictions [7]. The factors and their levels are detailed in Table 3.

Table 3. Etching control factors and their levels

Factor Level	Concentration of HF (% by weight)	Solution Temperature (°C)	Immersion Time (minutes)
-	3.5	20	15
0	6.5	30	25
+	9.5	40	35

According to the design of experiments methodology followed, a full factorial experiment investigating three control factors at three levels must involve all possible combinations, which leads to 27 experimental trials. In order to measure the effect of each factor combination, the experiment focused on mass of titanium removed and mass of tool steel removed as quality characteristics.

It was important to identify a solution capable of dissolving titanium at an industrially viable rate, while also entirely avoiding any damage to the tool steel, which in practice must adhere to strict geometric and mechanical requirements. Therefore, the chemical solution used throughout the experiment, inspired by the available relevant literature [6], was based upon that detailed in Table 4, albeit with varying concentrations of HF. It is worth mentioning that increasing the concentration of formic acid or triethanolamine beyond 2% by weight reportedly produces no additional benefits [6].

Table 4. Etching control factors and their levels

Constituent	Chemical Formula	Role	Concentration (% by weight)	Potential Alternatives
Hydrofluoric Acid	HF	Source of fluoride ions to dissolve titanium	6.5	Not recommended
Formic Acid	CH_2O_2	Source of COOH radicals to accelerate etching of titanium while inhibiting steel damage	2	Oxalic acid, tartaric acid
Triethanolamine	$C_6H_{15}NO_3$	Protects steel from HF and prevents smut formation	2	Sodium nitrite, potassium iodide

Due to the corrosive nature of HF, the solution had to be contained within a polypropylene beaker, which was then placed in a larger glass beaker containing water. Each trial began by simultaneously immersing one titanium sample and one tool steel sample, and starting a timer. This action would immediately trigger a significant exothermic reaction between the titanium and the etchant.

The temperature of the surrounding water was dependent on the heating or cooling requirements of the trial in question, so that the water could act as a heat sink or heater as required. Surrounding water temperature was maintained via immersed coolant circulation tubes and a laboratory hotplate, as necessary. This temperature was constantly monitored and any deviation from the required level quickly counteracted.

Once the desired time had elapsed, the two samples, if still solid, were then rinsed three times in a plastic beaker of water, with the water being replaced between each rinse, and then finally rinsed using ethanol and dried under a flow of air. After this procedure, the samples were safe to handle for measurement.

Between each trial, the used solution was safely disposed of and a new solution made, in order to avoid inconsistency due to contamination of the solution.

3. Results and Analysis

Upon completion of each trial, the final mass and initial mass of each sample were compared in order to calculate the mass loss experienced. Figures 1 and 2 show the *mean* mass losses at each level for each factor, for titanium and steel samples, respectively.

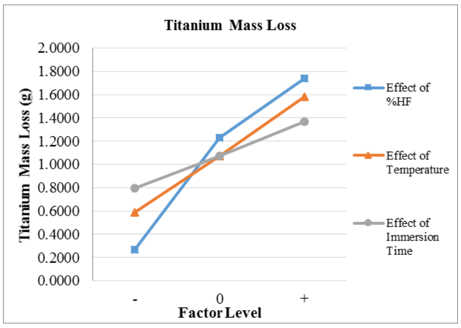

Figure 1. Effects plot for titanium mass loss

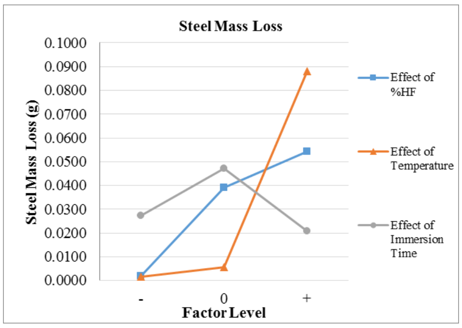

Figure 2. Effects plot for steel mass loss

For titanium samples it is clear that increasing the level of any of the three factors increased the mass dissolved, with HF concentration having the largest effect, and immersion time the smallest. Due to the extremely small mass losses, the results for steel are more difficult to interpret, although it remains evident that increasing HF concentration or temperature increased mass loss. Additionally, the effect of varying temperature was notably non-linear, likely due to the occurrence of surface flaking only at the high level, 40 °C. Curiously, immersion time alone did not appear to have an effect on steel mass loss.

In order to identify which effects are statistically significant and which occur due to the random variation inherent in the process, the statistical methods recommended by Grove and Davis as part of their design of experiments methodology [7] were adhered to. This methodology is inspired by Taguchi's statistical methods [8], although with several key differences, and utilises a combination of graphical and numerical methods to interpret the results in a simple yet useful manner.

By creating an $L_{27}(3^{13})$ orthogonal array it was possible to statistically separate 26 so-called contrasts – six contrasts representing a linear and a quadratic main effect for each factor, twelve contrasts representing the two-way interaction between each pair of factors, and eight contrasts representing three-way interactions between factors. Effects suspected to be statistically significant were identified using both normal and half-normal plots. These were then analysed further using ANOVA and F-tests. At a significance level (α) of 5%, the effects found to be significant are presented in Table 5.

Table 5. Statistically significant effects of factors for titanium mass loss and steel mass loss

Titanium Mass Loss Significant Factors	Steel Mass Loss Significant Factors
• HF concentration (linear) • Temperature (linear) • Interaction between HF concentration (linear) and temperature (linear) • Immersion time (linear) • Interaction between HF concentration (linear) and immersion time (linear)	• HF concentration (linear) • Temperature (linear) • Interaction between HF concentration (linear) and temperature (linear)

4. Discussion and Conclusions

It is clear that increasing the level of any or all of the factors leads to a significant increase in the mass of titanium dissolved and, were the only aim to maximise the amount of titanium dissolved, the obvious solution would be to simply raise all three factors to their highest practical levels. However, the issue is somewhat more complicated – due to the strict geometrical and mechanical tolerances associated with forming tools, as well as their high cost, it is crucial that the effect of the etching solution on the tool itself is kept to a negligible level.

The results show that both HF concentration and temperature have a significant effect on the steel – increasing either leads to increased steel mass loss, which would be detrimental to the tool being serviced. Furthermore, analysis reveals an existing interaction between these two factors. A temperature of 40 °C, when combined with an HF concentration of 6.5% or higher, results in flaking and smut formation on the steel surface, rendering all such parameter combinations unacceptable. On the other hand, despite the general risk of increasing HF concentration, there is also sufficient evidence to suggest that an HF concentration of 6.5% does not cause any considerable damage to steel, provided that the temperature does not exceed 30 °C. The results also suggest that immersion time alone does not have a significant effect on steel mass loss, and hence it appears that the time can safely be extended without any serious risk to the tool steel, provided that the other factors remain at low levels. It is therefore logical to recommend utilising the longest practical immersion time. Taking these considerations into account, the recommended suitable factor combinations are those listed in Table 6.

Table 6. Potentially suitable combinations of etching parameters

Trial Number	HF Concentration (% by weight)	Solution Temperature (°C)	Immersion Time (minutes)	Titanium Mass Loss (g)	Steel Mass Loss (g)
3	3.5	20	35	0.2904	0.0015
6	3.5	30	35	0.3570	0.0018
12	6.5	20	35	1.4737	0.0025

What is not discernible from the experiment is the effect of the ratio between the titanium and steel surface areas being etched. In a practical context, the surface area of the steel may be far greater than the tested samples, while the amount of titanium which needs to be removed may be extremely small. If the mass of galled titanium is minimal, there may be no great demand for a high titanium removal rate. In such a scenario, it is advisable to minimise the risk to the tool by using an HF concentration of 3.5% together with a solution temperature of 20 °C and an immersion time of 35 minutes, which results in a low titanium removal rate, but also poses the least risk of damage to the steel.

The experimental results presented provide a basis upon which to design a larger-scale process for servicing steel tools which have been affected by galled titanium during metal forming and SPD processes. This would necessarily involve larger equipment in order to sufficiently immerse the affected areas of the components. It is also recommended that the temperature control is improved by implementing an open-circuit cooling system and that a reliable structure is erected inside the coolant bath in order to support the solution container, which in this case would contain a steel tool of significant mass. In order to counter-act the heat released from the exothermic reaction of the galled titanium in the HF, an open-loop system of circulating 30% glycol-solution at the required temperature is recommended to maintain a temperature of 20 °C in a coolant bath surrounding the plastic etchant container. Additionally, as the large quantity of HF solution required would make replacing the solution for each operation both environmentally hazardous and expensive, it is recommended that the solution is stored safely and re-used until the colour of the solution darkens significantly, indicating the presence of significant amounts of titanium and other dissolved metals in the solution.

In summary, the work carried out led to the following key conclusions:

- Increasing HF concentration, etchant temperature or immersion time leads to a statistically significant increase in titanium mass loss during etching.
- Increasing HF concentration or solution temperature leads to a statistically significant increase in tool steel mass loss during etching.
- While several potentially suitable combinations were identified, a solution of 3.5% HF at 20 °C and an immersion time of 35 minutes is recommended for use if a high titanium removal rate is not required.
- The etching procedure and parameters discussed appear to be a potential method of combatting adhesive wear during SPD of CP-Ti.

Acknowledgements

The authors of this work would like to thank Ryan O'Neill and Kornelia Kondziolka of the Advanced Forming Research Centre for their help in carrying out acid etching tests.

References

[1] C.N. Elias, M.A. Meyers, R.Z. Valiev, S.N. Monteiro, Ultrafine grained titanium for biomedical implants: An overview of performance, *Journal of Materials Research and Technology* **2** (2013), 340-350.
[2] H. Choi et al, Experimental Investigation on Galling Performance of Tool Steel in Stamping of UHSS Sheets, *International Journal of Precision Engineering and Manufacturing* **15** (2014), 1101-1107.
[3] L. Pelcastre, J. Hardell, B. Prakash, Galling mechanisms during interaction of tool steel and Al-Si coated ultra-high strength steel at elevated temperature, *Tribology International* **67** (2013), 263-271.
[4] P. Walker, W.H. Tarn, *Handbook of Metal Etchants*, CRC Press LLC, Boca Raton, 1991.
[5] B.D. Craig, D.S. Anderson, *Handbook of Corrosion Data,* ASM International, Materials Park, 1994.
[6] E. Fannin, J. Gumbelevicius, *Patent No. US3749618 A*, USA, 1971.
[7] D.M. Grove, T.P. Davies, *Engineering Quality and Experimental Design,* Longman Scientific & Technical, Harlow, 1992.
[8] G. Taguchi, *System of Experimental Design,* White Plains, New York, 1987.