

MSE307 Engineering Alloys 2014-15 L5: Phase Metallurgy of Titanium Alloys

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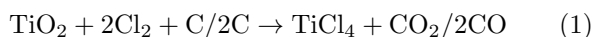
We turn now to a four-lecture primer on titanium alloys. We will focus on titanium *alloys* for high integrity aerospace applications, but will pause briefly towards the end to consider commercially pure (CP) titanium in chemical plant, armour applications and biomedical alloys. The first two lectures focus on the phases and the generation of microstructures through processing, whilst the second two lectures consider mechanical behaviour and fatigue phenomena. For books, the following are recommended

1. Lütjering and Williams. *Titanium*, Springer, 2007.
2. Collings. *The physical metallurgy of titanium alloys*, ASM, 1984.
3. Donachie, *Titanium: A technical guide*, ASM, 2000.

The primary reference is Lütjering and Williams. All three books are in the library.

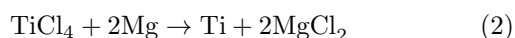
5.1. Production of titanium from the oxide

Titanium is produced by the *Kroll Process*, in which titanium tetrachloride is reduced by magnesium. TiO₂ is the 4th most abundant metallic element in the earth's crust and is usually mined from sand deposits, e.g. in Australia. It is widely used for pigment in everything from paint to cosmetics and so refined white TiO₂ powder is cheap and extremely common. The TiO₂ is then reacted with carbon in chlorine gas;



This is performed in a fluidised bed; the inclusion of carbon in the process acts to provide a thermodynamic boost, reducing the amount of heat that must be supplied. This is more efficient from a CO₂ standpoint than burning fossil fuels in power stations or using natural gas to heat the reaction vessel, and will continue to be so until a CO₂-free source of power is available. The product TiCl₄ is gaseous (boiling point 136°C and so the opportunity is taken to purify the titanium tetrachloride of other metal and titanium chlorides using fractional distillation.

The Kroll process, Figure 1, then reduces this product using flowing magnesium metal at around 800-850°C;



The magnesium chloride salt is then electrolysed to produce Mg and Cl₂, which are then recycled to make a closed-loop process. The Mg is mostly tapped off during the reduction run. At the end of the Kroll process, the Mg and

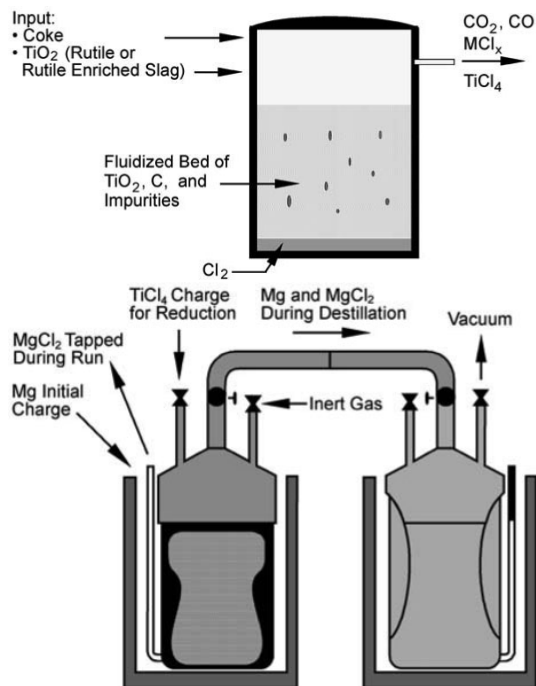


Figure 1: (Top) Schematic of a fluidised bed chlorinator for the production of TiCl₄. (Bottom) Schematic of a Kroll reaction vessel (left), together with (right) a second Kroll vessel for collection of the Mg and MgCl₂ that are removed during vacuum distillation after the main Kroll reduction run. From Lütjering and Williams, Figures 3.1 and 3.3.

MgCl₂ are separated by vacuum distillation. The product Ti is a porous, partially sintered 'sponge' of titanium, Figure 2. It is manually subdivided and crushed to produce particles a few cm in size.

As discussed in the melting and forging lecture, the sponge is then crushed and consolidated into briquettes, which are melted by vacuum arc remelting (VAR), Figure 3. The VAR ingot is then remelted a further two times, prior to breakdown forging to reduce the β phase grain size, followed finally by finish forging, usually in the $\alpha + \beta$ phase field. In practice, there are usually substantially more forging steps than this, but this is an adequate simplified description of the processing.

The Kroll process costs about 125 MWhr/tonne, or about £4/kg at 2003 prices just in power. The production cost is around £6/kg, although the market prices fluctuates significantly depending on market conditions. Over

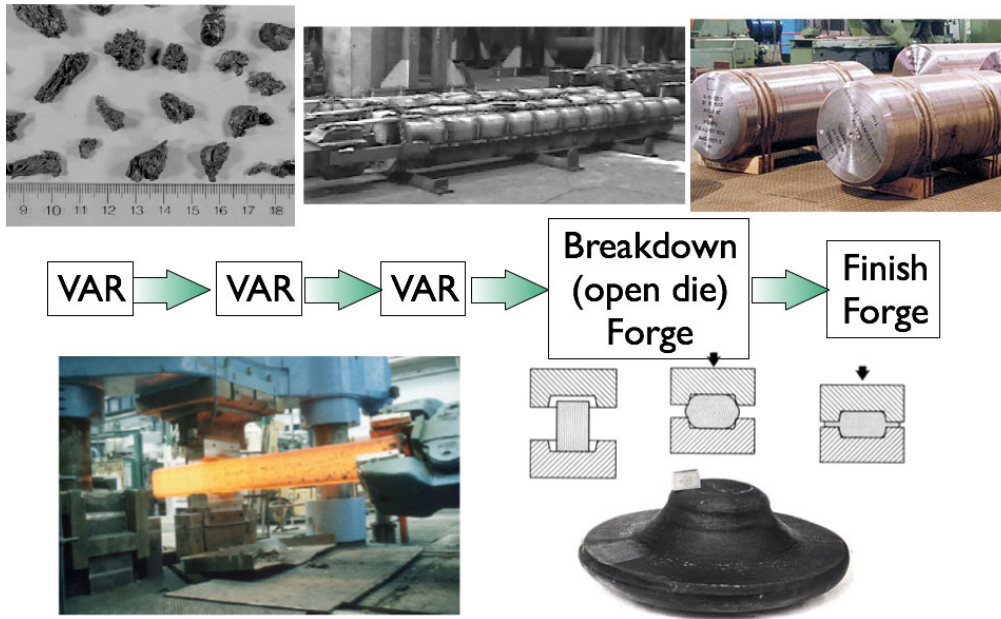


Figure 3: (From top left to bottom right: First the chips from the Kroll process and compacted into briquettes, which are then triple melted to make ingots. After skim machining, these are open die forged, followed by finish forging.



Figure 2: The largest single titanium sponge ever produced, at the 2011 world conference on titanium. Author photo.

70% of Ti production is used in aerospace applications and so, historically, open market Ti prices have varied significantly depending on the state of the aerospace industry. The major aerospace manufacturers have long term supply agreements in place with the titanium producers that mitigate this problem.

Total Kroll titanium production is $\sim 140,000$ t/yr, making this a several \$bn industry. For comparison, a single basic oxygen steelmaking furnace (200t per melt) will produce around $10\times$ this amount of steel per year; titanium manufacturing is a small, batch processing industry, but it is very high value. Typically, a single Kroll cell will produce several tonnes of titanium per run, with each run taking as long as 5 days.

In the Kroll process, the avoidance of the introduction of oxygen or nitrogen into either the Mg or Kroll processes

is critical to the avoidance of high-O/N hard α defects. Given the corrosive Cl environments, this is often challenging for the manufacturers.

There are other processes under active development for the production of titanium. One, the Fray Farthing Chen (FFC) process, involves the direct reduction of TiO_2 by CaCl_2 by electrolysis and is being commercialised by Metalysis, a startup company based in Rotherham. However, there have been many attempts over the decades to reduce the cost of production of titanium metal, and a level of skepticism is probably in order as to whether this can really be achieved. There are, however possibilities for supply chain compression which, together with a low cost titanium powder production route, might make low cost additively manufactured titanium parts possible in the 2020s.

5.2. Titanium phases and microstructures

Pure titanium has two main solid phases at room pressure; a high temperature bcc β phase and a low temperature hcp α phase. There are several archetypal binary phase diagrams which are shown schematically in Figure 4. So-called α stabilisers such as Al, O, N and C raise the transformation (solvus) temperature from the β to the α phase on cooling. Of course, this also opens up a 2-phase region, as required by the Gibbs phase rule. O in particular is a very effective α stabiliser and is always present in titanium alloys to some degree. Typically, very pure Ti will have an O level of around 500 ppmw, whereas heavily O-enriched alloys will have up to 2500 ppmw O.

There are two main groups of β stabilising elements (those which lower the solvus temperature), depending on

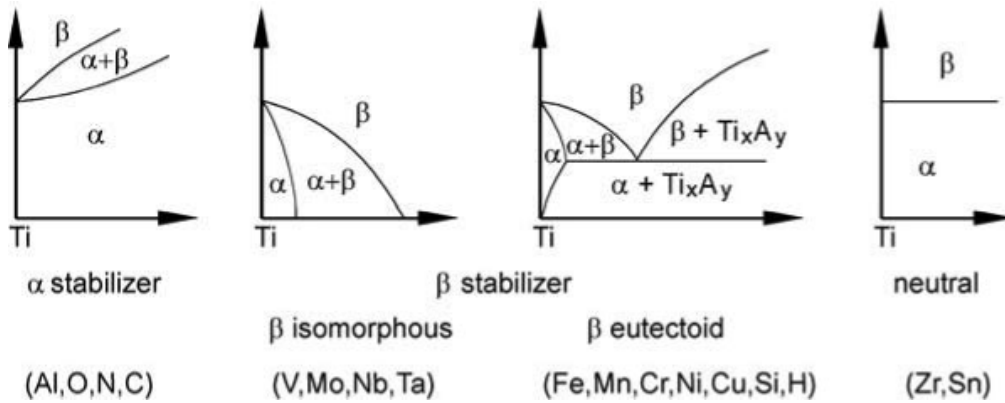


Figure 4: (Schematic archetypal titanium binary phase diagrams, from Lütjering and Williams (Fig 2.10).

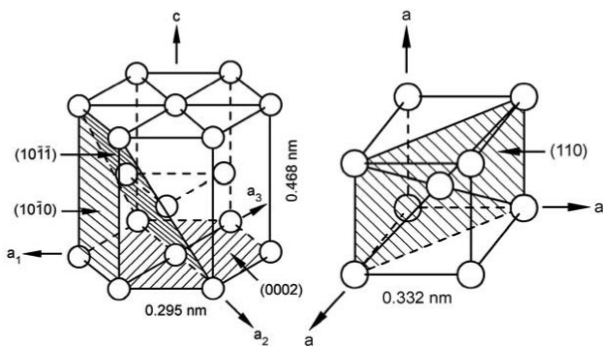


Figure 5: Unit cells of the hcp α (left) and bcc β (right) phases, from Lütjering and Williams (Figs 2.1-2).

the type of phase diagram. So-called isomorphous stabilisers like V, Mo, Nb and Ta open up a wide phase field which continues to widen down to low temperatures. In contrast, β eutectoid-type elements such as Fe, Mn, Cr, Ni, Cu, Si and H all give rise to a eutectoid phase diagram where intermetallics can be formed at excessive cooling rates and/or solute concentrations. These are usually brittle and so in many applications the isomorphous stabilisers are preferred.

Finally, there are the so-called neutral stabilisers, Zr and Sn. These have very little effect on the solvus temperature at low concentrations. Zr forms a continuous solid solution with Ti in both the bcc and hcp phases, as we have seen already in the course. Sn does eventually form a Ti_3Sn phase, however.

The body centred cubic (bcc) β unit cell and the hexagonal close packed (hcp) α phase are shown in Figure 5. The bcc phase has a lattice parameter of 3.3 Å whilst the hcp phase has cell parameters $a = 2.95$ Å and $c = 4.7$ Å. hcp packing is of sequential close packed layers in an ABABAB stacking sequence, as compared to fcc which is ABCABC stacking. The transformation from bcc to hcp occurs through a diffusional rearrangement of the atoms, but the two phases are symmetrically related. The $\{110\}$ planes in the bcc phase are a close match to the basal $\{0002\}$ plane in the hexagonal lattice, with the $\langle 111 \rangle$

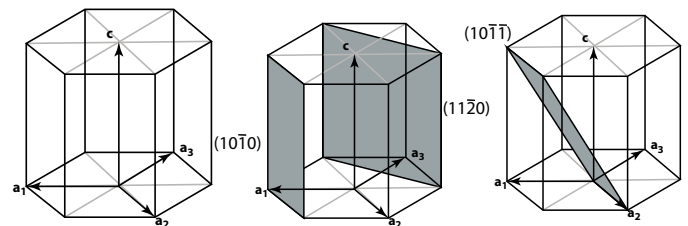


Figure 6: Definition of the lattice vectors in the 4-axis hexagonal notation, together with some sample hcp planes. A lattice vector in 4-axis hexagonal, $r = ua_1 + va_2 + ta_3 + wc$ obeys $u + v + t = 0$ (the same is also true for planes $(hkil)$). In this way, the Weiss zone law $hu + vk + tl + wl = 0$ is preserved.

direction parallel to the $\langle 11\bar{2}0 \rangle$. We can write the orientation relationship (OR) as:

$$\{110\} \parallel \{0002\}, \quad \langle 111 \rangle \parallel \langle 11\bar{2}0 \rangle \quad (3)$$

There are six different $\{110\}$ type planes, and two different $\langle 111 \rangle$ contained in each of these planes, so there are (in total) 12 different ways to satisfy this orientation relationship - each beta grain can give rise to 12 different orientation *variants* of the α phase. We will return to this topic in the next lecture.

The α phase therefore grows from the β in a very crystallographic fashion, Figure 7. First, grain boundary α will form, from which grows α along specific habit planes in the orientation relationship with the β . As it grows into the β , being purer in Ti it will reject solute β stabiliser until the β becomes stable enough to remain in the β phase. Immediately adjacent, another α lath will grow co-operatively - just like pearlite in steels, although a more exact comparison would be with the growth of *Widmanstätten* ferrite in steels. Therefore groups of similarly-oriented alpha grow - *colonies* of α , which eventually fill the grain. Lacking nucleation sites in the β , these will generally grow from the grain boundary.

In heavily β stabilised alloys containing slow diffusing elements, even quite moderate cooling rates may be fast enough that the β doesn't transform fast enough to complete transformation. Then, a second generation of fine

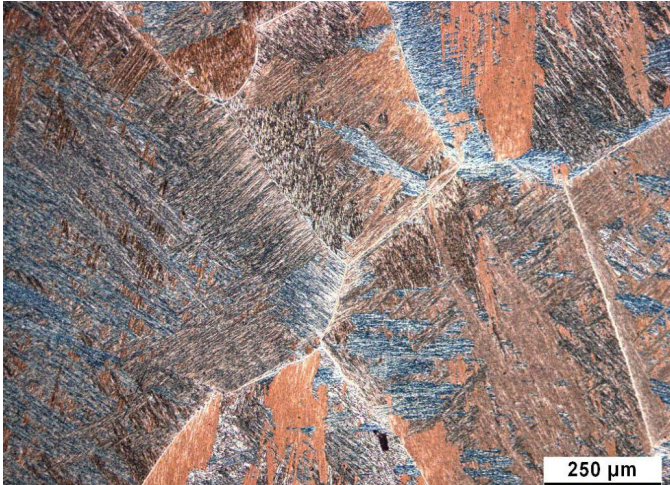


Figure 7: Ti-6246 in the transformed beta or colony microstructural condition (heat treated at 970°C and air cooled).

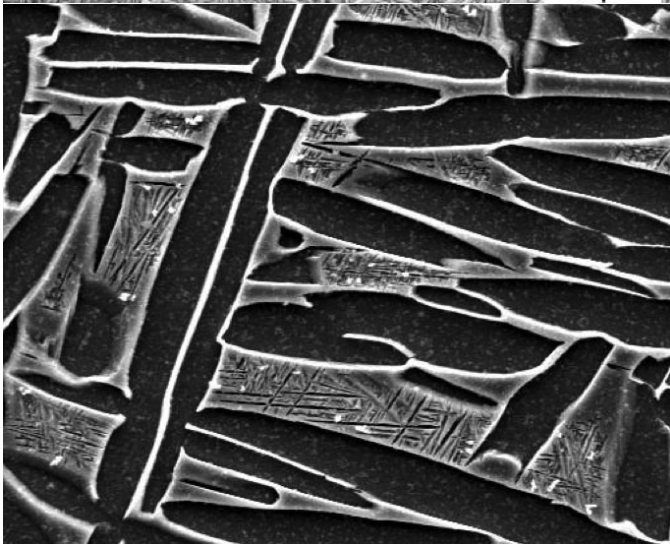
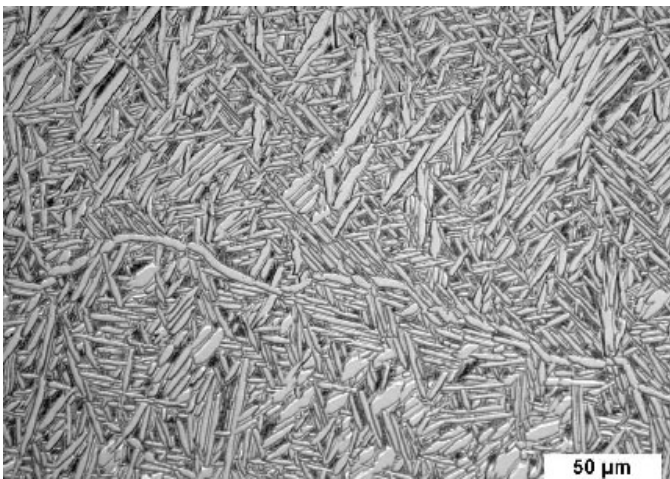


Figure 8: Ti-6246 in heat treated at 910°C, cooled at 2°C per minute to 820°C, held and then air cooled.

scale α can be produced, as in the two-step cooling shown in Figure 10. In comparison to the slowly-grown α laths,

which are a few microns thick, these α are < 100 nm in thickness, and consequently $\alpha - \beta$ microstructures can be produced which have very many interfaces providing high strength and high toughness to the material.

The α/β laths will grow with a particular habit plane, Figure 9. This is

$$\{1\bar{1}00\}_\alpha \parallel \{1\bar{1}2\}_\beta \quad (4)$$

Inspection will verify that $\{1\bar{1}2\} \perp \{110\}$, such that this is saying that the prism planes are the habit planes, perpendicular to the basal plane forming the OR with the β . Therefore the common direction along the habit plane is the $\{1\bar{1}1\} \parallel \{11\bar{2}0\}$.

Turning to consider the deformation mechanisms, recall the 2nd year lab on impact behaviour, where you examined Zn (hcp), iron (bcc) and Al (fcc). You found that Zn was relatively brittle as all temperatures, because it lacked easy c -axis deformation mechanisms. Titanium and zirconium are relatively unusual amongst hexagonal metals in that they are fairly ductile. In Ti the shortest Burgers vector is $\langle 11\bar{2}0 \rangle$ but the highest density atomic plane is the prism $\{10\bar{1}0\}$ plane, because $c/a = 1.57$, less than the ideal for hcp packing of 1.633 (if $c/a > 1.633$ then basal $\{0002\}$ slip would be preferred). Therefore prism $\langle a \rangle$ slip is the preferred slip mode.

However, as there is only one basal plane, despite there being three independent $\langle 11\bar{2}0 \rangle$ slip directions ($[11\bar{2}0]$, $[2\bar{1}\bar{1}0]$ and $[1\bar{2}10]$), only two are linearly independent of each other as only two vectors are required to define any vector in a plane. For general deformation, recall that we need five independent slip systems - a strain tensor has 6

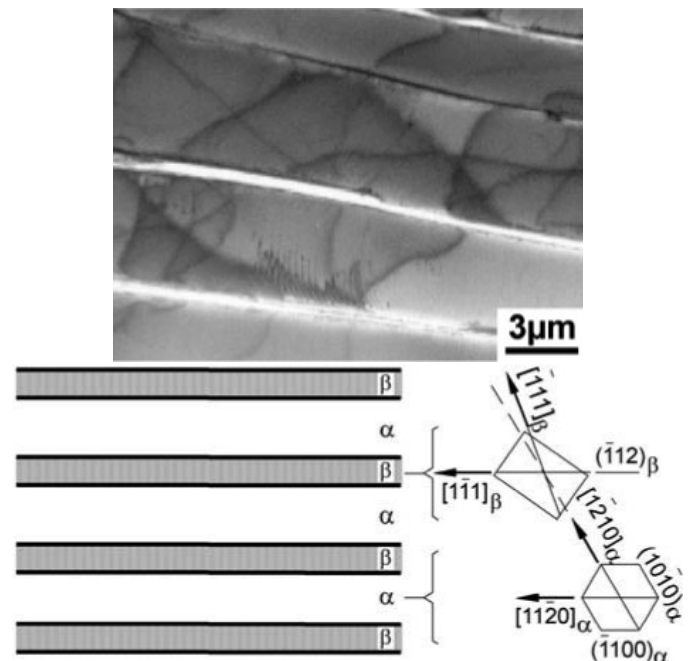


Figure 9: TEM micrograph of α laths grown in a β matrix (in Ti-6Al-4V), and schematic showing the habit plane and orientation relationship. From Lütiering and Williams, Figures 2.17 and 2.18.

independent components, the hydrostatic strain plus five shape changes that can be realised by plasticity (von Mises criterion). Therefore we need three further slip systems involving c -axis deformation in order for our hexagonal crystal to be ductile.

In commercially pure titanium these are provided by twinning, but the conventional wisdom is that alloying α -Ti with Al promotes $c + a$ slip at the expense of twinning, and for this reason nearly all commercial Ti alloys contain ~ 6 wt.% Al. Nevertheless, micro twins are still sometimes observed in alloyed α -Ti, and some workers suggest that twinning may occur during the hot forming of titanium alloys.

For a grain oriented with its c -axis along the loading axis, both $\langle a \rangle$ and pure $\langle c \rangle$ slip would have zero Schmid factor, and so the additional slip systems must be provided by $\langle c + a \rangle$ slip. For the same reason, the slip plane cannot be the $\{10\bar{1}0\}$, and so the actual operative slip mode is found to be the $\langle 11\bar{2}3 \rangle \{11\bar{2}2\}$ - this being preferred to the $\{10\bar{1}1\}$ as this slip plane is closer to 45° from the c -axis.

As the Burgers vector is greater and $U = \frac{1}{2}Gb^2$, this pyramidal $\langle c + a \rangle$ slip has about $3 \times$ greater critical resolved shear stress (CRSS) than prism $\langle a \rangle$ slip. This leads to the finding that only a few grains will actually undergo $\langle c + a \rangle$ slip, but these are vital to the ductility of the alloy.

In β -Ti, the usual bcc slip systems of $\langle 111 \rangle$ along the $\{110\}$, $\{112\}$ or $\{123\}$ planes apply.

Therefore, titanium is quite plastically anisotropic; there are hard-oriented and soft-oriented grains. In addition, in a lamellar structure, there will be one $\langle 11\bar{2}0 \rangle_\alpha$ that is near parallel to a $\langle 111 \rangle_\beta$ (Figure yy), and so one di-

Type	Slip Direction	Slip Plane	# Slip Systems Total	# Slip Systems Independent
$\langle a \rangle$	$\langle 11\bar{2}0 \rangle$	$\{0002\}$	3	2
$\langle c + a \rangle$	$\langle 11\bar{2}3 \rangle$	$\{11\bar{2}2\}$	6	5

Table 1: Preferred slip modes in the hexagonal α phase.

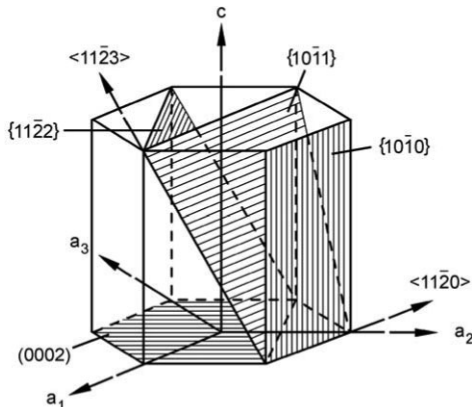


Figure 10: Unit cell of the α phase showing the slip planes and slip directions occurring. From Lütjering and Williams, Figure 2.6.

rection in which this composite is relatively permeable to dislocations, whereas all other directions will be hard.

5.3. Binary phase diagrams

We turn now to look at some real binary phase diagrams in the titanium system, Figure 11. First, Ti-Al is an alpha stabiliser and raises the β solvus temperature. It doesn't however, ever give rise to a very wide two phase $\alpha + \beta$ field - which is desired for forging operations. In addition, beyond about 6 or 7 wt.% Al (~ 12 at.%), we enter the two phase $\alpha + \alpha_2$ -Ti₃Al region at temperatures of around 550–650°C, which is sufficiently high that, at long ageing times, α_2 can form. This is significant as α_2 formation is generally considered to be undesirable as it is thought to give rise to a loss in ductility and fatigue resistance, as we shall see later.

In addition, notice the γ -TiAl phase, which is the basis for gamma titanium aluminides. These are being introduced into jet engine applications after more than 30 years' development as high temperature materials in the 450-650°C range, where they have better density-corrected strengths than nickel superalloys but do not suffer from problems of burn resistance like titanium alloys. One issue in their development has been that the high temperature equilibria around 1100-1200°C with the α_2 phase have been quite tricky to determine.

Turning to the Ti-Sn diagram, we see that Sn has almost no effect on the β solvus, and so tin is termed a neutral stabiliser. Hence it is quite widely used in titanium alloys for solution strengthening of the α phase. However, notice that there is a Ti₃Sn phase. It is found that Sn will tend to segregate to the Al site in the Ti₃Al α_2 phase, which we have already noted is usually undesirable. Therefore Sn levels in titanium alloys are usually limited to a few wt.%.

Mo is the archetypal isomorphous β stabiliser, having a dramatic effect on the β solvus temperature. Notice that at low temperatures, because Mo is a slow diffuser, the binary phase diagram is not provided. In addition, the solubility of Mo in α -Ti is very small - which is why it is a strong β stabiliser.

Cr is occasionally used, along with Fe, as a cheaper alternative β stabiliser than Mo, and at a lower density penalty. However, these have β eutectoid phase diagrams. So, whilst Cr reduced the β solvus and has limited solubility in the β phase, there is a eutectoid with the α TiCr₂ phase. Therefore enough other β stabilisers - such as Mo - must also be included to stabilise the β phase to room temperature, suppressing formation of the intermetallic phase.

5.4. Beta stabilisation

A ready-reckoner exists for summing-up the overall extent of β stabilisation that different β stabilisers contribute in a complex alloy. This is based upon establishing how much of each element is required to stabilise the β phase to room temperature on quenching model binary alloys,

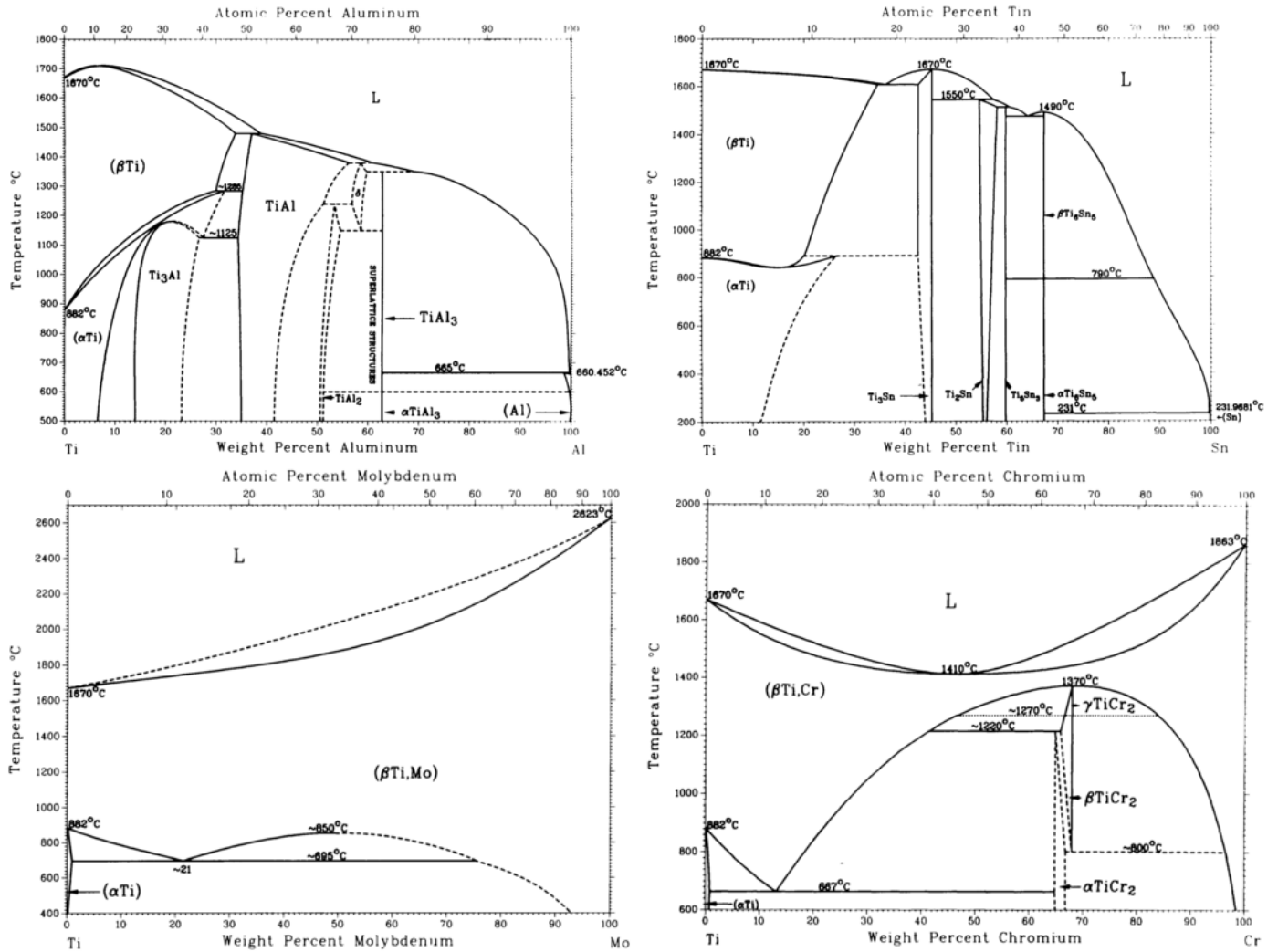


Figure 11: The Ti-Al, Ti-Sn, Ti-Mo and Ti-Cr binary phase diagrams, from the ASM handbook.

	V	Nb	Ta	Cr	Mo	W	Mn	Fe	Co	Ni
wt. %	15	36	50	8	10	25	6	4	6	8
at. %	14	23	21	7.4	5.2	8	5.3	3.4	4.9	6.6

Table 2: Concentration of β stabilising elements required to retain the β phase on quenching to room temperature in binary Ti alloys.

shown in Table 2. Normalising with respect to Mo gives rise to the following formula, for use with concentrations in wt. %;

$$\begin{aligned}
 \text{Mo}_{\text{eq}} = & [\text{Mo}] + & (5) \\
 & 2.5[\text{Fe}] + 1.7[\text{Co}] + 1.7[\text{Mn}] + 1.25[\text{Ni}] + 1.25[\text{Cr}] + \\
 & 0.67[\text{V}] + 0.4[\text{W}] + 0.28[\text{Nb}] + 0.2[\text{Ta}]
 \end{aligned}$$

Hence, it takes only 4 wt. % Fe to ‘fully stabilise’ the β , compared to 10 wt. % Mo, so Fe is $2.5\times$ as effective as Mo, as indicated in the formula. Therefore, according to the formula, a so-called ‘Mo equivalence’ of 10 would be required to produce an alloy in which the β phase was completely retained on quenching and would then be at

least metastable at room temperature.

Of course, this is a very idealised view of how alloying elements interact. It was inspired by the concept of carbon equivalence in steels, which examine the stability with respect to martensite formation as it applies to welds and hydrogen embrittlement of martensitic steel welds - and these sorts of ideas are generally found to be very good rules of thumb when working with alloys.

5.5. α_2 Ti_3Al

The Ti_3Al phase has arisen several times so far, so we turn now to briefly examine this phase. It is an ordered superstructure of the hcp α Ti lattice. 2×2 conventional unit cells of hcp α Ti are shown in the figure, with crystal structure hP3, $P6_3/mmc$. It is made up of stacked ABAB close packed layers, Figure 12.

If 1 in 4 on the Ti atoms are replaced with Al, and these are placed so as to create no Al bonds, the cell in Figure 12 is found. This is a DO_{19} , hP8 structure, again with a $P6_3/mmc$ space group - but now this is the conventional unit cell, not $2\times$ units of it.

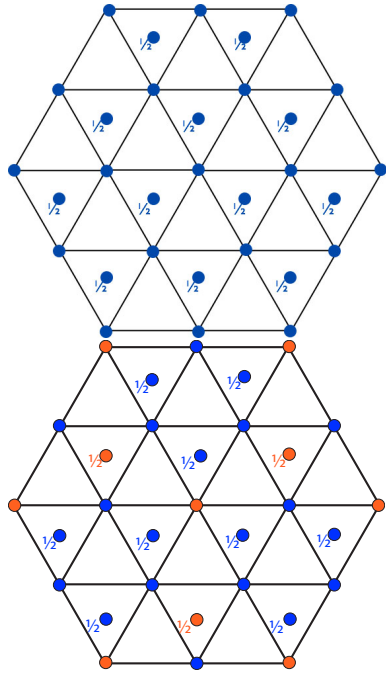


Figure 12: (Top) 2×2 of the hcp (A3 or hP3, $P6_3/mmc$) α Ti crystal structure. (Bottom) A single conventional unit cell of the α_2 crystal structure (DO_{19} or hP8, again with $P6_3/mmc$).

Therefore it is possible to imagine taking α -Ti containing 25 at.% Al, randomly distributed on the lattice, and observing it order into the α_2 lattice, without any long-scale diffusion taking place. Of course, in a real titanium such high Al concentrations will not be found, and so to form α_2 some clustering of the Al atoms must take place for the α_2 phase to form - a spinodal decomposition. Alternately, it might be possible for Ti of only 11 at.% Al to order and form two sublattices - this topic is still a topic of current research. Either way, in alloys with > 8 wt.% Al, Ti_3Al α_2 formation has been observed many times.

When titanium alloys that have been aged to contain α_2 are deformed, lower ductility is observed. In the TEM, the dislocations are observed to travel in pairs, Figure ?? and to shear the α_2 ; these are still $\langle a \rangle$ -type dislocations gliding on the prism planes, but they are seen to travel in pairs.

To consider why this must be so, consider Figure 14. If an $a/3 \langle 11\bar{2}0 \rangle$ α -Ti dislocation is passed that moves the atoms on the central row in the figure, then the structure is disrupted and a stacking defect occurs - the full dislocation in the superstructure would be double that length. Therefore we must pass these α -Ti dislocations through the α_2 phase in pairs in order to avoid creating stacking defects, just like in Ni superalloys. This situation is called Type I shear.

However, now consider passing that same $a/3 \langle 11\bar{2}0 \rangle$ α -Ti dislocation through the structure one row of atoms further up, termed Type II shear. Now, the stacking defect also creates Al-Al bonds. The whole point of forming the Ti_3Al superstructure was that we avoided Al-Al bonds,

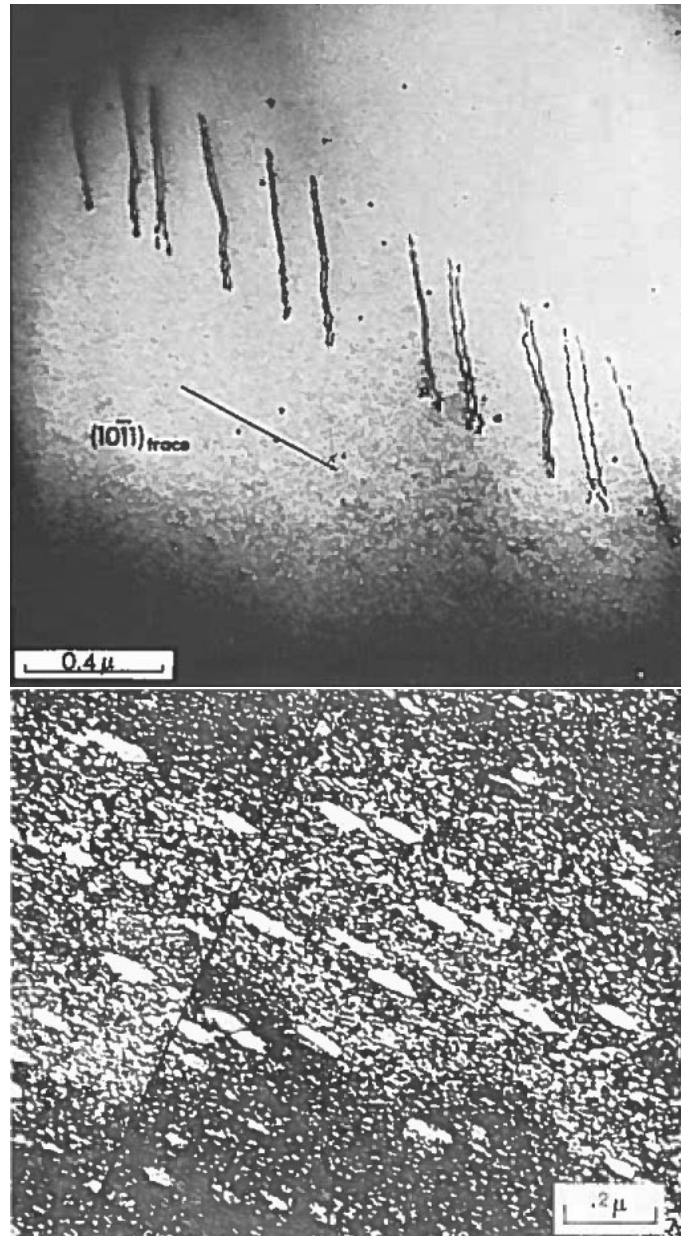


Figure 13: (Top) Example of dislocations in deformed Ti-8 wt.% Al, aged at $500^\circ C$. (Bottom) Example of α_2 precipitation in aged Ti-8.65 wt.% Al, where the particles have been sheared by deformation. Both from Blackburn and Williams, 1967.

presumably because these are energetically unfavourable compared to Al-Ti bonds (c.f. Enthalpy, MSE104 regular solution model). So this stacking defect must be much more energetic, and so Type I shear is preferred.

Therefore, the presence of the α_2 phase in the alloy leads to dislocations travelling in pairs, and to only alternate slip planes being available. Therefore, once slip begins on a particular plane, it is supposed to localise on that plane - more dislocation pairs keep gliding on that particular plane rather than on others. Therefore work hardening caused by dislocation tangling (forest hardening) does not occur, and so the alloy will not be ductile

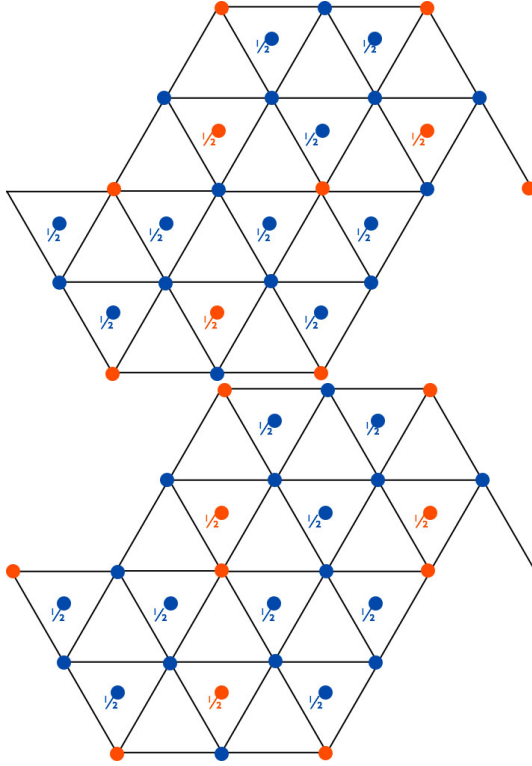


Figure 14: (Top) Type I and (Bottom) Type II shear in $\text{Ti}_3\text{Al } \alpha_2$. Passing a single $a/3 \langle 11\bar{2}0 \rangle$ α Ti dislocation creates a stacking defect in each case, but in the case of Type II shear, where Al-Al bonds are created, it is more more energetic.

according to Considère's criterion. On the fracture plane, the fracture mechanism is observed to be microvoid coalescence and growth, not cleavage, but the lack of work hardening has given rise to strain localisation.

This is actually a general point; it is very important in engineering microstructures of materials at the nanoscale not to create mechanisms by which the localisation of deformation can occur. When it does, this generally leads to a catastrophic loss of ductility.

This mechanism is the reason why α_2 phase formation is generally considered to be undesirable in titanium alloys.

5.6. Alpha stabilisation

Finally, there is a similar ready-reckoner for the degree of alpha stabilisation of an alloy, the aluminium-equivalence (in wt.%);

$$\text{Al}_{\text{eq}} = [\text{Al}] + \frac{1}{6}[\text{Zr}] + \frac{1}{3}[\text{Sn}] + 10[\text{O} + \text{C} + 2\text{N}] \quad (6)$$

This equation, due to Rosenberg, attempts to focus on the effect of α stabilisers on the solvus, but also the effect on the α phase boundary. Notice that Sn, is included, as when combined with Al, it acts to stabilise the α phase, whilst on its own it is neutral. Hence, there are limits to the utility of binary diagrams in understanding multicomponent systems.

The other thing to notice in this equation is that O is an extremely effective α stabiliser, which reinforces the problem with the avoidance of hard α defects arising prior to melting.

Often, both α and β stabilisers will be used. This acts to increase the size of the $\alpha + \beta$ phase field, widening the temperature interval over which $\alpha + \beta$ forging can be performed. Of course, this also permits more solid solution strengthening to be utilised in each phase.

Generally, it is said that Zr, Hf and Sn raise the α/β transformation temperature but do not affect the fraction very much. It is said that the Al-equivalence should be kept below 10 to avoid the production of Ti_3X hcp α_2 , but there are many exceptions to this guideline.

5.7. Summary

In this lecture we have introduced Ti alloys. We have found that titanium is expensive and time consuming to produce. It is truly a multi-\$bn cottage industry, with only a few suppliers in the world. The key feature of the phase metallurgy is the α/β phase transformation, which dominates the microstructures produced. We have divided the alloying elements into β stabilisers (Mo, Fe and others), and α stabilisers (Al, O and friends), and we have had an interesting discussion about the crystallography and deformation mechanisms, and the effect of the α_2 phase.

— END OF LECTURE —