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Titanium Developments in the UK

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This plenary paper describes some of the UK titanium activities since the last World Titanium Conference in 2003. The use of titanium by UK industry continues to increase in line with world trends as does the level of research activity on titanium in UK universities. Information is also given on important changes and initiatives that have taken place amongst various government and non-government research organisations in the UK and updates are included on the commercialisation of UK titanium technologies that have been announced at previous conferences.

Keywords: *extraction, titanium alloys, superplastic forming, joining, surface engineering, fabrication, MMC.*

1. Introduction

In common with the rest of the world, the UK has seen a major upsurge in titanium activity in the last three years. Large industrial users in the UK such as Airbus, Rolls-Royce and BAE Systems are using increasing amounts of titanium in their products, and this trend is expected to continue. UK universities, notably Imperial College, Birmingham, Sheffield, Swansea and Manchester continue to have strong titanium research groups. Advances on modelling techniques and new analytical tools, such as Electron Backscatter Diffraction (EBSD) and Synchrotron Microtomography, have led to new understanding in melting, metal processing and microstructure/property relationships.

Various structural and organisational changes affecting titanium activity in the UK have taken place since the last World Titanium Conference in 2003.

QinetiQ Ltd., the former Defence Evaluation and Research Agency (DERA), is now a fully privatised company but continues to have a large materials and titanium capability. The National Metals Technology Centre (NAMTEC), located in Rotherham and established in 2002, is a focus for training, information and industry development. The Titanium Information Group (TIG), the UK's forum for titanium users and producers, continues to prosper, with an increasing number of international members and in 2004 the management of the TIG was taken over by NAMTEC. Titanium activities at the newly established Advanced Manufacturing Park in Sheffield include machining and process development at the Advanced Manufacturing Research Centre (AMRC), laser processing and joining echnology at TWI Technology Centre (Yorkshire) and Titanium casting at Castings Technology International Cti).

Some titanium activities which have featured strongly previous World Titanium Conferences are now firmly established manufacturing techniques for example, superplastic forming and diffusion bonding (SPFB) is used by Rolls-Royce in the Trent engine hollow fan blade (Figure 1). Other well publicised technologies, such as titanium fibre-reinforced metal matrix composites, the FFC Cambridge process for titanium production and titanium gamma aluminides are at different stages of development but have not yet reached commercial exploitation.

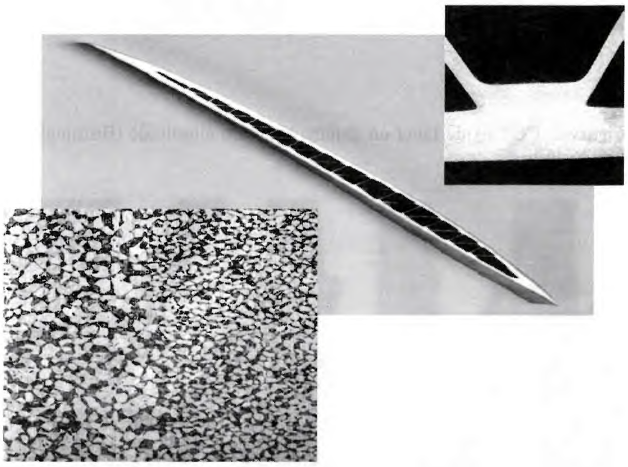

Figure 1. Rolls-Royce SPFDB fan core geometry and diffusion bond details (Rolls-Royce plc)

2. Surface Engineering

A group led by Dr H Dong at Birmingham University has developed a new surface coating system for titanium called Ceramic Conversion Treatment (CCT). The process generates an enhanced oxide layer with improved surface protection properties. The new process has been used to improve the tribological performance of gamma titanium aluminide, TiAl. CCT was used to convert the surface of TiAl intermetallic into the ceramic layer ($A1_2O_3$ doped with TiO_2) shown in Figure 2. The treatment improved wear resistance by more than two orders of magnitude and some TiAl valves (Figure 3) have been successfully treated and are being tested for use in car engines.

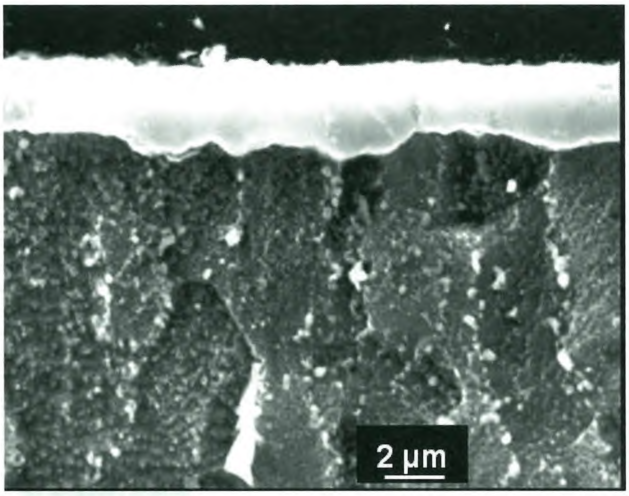

Figure 2. CCT oxide layer on gamma titanium aluminide (Birmingham University)

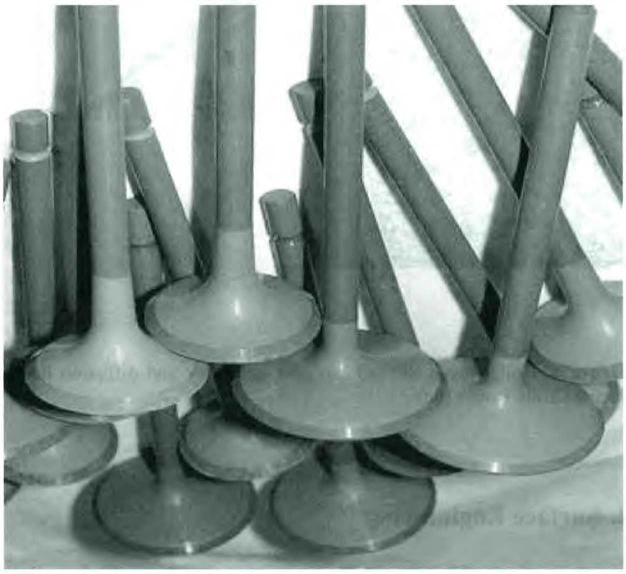

Figure 3. CCT coated TiAl engine valves (Birmingham University)

In another potential application, the process has been applied to NiTi shape memory alloys (SMA) for medical devices such as orthopaedic and orthodontic implants (Figure 4). Such biomedical applications have raised concerns over their biocompatibility owing to dissolution and release of Ni ions during surface degradation. The effect of CCT on the fretting corrosion behaviour of NiTi alloy was investigated using tests in Ringer's solution. The experimental results have shown that the CCT treatment can convert the surface of NiTi into a TiO_2 layer, which can effectively improve the fretting corrosion resistance of NiTi alloy and significantly reduce Ni ion release into the Ringer's solution (Figure 5).

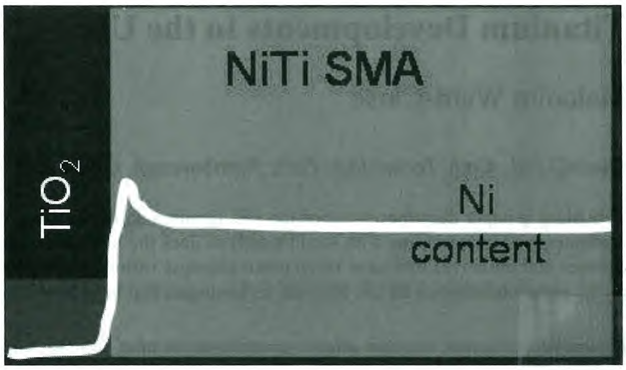

Figure 4. CCT coating on NiTi - layer structure and Ni distribution (Birmingham University)

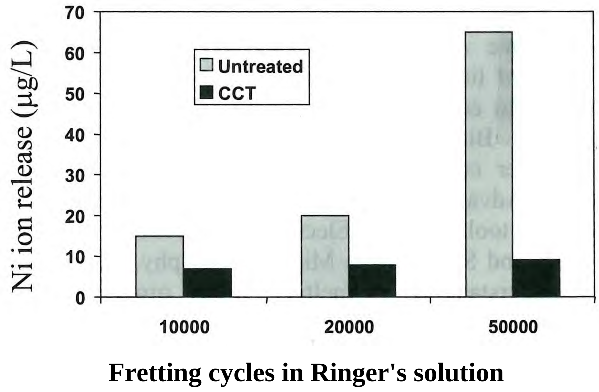

Figure 5 CCT coating on NiTi — Ni ion release under fretting conditions (Birmingham University)

3. Casting

The Rolls-Royce Centre of Excellence for Casting at Birmingham University has a 5 kg cold wall melting furnace for investment casting of titanium and TiAl based alloys. Figure 6 illustrates some TiAl parts made in this facility.

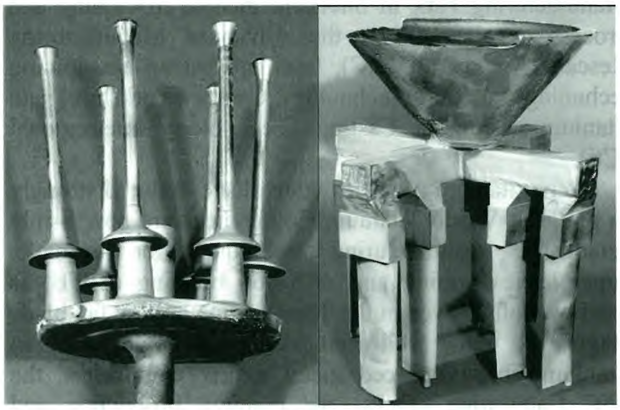

Figure 6. Examples of TiAl investment cast parts (Birmingham IRC)

Castings Technology International (Cti) has invested heavily in state-of-the-art technology for the fast manufacture of precision, thin-wall titanium castings. Two melting units are fully operational and capable of producing 30kg and 90kg of titanium alloys respectively. Both are based on induction skull 'cold crucible' melting technology from ALD GmbH (Figure 7).

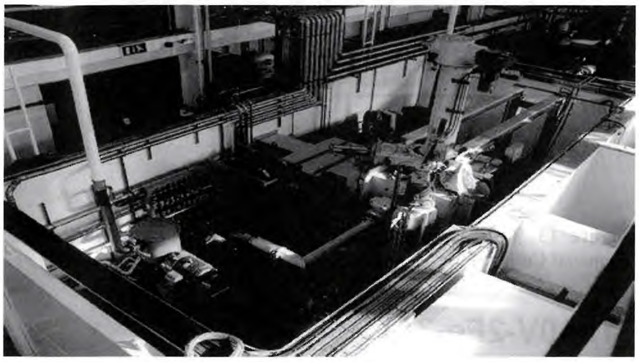

Figure 7. Cti titanium casting facility.

4. Joining

TWI (The Welding Institute) have announced the latest development of their friction stir welding (FSW) process for titanium, called the Static Shoulder FSW System. Friction stir welding is a solid state joining process where a rotating metal tool is driven along the interface between the metal parts being joined. In the past, titanium application has been inhibited by problems caused by the poor thermal conductivity and relatively narrow hot working temperature range of alloys such as Ti 6-4. The new method in which only the pin of the FSW tool rotates, not the shoulder, causes the heat to be generated by the pin, and evenly distributed through the thickness thus making the process more stable. It also gives a good surface finish. The process is shown schematically in Figure 8 and an example of a welded titanium alloy plate is shown in Figure 9.

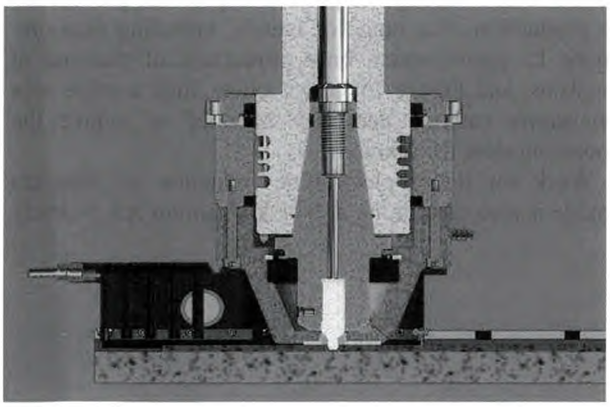

Figure 8. Static Shoulder Friction Stir Welding System (TWI)

Figure 9. Metallographic section through Static Shoulder Friction Stir Weld in 7 mm Ti-6A1-4V plate (TWI).

In a related piece of work, TWI has also proposed a new rapid prototyping method that uses multiple FSW passes to build complex shapes. Excess material is machined away to the give final shape (Figure 10).

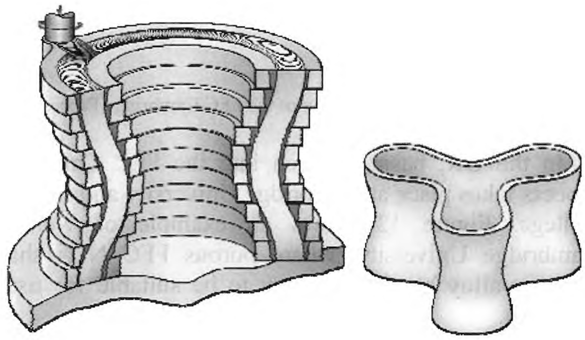

Figure 10. Concept for a titanium rapid prototyping method based on multi-pass friction stir welding (TWI).

TWI also continues to develop linear friction welding of titanium alloys for various applications, including bladed discs (blisks). Their new, fully hydraulically activated, LinFric® machine can weld up to 2000 mm^2 of Ti-6A1-4V, using an energy storage system to give significant cost advantages.

5. Titanium Extraction

The FFC Cambridge Process has received much research attention in the last four years, with several companies worldwide initiating development programmes. Briefly, the FFC Cambridge process, illustrated in Figure 11, is an electrolytic method for reducing metal oxides directly to metal. Electrolysis takes place in a molten salt in the temperature range 750-1000°C. The cathode consists of sintered metal oxide and the anode is carbon. Electrolysis takes place at approximately 3 V and during the process oxygen is removed from the cathode and released at the anode, mainly as carbon monoxide. By using mixed metal oxides in the sintered cathode, alloys can be formed directly. The product is normally fine grained, porous titanium or titanium alloy. This simple process has the potential to produce titanium alloys, and many other metals and alloys, at substantially lower cost than conventional routes.

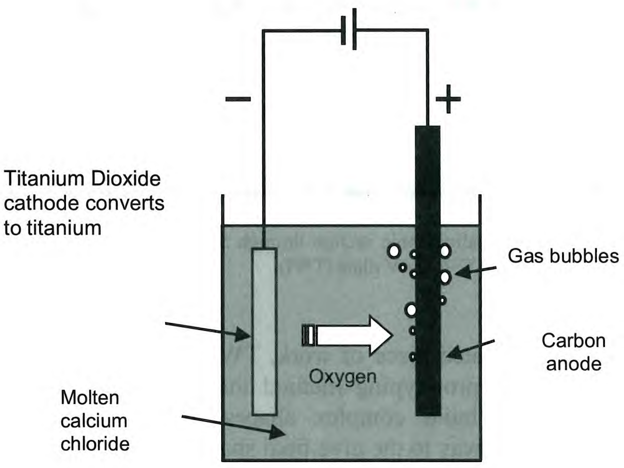

Figure 11. A schematic illustration of the FFC Cambridge Process

In the UK, basic research into the FFC Cambridge process takes place at Cambridge University and Imperial College. Figure 12 shows an example of work at Cambridge University, where porous FFC NiTi shape memory alloy has been shown to be suitable for tissue ingrowth.

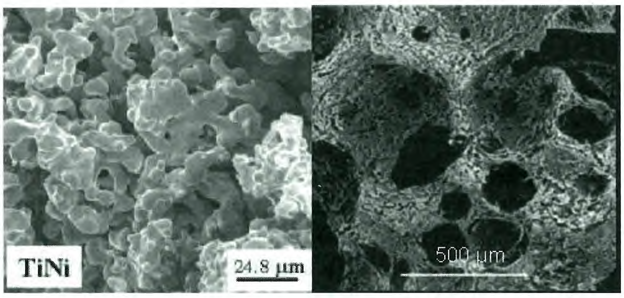

Figure 12. FFC NiTi alloy (left) and growth of human MG63 cells on the NiTi (Cambridge University)

The team at Imperial College have explored the potential of the FFC process to produce a range of different titanium alloys and microstructures, some conventional compositions and some compositions that would not normally be suitable for ingot casting (Figures 13 and 14). Because the FFC process forms alloys isothermally and at a relatively low temperature, they are normally very uniform and fine grained. Unlike ingot casting, there is no opportunity for gross chemical segregation or the formation of large grains.

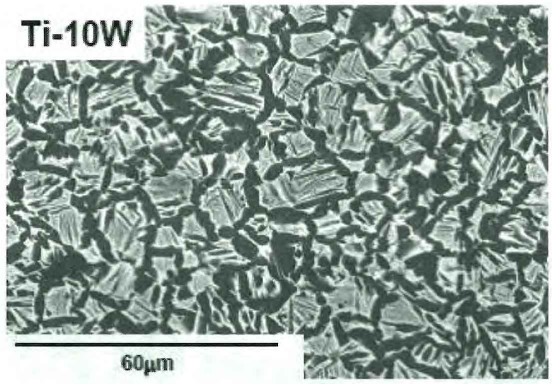

Figure 13. Ti-10W alloy produced by the FFC Cambridge Process (Imperial College)

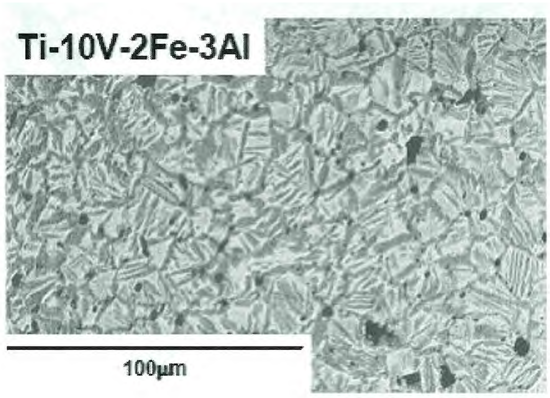

Figure 14. Ti-10-2-3 alloy produced by the FFC Cambridge Process (Imperial College)

Since the last World Titanium Conference in 2003, QinetiQ has transferred all its FFC activities and intellectual property to Metalysis Ltd., the company set up by Cambridge University to exploit the FFC process. Similarly, Metalysis have acquired the rights to the closely related BHP Polar Process. Metalysis are now the UK focus for commercial development of the FFC process. The company has plans to exploit the process for the production of a range of metals, including titanium. Figure 15 shows recent bulk production of titanium at Metalysis, and Figure 16 shows a new, high surface area honeycomb cathode geometry intended to reduce the processing time for titanium. Work on direct electrolytic reduction of titanium dioxide is also continuing at Norsk Titanium AS, Norway.

Figure 15. Bulk titanium production at Metalysis Ltd.

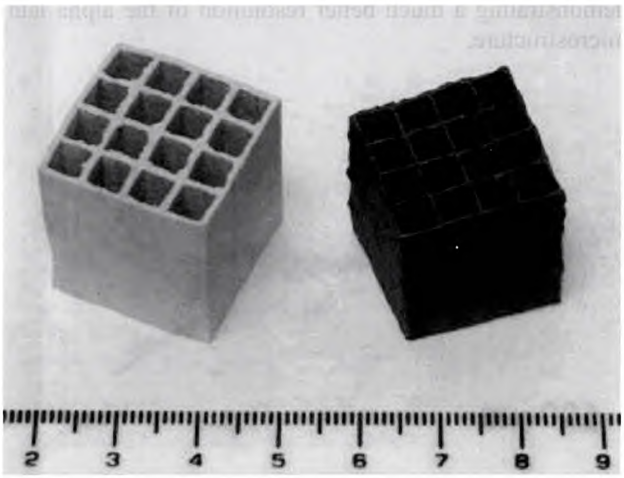

Figure 16. Honeycomb cathode design for high rate production of FFC titanium, sintered oxide (left) and titanium product (right) (Metalysis Ltd)

6. Ingot Processing

At the previous World Titanium Conference in 2003 Timet UK Ltd presented their work on the validation of the 'SOLAR' (SOLidification during Arc Remelting) model of vacuum arc remelting. A non-conflicting group of industrial melters has continued to fund the improvement of its capabilities by its originators at the School of Mines in Nancy. This now includes a model of cathode heating and melting, which can be used to predict the melt rate, and a particle trajectory model. The SOLAR model is used routinely in the development of VAR melting technology and as a quality tool at Timet UK Ltd. Figure 17 illustrates how it has been used to study the effect of magnetic stirring parameters on turbulence in the liquid pool.

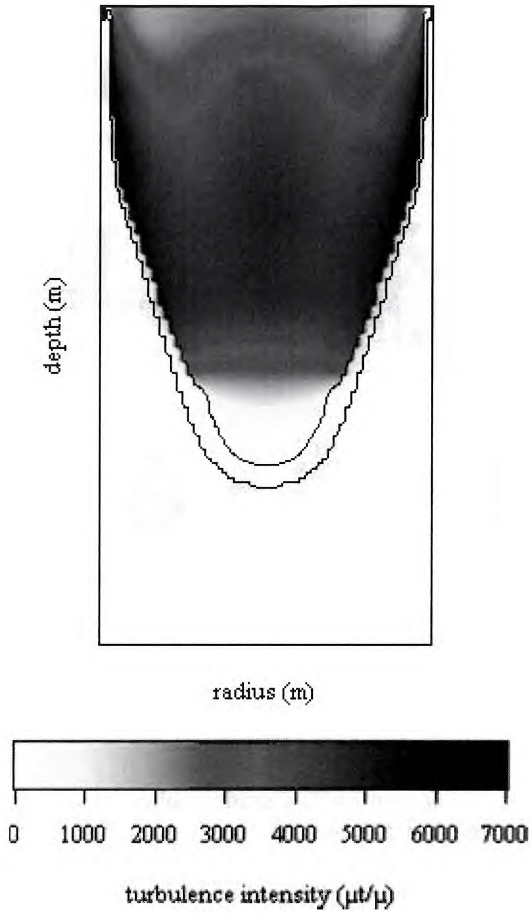

Figure 17. Predicted maximum turbulence, which occurred shortly after magnetic stirring reversal, due to the momentum of the pool (Timet UK).

7. Component Fabrication

QinetiQ Ltd (UK) and PM-Technology (Italy) have announced a new, low-contamination metal injection moulding (MIM) system for titanium, which uses only environmentally safe and non-hazardous chemicals. The MIM process is ideal for the production of small complex parts (Figure 18) that would otherwise be expensive to machine and wasteful of material. The MIM process is illustrated schematically in Figure 19.

Figure 18. Typical MIM parts

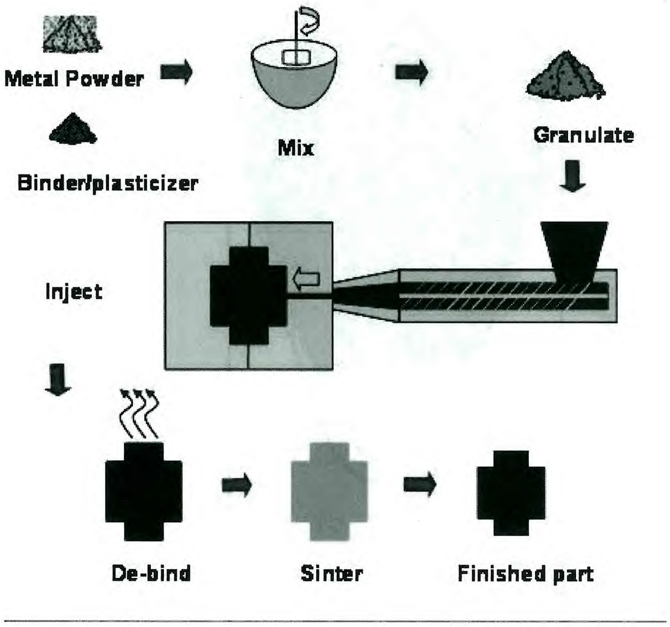

Figure 19. Schematic illustration of the MIM process

MIM of CP titanium for low grade applications, such as jewellery and watch cases, has been in use for some years. However, to date, excess reaction with the binder has prevented the use of titanium MIM for demanding applications. In order to meet ASTM standards and provide satisfactory mechanical performance, increases in interstitial contamination due to the MIM process must not exceed 1000 ppm oxygen and 600 ppm carbon.

The new low-contamination binder was used to produce MIM test bars with -45 µm Ti-6/4 spherical powder, sintered to 95% density, Figure 20. Chemical analysis confirmed that the interstitial pick-up was within the target range (oxygen 757 ppm and carbon 281 ppm).

Figure 20. Metal Injection Moulded (MIMed) and sintered Ti-6A1-4V test bars (QinetiQ Ltd.)

8. Analytical Techniques

A team at Manchester University School of Materials have recently announced the application of a new X-ray technique for 3D microstructural imaging based on synchrotron microtomography. Previously, X-ray microtomography has been limited to resolutions in the range 10-500 gm and, due to poor attenuation contrast, has been unable to image fine microstructural features. The new method uses interference of phase modulations between two parallel X-ray beams passing either side of a microstructural feature to give a resolution of 0.7 lam and greatly improve contrast and edge detection.

Using this new technique, researchers have studied in situ high cycle fatigue crack propagation in titanium alloy Ti-6246 and identified interactions between the growing crack and the microstructure.

Figure 21 compares tomographs of the same iso-surface, imaged using conventional attenuation contrast and the new phase imaging technique; the new technique demonstrating a much better resolution of the alpha lath microstructure.

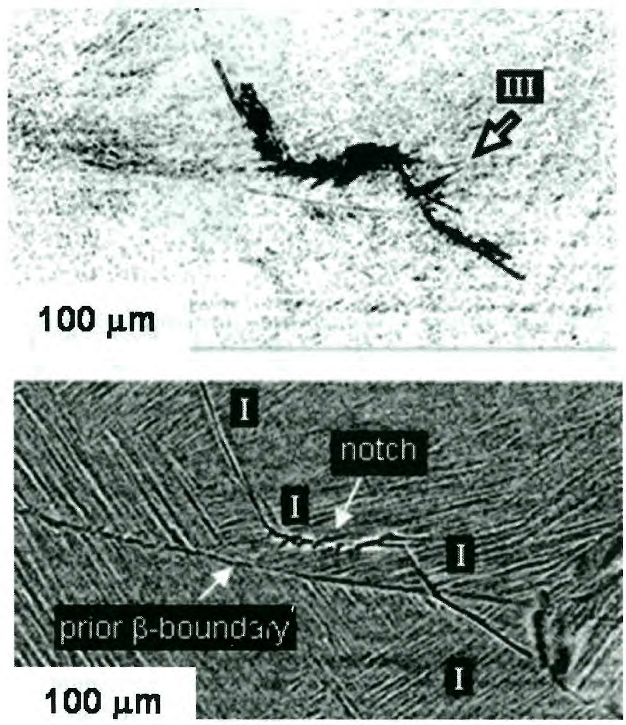

Figure 21. A conventional attenuation-contrast tomograph of Ti-6246 containing a fatigue crack (top), compared with the same iso-surface imaged with the new phase-contrast technique (bottom), (the numerals refer to different fracture modes) (Manchester University)

In Figure 22 the new method has been used to create a 3D tomograph combining damage (crack) and microstructure.

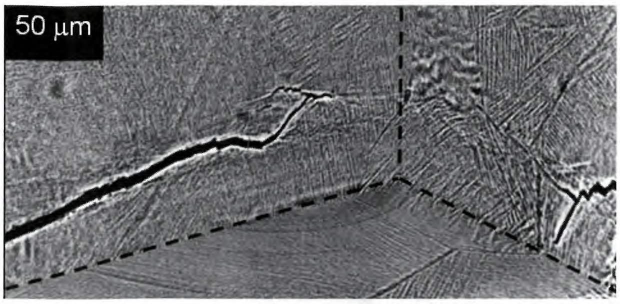

Figure 22. 3D microtomograph of Ti-6246, showing combined damage (crack) and microstructure. (Manchester University)

9. Metal Matrix Composites

In 2005, the QinetiQ "Sigma" SiC fibre and titanium MMC fabrication business was subject to a management buy-out. TISICS Ltd is the new company name and is now in the process of moving premises. It is anticipated that production of the SiC monofilament will resume in the last quarter of 2007.

Work continues at QinetiQ on the development of continuously reinforced SiC/titanium alloy MMC using the QinetiQ Matrix Coated Fibre (MCF) process (Figure 23).

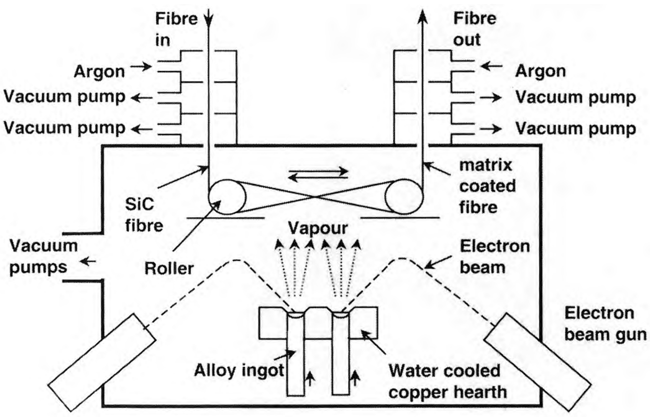

Figure 23. A schematic representation of the QinetiQ Matrix Coated Fibre Process

This method uses high power electron beam evaporation to coat the silicon carbide fibre with a thick layer of titanium alloy. The 'matrix coated fibre' can then be filament-wound into a titanium assembly and hot consolidated to give a fully dense, high quality, fibre reinforced MMC component. All the titanium originates from the PVD coating and this method automatically gives near perfect geometrical distribution of the fibre, with no touching or misaligned fibres.

The fibre coating system uses two electron beam heated evaporation baths. For Ti-6A1-4V both baths are Ti-6/4 alloy. For the more complex, higher temperature, refractory containing alloys, two different master alloys are evaporated simultaneously, producing a micro layered coating on the fibre. During subsequent thermal processing the micro layers interdiffuse to give the target alloy. Figure 24 shows an example of a microlayered Ti-alloy/Mo coating on an SCS6 SiC fibre.

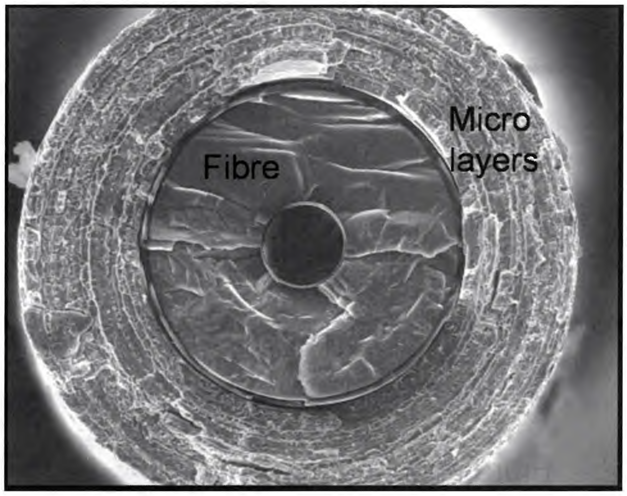

Figure 24. 140 gm diameter SiC fibre coated with titanium alloy/molybdenum microlayers (SEM image of fractured fibre)

Using this technique QinetiQ have produced silicon carbide fibre coated with established creep resistant alloys. In a related piece of work, QinetiQ have experimented with alternative high temperature titanium alloy compositions, intended to give similar performance to conventional high temperature alloy in an MMC but avoiding the use of expensive master alloys in the vapour coating process. The approach was to use Ti-6A1-4V in one evaporation bath and pure Mo, Nb or Zr in the second bath. Vapour coating was successful in each case, and several promising new MMC titanium alloys have been identified. Figure 25 shows a Nb containing alloy with a fine alpha/beta microstructure and a 10-15 µm grain size.

The QinetiQ fibre coating facility, shown in Figure 26, is able to supply up to 5,000 m continuous lengths of Ti-6A1-4V alloy coated silicon carbide fibre for evaluation and component development.

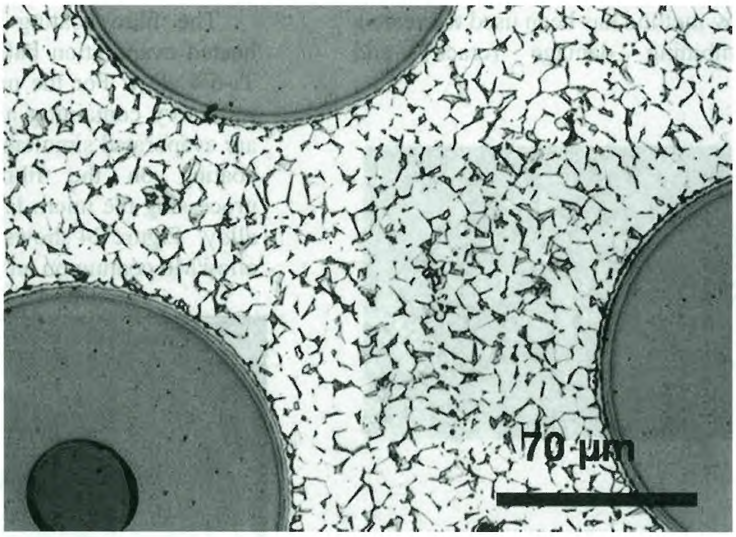

Figure 25. Titanium alloy MMC produced using the MCF process — Ti-4.5A1-4V-1.9Nb alloy reinforced with SMI SCS6 SiC fibre (QinetiQ Ltd)

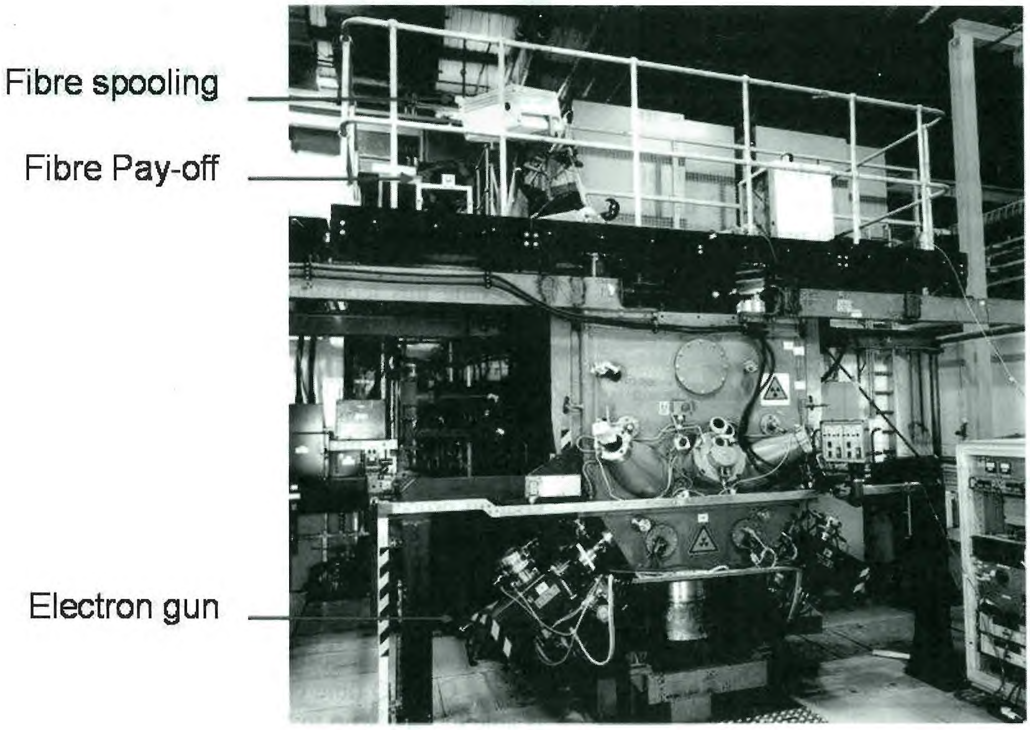

Figure 26. The QinetiQ matrix coated fibre (MCF) facility.

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