Metallographic preparation of titanium

Struers

Application Notes

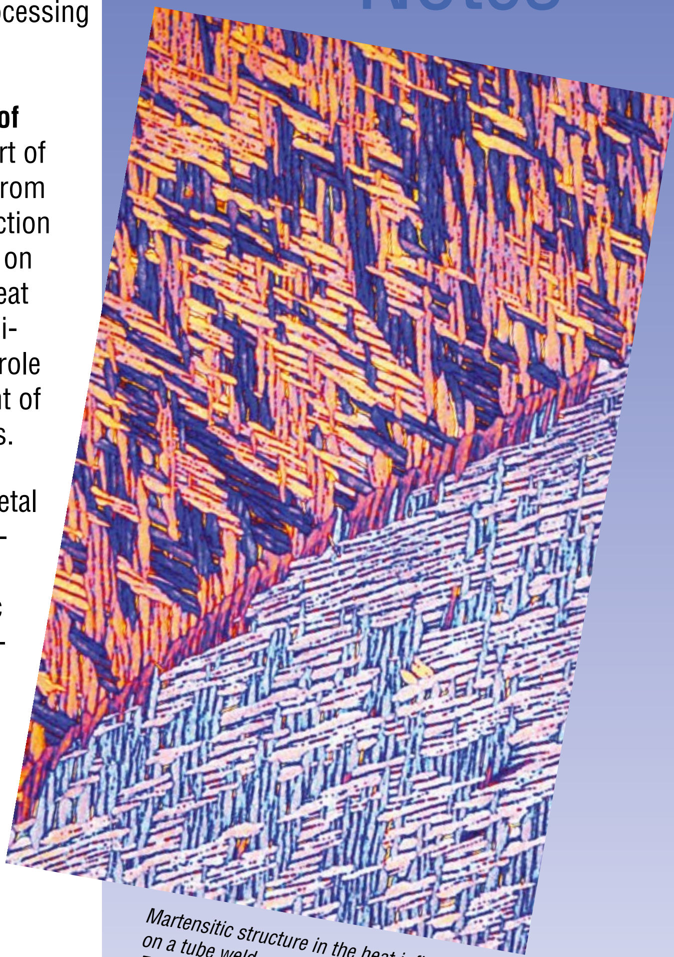
Titanium is a relatively new metal and expensive to produce, but its outstanding properties of high strength to weight ratio, excellent corrosion and heat resistance have made titanium and its alloys well established engineering materials.

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:*

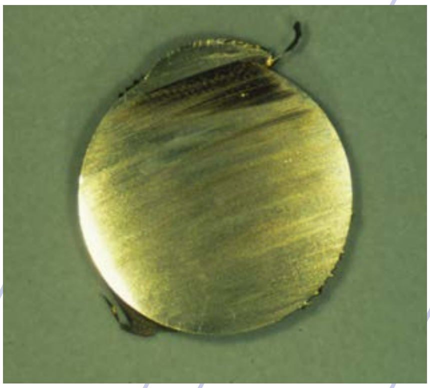


Fig. 1

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

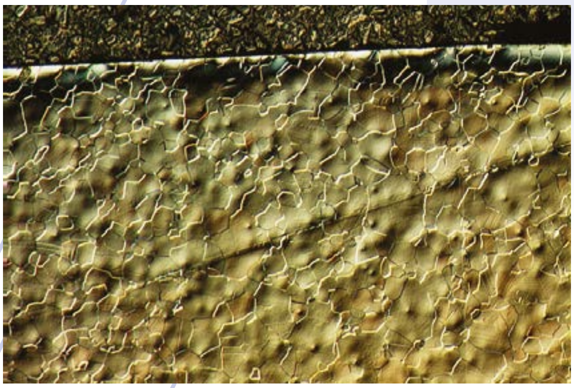


Fig. 2 *DIC, 50 x*

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 (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 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 jewellery, golf clubs, eyeglasses, bikes and watches, and in architecture it is used for decorative façades (Fig. 4)

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

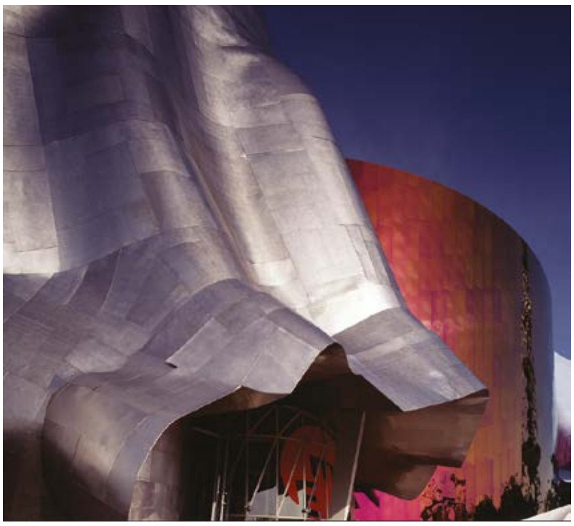


Fig. 4: Entrance Experience Music Project, Seattle.

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. 20S30 and 20S35).

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 (MultiFast) 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.

Preparation Method

Grinding

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

Polishing

			OP	
Step			OP	
Surface			MD-Chem	
Abrasive	Type		Collodial 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_2O_2 (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.*

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.

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 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 repetable cleaning method can be done using automatic cleaning equipment like Lavamin.

Preparation Method

Grinding

Step		PG	FG	OP
Surface		Foil/Paper	MD-Largo	MD-Chem
Abrasive	Type	SiC	Diamond	Collodial Silica
	Size	#320	9 µm	0.04 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_2O_2 (30%) + 10% NH_4OH (25%)*

Equipment:	LectroPol-5
Electrolyte:	A3
Mask size:	1 cm^2
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.*

As an alternative to mechanical polishing, **electrolytical 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, electrolytical 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 electrolytical polishing, but also α-β alloys can be polished electrolytically.

The electrolytical 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 electrolytical polishing, the polished specimen is examined in polarized light or etched chemically (for etchants, see under “Etching and Interpretation”).

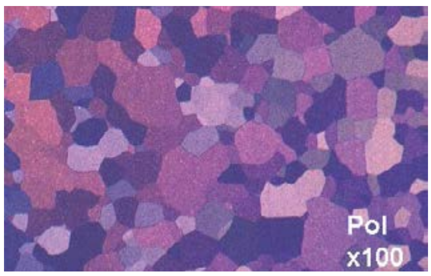


Fig. 8: Cross-section of bar, commercially pure titanium, electrolytically polished, 100 x, polarized light.

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 β 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; α and near α alloys such as Ti-6Al-2Sn-4Zr-2Mo; α-β alloys, of which Ti-6Al-4V is the most well known, and β alloys that have a high content of vanadium, chromium and molybdenum.

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

This transformation allows alloys with α, β, or mixed α/β 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.

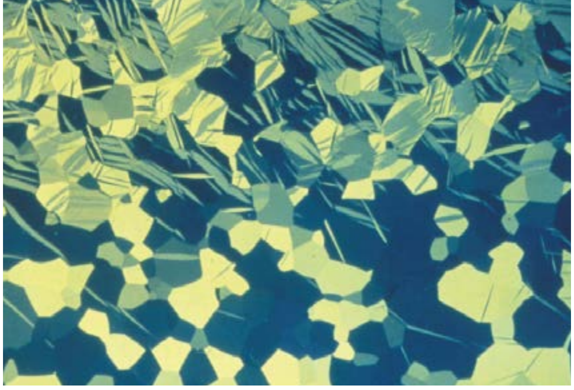


Fig. 9: Grain structure of a commercially pure titanium, polarized light, 100 x

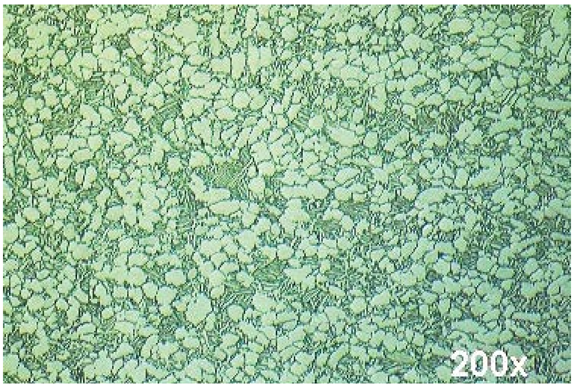


Fig.10: Structure of a forged α-β Ti-6Al-4V, 400 x

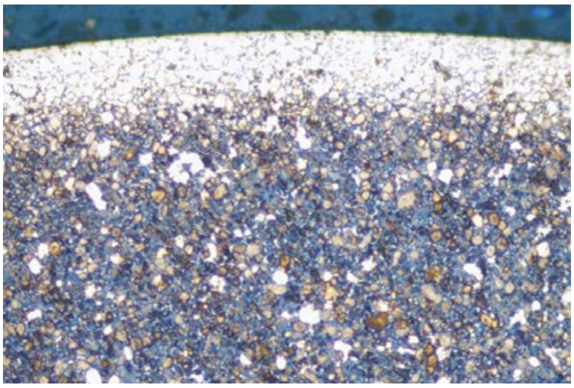


Fig.11: α-β Ti-6Al-4V with a white, brittle "α-case" surface layer, 50 x

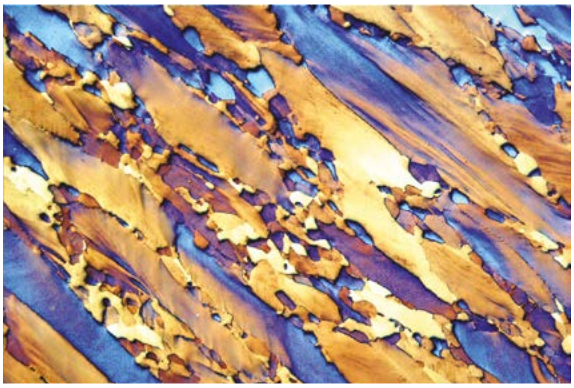


Fig.12: β Ti-15V-3Al-3Sn-3Cr, heat tinted, 50 x

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 α-β Ti-6Al-4V of an orthopaedic implant in the annealed condition, etchant: Kroll's reagent.

Fig.11 shows an α-β Ti-6Al-4V with a white, brittle "α-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, "α-case". This is a very brittle layer and can only be removed mechanically. (Note: α-case does not show up with Kroll's etchant, but with the bifluoride).

Fig. 12 shows the β 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.

Application Notes

Metallographic preparation of titanium

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Acknoledgements:
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.

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Metals Handbook, Desk edition, ASM, 1984

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02.2016 / 62140202 Printed in Denmark