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Electrolytic Etching of Platinum-Aluminium Based Alloys

Enhanced microstructural analysis with improved safety using chloride solutions

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The microstructures of as-cast and annealed platinum alloys of different compositions were revealed after electrolytic etching in hydrochloric acid/sodium chloride solution using direct current. It was shown that the etching process enhances good microstructural images of platinum-aluminium based alloys.

1. Introduction

Etching of Pt-Al based alloys has been problematic because most of the alloys are designed to withstand oxidation and corrosion. Currently, binary Pt-Al alloys have been patented in the USA (1) as a catalyst for use in fuel cells. However, in this work higher order Pt-Al based alloys are being investigated as potential replacement for nickel-based superalloys used in high temperature and aggressive environments. The resistance to oxidation and corrosion is attributed to the formation of a protective Al oxide scale (2). Electrolytic etching can be considered as 'forced corrosion', where a previously polished specimen surface corrodes inhomogeneously, revealing the different microstructural features (3,4).

Previously in South Africa (5–7), microstructural imaging of Pt-Al based alloys was done using scanning electron microscopy (SEM) in the backscattered electron mode. All the samples had been metallographically prepared by grinding using silicon carbide down to 1200 grit, diamond polishing down to 1 μm and finally polishing with oxide polishing system (OP-S, Struers A/S, Denmark) by which polishing is achieved through a combination of chemical treatment (the solution has a pH of 8) and gentle abrasive action. It allows selective polishing of softer phases thereby achieving a limited etching effect. Although some of the images derived from this method had reasonably good contrast, in some cases, the contrast was poor to the extent that analysis was rendered impossible. **Figures 1–6** are examples of some of the images of Pt-Al based alloys taken using SEM in the backscattered electron mode. In alloy

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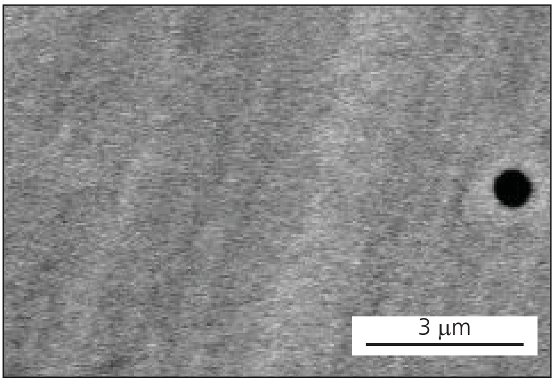

Fig. 1. SEM-BSE of unetched, as-cast $Pt_{60}:Al_{2}:Cr_{38}$ *(at%), showing cored single phase ~CrPt and scratches (7)*

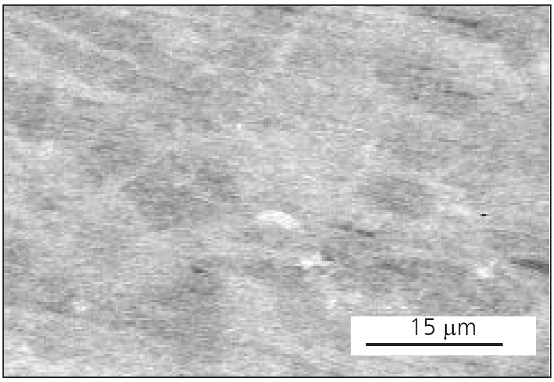

Fig. 2. SEM-BSE image of unetched, as-cast $Pt_{63}:Al_{22}:Cr_{15}$ *(at%), showing cored single phase* ~Pt_3Al *(7)*

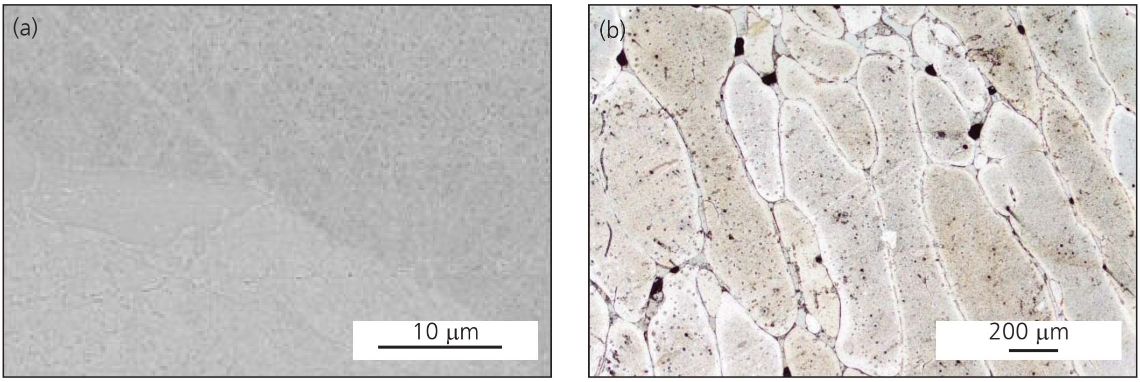

Fig. 3. (a) SEM-BSE image of unetched, annealed $Pt_{81.5}:Al_{11.5}:Cr_{4.5}:Ru_{2.5}$ *(at%), showing fine dark* ~Pt_3Al *precipitates in light (Pt) matrix (6); (b) optical microscope image of annealed* $Pt_{81.5}:Al_{11.5}:Cr_{4.5}:Ru_{2.5}$ *(at%), after electrolytic etching in HCl/NaCl solution, showing fine dark* ~Pt_3Al *precipitates in light (Pt) matrix more clearly*

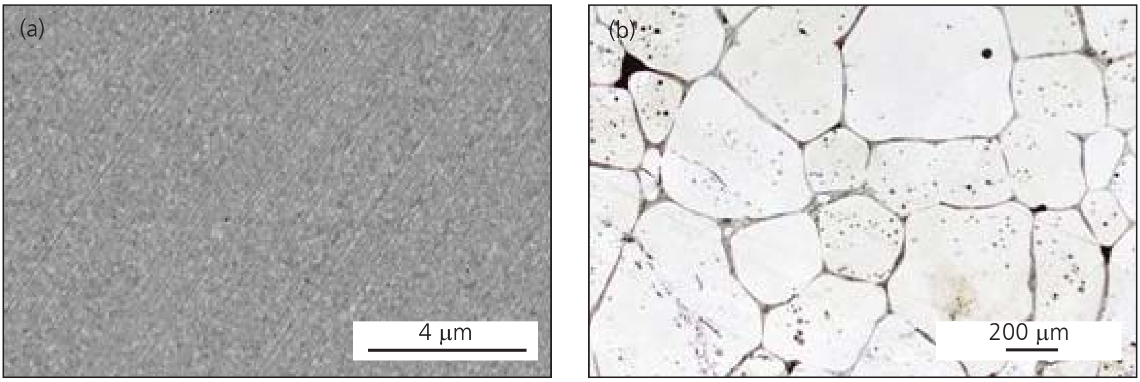

Fig. 4. (a) SEM-BSE image of unetched, annealed $Pt_{78}:Al_{15.5}:Cr_{4.5}:Ru_{2}$ *(at%), showing fine dark* ~Pt_3Al *precipitates in light (Pt) matrix (6); (b) SEM-BSE image of etched, annealed* $Pt_{78}:Al_{15.5}:Cr_{4.5}:Ru_{2}$ *(at%), showing fine* ~Pt_3Al *in light (Pt) matrix (6)*

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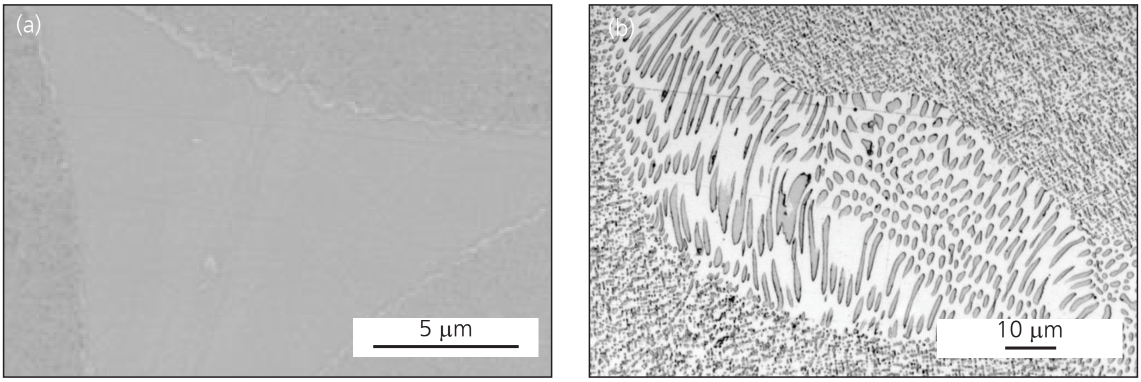

Fig. 5. (a) SEM-BSE image of unetched, annealed Pt_{82}:Al_{12}:Cr_4:Ru_2 (at%), showing ~Pt_3Al precipitates in light (Pt) matrix (6); (b) optical microscope image of annealed Pt_{82}:Al_{12}:Cr_4:Ru_2 (at%) after electrolytic etching in HCl/NaCl solution, showing ~Pt_3Al precipitates in light (Pt) matrix as well as a eutectic

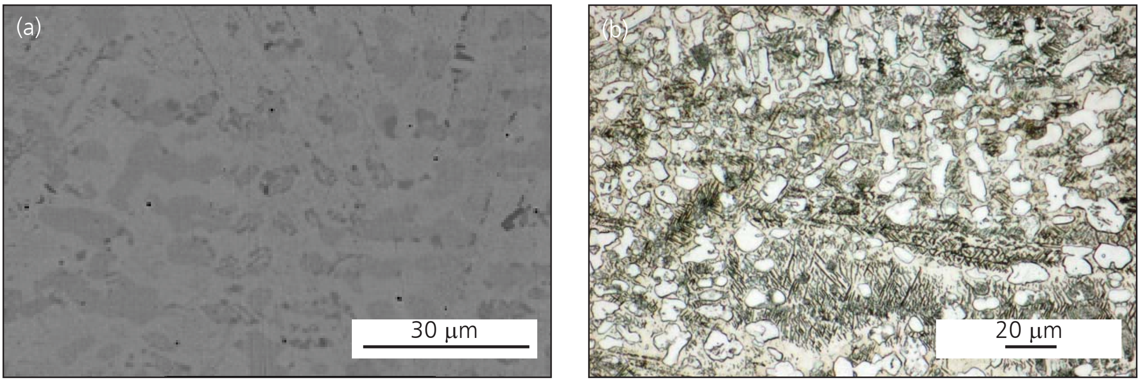

Fig. 6. (a) SEM-BSE image of unetched, annealed $Pt_{64.7}$:$Al_{26.2}$:$V_{9.1}$ (at%), showing medium contrast ~Pt_3Al, light ~Pt_5Al_3 and dark ~PtV (5); (b) optical microscope image of etched, annealed $Pt_{64.7}$:$Al_{26.2}$:$V_{9.1}$ (at%), showing light ~Pt_3Al, dark ~Pt_5Al_3 with oriented needle-like precipitates

Pt_{60}:Al_2:Cr_{38} (at%) (**Figure 1**), X-ray diffraction (XRD) analysis confirmed single phase ~CrPt (cored) and remnants of ~$CrPt_3$ from incomplete ordering. The poor contrast in the image made it impossible to deduce the phases from the microstructure and plot of the energy dispersive X-ray (EDX) composition analysis. The same applied to alloy Pt_{63}:Al_{22}:Cr_{15} (**Figure 2**) whose XRD analysis confirmed the microstructure as single phase ~Pt_3Al (cored). The other four alloys were electrolytically etched in HCl/NaCl solution and their microstructure in the unetched and etched conditions are discussed subsequently.

In Germany (8, 9), electrolytic etching of Pt-Al based alloys has been done in aqueous potassium cyanide (KCN) solution for microstructure investigation. However, there are serious health and safety concerns regarding the use of KCN and its use in South Africa is very restricted, especially in laboratories. Two images of Pt-Al based alloys etched electrolytically in aqueous KCN solution are shown in **Figures 7** and **8**. Heat treatment of as-cast samples by two-stage ageing (variant B) resulted in the formation of coarse γ matrix and γ′ regions in alloy Pt_{77}:Al_{12}:Cr_6:Ni_5 (at%) (**Figure 7**) (8). Spherical precipitates of γ′ in a γ matrix were observed in alloy Pt_{79}:Al_{10}:Cr_3:Ni_8 (at%) after solution heat treatment at 1450ºC for 24 h and ageing at 1000ºC for 120 h (**Figure 8**) (9).

Most electrolytic reagents are simple in composition, being acidic, alkaline or salt solutions. The sample is nearly always the anode, although a few cathodic etching solutions have been developed (10). Direct current (DC) is mostly used, although a few solutions require alternating current (AC). In electrolytic etching, the process is controlled by varying the voltage and time (10).

Battaini (3, 4) obtained the best results for Pt alloys in saturated HCl/NaCl solution with an AC power supply when the voltage varied from 0. 1 V to 10 V

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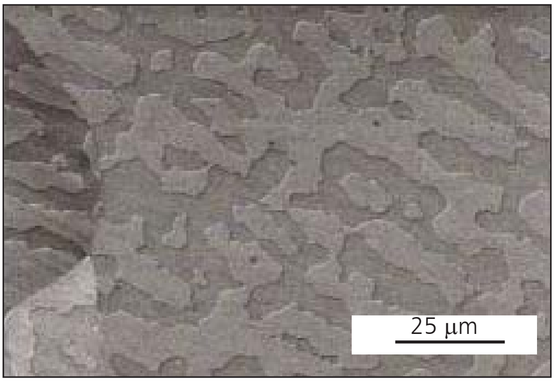

Fig. 7. SEM-BSE image of $Pt_{77}:Al_{12}:Cr_6:Ni_5$ (at%) after two-stage ageing (variant B) and electrolytically etched in aqueous KCN solution, showing coarse γ matrix and γ′ regions (8)

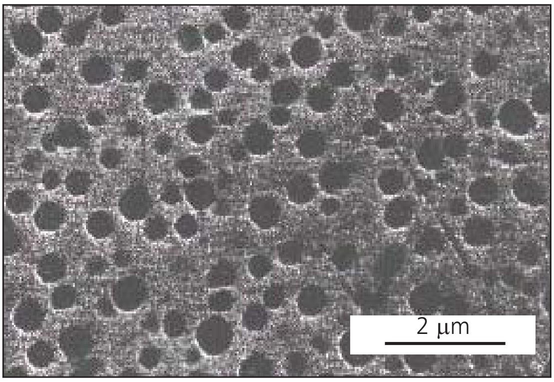

Fig. 8. SEM-BSE image of $Pt_{79}:Al_{10}:Cr_3:Ni_8$ (at%) after solution heat treatment and ageing, electrolytically etched in aqueous KCN solution, showing spherical γ′ precipitates in γ matrix (9)

and the power supply provided a current of at least 10 A. Some of the electrolytic conditions are shown in **Table I**. However, the present work has shown that it is possible to get good results using a DC power supply.

Table I

Electrolytic Etching Solutions for Use with Platinum Alloys (3)

Composition	Type
100 cm^3 HCl (37%) + 10 g NaCl	Electrolytic, 3–6 V AC
10 cm^3 HCl + 90 cm^3 H_2O + 1 g $FeCl_3$	Electrolytic, 3–6 V AC

2. Experimental Procedure

The specimens were ground by silicon carbide down to 1200 grit and then diamond polished down to 1 µm. The samples were then etched in a solution of 10 g NaCl in 100 cm^3 HCl (32% concentration). Etching was done in a fume cupboard using a DC power supply, and a voltage range of 9 V to 12 V gave adequate results. The current density in the electrolyte was ~100 A m^{-2}. The counter electrode was a stainless steel wire suspended in the electrolyte solution. Images were taken using an optical microscope.

3. Results and Discussion

The electron beam voltage used to obtain the SEM-backscattered electron (SEM-BSE) images was 20 kV. **Figure 3(a)** and **Figure 4(a)** are SEM-BSE images of alloys $Pt_{81.5}:Al_{11.5}:Cr_{4.5}:Ru_{2.5}$ (at%) and $Pt_{78}:Al_{15.5}:Cr_{4.5}:Ru_2$ (at%), while **Figure 3(b)** and **Figure 4(b)** are the optical microscope images of the same alloys after electrolytic etching in HCl/NaCl solution.

Both alloys had very fine dark ~Pt_3Al precipitates in light (Pt) matrices, which were difficult to discern from the SEM-BSE images. The contrast after etching is better and shows more clearly the dark ~Pt_3Al precipitates in the light (Pt) matrix, as well as the grain boundaries.

Figure 5(a) is a SEM-BSE image of alloy $Pt_{82}:Al_{12}:Cr_4:Ru_2$ (at%) which had a very poor contrast and after XRD analysis it was concluded that it had rounded dark ~Pt_3Al precipitates in light (Pt) matrix. After etching (**Figure 5(b)**), the optical microscope image showed a eutectic, as well as the dark ~Pt_3Al precipitates in light (Pt) matrix. **Figure 6(a)** is an example of an SEM-BSE image which had a reasonably good contrast and its optical microscope image after etching is shown in **Figure 6(b)**.

4. Conclusions

There was a large improvement in contrast when the SEM-BSE images of alloys $Pt_{81.5}:Al_{11.5}:Cr_{4.5}:Ru_{2.5}$, $Pt_{78}:Al_{15.5}:Cr_{4.5}:Ru_2$ and $Pt_{82}:Al_{12}:Cr_4:Ru_2$ (at%) in the unetched conditions (**Figures 3(a)–5(a)**) were compared to the images of the same alloys (**Figures 3(b)–5(b)**) after being etched. Therefore,

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electrolytic etching of Pt-Al based alloys in HCl/NaCl solution using direct current gives good results, and it is safer than using aqueous KCN solution.

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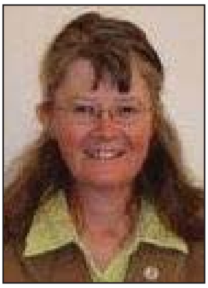

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