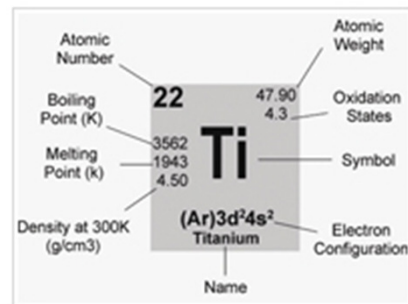


# Titânio e suas ligas

André Paulo Tschiptschin



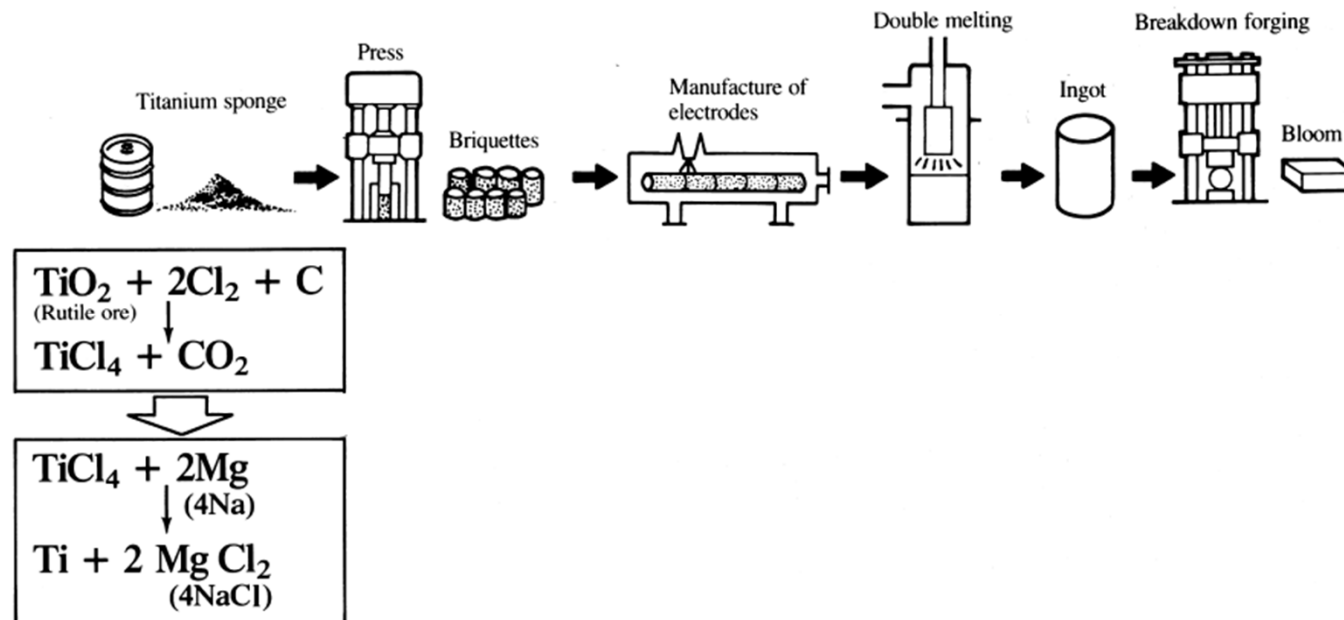


# Titânio - obtenção

- Identificado como um novo elemento metálico por Gregor, na Inglaterra, em 1791.
- Sua produção era muito difícil devido à forte tendência a reagir com oxigênio e nitrogênio.
- Somente em meados do século 20 (1938 a 1940) foi desenvolvido processo comercial de obtenção de titânio.
- Somente na segunda metade do século 20 começou a ser utilizado como liga industrial e em projetos.

# Processo Kroll

- Desenvolvido em Luxemburgo  $\Rightarrow$  redução do tetracloreto de titânio com magnésio em um atmosfera de gás inerte.
- Obtenção de titânio na forma de esponja.





# Propriedades

- Metal de baixa densidade ( $\rho_{Al} < \rho_{Ti} < \rho_{Fe}$ ) cerca de 60% da densidade do ferro.
- Limite de resistência equivalente ao de aços. martensíticos de menor resistência. Limites de escoamentos entre 500 MPa e 1100 MPa.
- Pode ser usado em temperaturas entre 540°C e 600 °C.



Fig. 1.1 SR71 aircraft: first use of beta alloys in aerospace structures. Courtesy Lockheed California Co.

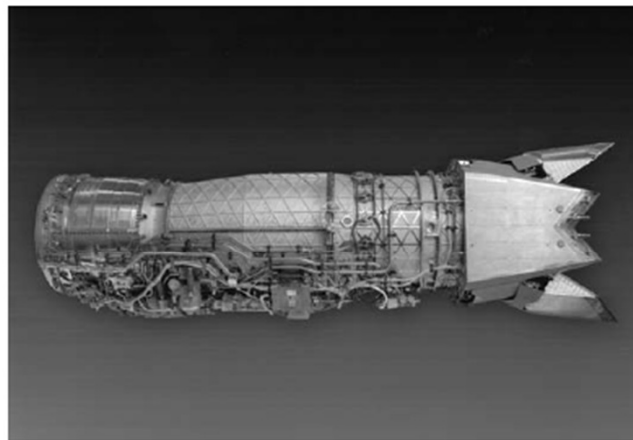


Fig. 1.2 F119 engine by Pratt & Whitney powering the F22 Raptor aircraft





# Resistência à corrosão

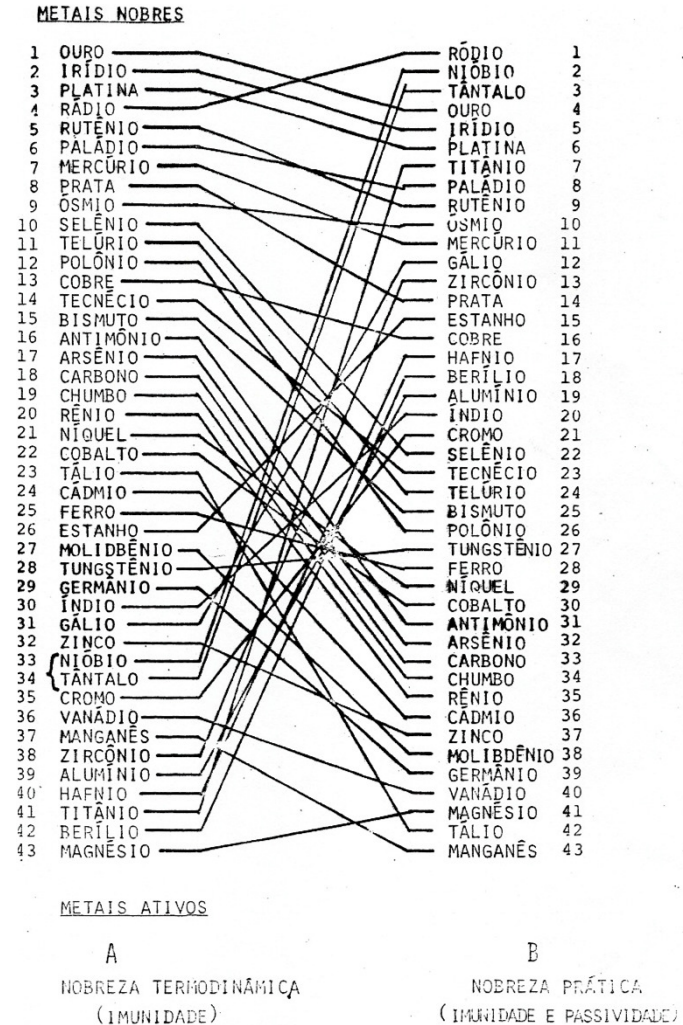
- O Titânio é muito resistente à corrosão. Sua resistência à corrosão é melhor que a do aço inoxidável na maioria dos ambientes.
- Muito boa biocompatibilidade no corpo humano.
- O titânio é imune aos fluidos corpóreos contendo cloretos e pH tendendo para o ácido.





# Escala de nobreza prática

- Ti forma película passiva de  $TiO_2$  que torna as ligas nobres se considerarmos a escala de nobreza prática.
- Utilização em reatores químicos e implantes cirúrgicos.



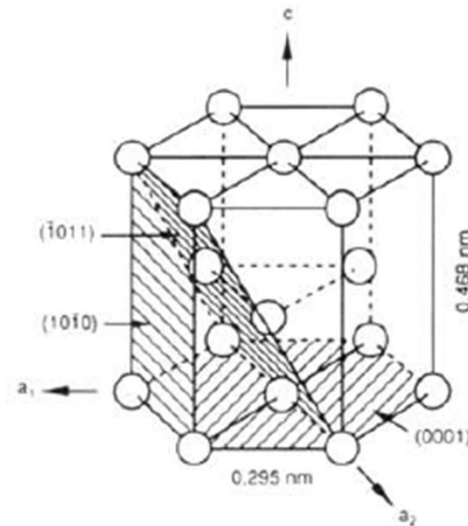


# Propriedades de fabricação

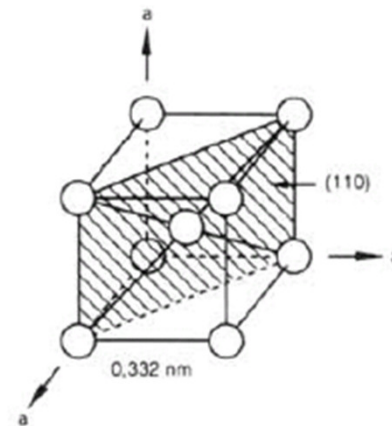
- Pode ser forjado ou trabalhado por técnicas convencionais.
- Apresenta boas propriedades de fundição.
- Metalurgia do pó.
- Boa soldabilidade.
- Usinabilidade muito difícil, requer técnicas especiais de usinagem.

# Transformações de fase

- Titânio sofre transformação de fase a  $882^{\circ}\text{C}$  passando de fase  $\beta$  (CCC) estável em alta temperatura para fase  $\alpha$  (HCP) estável em baixa temperatura.



a) hcp  $\alpha$  phase



b) bcc  $\beta$  phase

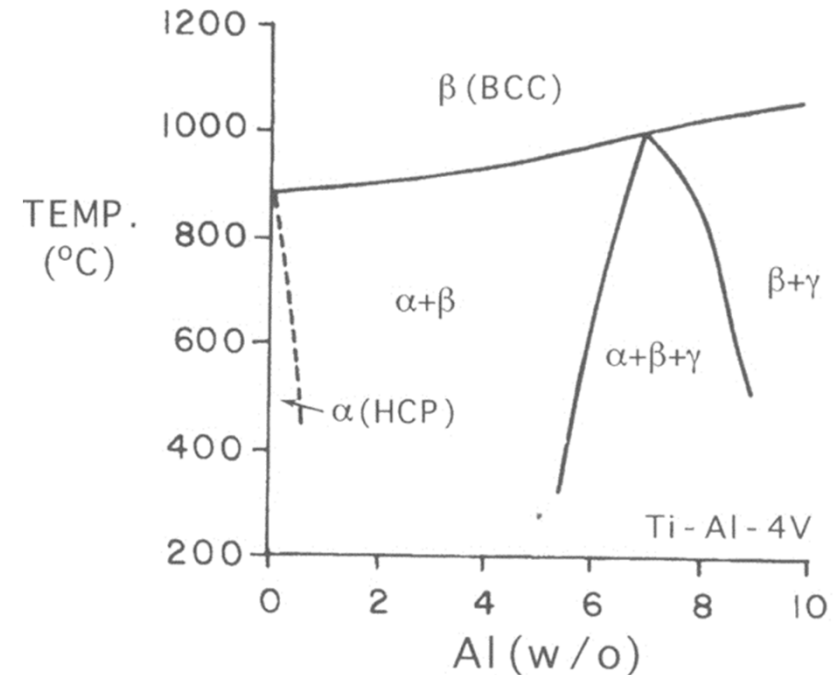




METMAT

# Transformações de fase

- A temperatura de transformação pode ser aumentada ou diminuída pela adição de elementos de liga
- Duas temperaturas são importantes:
  - Alfa transus, abaixo da qual a liga é totalmente alfa
  - Beta transus, acima da qual a liga é totalmente beta
  - Entre as duas temperaturas as ligas são ( $\alpha+\beta$ )

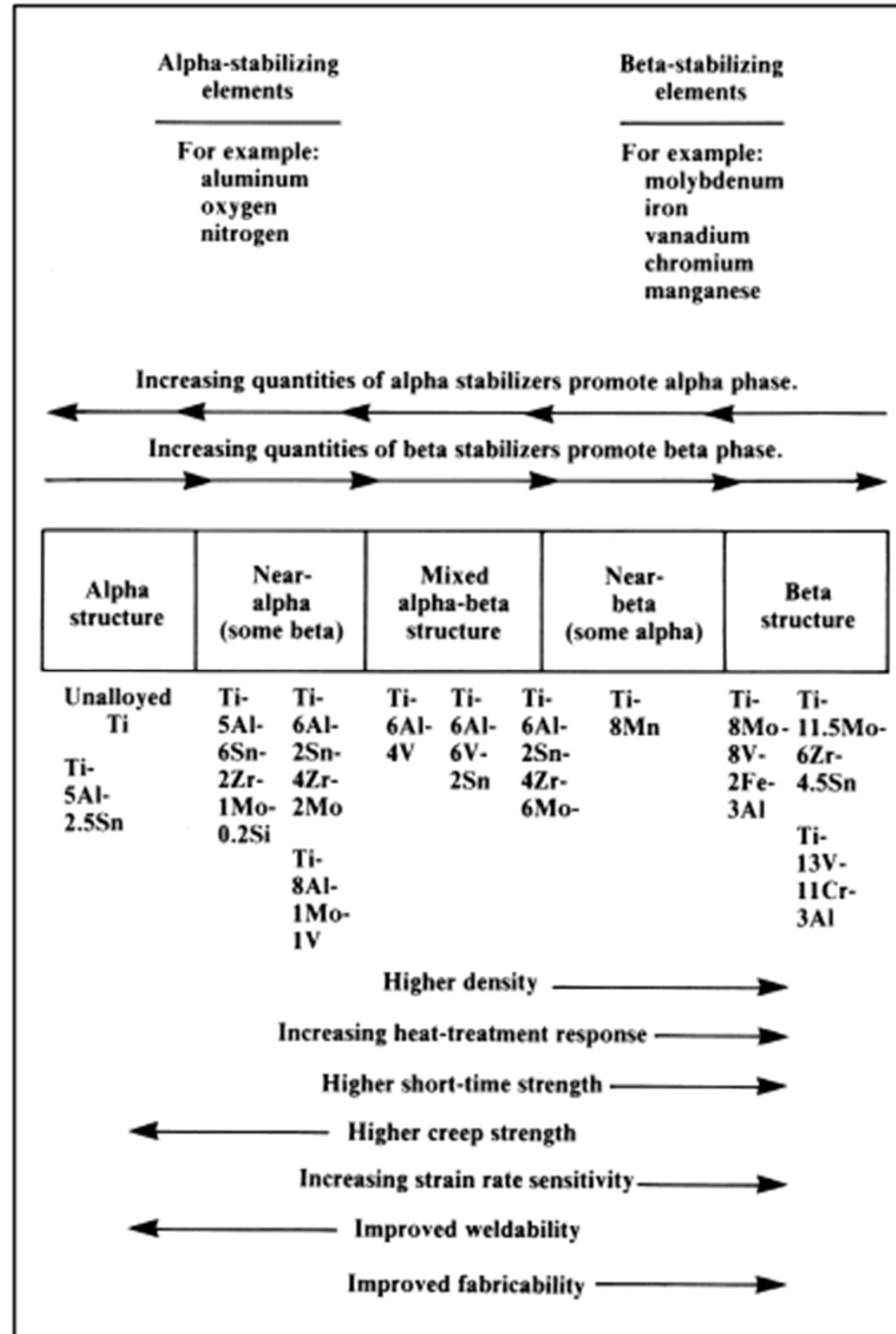


Part of phase diagram of Ti-Al-V at 4 w/o V [Smith and Hug



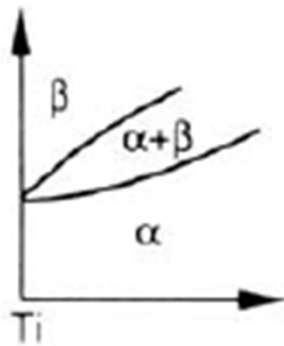
# Classes de titânio

- As ligas de titânio podem ser classificadas em quatro classes, de acordo com a sua microestrutura
  - Alfa
  - Próximo de alfa (near alpha)
  - Alfa-beta
  - Beta



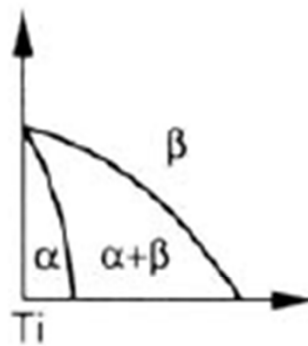
# Transformações de fase

- Efeito dos elementos de liga nos diagramas de equilíbrio Ti-X.



$\alpha$  stabilizer

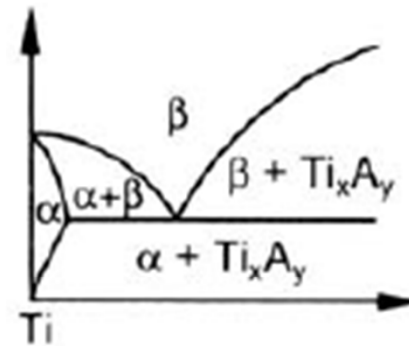
(Al,O,N,C)



$\beta$  stabilizer

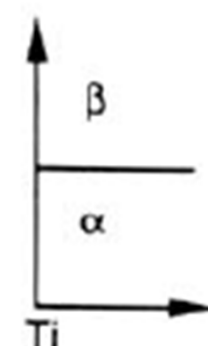
$\beta$  isomorphous

(V,Mo,Nb,Ta)



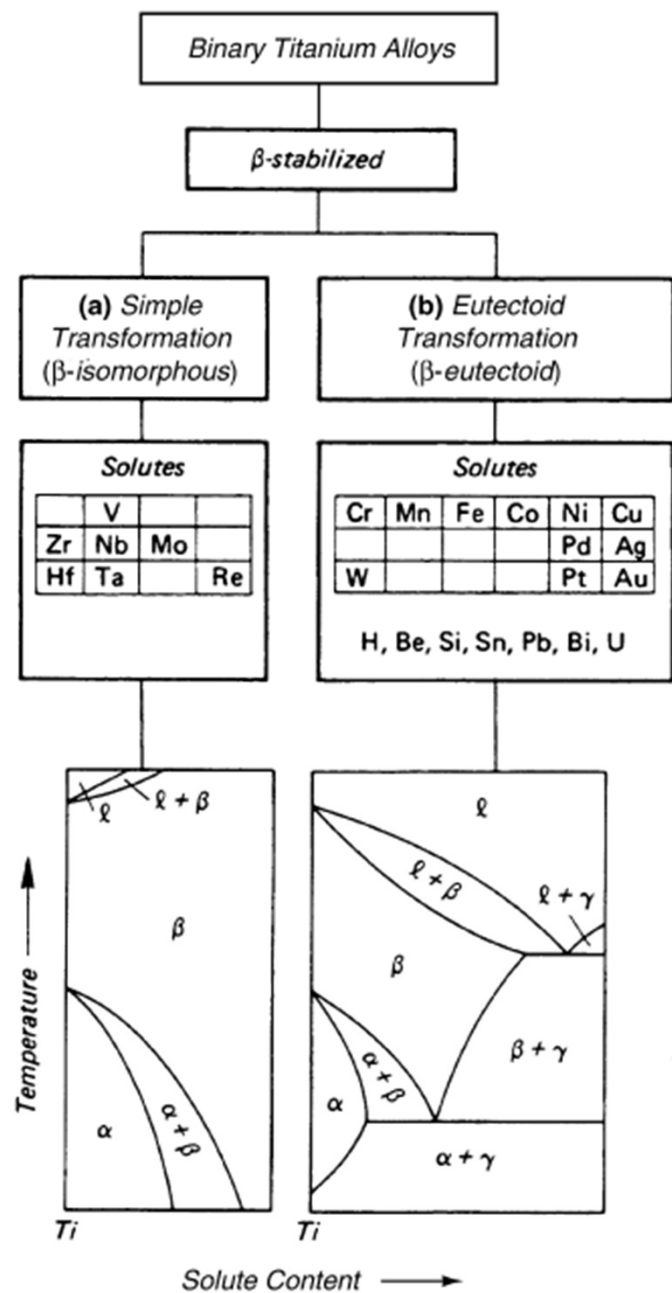
$\beta$  eutectoid

(Fe,Mn,Cr,Co,Cu,Si,H)



neutral

(Zr,Sn)



**Fig 3.13** Phase diagram schematics for beta-stabilized alloys (a) beta isomorphous and (b) beta eutectoid

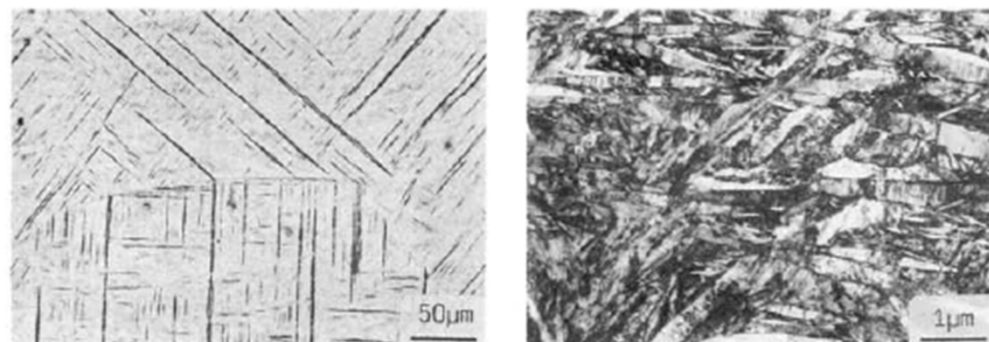


Fig. 7: "Acicular" martensite in Ti-6Al-4V quenched from the β phase field.

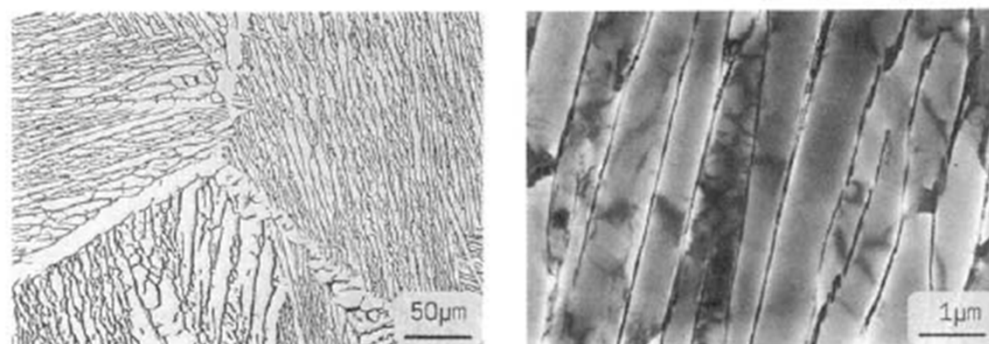
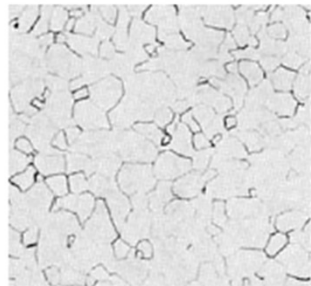
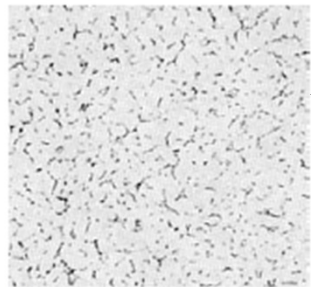


Fig. 8: Lamellar α+β microstructure in Ti-6Al-4V slowly cooled from the β phase field.





(a)



(b)

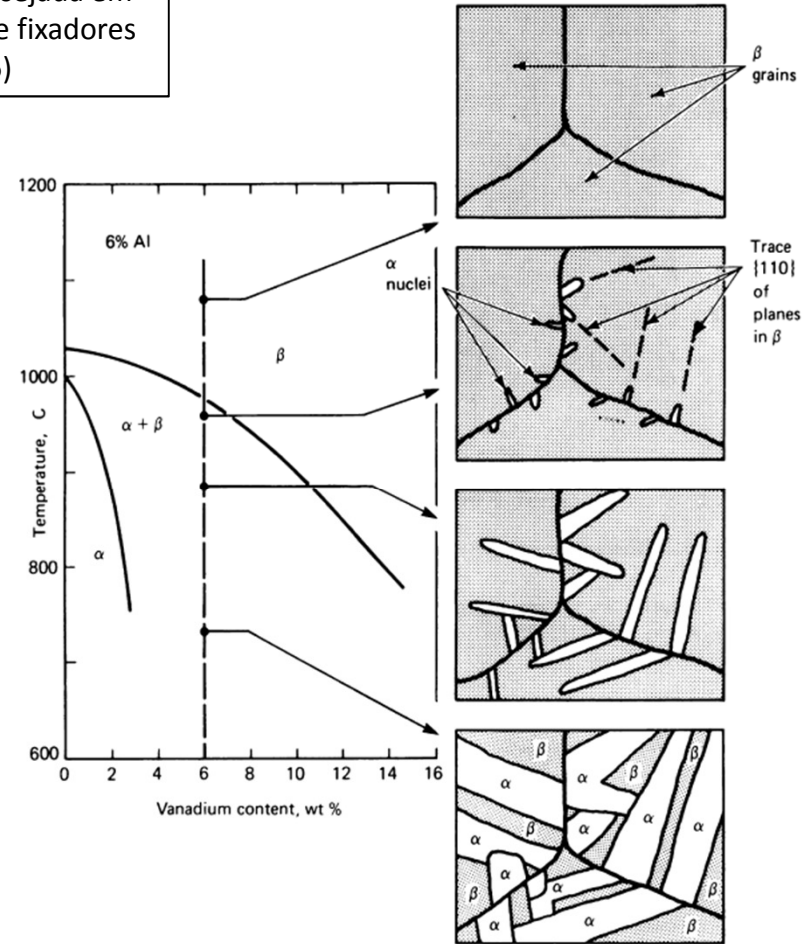


(c)



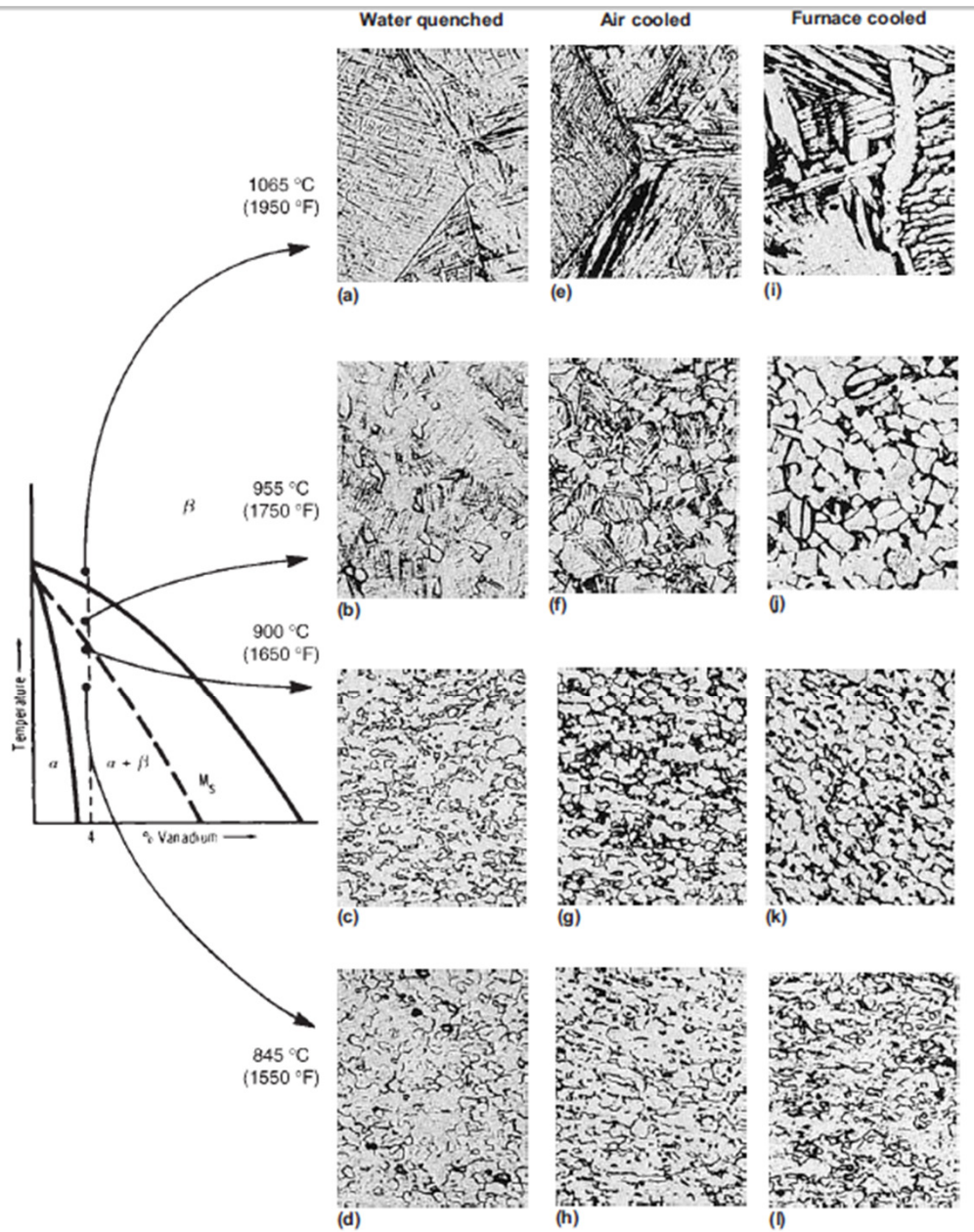
(d)

Microestrutura desejada em parafusos, placas e fixadores de ligas de Ti ( $\alpha+\beta$ )

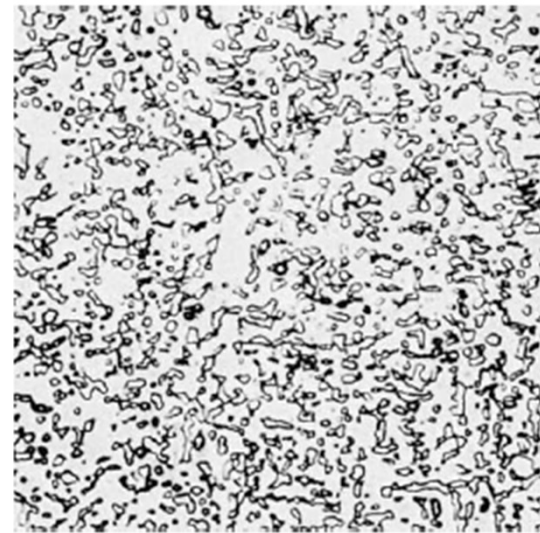


Microstructures achieved at various intermediate temperatures by slowly cooling from above the  $\beta$  transus. Final microstructure consists of plates of  $\alpha$  (white) separated by the  $\beta$  phase (dark).

**Fig. 3.2** Typical microstructures of alpha, alpha-plus-beta, and beta titanium alloys. (a) Equiaxed  $\alpha$  in unalloyed Ti after 1 h at 699 °C (1290 °F). (b) Equiaxed  $\alpha + \beta$ . (c) Acicular  $\alpha + \beta$  in Ti-6Al-4V. (d) Equiaxed  $\beta$  in Ti-13V-11Cr-3Al

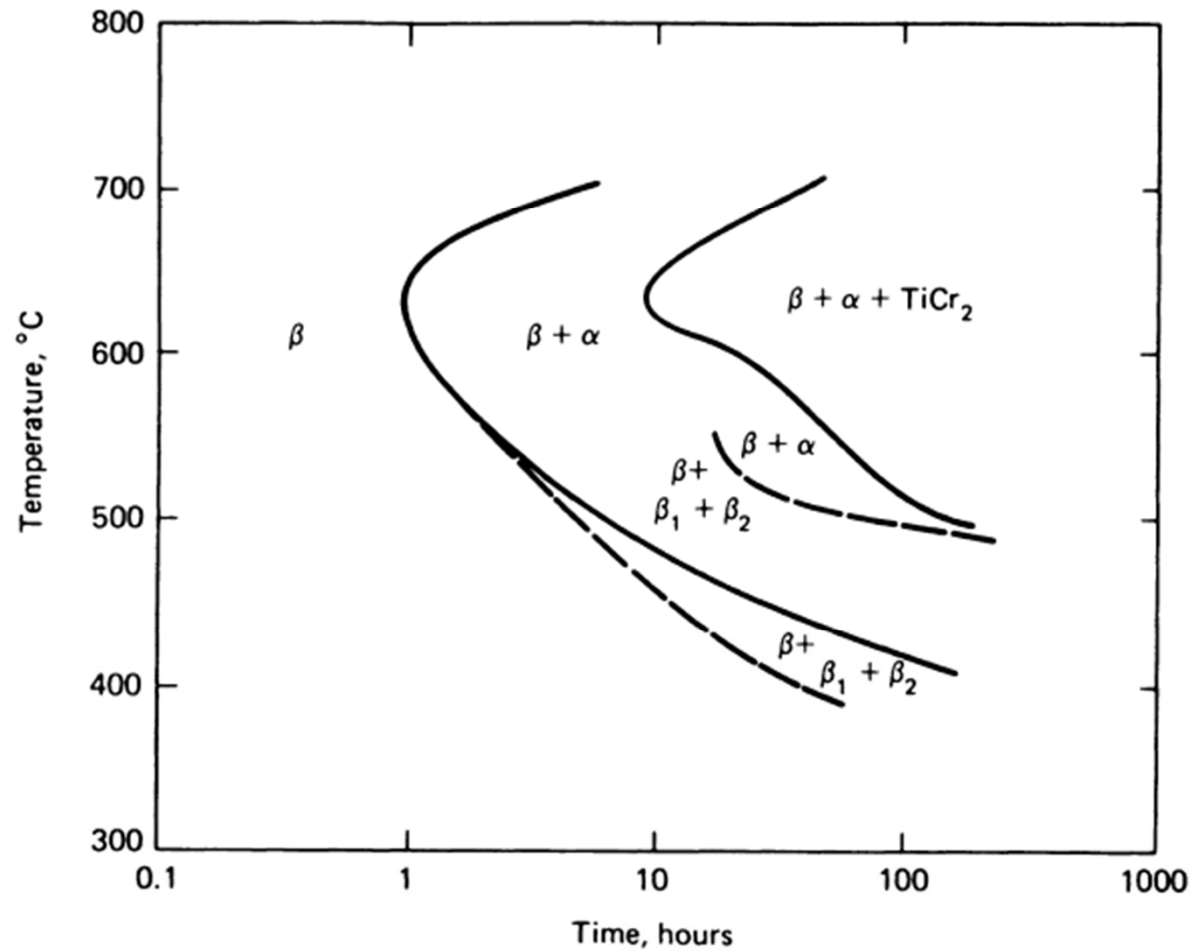


**Fig. 3.11** Effect of cooling rate on the microstructure of an alpha-beta alloy (Ti-6Al-4V). (a)  $\alpha' + \beta$ ; prior beta grain boundaries. (b) Primary  $\alpha$  and  $\alpha' + \beta$ . (c) Primary  $\alpha$  and  $\alpha' + \beta$ . (d) Primary  $\alpha$  and metastable  $\beta$ . (e) Acicular  $\alpha + \beta$ ; prior beta grain boundaries. (f) Primary  $\alpha$  and acicular  $\alpha + \beta$ . (g) Primary  $\alpha$  and acicular  $\alpha + \beta$ . (h) Primary  $\alpha$  and  $\beta$ . (i) Plate-like  $\alpha + \beta$ ; prior grain boundaries. (j) Equiaxed  $\alpha$  and intergranular  $\beta$ . (k) Equiaxed  $\alpha$  and intergranular  $\beta$ . (l) Equiaxed  $\alpha$  and intergranular  $\beta$ . Etchant: 10 HF, 5 HNO<sub>3</sub>, 85 H<sub>2</sub>O. 250x



**Fig. 3.12** Structure of mill-annealed alpha-beta alloy (Ti-6Al-4V). Structure is globular particles of  $\beta$  in a matrix of  $\alpha$ . Optical micrograph. ~500x





**Fig. 3.14** Time-temperature transformation diagram for a beta alloy (Ti-1 3V-11Cr-4Al). Alloy was initially solution treated in the  $\beta$  region for 2 h at 760 °C (1400 °F); then air cooled at 25 °C (77 °F); then aged.

# Endurecimento da fase $\beta$

## Fases $\omega$ e $\beta'$

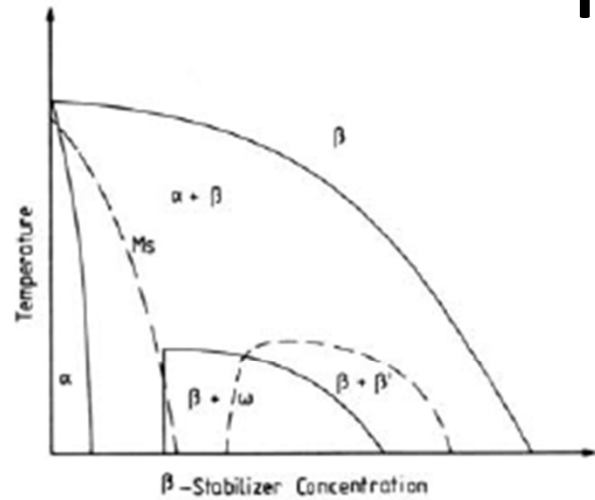


Fig. 11: Metastable  $\beta + \omega$  and  $\beta + \beta'$  phase fields within  $\beta$ -isomorphous equilibrium phase diagram (schematically).

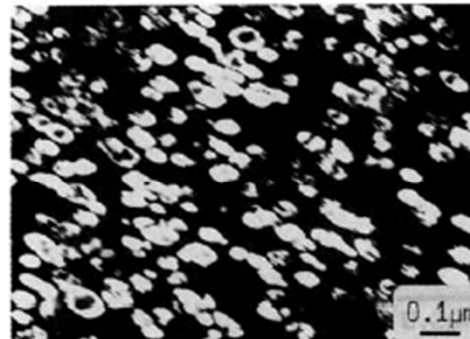


Fig. 12: Dark field micrograph of  $\omega$  precipitates in the Ti-16Mo alloy aged for 48h at 450°C (TEM).



Fig. 13: Bright field micrograph of  $\alpha$  platelets in the Ti-alloy  $\beta$ -CEZ aged for 8h at 580°C (TEM).



# Transformação $\beta$ (CCC) $\Rightarrow$ $\alpha$ (HCP)

- Relação cristalográfica:

$$\begin{aligned} \{110\}_{\beta} // (0002)_{\alpha} \\ \langle 111 \rangle_{\beta} // \langle 1120 \rangle_{\alpha} \end{aligned}$$

- A fase  $\beta$  pode transformar para 12 variantes hexagonais com diferentes orientações.
- A transformação pode ser martensítica ou por nucleação e crescimento controlado por difusão.



# Martensitas atérmicas

- Martensita  $\alpha'$  hexagonal
  - Massiva ou em ripas em ligas muito diluídas
  - Acicular em ligas mais carregadas de elementos
- Martensita  $\alpha''$  ortorrômbica

Table 2.2 Some commercial and semicommercial grades and alloys of titanium

Designation	Tensile strength (min)		0.2% yield strength (min)		Impurity limits, wt% (max)					Nominal composition, wt%				
	MPa	ksi	MPa	ksi	N	C	H	Fe	O	Al	Sn	Zr	Mo	Others
<b>Unalloyed grades</b>														
ASTM grade 1	240	35	170	25	0.03	0.08	0.015	0.20	0.18	...	...	...	...	...
ASTM grade 2	340	50	280	40	0.03	0.08	0.015	0.30	0.25	...	...	...	...	...
ASTM grade 3	450	65	380	55	0.05	0.08	0.015	0.30	0.35	...	...	...	...	...
ASTM grade 4	550	80	480	70	0.05	0.08	0.015	0.50	0.40	...	...	...	...	...
ASTM grade 7	340	50	280	40	0.03	0.08	0.015	0.30	0.25	...	...	...	...	0.2Pd
ASTM grade 11	240	35	170	25	0.03	0.08	0.015	0.20	0.18	...	...	...	...	0.2Pd
<b><math>\alpha</math> and near-<math>\alpha</math> alloys</b>														
Ti-0.3Mo-0.8Ni	480	70	380	55	0.03	0.10	0.015	0.30	0.25	...	...	...	0.3	0.8Ni
Ti-5Al-2.5Sn	790	115	760	110	0.05	0.08	0.02	0.50	0.20	5	2.5	...	...	...
Ti-5Al-2.5Sn-ELI	690	100	620	90	0.07	0.08	0.0125	0.25	0.12	5	2.5	...	...	...
Ti-8Al-1Mo-1V	900	130	830	120	0.05	0.08	0.015	0.30	0.12	8	...	...	1	1V
Ti-6Al-2Sn-4Zr-2Mo	900	130	830	120	0.05	0.05	0.0125	0.25	0.15	6	2	4	2	0.08Si
Ti-6Al-2Nb-1Ta-0.8Mo	790	115	690	100	0.02	0.03	0.0125	0.12	0.10	6	...	...	1	2Nb, 1Ta
Ti-2.25Al-11Sn-5Zr-1Mo	1000	145	900	130	0.04	0.04	0.008	0.12	0.17	2.25	11	5	1	0.2Si
Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si	1030	149	910	132	0.03	0.08	0.006	0.05	0.15	5.8	4	3.5	0.5	0.7Nb, 0.35Si
<b><math>\alpha</math>-<math>\beta</math> alloys</b>														
Ti-6Al-4V(a)	900	130	830	120	0.05	0.10	0.0125	0.30	0.20	6	...	...	...	4V
Ti-6Al-4V-ELI(a)	830	120	760	110	0.05	0.08	0.0125	0.25	0.13	6	...	...	...	4V
Ti-6Al-6V-2Sn(a)	1030	150	970	140	0.04	0.05	0.015	1.0	0.20	6	2	...	...	0.75Cu, 6V
Ti-8Mn(a)	860	125	760	110	0.05	0.08	0.015	0.50	0.20	...	...	...	...	8.0Mn
Ti-7Al-4Mo(a)	1030	150	970	140	0.05	0.10	0.013	0.30	0.20	7.0	...	...	4.0	...
Ti-6Al-2Sn-4Zr-6Mo(b)	1170	170	1100	160	0.04	0.04	0.0125	0.15	0.15	6	2	4	6	...
Ti-5Al-2Sn-2Zr-4Mo-4Cr(b)(c)	1125	163	1055	153	0.04	0.05	0.0125	0.30	0.13	5	2	2	4	4Cr
Ti-6Al-2Sn-2Zr-2Mo-2Cr(c)	1030	150	970	140	0.03	0.05	0.0125	0.25	0.14	5.7	2	2	2	2Cr, 0.25Si
Ti-3Al-2.5V(d)	620	90	520	75	0.015	0.05	0.015	0.30	0.12	3	...	...	...	2.5V
Ti-4Al-4Mo-2Sn-0.5Si	1100	160	960	139	(e)	0.02	0.0125	0.20	(e)	4	2	...	4	0.5Si
<b><math>\beta</math> alloys</b>														
Ti-10V-2Fe-3Al(a)(c)	1170	170	1100	160	0.05	0.05	0.015	2.5	0.16	3	...	...	...	10V
Ti-13V-11Cr-3Al(b)	1170	170	1100	160	0.05	0.05	0.025	0.35	0.17	3	...	...	...	11.0Cr, 13.0V
Ti-8Mo-8V-2Fe-3Al(b)(c)	1170	170	1100	160	0.03	0.05	0.015	2.5	0.17	3	...	...	8.0	8.0V
Ti-3Al-8V-6Cr-4Mo-4Zr(a)(c)	900	130	830	120	0.03	0.05	0.20	0.25	0.12	3	...	4	4	6Cr, 8V
Ti-11.5Mo-6Zr-4.5Sn(a)	690	100	620	90	0.05	0.10	0.020	0.35	0.18	...	4.5	6.0	11.5	...
Ti-15V-3Cr-3Al-3Sn	1000(b)	145(b)	965(b)	140(b)	0.05	0.05	0.015	0.25	0.13	3	3	...	...	15V, 3Cr
	1241(f)	180(f)	1172(f)	170(f)										
Ti-15Mo-3Al-2.7Nb-0.2Si	862	125	793	115	0.05	0.05	0.015	0.25	0.13	3	...	...	15	2.7Nb, 0.2Si

(a) Mechanical properties given for the annealed condition; may be solution treated and aged to increase strength. (b) Mechanical properties given for the solution-treated-and-aged condition; alloy not normally applied in an annealed condition. (c) Semicommercial alloy; mechanical properties and composition limits subject to negotiation with suppliers. (d) Primarily a tubing alloy; may be cold drawn to increase strength. (e) Combined  $O_2 + 2N_2 = 0.27\%$ . (f) Also solution treated and aged using an alternative aging temperature (480 °C, or 900 °F)



Code/Designation	Alloy Composition (wt.%)	T <sub>β</sub> (°C)
<b>α-alloys</b>		
Grade 1	CP-Ti (0.2 Fe, 0.18 O)	890
Grade 2	CP-Ti (0.3 Fe, 0.25 O)	915
Grade 3	CP-Ti (0.3 Fe, 0.35 O)	920
Grade 4	CP-Ti (0.5 Fe, 0.40 O)	950
Grade 6	Ti-5Al-2.5Sn	1040
Grade 7	Ti-0.2Pd	915
Grade 12	Ti-0.3Mo-0.8Ni	880
<b>α + β alloys</b>		
Ti-8-1-1	Ti-8Al-1V-1Mo	1040
Ti-11	Ti-6Al-2Sn-1.5Zr-1Mo-0.35Bi-0.1Si	1015
TIMETAL 1100	Ti-5.9Al-2.6Sn-3.8Zr-0.4Mo-0.45Si	1010
IMI 679	Ti-2.5Al-11Sn-5Zr-1Mo-0.2Si	945
IMI 685	Ti-6Al-5Zr-0.5Mo-0.25Si	1020
IMI 829	Ti-5.5Al-3.5Sn-3Zr-1Nb-0.25Mo-0.3Si	1015
IMI 834	Ti-5.8Al-4Sn-3.5Zr-0.5Mo-0.7Nb-0.35Si-0.06C	1045
Ti-56-21-S	Ti-5Al-6Sn-2Zr-0.8Mo-0.25Si	1005
Ti-6-2-4-2	Ti-6Al-2Sn-4Zr-2Mo-0.1Si	995
Ti-55-22-S	Ti-5Al-5Sn-2Zr-2Mo-0.25Si	980
Ti-3-2.5	Ti-3Al-2.5V	935
Ti-6-4	Ti-6Al-4V	995
Ti-6-6-2	Ti-6Al-6V-2Sn	945
IMI 550	Ti-4Al-2Sn-4Mo-0.5Si	975
Ti-55-24-S	Ti-5Al-5Sn-2Zr-4Mo-0.25Si	960
Ti-6-Q2	Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si	970
Ti-6-2-4-6	Ti-6Al-2Sn-4Zr-6Mo	940
TIMETAL 62S	Ti-6Al-2Fe-0.1Si	1015
Corona 5	Ti-4.5Al-5Mo-1.5Cr	935
Ti-17	Ti-5Al-2Sn-2Zr-4Mo-4Cr	890
<b>Metastable β-Alloys</b>		
B 120 VCA	Ti-13V-11Cr-3Al	720
Beta III	Ti-11.5Mo-6Zr-4.5Sn	760
Beta C	Ti-3Al-8V-6Cr-4Mo-4Zr	795
TIMETAL 10-2-3	Ti-10V-2Fe-3Al	800
TIMETAL 15-3	Ti-15V-3Cr-3Al-3Sn	760
TIMETAL 21S	Ti-15Mo-2.7Nb-3Al-0.2Si	815
TIMETAL LCB	Ti-4.5Fe-6.8Mo-1.5Al	810
Beta-CEZ	Ti-5Al-2Sn-2Cr-4Mo-4Zr-1Fe	890
SP 700	Ti-4.5Al-3V-2Mo-2Fe	900

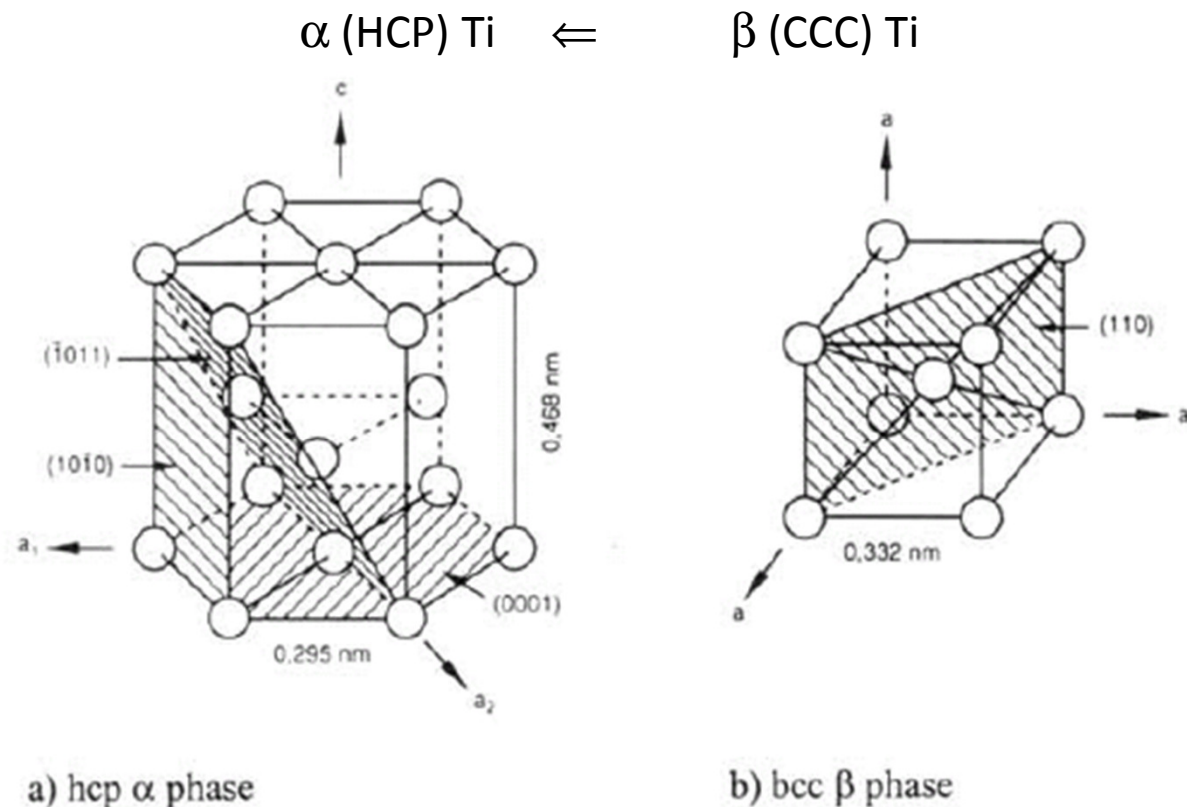


**Table 2.5 Some titanium applications**

<b>Aerospace</b>	<b>Automotive</b>	<b>Oil, gas, and petroleum processing</b>	<b>Sports</b>
Gas turbine engines	Body panels	Tubing and pipe	Golf clubs
Aircraft structures	Connecting rods	Liners	Bicycle frames, gears, etc.
Spacecraft	Valves and valve springs	Springs	Lacrosse sticks
Helicopter rotors	Rocker arms	Valves	Racing wheelchairs
<b>Power generation</b>	<b>Marine</b>	Risers	Horseshoes
Gas turbines	Surface ship hulls	<b>Biomedical</b>	Tennis rackets
Steam turbines	Deep-sea submersibles	Artificial joint prostheses	Scuba gas cylinders
Piping systems	Pleasure boat components	Bone plates, intramedullary rods, etc.	Skis
Heat exchangers	Racing yacht components	Heart valves	Pool cues
Flue gas desulphurization systems	Shipboard cooling systems	Pacemakers	<b>Miscellaneous</b>
<b>Chemical processing industries</b>	Ship propellers	Dental implants	Shape memory alloys
Pressure and reaction vessels	Service water systems	Attachment wire	Pollution control systems
Heat exchangers	Ducting	Surgical instruments	Hand tools
Pipe and fittings	Fire pumps	Wheelchairs	Desalination systems
Liners	Water jet propulsion systems	<b>Architectural</b>	Military vehicle armor
Tubing	<b>Fashion and apparel</b>	Roofing	Hunting knives
Pumps	Eyeglasses	Window frames	Backpack cookware
Condensers	Jewelry	Eaves and gables	
Valves, ducting, and filters	Watches	Railings	
Agitators	Writing instruments	Ventilators	

# Propriedades elásticas

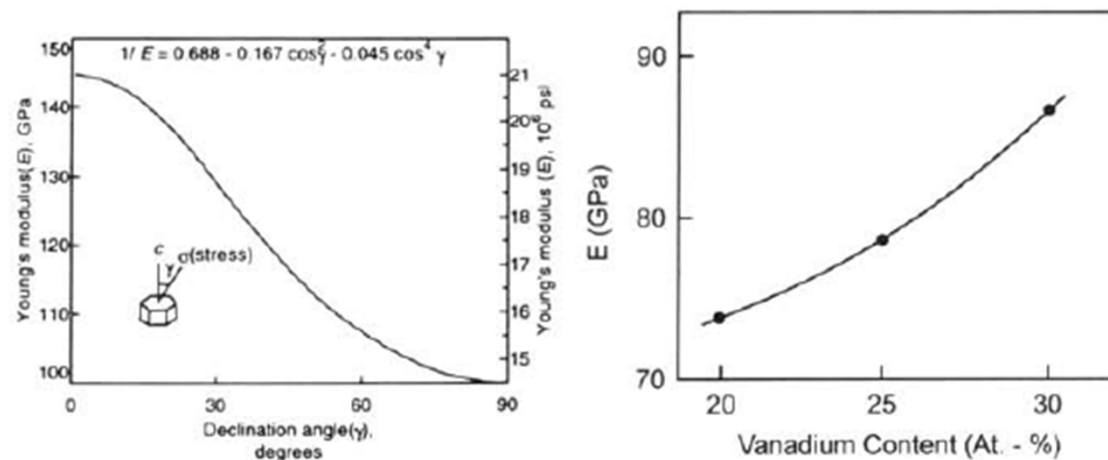
- Módulo de elasticidade (HCP) depende da direção.





# Propriedades elásticas

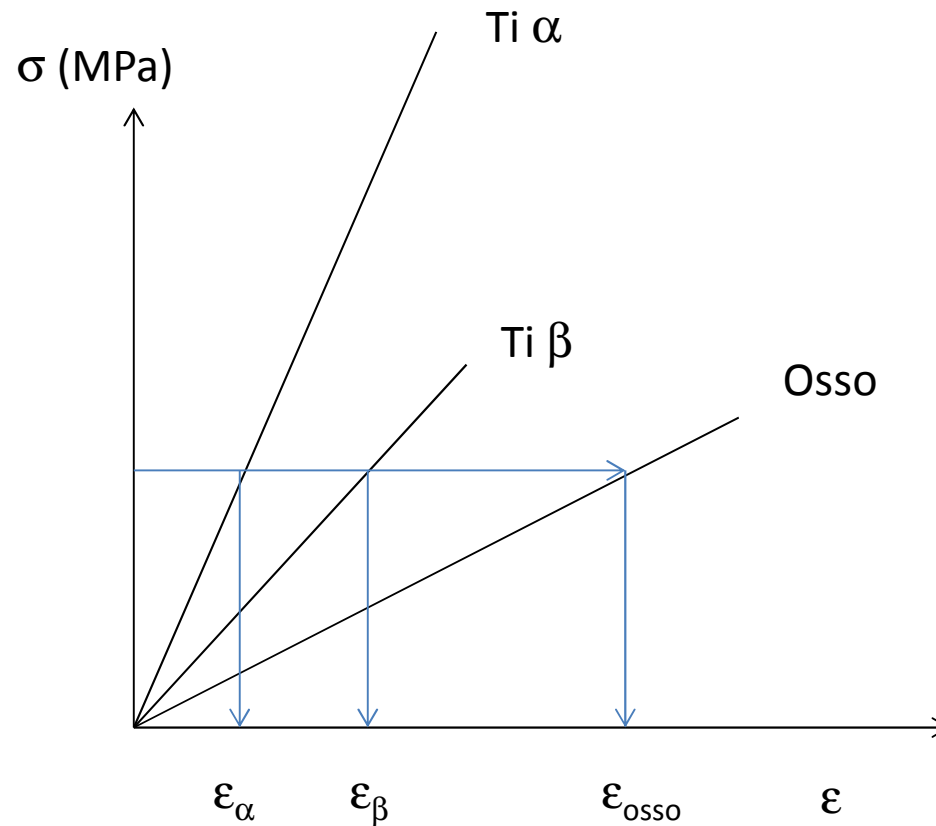
- Módulo de elasticidade (HCP) depende da direção. (100 a 140 Mpa).



- Módulo de elasticidade do CCC é sempre menor (70 a 90 MPa) e depende da composição.

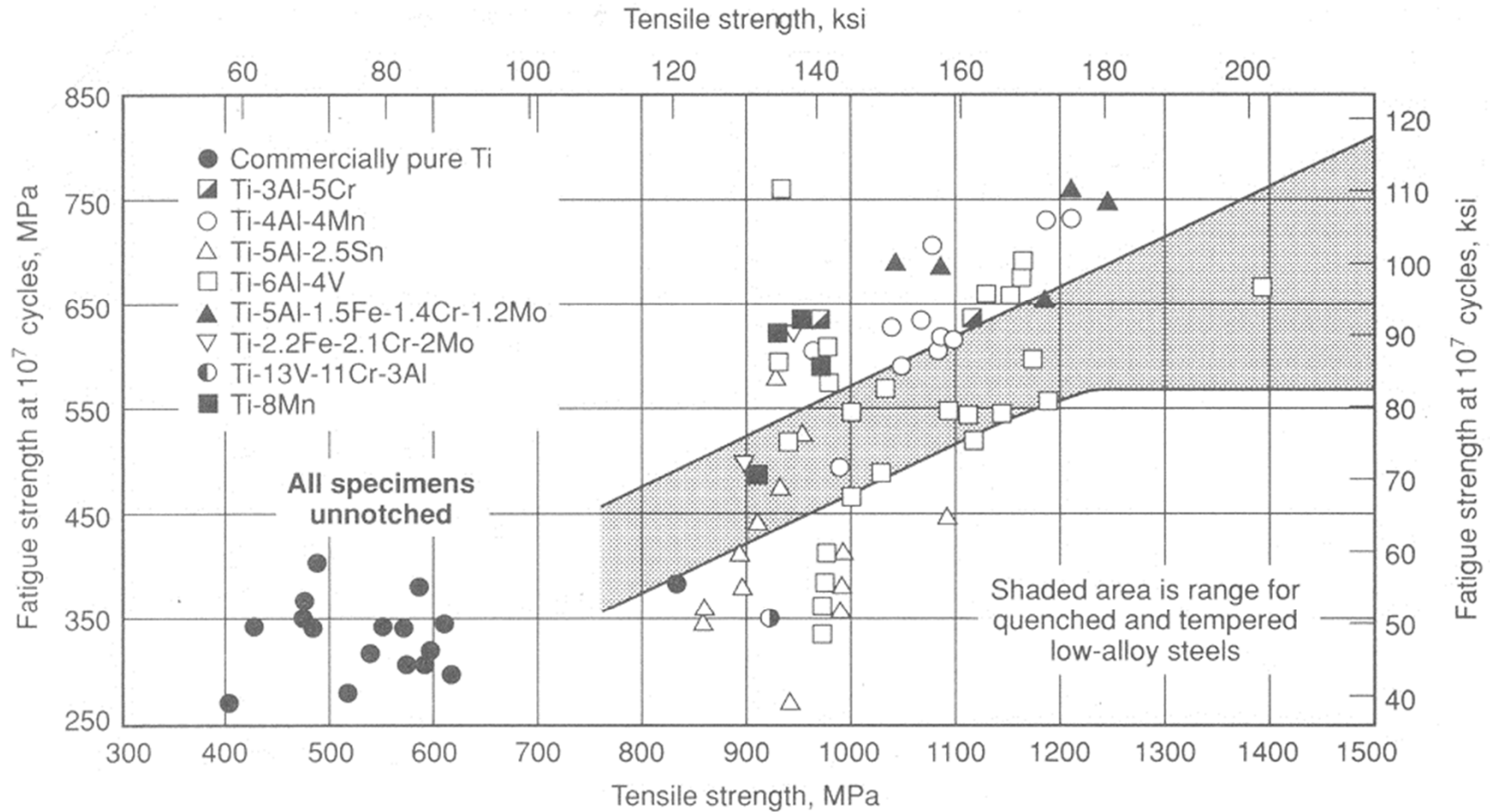


# Compatibilidade mecânica



Ligas  $Ti\ \beta$  apresentam maior compatibilidade mecânica e resultam em menor número de falhas por adesão do implante ao osso.

# Resistência à fadiga comparada com a de aços

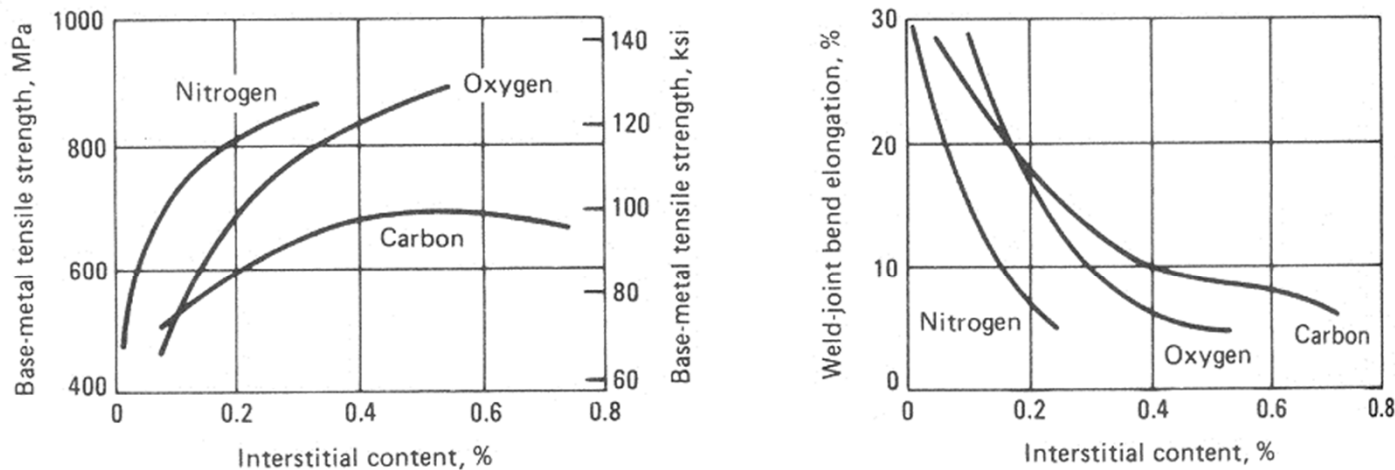


Fatigue data for titanium and titanium alloys, compared with quenched and tempered low-alloy steels



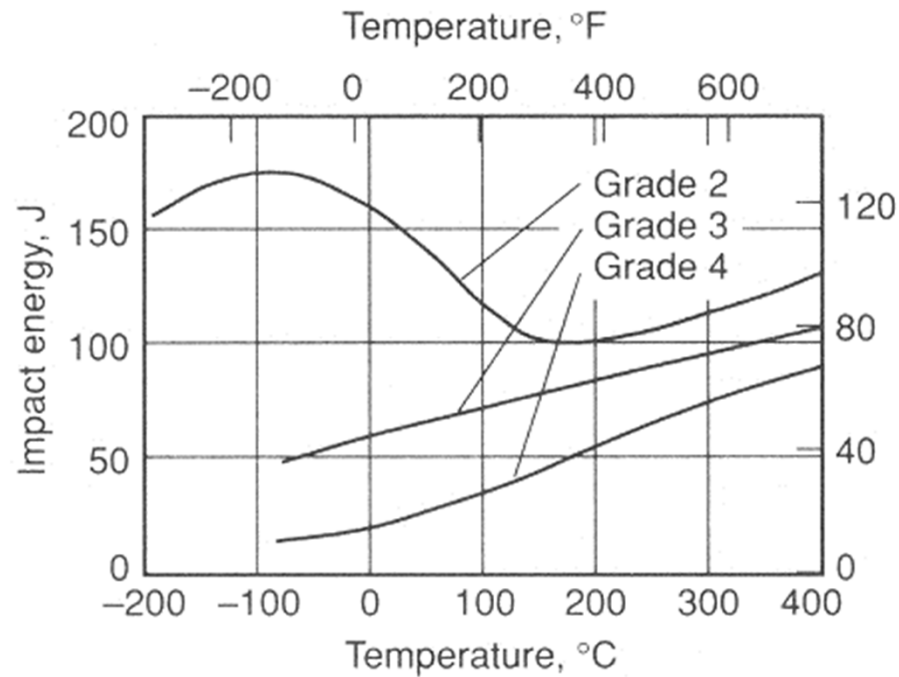
# Efeito de intersticiais nas propriedades mecânicas do Ti

- Os níveis de oxigênio e ferro determinam o nível de resistência de titânio comercialmente puro.
- O carbono e o nitrogênio são mantidos em níveis mínimos para evitar fragilização.
- Quando se requer ductilidade e tenacidade muito boas são utilizados os graus extra baixo intersticial (ELI)



Effects of interstitial-element content on strength and ductility of unalloyed titanium

# Efeito de intersticiais na tenacidade

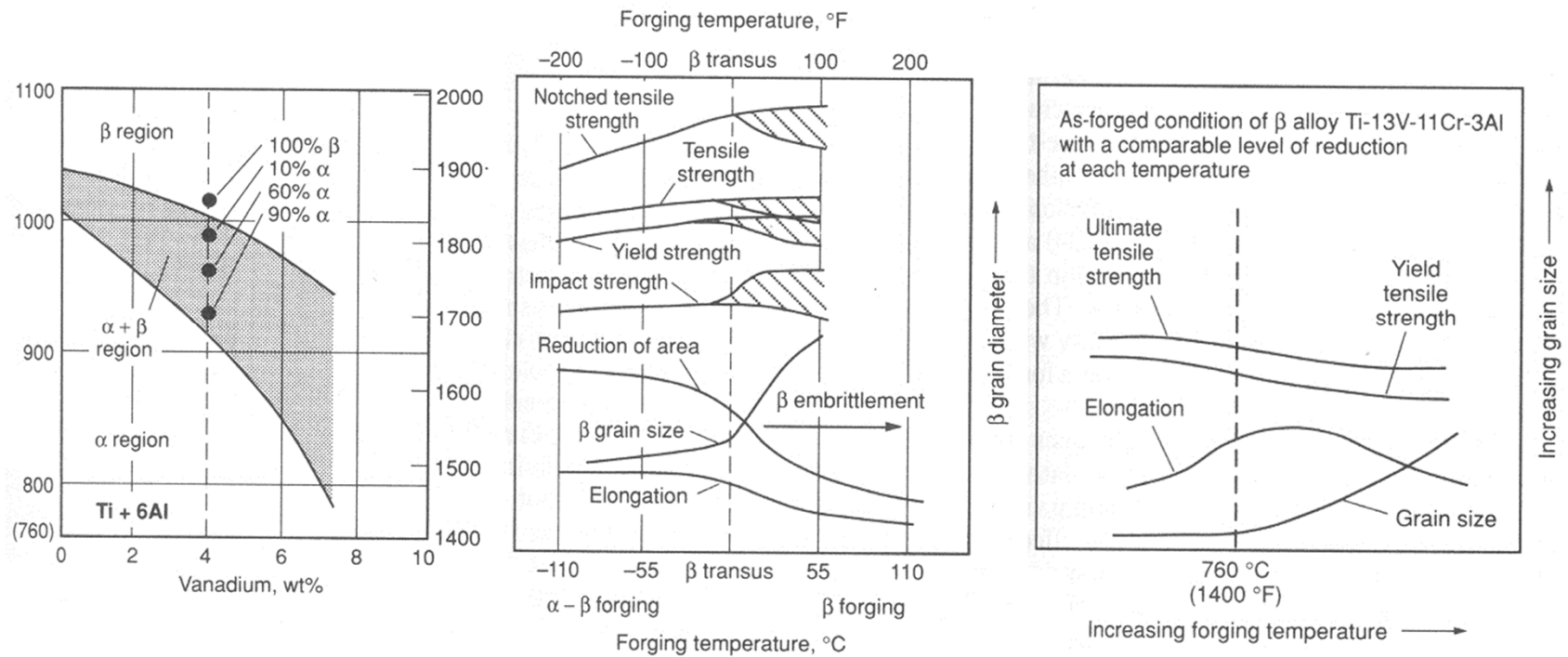


**TABLE 1.6** Chemical Compositions of Ti and Its Alloy  
 [American Society for Testing and Materials, F67-89, p.39;  
 F136-84, p.55, 1992]

Element	Grade 1	Grade 2	Grade 3	Grade 4	Ti6Al4V <sup>a</sup>
Nitrogen	0.03	0.03	0.05	0.05	0.05
Carbon	0.10	0.10	0.10	0.10	0.08
Hydrogen	0.015	0.015	0.015	0.015	0.0125
Iron	0.20	0.30	0.30	0.50	0.25
Oxygen	0.18	0.25	0.35	0.40	0.13
Titanium					Balance

<sup>a</sup> Aluminum 6.00% (5.50~6.50), vanadium 4.00% (3.50~4.50), and other elements 0.1% maximum or 0.4% total. All are maximum allowable weight percent.

# Efeito da temperatura de processamento nas propriedades



## Comparação entre morfologias equiaxiais e aciculares e Ti alfa e próximo de alfa.

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### Table 8 Relative advantages of equiaxed and acicular morphologies in near-alpha and alpha-beta alloys

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#### **Equiaxed:**

Higher ductility and formability  
Higher threshold stress for hot-salt stress corrosion  
Higher strength (for equivalent heat treatment)  
Better low-cycle fatigue (initiation) properties

#### **Acicular:**

Superior creep properties  
Higher fracture-toughness values  
Slight drop in strength (for equivalent heat treatment)  
Superior stress-corrosion resistance  
Lower crack-propagation rates

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## Aplicações biomédicas

- Titânio puro e titânio  $\alpha+\beta$ , incluindo Ti-6Al-4V ELI e Ti-6Al-4V são ligas que foram projetadas para uso estrutural para a indústria aeroespacial. Posteriormente foram utilizadas em aplicações biomédicas.
- A toxicidade do V, elemento estabilizador da fase  $\beta$  foi demonstrada e o V foi substituído por outros elementos estabilizadores de  $\beta$  como o Fe ou o Nb.
- Duas ligas tipo ( $\alpha+\beta$ ) Ti-5Al-2.5Fe e Ti-6Al-7Nb, foram normatizadas.
- Mais, recentemente concluiu-se que o módulo elástico dos biomateriais metálicos deve ser baixo para garantir compatibilidade mecânica entre o osso e o implante.
- As ligas  $\beta$  foram desenvolvidas.



# Aplicações biomédicas

**Table 1 Titanium alloys for biomedical applications**

1. Pure Ti (ASTM F67-89)

Grade 1, 2, 3 and 4

Purity → Decrease (add N, Fe and O)

Strength → Increase

Ductility → Decrease

2. Ti-6Al-4V ELI (ASTM F136-84, F620-87) :  $\alpha+\beta$  type

3. Ti-6Al-4V (ASTM F1108-88) :  $\alpha+\beta$  type

○ 4. Ti-6Al-7Nb (ASTM F1295-92, ISO5832-11)

:  $\alpha+\beta$  type (Swiss)

○ 5. Ti-5Al-2.5Fe (ISO5832-10) :  $\alpha+\beta$  type (Germany)

○ 6. Ti-5Al-3Mo-4Zr :  $\alpha+\beta$  type (Japan)

○ 7. Ti-15Sn-4Nb-2Ta-0.2Pd :  $\alpha+\beta$  type (Japan)

○ 8. Ti-15Zr-4Nb-2Ta-0.2Pd :  $\alpha+\beta$  type (Japan)

○ 9. Ti-13Nb-13Zr (ASTM F1713-96) : near  $\beta$  type (U.S.A.), Low modulus

○ 10. Ti-12Mo-6Zr-2Fe (ASTM F1813-97):  $\beta$  type (U.S.A.), Low modulus

○ 11. Ti-15Mo :  $\beta$  type (U.S.A.), Low modulus

12. Ti-16Nb-10Hf :  $\beta$  type (U.S.A.), Low modulus

13. Ti-15Mo-5Zr-3Al :  $\beta$  type (Japan), Low modulus

14. Ti-15Mo-2.8Nb-0.2Si-0.26O :  $\beta$  type (U.S.A.), Low modulus

○ 15. Ti-35Nb-7Zr-5Ta :  $\beta$  type (U.S.A.), Low modulus

○ 16. Ti-29Nb-13Ta-4.6Zr :  $\beta$  type (Japan), Low modulus

○ 17. Ti-40Ta, Ti-50Ta :  $\beta$  type (U.S.A.), High corrosion resistance