

# Metallographic preparation of titanium

## Application Notes

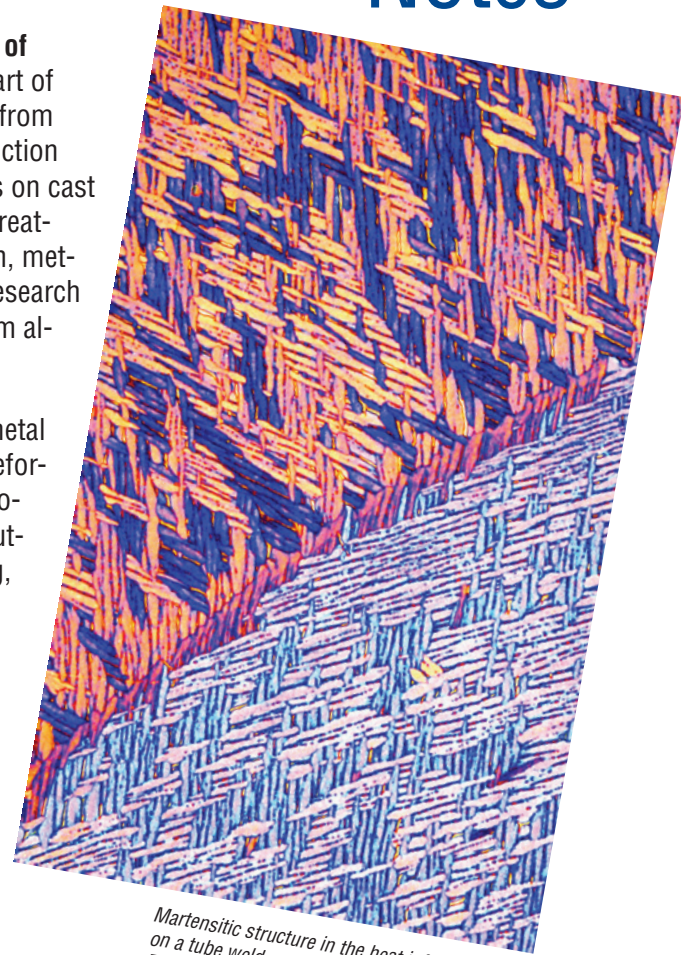
**Titanium** is a relatively new metal and expensive to produce, but its outstanding properties of high strength to weight ratio, excellent corrosion and heat resistance have made titanium and its alloys well established engineering materials.

Titanium is exceptionally resistant to corrosion by a wide range of chemicals. Its high affinity for oxygen results in a thin, but dense, self-healing stable oxide layer, which provides an effective barrier against incipient corrosion. In addition, it is the high strength to weight ratio, maintained at elevated temperatures, which makes titanium and its alloys attractive for many critical applications.

Titanium and its alloys are widely used in the aerospace and aircraft, chemical and medical industry, where high safety is essential. Consequently, quality control of titanium production and processing is extremely important.

This is why **metallography of titanium** is an integrated part of quality control of titanium, from monitoring the initial production process, to porosity checks on cast parts and controlling heat treatment processes. In addition, metallography plays a role in research and development of titanium alloys and products.

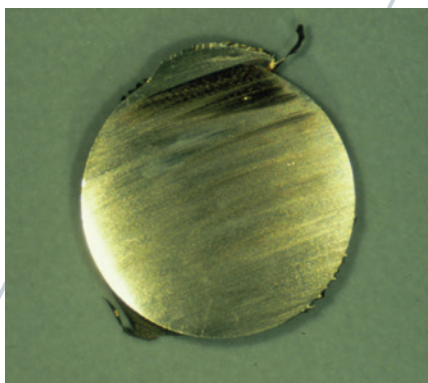
Titanium is a very ductile metal and prone to mechanical deformation. For the abrasive processes in metallographic cutting, grinding and polishing, this aspect has to be taken into consideration.



*Martensitic structure in the heat influenced zone on a tube weld.  
Etchant: Weck's reagent, 1000 x*

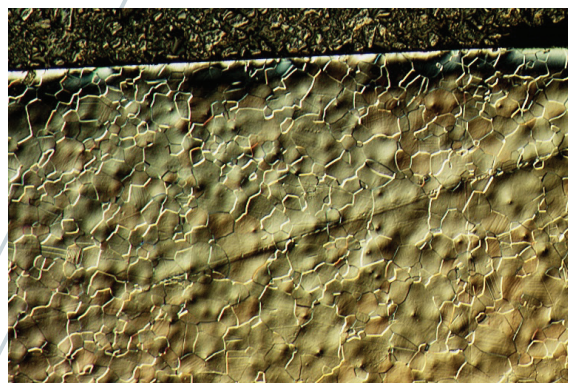
### Difficulties during metallographic preparation

**Cutting:** *Titanium can easily overheat during cutting and large burrs can occur:*



*Fig. 1*

**Grinding and polishing:** *Due to its ductility titanium deforms and scratches easily:*



*Fig. 2*

*DIC, 50 x*

### Solution:

*Special cut-off wheel for titanium.*

*Chemical-Mechanical polishing.*

*Electrolytical polishing.*

# Production and applications of titanium

The production of titanium is a three-step process:

1. The first step is the manufacture of titanium sponge and involves the chlorination of rutile ore ( $\text{TiO}_2$ ).

Chlorine gas and coke are combined with the rutile and react to form titanium tetrachloride. This is purified by distillation and then reduced with magnesium to titanium sponge and magnesium chloride.

2. This titanium sponge is then crushed into grainy powder, mixed with scrap and/or alloying metals such as vanadium, aluminium, molybdenum, tin and zirconium, and melted in a vacuum arc reduction furnace to produce titanium ingots.

3. These ingots from the first melt are then used in a second melt as consumable electrodes. This process is called "double consumable-electrode vacuum melting process". For very pure and clean titanium with very homogenous structures, an additional third melt can be carried out.

In a first fabrication step, the cast ingots, either cylindrical and 15 metric tons, or square and 10 metric tons, are hot forged into general mill products such as smaller billets, slabs, bar and plate. As cast ingots can have an inherent coarse microstructure, which makes them sensitive to cracking, close temperature and process control are maintained during forging operation.

The finished products consist of forgings for aerospace applications as well as slab, bar, and other feedstock for further processing into bar, rod, wire, sheet or plate.

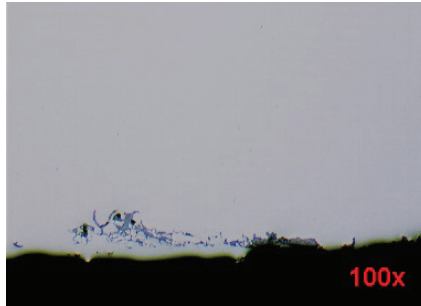


Fig. 3: Grey oxide (defect) rolled into surface of bar.

Fig. 3 shows a defect on a rolled titanium bar, grey oxide has been rolled into the surface.

Secondary fabrication for producing parts from mill products includes manufacturing processes such as die forging, extrusion, hot and cold forming etc. Hot forming of titanium is not only a shaping procedure, but a method to produce and control the microstructure.

The high strength/low density of titanium make it a crucial material in the aerospace industry. Its main gas turbine engine applications include compressor rings, discs, and spacer casings, ducts and shrouds. In aeroplane structural frames, titanium alloys are used in under carriage parts, engine mountings, and control mechanism parts, sheet and fasteners for outer body construction.

Titanium's superior corrosion resistance and biocompatibility make it an ideal



Fig. 4: Entrance Experience Music Project, Seattle.



Fig. 5: Screws and bone plate electro-chemically oxidized for colour coding. The colours are the result of different thickness of the oxide layer.

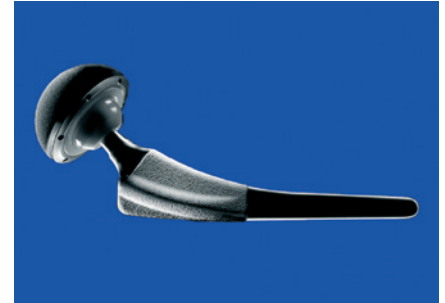


Fig. 6: Hip implant with CaP-coating

material for the chemical, medical and food industry, and for ocean research and development. With its passive oxide film it has a high corrosion resistance against salt solutions, nitric acid solutions, seawater, body fluids, fruit and vegetable juices. Typical products are reaction vessels, heat exchangers, valves, and pumps; prosthetic devices such as implants, artificial bones, artificial heart pumps and valve parts. The most widely used alloy for these products is Ti-6Al-4V.

Its light weight combined with aesthetic design has made it a favorite for high class consumer goods such as jewelry, golf clubs, eyeglasses, bikes and watches, and in architecture it is used for decorative façades (Fig. 4)



# Difficulties in the preparation of titanium



The main problem of preparing titanium for microscopic observation is its high ductility, which makes titanium difficult to cut, grind and polish. In the following recommendations, specific advice is given on how to overcome this typical behavior of titanium.

## Recommendations for the preparation of titanium and its alloys

**Cutting:** Due to its high ductility, titanium produces long chips when machined or cut, which makes metallographic cutting with regular aluminium oxide cut-off wheels very ineffective. Heat damage can occur easily (see Fig.1) and therefore silicon carbide cut-off wheels have been developed specifically for sectioning of titanium (e.g. 20SXX).



Cutting titanium also generates a characteristic smell that can become pronounced when cutting large pieces or quantities. In these cases, it is recommended to connect a fume extraction to the cut-off machine.

**Mounting:** In primary production control labs, which check mainly ingots, billets and slabs, large samples of titanium are metallographically processed unmounted. For smaller manufactured parts that need to be mounted, such as wires or fasteners, hot compression mounting with phenolic resin (Multi-Fast) or cold mounting with slow curing epoxy (EpoFix) are recommended.



**Grinding and polishing:** Its extreme ductility makes titanium prone to mechanical deformation and scratching, which necessitates a chemical-mechanical polish. The three-step, automatic method described in Table 1 is a proven procedure, which gives excellent, reproducible results for titanium alloys.

The first step is a plane grinding with resin bonded diamonds in a rigid disc. Plane grinding is followed by a single fine grinding step on a hard surface such as MD-Largo or MD-Plan. As abrasive 9 µm diamond suspension DiaPro Allegro/Largo 9 or DiaPro Plan 9 is used.

Pure titanium should always be ground using silicon carbide foil for plane grinding, see table 2.

The third and final step for titanium alloys is a **chemical-mechanical polishing** with a mixture of colloidal silica (OP-S) and hydrogen peroxide (30%). The concentration can vary between 10-30%.

Unlike some other colloidal silica, OP-S was developed to accommodate chemical additions without transforming into a gel-like consistency, and is therefore well suited for polishing titanium and titanium alloys. During chemical-mechanical polishing, the reaction product of the hydrogen peroxide with titanium is continuously removed from the sample surface with the silica suspension and leaves the surface free of mechanical deformation. References in the relevant literature also mention nitric and hydrofluoric acid mixtures for chemical-mechanical polishing of titanium.

## Preparation Method

### Grinding

Step		PG	FG
	Surface		
	Abrasive	Type	Diamond
		Size	#220
	Suspension/Lubricant	Water	DiaPro Allegro/Largo 9
	rpm	300	150
	Force [N]/specimen	40***	30
	Time (min)	Until Plane	5

### Polishing

Step		OP	
	Surface		
	Abrasive	Type	Colloidal Silica
		Size	0.04 µm
	Suspension/Lubricant	OP-S*	
	rpm	150	
	Force [N]/specimen	30	
	Time (min)	5**	

**Table 1** shows a general, automatic preparation method for titanium alloys with grade 5 or higher, unmounted samples, 30 mm dia. Please be aware that the polishing time can vary depending on the purity of the titanium and the area of the sample surface.

\* Mix 90% OP-S with 10-30% H<sub>2</sub>O<sub>2</sub> (30%).

\*\* The polishing time depends on the sample area. Very large samples require more polishing time than small ones.

\*\*\* Decrease to 25 N to avoid pencil shapes in single sample preparation of mounted samples.

**Note:** during the last 20-30 seconds of the preparation step with OP-S, the rotating cloth is flushed with water. This will clean the samples, holder and cloth.

These reagents may work faster, however, Struers does not recommend to use them for polishing, because they are more corrosive than hydrogen peroxide and proper precautions have to be observed when handling these acids in the polishing procedure. When working with hydrogen peroxide it is recommended to wear rubber gloves.

If this chemical-mechanical polish is not used, the surface of the titanium sample will exhibit a very scratched appearance, and it is almost impossible to achieve a good polish with diamond only.

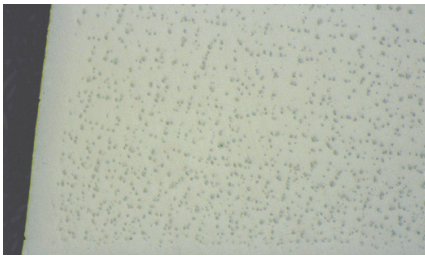


Fig. 7: Titanium after 3 μm diamond polish, deformation and scratches are not removed.

Contrary to the usual procedure of using finer and finer diamond for polishing, diamond polishing actually introduces continuously mechanical deformation which leaves scratches and smearing on the surface (see Fig. 7). Once introduced, this layer of deformation is difficult to remove even with the colloidal silica and hydrogen peroxide mixture. Therefore diamond polishing should be avoided, especially with commercially pure titanium.

The preparation time depends on the sample area and the alloy.

The larger the sample and the purer the titanium, the longer the preparation time for the final oxide polishing step, which can take up to 45 minutes for commercially pure titanium. A properly polished, unetched titanium surface looks white when examined in the optical microscope, and polishing has to continue until this state of the surface is reached.

Due to the production process, titanium and its alloys are very clean, which means that little black dots, appearing on a polished surface, are remains from grinding deformation and not inclusions or part of the structure.

This artefact needs to be removed with further chemical-mechanical polishing. Once the surface is polished sufficiently, the structure can be seen in polarised light without etching. (See Fig. 8).

**Note:** When working with colloidal silica (OP-S) it is important to wet the cloth with water before starting the polishing. To clean the samples, it is essential to flush the rotating cloth with water approximately 20-30 seconds before the machine stops. The water washes off the OP-S from the samples, holder and cloth. The samples are then cleaned again individually with neutral detergent and tap water, and then dried with ethanol

## Preparation Method

### Grinding

Step	PG	FG	OP
Surface	Foil/Paper	MD-Largo	MD-Chem
Abrasive	Type	Diamond	Colloidal Silica
	Size	#320	9 μm
Suspension/Lubricant	Water	DiaPro Allegro/Largo 9	OP-S*
rpm	300	150	150
Force [N]/specimen	15	20	20
Time (min)	Until Plane	5	25 (or longer)

Table 2 shows a general, automatic preparation method for pure titanium (grade 1-4) with unmounted samples, 30 mm dia. Please be aware that the polishing time can vary depending on the purity of the titanium and the area of the sample surface.

\*80% OP-S + 10% H<sub>2</sub>O<sub>2</sub> (30%) + 10% NH<sub>4</sub>OH (25%)

Equipment:	LectroPol-5
Electrolyte:	A3
Mask size:	1 cm <sup>2</sup>
Temperature:	Room temperature 18-20°C
Flow rate:	10-15
Voltage:	35-45 V
Time:	20-30 sec.

Table 3 shows a general, electrolytic preparation method for pure titanium and titanium alloys.

and a strong stream of air. If after the cleaning step residue of OP-S is seen on the surface of the sample, the cleaning has not been carried out properly and has to be repeated. An efficient and repeatable cleaning method can be done using automatic cleaning equipment like Lavamin.



As an alternative to mechanical polishing, **electrolytic polishing** can be recommended when fast results are required. Electrolytic polishing methods are particularly appropriate for the following reasons: speed of results

(especially for pure titanium which needs very long polishing times), ease of operation, reproducibility. Also, electrolytic polishing leaves no mechanical deformation on the sample surface. This could be especially relevant for research applications. α alloys, which have a homogenous structure, are particularly well suited for electrolytic polishing, but also α-β alloys can be polished electrolytically.

The electrolytic polishing procedure requires a fine ground surface with SiC #1200 or finer. Table 3 shows a general procedure for titanium and titanium alloys. After the electrolytic polishing, the polished specimen is examined in polarized light or etched chemically (for etchants, see under "Etching and Interpretation").

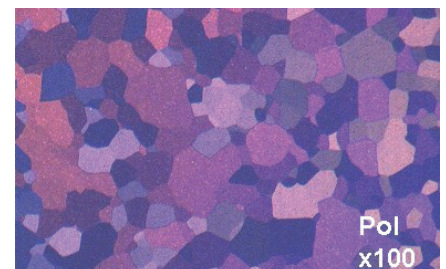


Fig. 8: Cross-section of bar, commercially pure titanium, electrolytically polished, 100 x, polarized light.

# Etching and interpretation

As mentioned before, the surface of a well-polished titanium sample can already be observed unetched in polarized light. The contrast with this illumination is not always very pronounced, but it is ideal for a general check to see if the polish is sufficient.

The most common chemical etchant for titanium is Kroll's reagent:

100 ml water  
1-3 ml hydrofluoric acid  
2-6 ml nitric acid

The concentration can vary depending on the alloy and can be adjusted individually. It colors the  $\beta$  phase dark brown. Titanium can be colour etched with Weck's reagent:

100 ml water  
5 g ammonium bifluoride

## Metallurgy and microstructures

Commercial titanium grades and alloys are divided into four groups: commercially pure titanium;  $\alpha$  and near  $\alpha$  alloys such as Ti-6Al-2Sn-4Zr-2Mo;  $\alpha$ - $\beta$  alloys, of which Ti-6Al-4V is the most well known, and  $\beta$  alloys that have a high content of vanadium, chromium and molybdenum.

Titanium undergoes an allotropic change from a low temperature close packed hexagonal structure ( $\alpha$ ) to a body centred cubic phase ( $\beta$ ), at a temperature of 882°C.

This transformation allows alloys with  $\alpha$ ,  $\beta$ , or mixed  $\alpha/\beta$  microstructures, and the possibility of using heat treatment and thermo-mechanical treatment.

Consequently a wide range of properties can be obtained from a relatively small number of alloy compositions.

To ensure the desired combination of microstructure and properties, close process control has to be maintained.

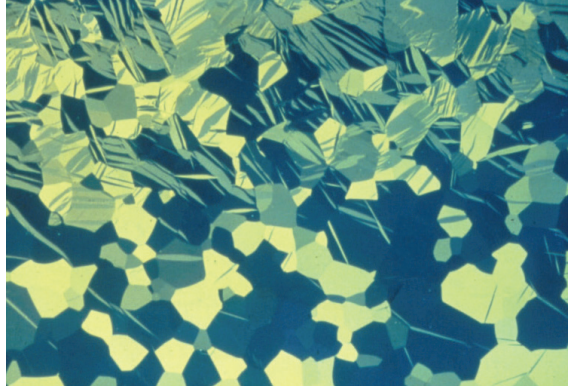


Fig. 9:  
Grain structure of a commercially pure titanium, polarized light, 100 x

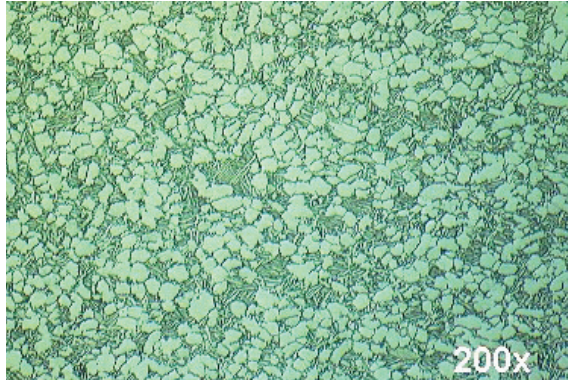


Fig. 10:  
Structure of a forged  $\alpha$ - $\beta$  Ti-6Al-4V, 400 x

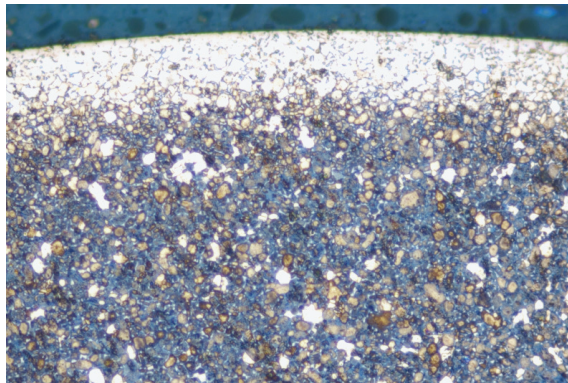


Fig. 11:  
 $\alpha$ - $\beta$  Ti-6Al-4V with a white, brittle "alpha-case" surface layer, 50 x

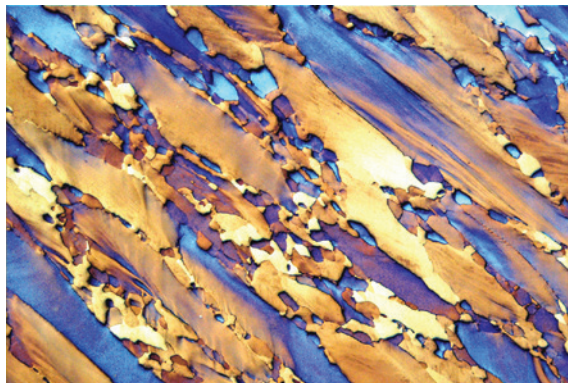


Fig. 12:  
 $\beta$  Ti-15V-3Al-3Sn-3Cr, heat tinted, 50 x

Consequently metallography plays an important role in ensuring that products have the correct microstructure, which in turn reflects the appropriate degree of process control. The relations between hot forming, heat treatment, microstructure and physical properties in the production of titanium are very complex. In the following, only a few examples of the most common types of titanium microstructures are described.

Fig. 9 shows the grain structure of a commercially pure titanium part that has been mechanically deformed through bending. Twinning due to mechanical deformation is visible.

Fig. 10 shows the structure of a forged  $\alpha$ - $\beta$  Ti-6Al-4V of an orthopaedic implant in the annealed condition, etchant: Kroll's reagent.

**Struers ApS**  
 Pederstrupvej 84  
 DK-2750 Ballerup, Denmark  
 Phone +45 44 600 800  
 Fax +45 44 600 801  
 struers@struers.dk  
 www.struers.com

**NETHERLANDS**  
**Struers GmbH Nederland**  
 Zomerdijk 34 A  
 3143 CT Maassluis  
 Telefoon +31 (10) 599 7209  
 Fax +31 (10) 5997201  
 netherlands@struers.de

**NORWAY**  
**Struers ApS, Norge**  
 Sjøskogenveien 44C  
 1407 Vinterbro  
 Telefon +47 970 94 285  
 info@struers.no

**AUSTRIA**  
**Struers GmbH**  
 Zweigniederlassung Österreich  
 Betriebsgebiet Puch Nord 8  
 5412 Puch  
 Telefon +43 6245 70567  
 Fax +43 6245 70567-78  
 austria@struers.de

**POLAND**  
**Struers Sp. z o.o.**  
 Oddział w Polsce  
 ul. Jasnogórska 44  
 31-358 Kraków  
 Phone +48 12 661 20 60  
 Fax +48 12 626 01 46  
 poland@struers.de

**ROMANIA**  
**Struers GmbH, Sucursala Bucuresti**  
 Str. Preciziei nr. 6R  
 062203 sector 6, Bucuresti  
 Phone +40 (31) 101 9548  
 Fax +40 (31) 101 9549  
 romania@struers.de

**SWITZERLAND**  
**Struers GmbH**  
 Zweigniederlassung Schweiz  
 Weissenbrunnenstraße 41  
 CH-8903 Birmensdorf  
 Telefon +41 44 777 63 07  
 Fax +41 44 777 63 09  
 switzerland@struers.de

**SINGAPORE**  
**Struers Singapore**  
 627A Aljunied Road,  
 #07-08 BizTech Centre  
 Singapore 389842  
 Phone +65 6299 2268  
 Fax +65 6299 2661  
 struers.sg@struers.dk

**SPAIN**  
**Struers España**  
 Camino Cerro de los Gamos 1  
 Building 1 - Pozuelo de Alarcón  
 CP 28224 Madrid  
 Teléfono +34 917 901 204  
 Fax +34 917 901 112  
 struers.es@struers.es

**FINLAND**  
**Struers ApS, Suomi**  
 Hietalahdenranta 13  
 00180 Helsinki  
 Puhelin +358 (0)207 919 430  
 Faksi +358 (0)207 919 431  
 finland@struers.fi

**SWEDEN**  
**Struers Sverige**  
 Box 20038  
 161 02 Bromma  
 Telefon +46 (0)8 447 53 90  
 Telefax +46 (0)8 447 53 99  
 info@struers.se

**UNITED KINGDOM**  
**Struers Ltd.**  
 Unit 11 Evolution @ AMP  
 Whittle Way, Catcliffe  
 Rotherham S60 5BL  
 Tel. +44 0845 604 6664  
 Fax +44 0845 604 6651  
 info@struers.co.uk

**USA**  
**Struers Inc.**  
 24766 Detroit Road  
 Westlake, OH 44145-1598  
 Phone +1 440 871 0071  
 Fax +1 440 871 8188  
 info@struers.com

**AUSTRALIA & NEW ZEALAND**  
**Struers Australia**  
 27 Mayneview Street  
 Milton QLD 4064  
 Australia  
 Phone +61 7 3512 9600  
 Fax +61 7 3369 8200  
 info.au@struers.dk

**BELGIUM (Wallonie)**  
**Struers S.A.S.**  
 370, rue du Marché Rollay  
 F- 94507 Champigny  
 sur Marne Cedex  
 Téléphone +33 1 5509 1430  
 Télécopie +33 1 5509 1449  
 struers@struers.fr

**BELGIUM (Flanders)**  
**Struers GmbH Nederland**  
 Zomerdijk 34 A  
 3143 CT Maassluis  
 Telefoon +31 (10) 599 7209  
 Fax +31 (10) 5997201  
 netherlands@struers.de

**CANADA**  
**Struers Ltd.**  
 7275 West Credit Avenue  
 Mississauga, Ontario L5N 5M9  
 Phone +1 905-814-8855  
 Fax +1 905-814-1440  
 info@struers.com

**CHINA**  
**Struers Ltd.**  
 No. 1696 Zhang Heng Road  
 Zhang Jiang Hi-Tech Park  
 Shanghai 201203, P.R. China  
 Phone +86 (21) 6035 3900  
 Fax +86 (21) 6035 3999  
 struers@struers.cn

**CZECH REPUBLIC & SLOVAKIA**  
**Struers GmbH Organizační složka**  
 vědeckotechnický park  
 Přilepská 1920,  
 CZ-252 63 Roztoky u Prahy  
 Phone +420 233 312 625  
 Fax +420 233 312 640  
 czechrepublic@struers.de  
 slovakia@struers.de

**GERMANY**  
**Struers GmbH**  
 Carl-Friedrich-Benz-Straße 5  
 D- 47877 Willich  
 Telefon +49 (0) 2154 486-0  
 Fax +49 (0) 2154 486-222  
 verkauf@struers.de

**FRANCE**  
**Struers S.A.S.**  
 370, rue du Marché Rollay  
 F-94507 Champigny  
 sur Marne Cedex  
 Téléphone +33 1 5509 1430  
 Télécopie +33 1 5509 1449  
 struers@struers.fr

**HUNGARY**  
**Struers GmbH**  
 Magyarországi Fióktelepe  
 2040 Budaörs  
 Szabadság utca 117  
 Phone +36 2380 6090  
 Fax +36 2380 6091  
 Email: hungary@struers.de

**IRELAND**  
**Struers Ltd.**  
 Unit 11 Evolution@ AMP  
 Whittle Way, Catcliffe  
 Rotherham S60 5BL  
 Tel. +44 0845 604 6664  
 Fax +44 0845 604 6651  
 info@struers.co.uk

**ITALY**  
**Struers Italia**  
 Via Monte Grappa 80/4  
 20020 Arese (MI)  
 Tel. +39-02/38236281  
 Fax +39-02/38236274  
 struers.it@struers.it

**JAPAN**  
**Marumoto Struers K.K.**  
 Takanawa Muse Bldg. 1F  
 3-14-13 Higashi-Gotanda,  
 Shinagawa  
 Tokyo  
 141-0022 Japan  
 Phone +81 3 5488 6207  
 Fax +81 3 5488 6237  
 struers@struers.co.jp

## Application Notes

Metallographic preparation of titanium

Bill Taylor,  
 Struers Ltd, Glasgow

Elisabeth Weidmann,  
 Struers ApS, Copenhagen

### Acknowledgements:

We wish to thank Fa. Aesculap, Tuttlingen, Germany, for supplying information on titanium, and the permission to reproduce Figs 5, 6 and 11.

We thank Wah Chang North, Albany, Oregon, USA for supplying sample material, and Mr. Paul Danielson from Albany Research Centre, Albany, Oregon, USA for the color micrographs on the front page and Fig. 12. We thank Lindberg, Aabyhøj, Denmark, for letting us reproduce the image of the eyeglasses, model Air Titanium, and Experience Music Project, Seattle, USA for reproducing Fig. 4.

### Bibliography:

Metals Handbook, Desk edition, ASM, 1984

Fig.11 shows an  $\alpha$ - $\beta$  Ti-6Al-4V with a white, brittle “ $\alpha$ -case” surface layer, etchant: Weck’s reagent. Although hot forming processes are carried out under controlled atmosphere, titanium can absorb oxygen already at lower temperatures, which results in a surface hardened zone, “ $\alpha$ -case”. This is a very brittle layer and can only be removed mechanically. (Note:  $\alpha$ -case does not show up with Kroll’s etchant, but with the bifluoride).

Fig. 12 shows the  $\beta$  structure of the longitudinal section of a Ti-15V-3Al-3Sn-3Cr alloy plate. It is used in the aerospace industry because of its superior mechanical properties. Etchant: heat tinting.

## Summary

Titanium is a very ductile, low weight - high strength metal with an excellent corrosion resistance and biocompatibility. Its ductility requires a specific metallographic preparation, using special cut-off wheels for sectioning and a chemical-mechanical polish with a mixture of hydrogen peroxide and colloidal silica. This polishing method, carried out with automatic equipment, gives consistently excellent and reproducible results.



Details of a titanium frame for eye-glasses. The high strength and ductility of titanium make screws and solder on these frames obsolete.