Materiali ceramici

Definizione

Che cos'è un materiale ceramico?

- ✓ **Ceramics** *can be defined as solid compounds that are formed by the application of heat, and sometimes heat and pressure, comprising at least two elements provided one of them is a non-metal or a nonmetallic elemental solid. The other element(s) may be a metal(s) or another nonmetallic elemental solid(s)*
- ✓ A somewhat simpler definition was given by Kingery who defined ceramics as, ‘‘the art and science of making and using solid articles, which have, as their essential component, and are composed in large part of, inorganic nonmetallic materials’’. In other words, what is neither a metal, a semiconductor or a polymer is a ceramic

I materiali ceramici sono materiali inorganici non metallici, costituiti da elementi metallici e non metallici legati fra loro prevalentemente da legami ionici e/o covalenti

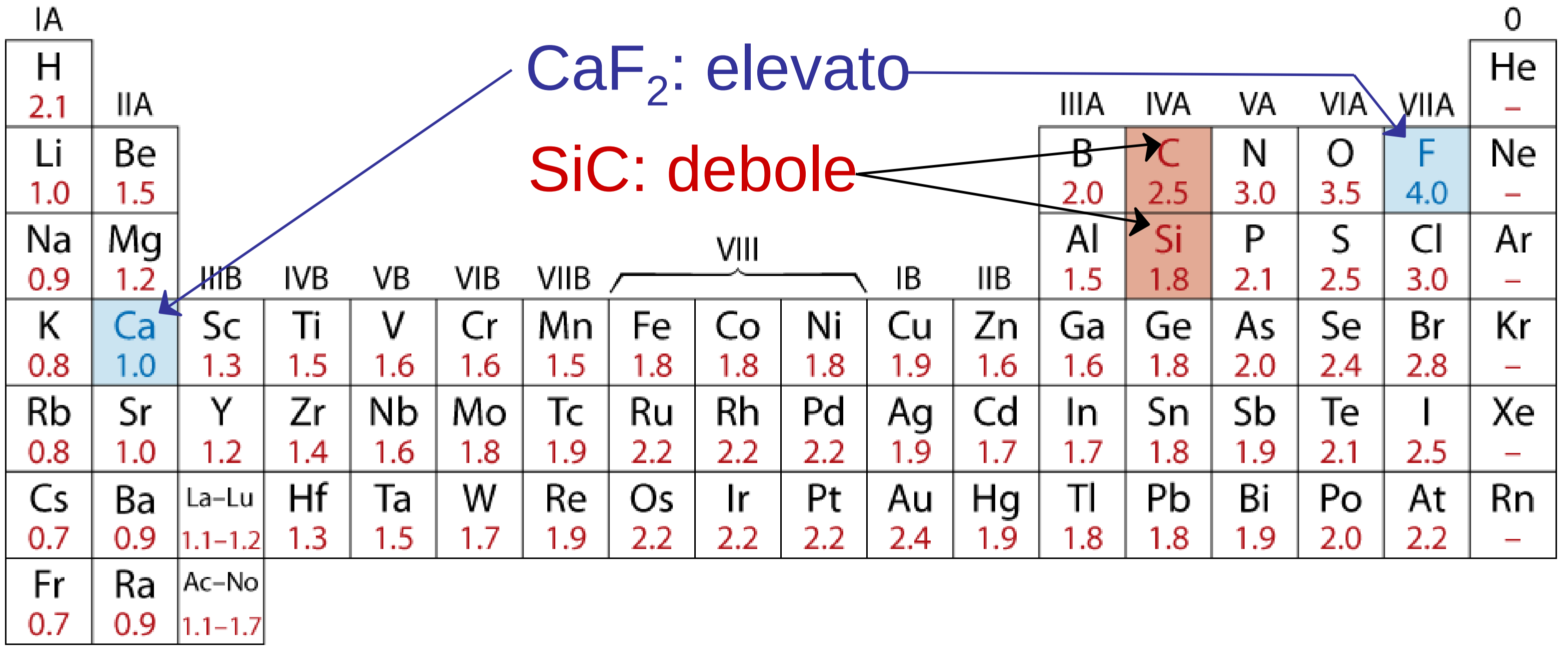
“Legame Ceramico”

- Legame:

  -- Prevalentemente ionico, con una componente covalente

  -- % carattere ionico aumenta con la differenza di elettronegatività

- Elevato vs. debole carattere ionico del legame:



CaF_2: elevato

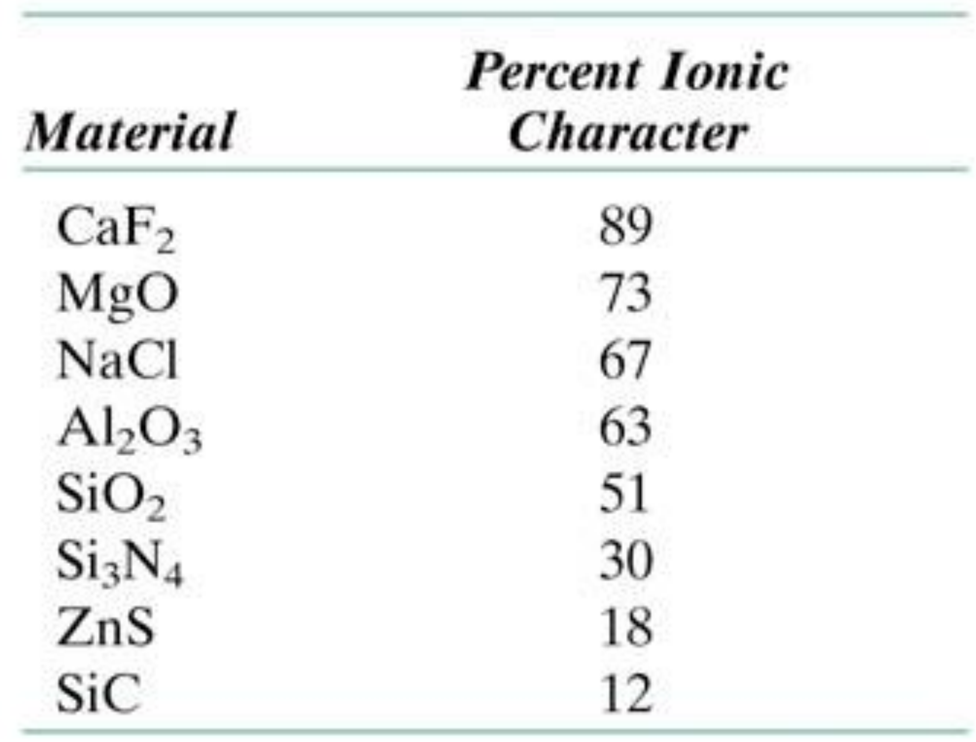
SiC: debole

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

La percentuale di carattere ionico (% IC) di un legame atomico tra gli elementi A e B (con A l'elemento più elettronegativo) può essere ottenuta mediante la seguente relazione:

$$\% \, IC = \{1 - exp[-(0{,}25)(X_A - X_B)^2]\} x100$$

ove X_A e X_B sono le elettronegatività dei rispettivi elementi



Material	***Percent Ionic Character***
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

GENERAL PROPERTIES

- ✓ Ceramics generally have specific properties associated with them although this can be a misleading approach to defining a class of materials

- ✓ **Brittleness**. This probably comes from personal experiences such as dropping a glass beaker or a dinner plate. The reason that the majority of ceramics are brittle is the mixed ionic–covalent bonding that holds the constituent atoms together. At high temperatures (above the glass transition temperature) glass no longer behaves in a brittle manner; it behaves as a viscous liquid. That is why it is easy to form glass into intricate shapes. So what we can say is that *most ceramics are brittle at room temperature but not necessarily at elevated temperatures*

- ✓ **Poor electrical and thermal conduction**. The valence electrons are tied up in bonds, and are not free as they are in metals. In metals it is the free electrons—the electron gas—that determines many of their electrical and thermal properties. Diamond, which is classified as a ceramic, has the highest thermal conductivity of any known material. The conduction mechanism is due to phonons, not electrons

- ✓ Ceramics can also have high electrical conductivity: the oxide ceramic, ReO_3, has an electrical conductivity at room temperature similar to that of copper

- ✓ **Compressive strength**. Ceramics are stronger in compression than in tension, whereas metals have comparable tensile and compressive strengths. This difference is important when we use ceramic components for load-bearing applications. It is necessary to consider the stress distributions in the ceramic to ensure that they are compressive. An important example is in the design of concrete bridges—the concrete, a CMC, must be kept in compression. Ceramics generally have low toughness, although combining them in composites can dramatically improve this property

- ✓ **Chemical insensitivity**. A large number of ceramics are stable in both harsh chemical and thermal environments. Pyrex glass is used widely in chemistry laboratories specifically because it is resistant to many corrosive chemicals, stable at high temperatures (it does not soften until 1100 K), and is resistant to thermal shock because of its low coefficient of thermal expansion (33×10^{-7} K^{-1}). It is also widely used in bakeware

TYPES OF CERAMIC AND THEIR APPLICATIONS

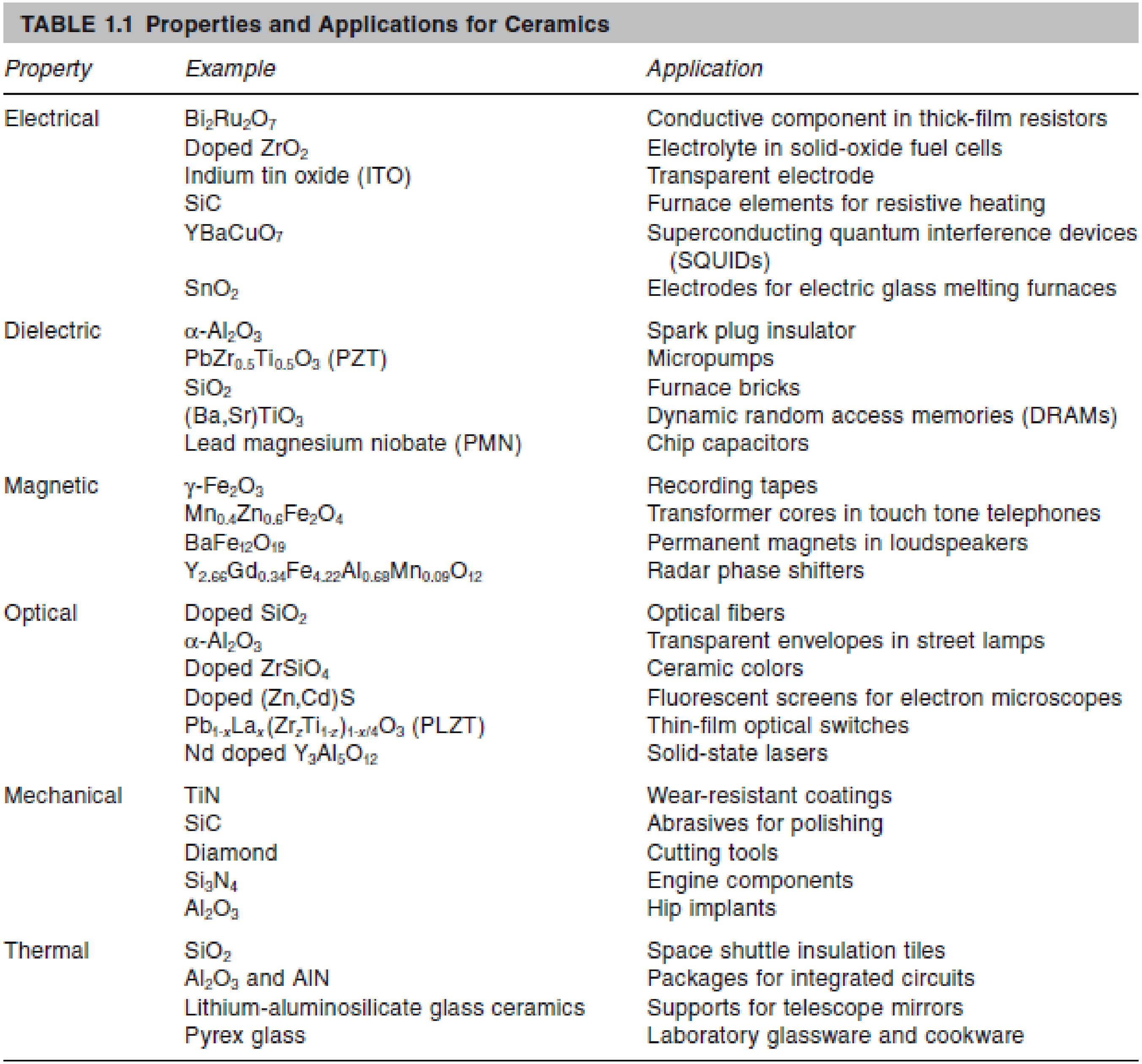


TABLE 1.1 Properties and Applications for Ceramics

Property	*Example*	*Application*
Electrical	$Bi_2Ru_2O_7$	Conductive component in thick-film resistors
	Doped ZrO_2	Electrolyte in solid-oxide fuel cells
	Indium tin oxide (ITO)	Transparent electrode
	SiC	Furnace elements for resistive heating
	$YBaCuO_7$	Superconducting quantum interference devices (SQUIDs)
	SnO_2	Electrodes for electric glass melting furnaces
Dielectric	α-Al_2O_3	Spark plug insulator
	$PbZr_{0.5}Ti_{0.5}O_3$ (PZT)	Micropumps
	SiO_2	Furnace bricks
	$(Ba,Sr)TiO_3$	Dynamic random access memories (DRAMs)
	Lead magnesium niobate (PMN)	Chip capacitors
Magnetic	γ-Fe_2O_3	Recording tapes
	$Mn_{0.4}Zn_{0.6}Fe_2O_4$	Transformer cores in touch tone telephones
	$BaFe_{12}O_{19}$	Permanent magnets in loudspeakers
	$Y_{2.66}Gd_{0.34}Fe_{4.22}Al_{0.68}Mn_{0.09}O_{12}$	Radar phase shifters
Optical	Doped SiO_2	Optical fibers
	α-Al_2O_3	Transparent envelopes in street lamps
	Doped $ZrSiO_4$	Ceramic colors
	Doped (Zn,Cd)S	Fluorescent screens for electron microscopes
	$Pb_{1-x}La_x(Zr_zTi_{1-z})_{1-x/4}O_3$ (PLZT)	Thin-film optical switches
	Nd doped $Y_3Al_5O_{12}$	Solid-state lasers
Mechanical	TiN	Wear-resistant coatings
	SiC	Abrasives for polishing
	Diamond	Cutting tools
	Si_3N_4	Engine components
	Al_2O_3	Hip implants
Thermal	SiO_2	Space shuttle insulation tiles
	Al_2O_3 and AlN	Packages for integrated circuits
	Lithium-aluminosilicate glass ceramics	Supports for telescope mirrors
	Pyrex glass	Laboratory glassware and cookware

- ✓ In addition to dividing ceramics according to their properties and applications, it is common to class them as ***traditional*** or ***advanced***
- ✓ **Traditional ceramics** are usually based on clay and silica. There is sometimes a tendency to equate traditional ceramics with low technology, however, advanced manufacturing techniques are often used. Competition among producers has caused processing to become more efficient and cost effective. Complex tooling and machinery is often used and may be coupled with computer-assisted process control
- ✓ **Advanced ceramics** are also referred to as “special,” “technical,” or “engineering” ceramics. They exhibit superior mechanical properties, corrosion/oxidation resistance, or electrical, optical, and/or magnetic properties. While traditional clay-based ceramics have been used for over 25,000 years, advanced ceramics have generally been developed within the last 100 years

Settori dell'industria ceramica tradizionale

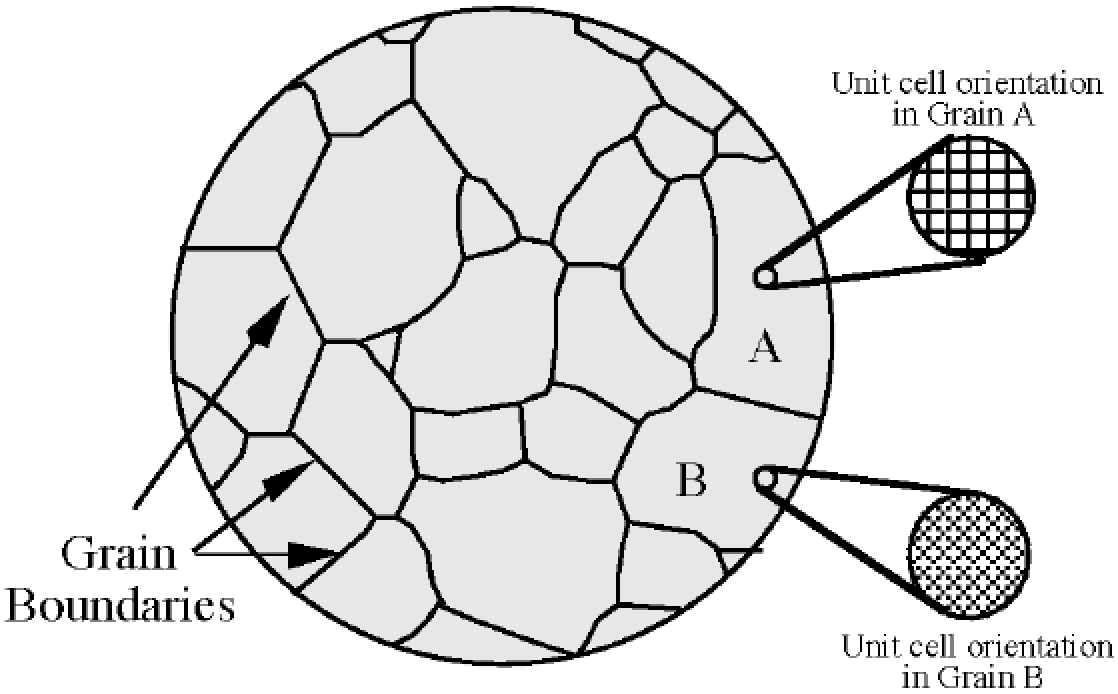
- Prodotti strutturali da argilla (mattoni, grondaie, condotti per fognature, tegole, canne fumarie, piastrelle)
- Porcellane (stoviglie, piastrelle, sanitari, porcellana decorativa, protesi dentali)
- Refrattari (mattoni e prodotti monolitici e prodotti colabili nell'industria dell'acciaio, dei metalli non ferrosi, conversione energetica, trasformazione del petrolio e industria chimica)
- Vetri (vetro piano, contenitori, bottiglie, vetro soffiato, fibre di vetro, fibre ottiche)
- Abrasivi (naturali (diamanti..) e sintetici (allumina, carburo di silicio) usati per smerigliatura, lucidatura, taglio, sabbiatura)
- Cementi (usati nella costruzione di edifici, ponti, strade, dighe)

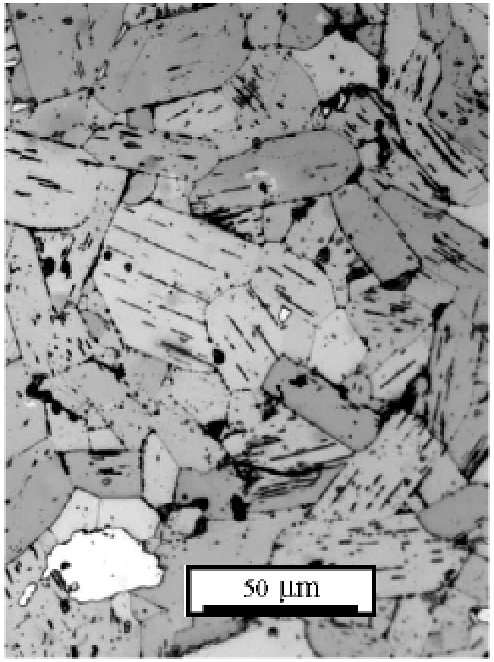
Le principali classi di ceramici avanzati

Ossidi monocomponente	Allumina (Al_2O_3) Zirconia (ZrO_2) Titania (TiO_2) Ossido di magnesio (MgO) Yttria (Y_2O_3)
Ossidi misti	Mullite ($3Al_2O_3 2SiO_2$) Spinello ($MgO\ Al_2O_3$)
Carburi	Carburo di silicio (SiC) Carburo di boro (B_4C) Carburo di titanio (TiC)
Nitruri	Nitruro di boro (BN) Nitruro di silicio (Si_3N_4) Nitruro di titanio (TiN)
Boruri	Boruro di zirconio (ZrB_2) Boruro di afnio (HfB_2)

Ceramic Microstructures

- ✓ Most ceramics are crystalline. The exception is glass
- ✓ Typically, in ceramics the grains are in the range of 1 to 50 µm





Strutture cristalline dei ceramici

- Strutture cristalline più complesse di quelle dei metalli (i ceramici sono composti da almeno 2 elementi)

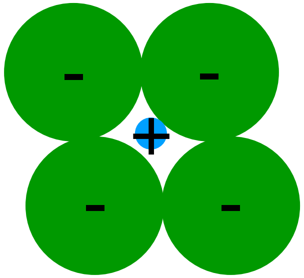
- Il legame varia da puramente ionico a totalmente covalente

- Per i ceramici aventi un legame prevalentemente ionico, le strutture cristalline si possono pensare composte di ioni invece che di atomi

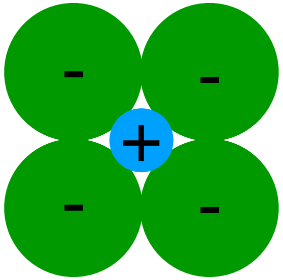
- Due caratteristiche degli ioni costituenti influenzano la struttura cristallina:
  - il valore della carica di ciascuno ione costituente
  - le dimensioni relative dei cationi e degli anioni (r_c/r_a)

1. Dimensione - Strutture stabili:

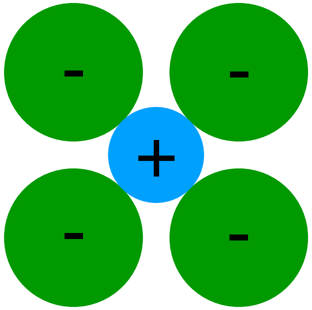
--si massimizza il # di vicini di carica opposta



instabile



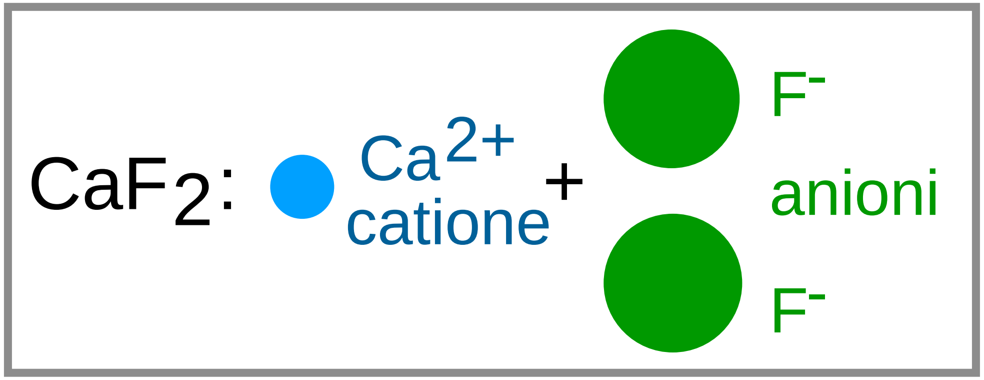
stabile



stabile

2. Neutralità della carica:

--La carica netta nella struttura deve essere nulla

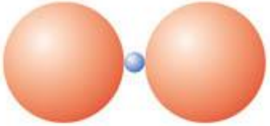
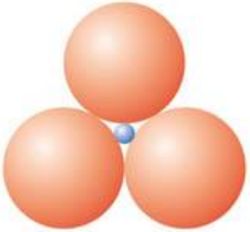
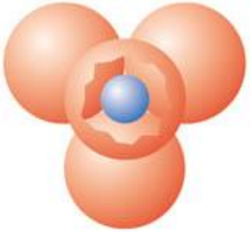
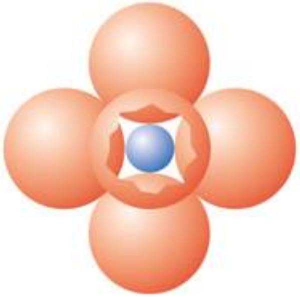
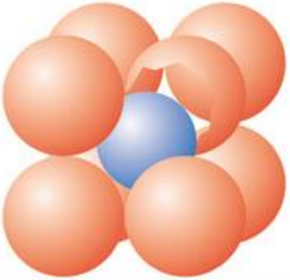


CaF$_2$: Ca^{2+} catione + F$^-$ F$^-$ anioni

--Forma generale:

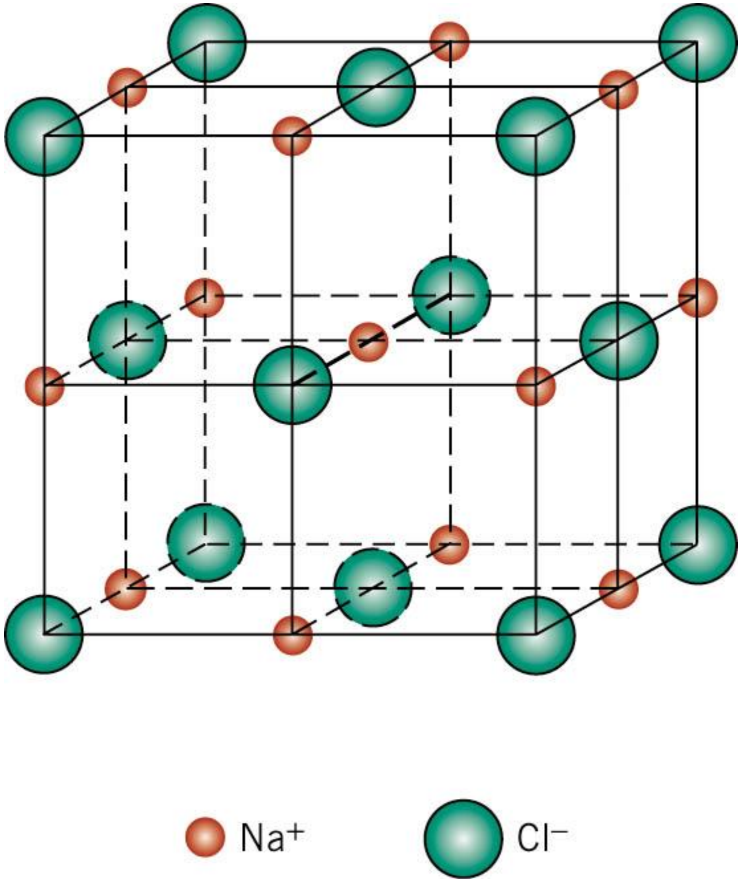
$$A_m X_p$$

m, p determinati dalla neutralità della carica

Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Più comuni

Strutture del tipo AX (tipo NaCl)

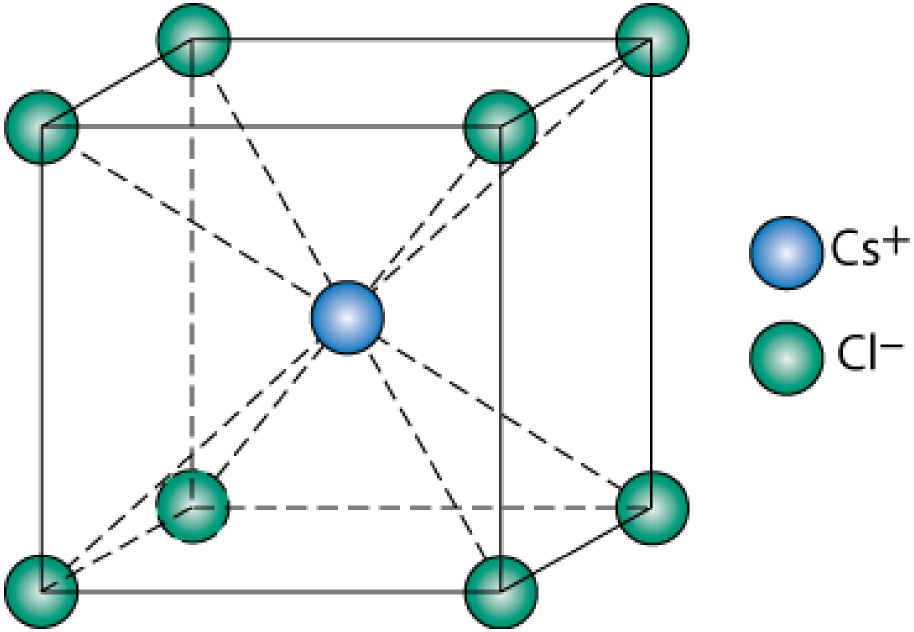


NaCl, MgO, MnS, LiF, FeO

Numero di coordinazione = 6

Uguale numero di cationi e anioni
A = catione
X = anione

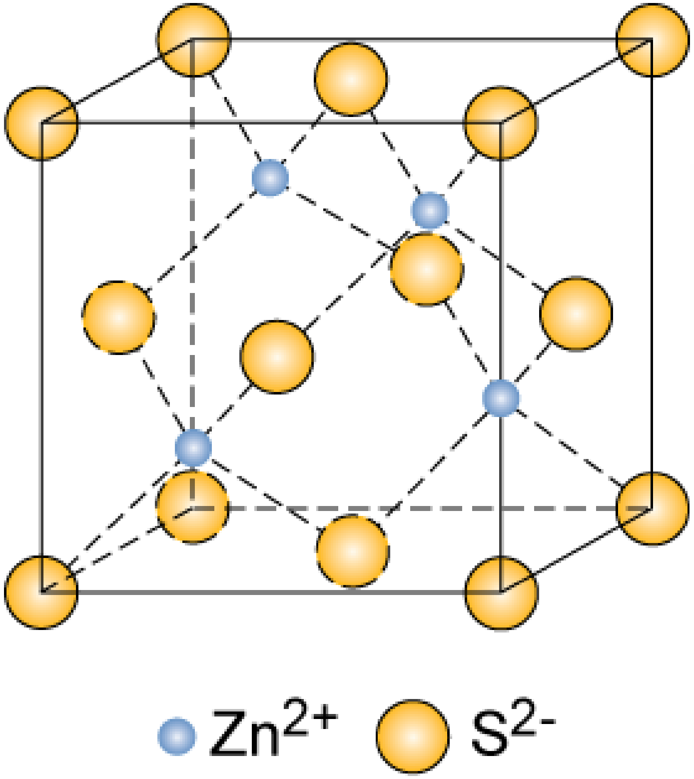
Strutture del tipo AX
(tipo CsCl)



$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

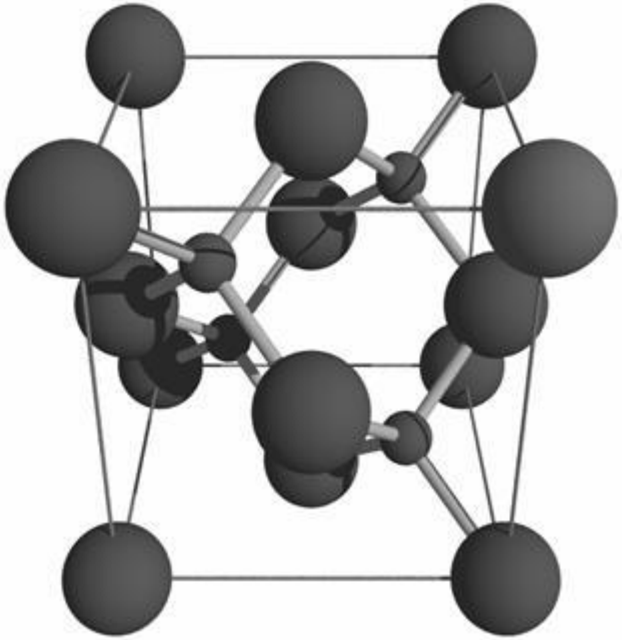
Numero di coordinazione = 8

Strutture del tipo AX
(tipo ZnS, zincoblenda)



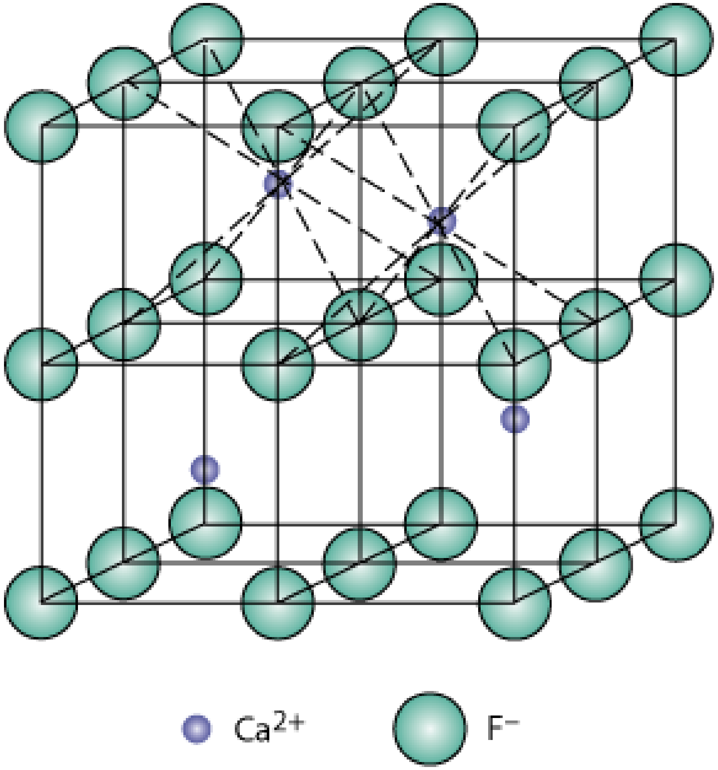
Ex: ZnS, SiC

Numero di coordinazione = 4



Coordinazione tetraedrica tra gli ioni
Materiali che esibiscono questa struttura spesso hanno legame molto covalente

Strutture del tipo A_mX_n



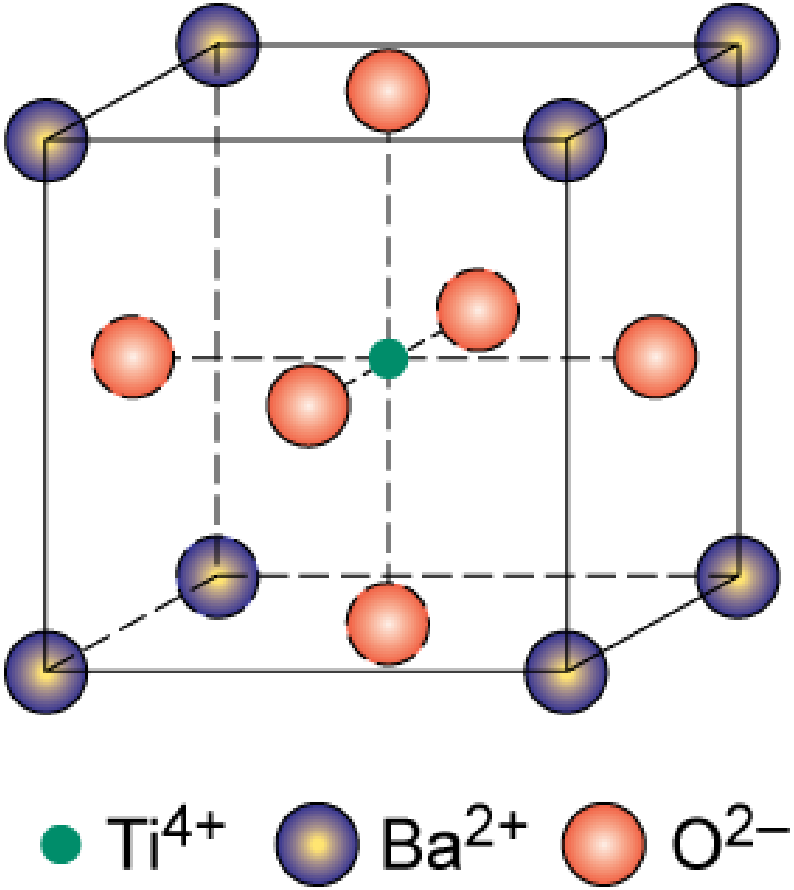
Struttura della fluorite CaF_2

Numero di coordinazione = 8

Strutture del tipo $A_mB_nX_p$

Perovskiti

ABO_3



$BaTiO_3$

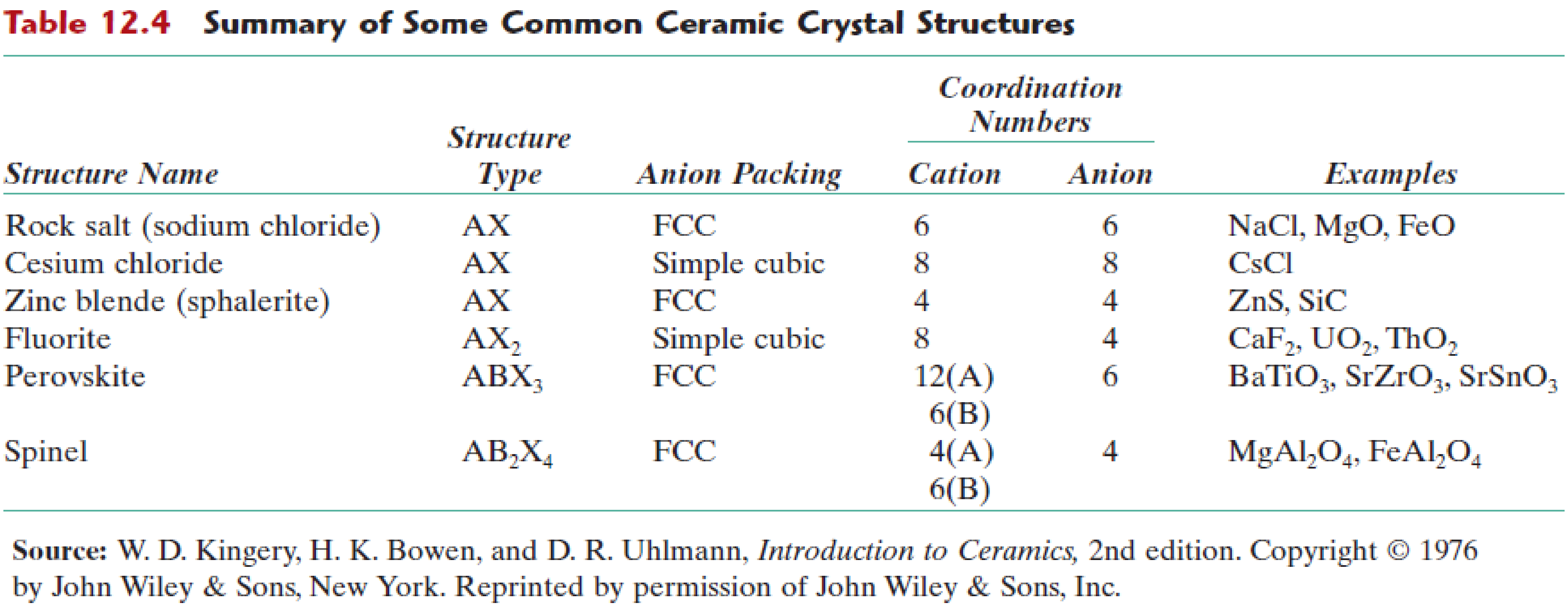


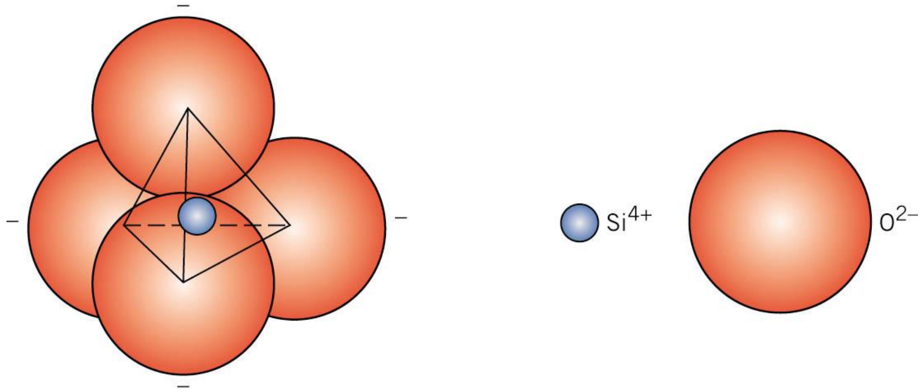
Table 12.4 **Summary of Some Common Ceramic Crystal Structures**

Structure Name	*Structure Type*	*Anion Packing*	*Coordination Numbers*		*Examples*
			Cation	*Anion*	
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12(A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

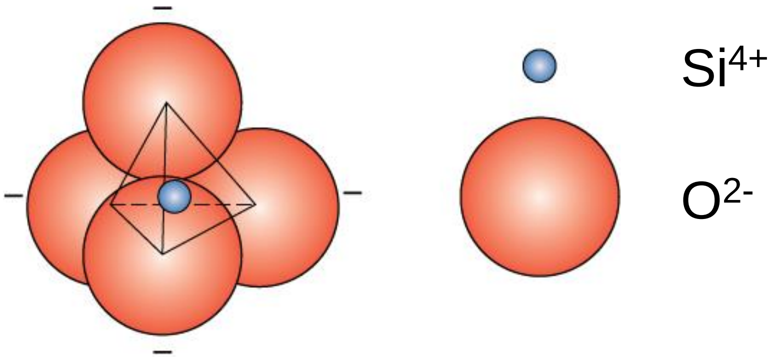
Source: W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics,* 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

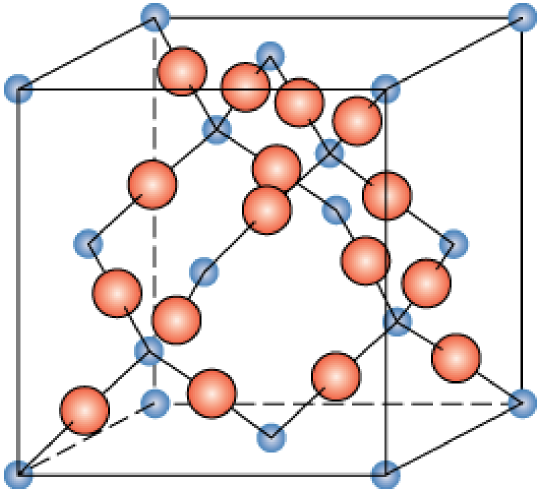
Silicati

- *Sono composti principalmente da Si & O*
- *La struttura cristallina viene caratterizzata sulla base della disposizione del tetraedro* SiO^{4-}_4
- *I silicati non vengono in genere considerati ionici a causa del significativo carattere covalente dei legami Si-O, che sono direzionali e relativamente forti*
- *Le diverse strutture dei silicati hanno origine dalle diverse disposizioni delle unità tetraedriche in una, due o tre dimensioni*



Silice





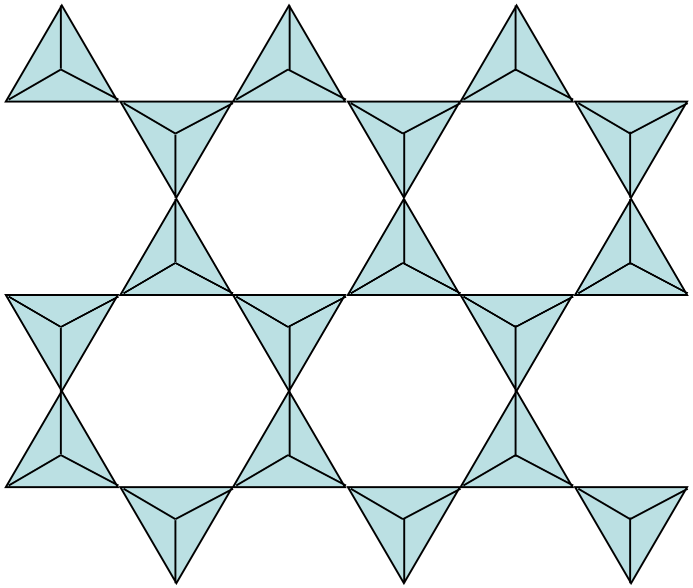
cristobalite

- ✓ Quarzo, cristobalite e tridimite (SiO_2)

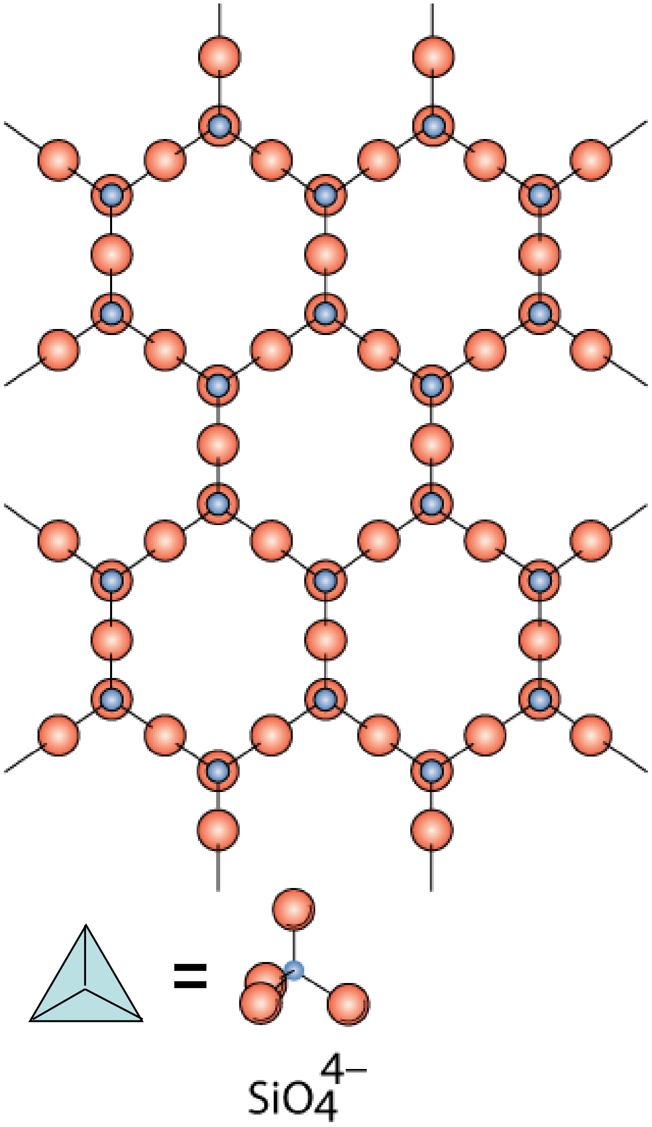
Il forte legame Si-O genera una elevata temperatura di fusione (1710°C)

Layered Silicates

- Layered silicates (clay silicates)
  - SiO_4 tetrahedra connected together to form 2-D plane



- $(Si_2O_5)^{2-}$
- So need cations to balance charge

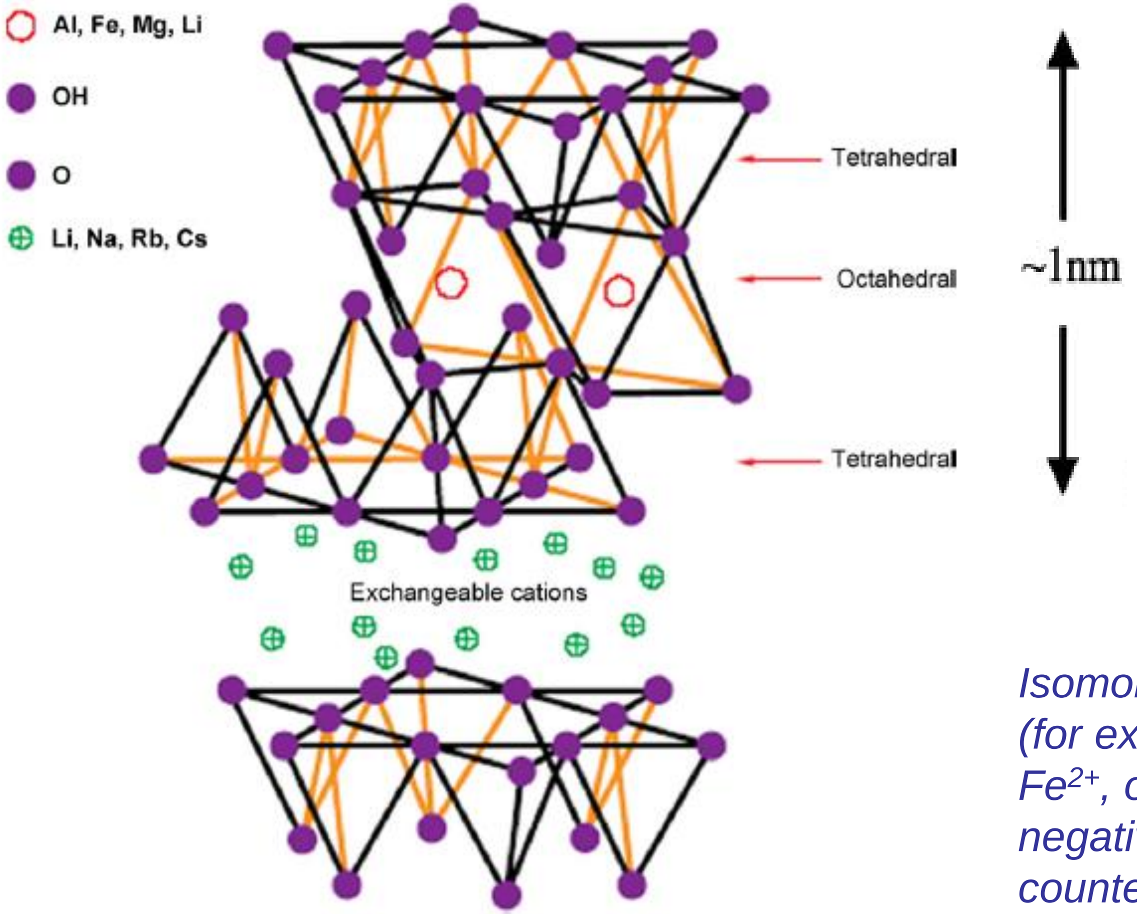


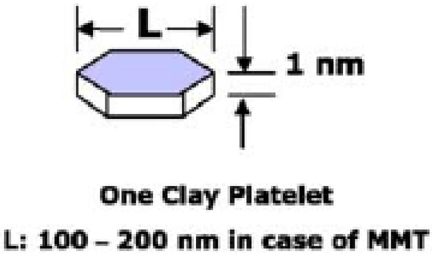
Structure and characteristics of layered silicates

- ✓ Layered silicates are natural or synthetic minerals, consisting of very thin layers that are usually bound together with counter-ions. Their basic building blocks are tetrahedral sheets in which silicon is surrounded by four oxygen atoms, and octahedral sheets in which a metal like aluminum is surrounded by eight oxygen atoms. Therefore, in 1:1 layered structures (e.g. in kaolinite) a tetrahedral sheet is fused with an octahedral sheet, whereby the oxygen atoms are shared

- ✓ On the other hand, the crystal lattice of 2:1 layered silicates (or 2:1 phyllosilicates), consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Therefore, the aspect ratio of these layers (ratio length/thickness) is particularly high. Stacking of the layers leads to a gap between the layers called the *interlayer or gallery*. Silica is a main component of a tetrahedral sheet whilst octahedral sheet comprises diverse elements such as Al, Mg, and Fe

The structure of a 2:1 layered silicate

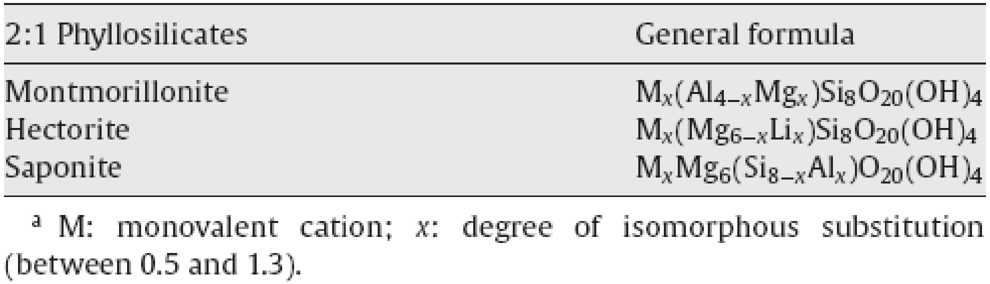




One Clay Platelet

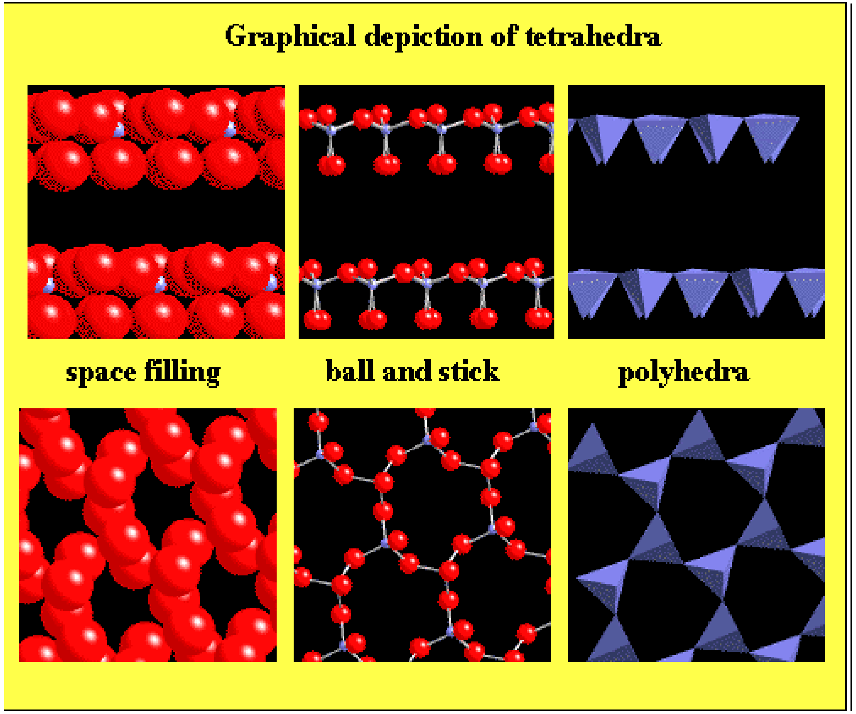
L: 100 – 200 nm in case of MMT

Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} replaced by Li^{1+}) generates negative charges that are counterbalanced by alkali and alkaline earth cations situated inside the galleries

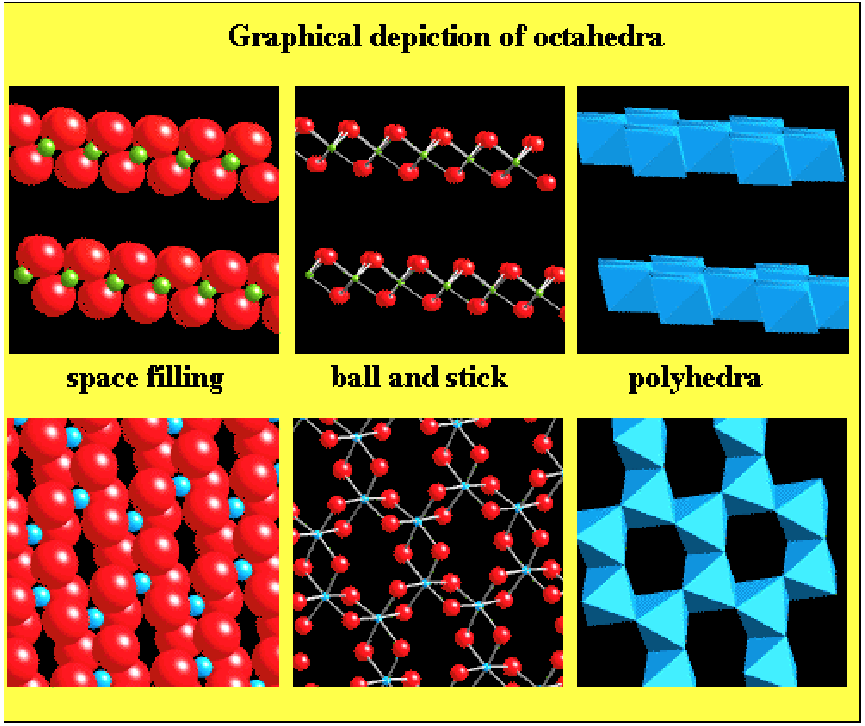


2:1 Phyllosilicates	General formula
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$

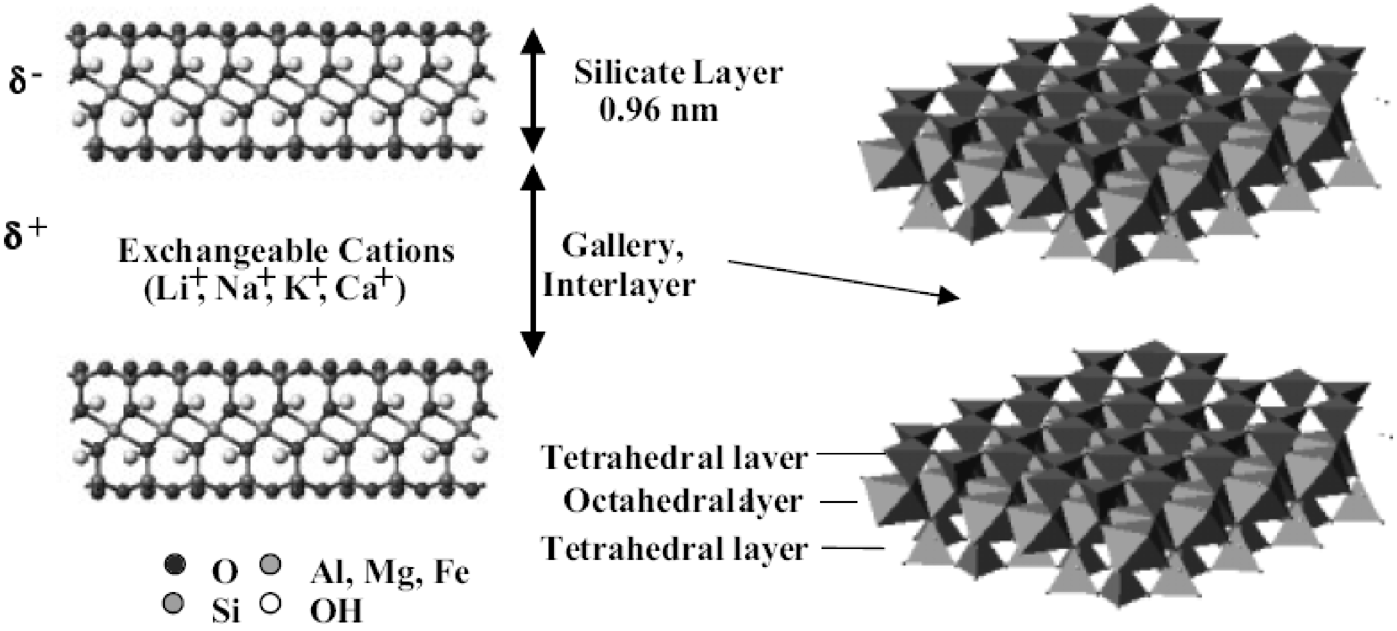
[a] M: monovalent cation; x: degree of isomorphous substitution (between 0.5 and 1.3).



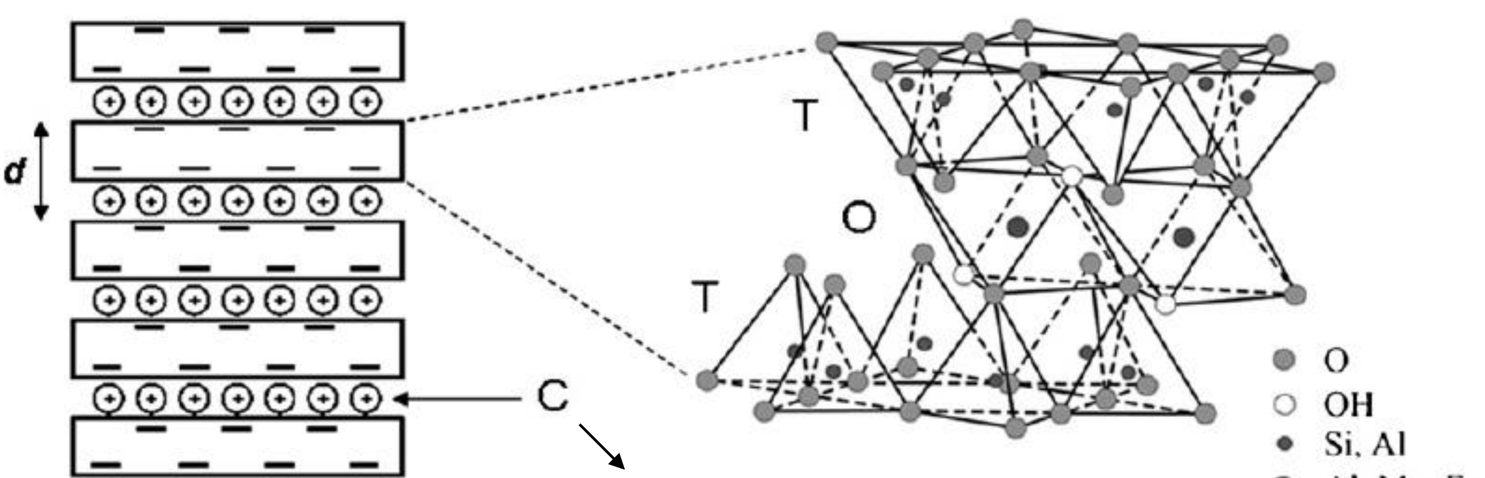
Graphical depiction of tetrahedra



Graphical depiction of octahedra



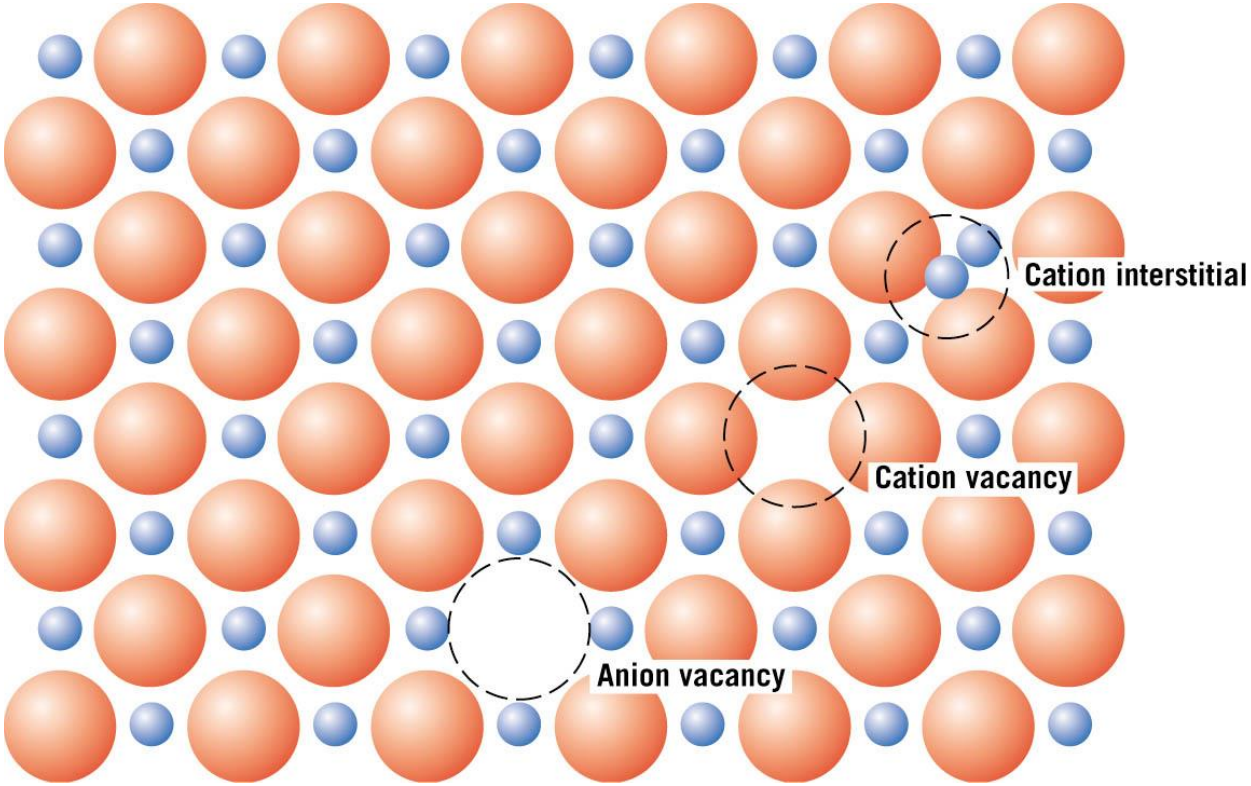
interlayer distance



intercalated cations

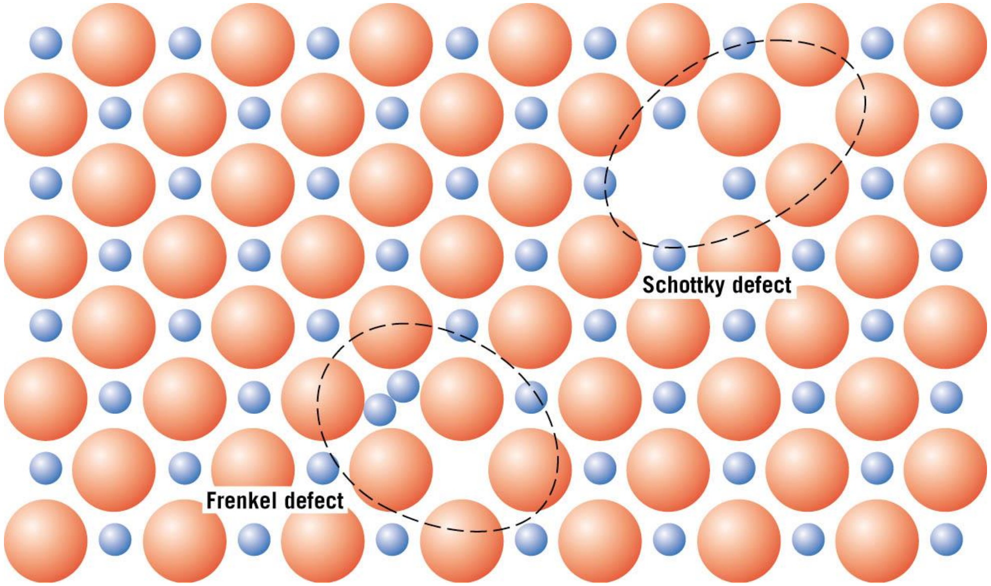
Difetti nei materiali ceramici

- L'esistenza di difetti nei ceramici deve garantire l'elettroneutralità



Difetti nei materiali ceramici

- Difetto di Frenkel
  -- catione fuori posizione
- Difetto di Shottky
  --una coppia di vacanze anionica e cationica

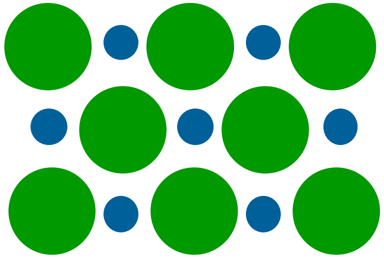


Impurezze

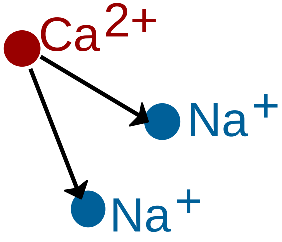
Sono possibili soluzioni solide sostituzionali e interstiziali

Anche le impurezze devono mantenere l’elettroneutralità

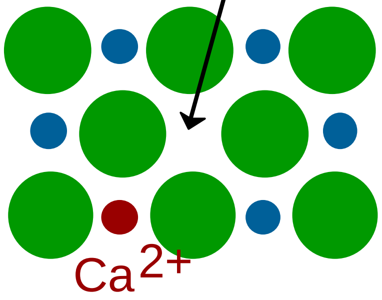
- Es: NaCl Na^+ ● Cl^- ●
- Impurezza sostituzionale cationica



geometria iniziale

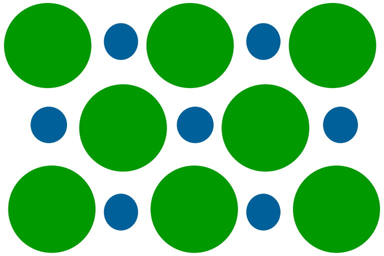


Ca^{2+} impurezza

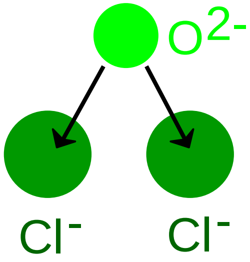


geometria risultante

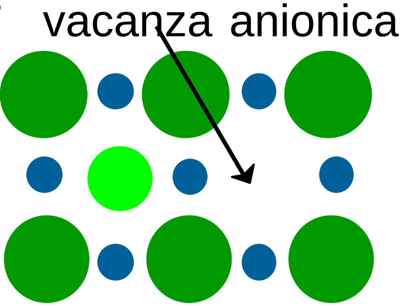
- Impurezza sostituzionale anionica



geometria iniziale



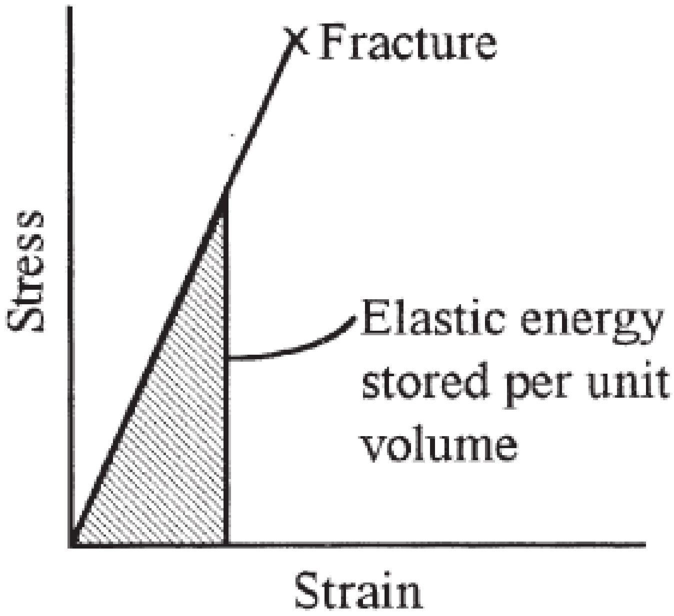
O^{2-} impurezza

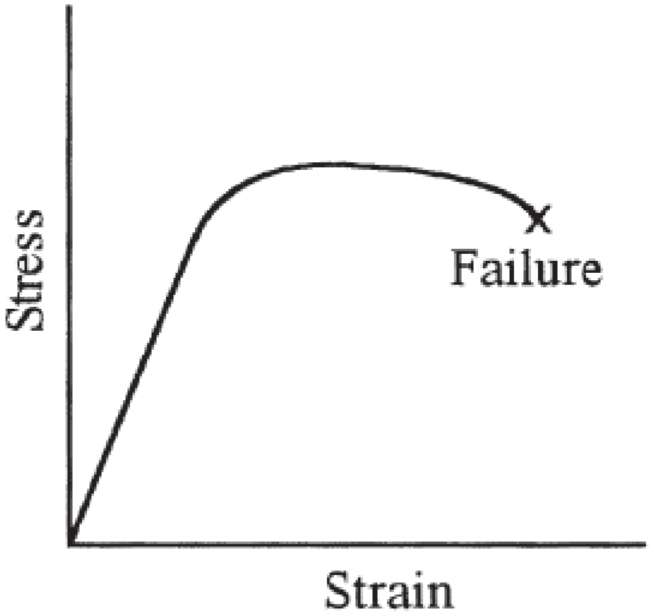


geometria risultante

Proprietà meccaniche

- Elevata rigidezza
- Elevata resistenza (soprattutto in compressione)
- A *T* ambiente mostrano un comportamento fragile fino a rottura senza apprezzabile deformazione plastica (dovuto al tipo di legame)
- Resistenza determinata da difetti inizialmente presenti nel materiale (spesso creati durante la fabbricazione)
- Buona stabilità chimica
- Elevata stabilità ad alta *T* (vero per i ceramici cristallini)


Fracture
Stress
Elastic energy stored per unit volume
Strain


Stress
Failure
Strain

Modulo elastico

- Il valore del modulo elastico è determinato dalla resistenza dei legami atomici del materiale. Più forte è il legame, maggiore sarà il valore del modulo elastico

- Ceramici con deboli legami ionici hanno bassi valori di *E* (Es. NaCl ha modulo pari a 44,2 GPa)

- Ceramici con forti legami covalenti hanno elevati valori di *E* (Es. Diamante ha modulo pari a 1035 GPa)

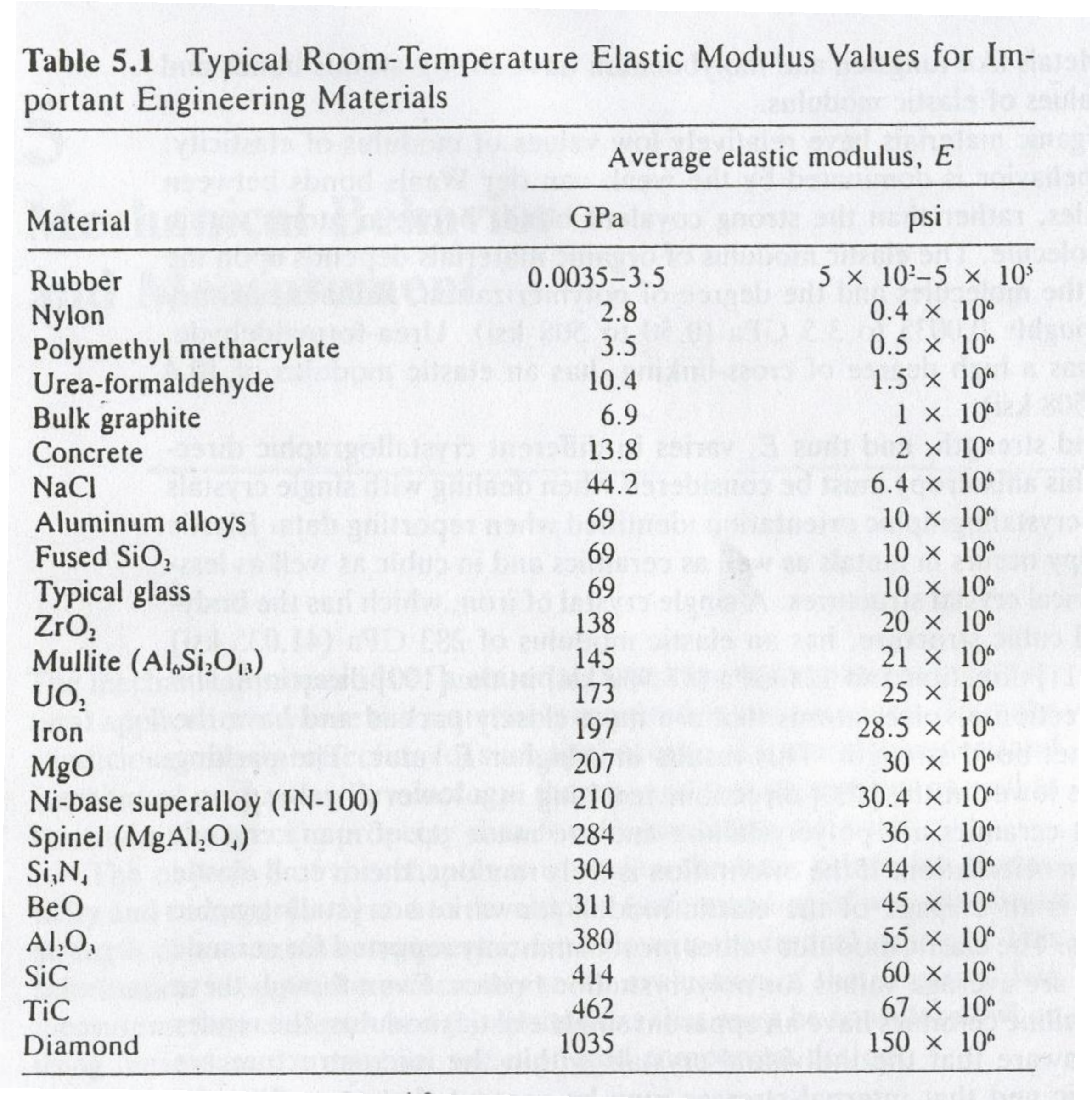


Table 5.1 Typical Room-Temperature Elastic Modulus Values for Important Engineering Materials

Material	Average elastic modulus, *E*	
	GPa	psi
Rubber	0.0035–3.5	5×10^2–5×10^5
Nylon	2.8	0.4×10^6
Polymethyl methacrylate	3.5	0.5×10^6
Urea-formaldehyde	10.4	1.5×10^6
Bulk graphite	6.9	1×10^6
Concrete	13.8	2×10^6
NaCl	44.2	6.4×10^6
Aluminum alloys	69	10×10^6
Fused SiO_2	69	10×10^6
Typical glass	69	10×10^6
ZrO_2	138	20×10^6
Mullite ($Al_6Si_2O_{13}$)	145	21×10^6
UO_2	173	25×10^6
Iron	197	28.5×10^6
MgO	207	30×10^6
Ni-base superalloy (IN-100)	210	30.4×10^6
Spinel ($MgAl_2O_4$)	284	36×10^6
Si_3N_4	304	44×10^6
BeO	311	45×10^6
Al_2O_3	380	55×10^6
SiC	414	60×10^6
TiC	462	67×10^6
Diamond	1035	150×10^6

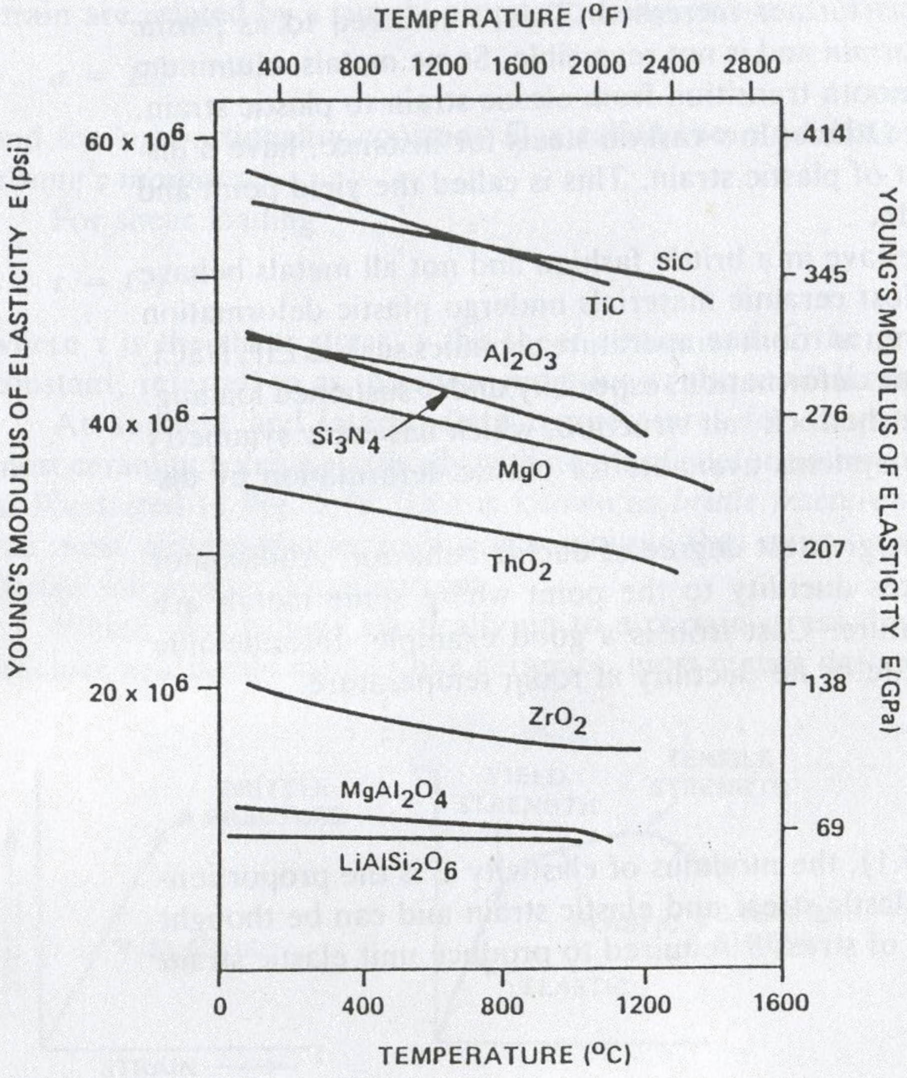


Figure 5.2 Effect of temperature on the elastic modulus.

E diminuisce leggermente all'aumentare della *T*

Ciò è dovuto all'aumento della distanza interatomica

All'aumentare della distanza interatomica, è richiesta meno forza per provocare ulteriore separazione

Resistenza

- La resistenza teorica dei ceramici varia da 1/10 a 1/5 del modulo elastico (presenza di difetti!)
- Tuttavia la resistenza *misurata* di un materiale ceramico è sostanzialmente inferiore a quella *teorica* (derivata dalla teoria sulle forze di legame interatomiche)

Materiale	E [GPa]	Resistenza Teorica [GPa]	Resistenza Misurata Fibre [GPa]	Resistenza Misurata Campione Policristallino [GPa]
Al_2O_3	380	38	2,5-3,5	0,4
SiC	440	44	~4,5-6	0,7

Resistenza

- Tale comportamento è dovuto alla presenza di difetti all’interno del materiale che favoriscono la frattura per livelli di sollecitazione ben al di sotto di quelli teorici
- Tali difetti agiscono da intensificatori degli sforzi
- La misura della capacità di un materiale ceramico di resistere alla frattura in presenza di una cricca è specificata in termini di *tenacità alla frattura* (K_{Ic})
- Più elevato è K_{Ic}, più difficile sarà l’innesco e la propagazione di una cricca
- I valori di K_{Ic} per i ceramici sono inferiori a quelli dei metalli (tipicamente sono inferiori a 10 MPa $m^{1/2}$)

Resistenza

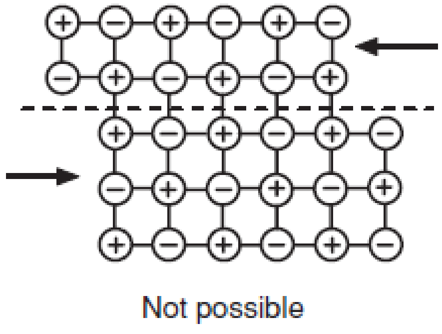
Le dislocazioni sono quasi completamente immobili (a T ambiente) nei materiali ceramici a causa della direzionalità dei legami e delle complesse strutture cristalline

In generale non si verifica deformazione plastica

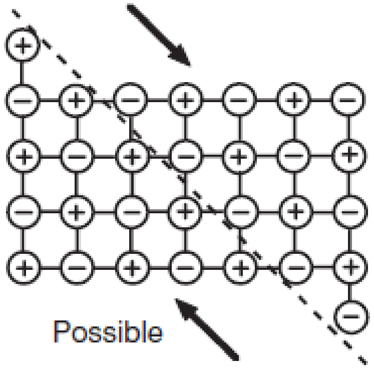
La frattura si verifica tipicamente per clivaggio, di solito con cricche iniziali che crescono e si propagano. I pori che rimangono al termine della compattazione possono agire da cricche iniziali e causare il cedimento per propagazione delle cricche. Tali cricche, una volta innescate, non essendoci deformazione plastica apprezzabile, non possono essere "scaricate" ⟶ Per tali motivi la tenacità a frattura dei ceramici è bassa.

A causa della elevata sensibilità dei ceramici per le cricche, anche piccoli difetti possono determinarne la resistenza. Di solito i ceramici contengono cricche di diverse dimensioni ed orientazioni. Sotto carichi di trazione, tali cricche possono essere sollecitate in tutti e tre i modi (I, II, III), mentre in compressione solo nei modi II e III. Visto che la tenacità a frattura è molto più piccola per il modo I che per gli altri, i ceramici a trazione tendono a cedere per il modo I e sono perciò più sensibili alla trazione che non alla compressione. La resistenza a compressione dei ceramici è da circa 10 a 15 volte più grande di quella a trazione.

- ✓ Ceramics tend to be brittle because the number of independent slip systems is limited. In an ionically bonded crystal, the slip plane and direction must be such that during slip there is not close contact between ions of like sign



a



b

Slip system	Critical resolved shear stress, τ_c,	(MPa)
	25°C	1,000°C
$(0001)\langle 2\overline{11}0\rangle$	30,000 (extrapolated)	130
$(0\bar{1}10)\langle 2\overline{11}0\rangle$	5,000	330

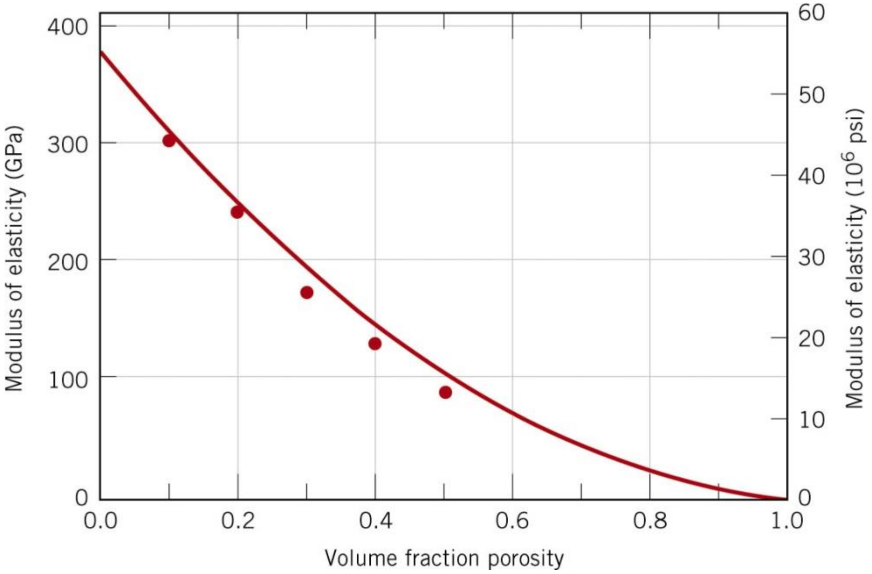
Structure			Slip systems	No. of independent slip systems
Rock salt	NaCl(LiF, MgO)	(RT)	<110>{110}	2
		(high temp)	&<110>{001}	3
Rock salt	AgCl	(RT)	<110>{001}, <110>{001}	
			&<110>{111}	5
Cubic cesium Chloride	CsCl(CsBr)	(RT)	<100>{001}	3
Cubic fluorite	$CaF_2(BaF_2)$	(RT)	<110>{001}	3
	” &UO_2	(high temp)	&<110>{110}	3
Rutile	TiO_2	(high temp)	$\langle 110\rangle\{1\bar{1}0\}$&<110>{001}	3
Hexagonal	graphite,			
	Al_2O_3, BeO	(high temp)	$\langle 11\bar{2}0\rangle(0001)$	2

Table 11.1 Data for Young's modulus Y, Poisson's ratio, and K_{Ic} values of selected ceramics at ambient temperatures[†]

	Y, (GPa)	Poisson's ratio	K_{Ic}, $MPa \cdot m^{1/2}$	Vickers hardness, GPa
Oxides				
Al_2O_3	390	0.20–0.25	2.0–6.0	19.0–26.0
Al_2O_3 (single crystal, $10\bar{1}2$)	340		2.2	
Al_2O_3 (single crystal, 0001)	460		>6.0	
$BaTiO_3$	125			
BeO	386	0.34		0.8–1.2
HfO_2 (monoclinic)	240			
MgO	250–300	0.18	2.5	6.0–10.0
$MgTi_2O_5$	250			
$MgAl_2O_4$	248–270		1.9–2.4	14.0–18.0
Mullite [fully dense]	230	0.24	2.0–4.0	15.0
Nb_2O_5	180			
$PbTiO_3$	81			
SiO_2 (quartz)	94	0.17		12.0 (011)
SnO_2	263	0.29		
TiO_2	282–300			10.0 ± 1.0
ThO_2	250		1.6	10.0
Y_2O_3	175		1.5	7.0–9.0
$Y_3Al_5O_{12}$				18.0 ± 1.0
ZnO	124			2.3 ± 1.0
$ZrSiO_4$ (zircon)	195	0.25		≈15.0
ZrO_2 (cubic)	220	0.31	3.0–3.6	12.0–15.0
ZrO_2 (partially stabilized)	190	0.30	3.0–15.0	13.0
Carbides, Borides, and Nitrides and Silicides				
AlN	308	0.25		12.0
B_4C	417–450	0.17		30.0–38.0
BN	675			
Diamond	1000			
$MoSi_2$	400			
Si	107	0.27		10.0
SiC [hot pressed]	440 ± 10	0.19	3.0–6.0	26.0–36.0
SiC (single crystal)	460		3.7	
Si_3N_4 Hot Pressed (dense)	300–330	0.22	3.0–10.0	17.0–30.0
TiB_2	500–570	0.11		18.0–34.0
TiC	456	0.18	3.0–5.0	16.0–28.0
WC	450–650		6.0–20.0	
ZrB_2	440	0.14		22.0
Halides and Sulfides				
CaF_2	110		0.80	1.800
KCl (forged single crystal)	24		≈0.35	0.120
MgF_2	138		1.00	6.000
SrF_2	88		1.00	1.400
Glasses and Glass Ceramics				
Aluminosilicate (Corning 1720)	89	0.24	0.96	6.6
Borosilicate (Corning 7740)	63	0.20	0.75	6.5
Borosilicate (Corning 7052)	57	0.22		
LAS (glass-ceramic)	100	0.30	2.00	
Silica (fused)	72	0.16	0.80	6.0–9.0
Silica (96%)	66		0.70	
Soda Lime Silica Glass	69	0.25	0.82	5.5

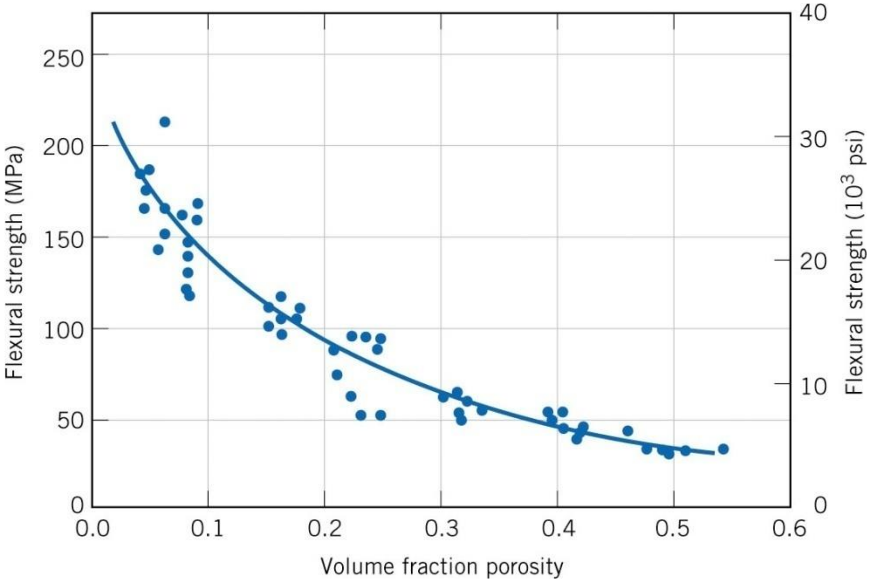
[†] The fracture toughness is a function of microstructure. The values given here are mostly for comparison's sake.

Influenza della porosità



$E=E_0(1-1,9P+0,9P^2)$

P= frazione in volume di porosità
E_0= Modulo elastico del materiale non poroso



$\sigma_{fs}=\sigma_0 \exp(-nP)$

σ_0 ed n sono costanti sperimentali

Shock Termico

A causa della loro fragilità e della bassa conducibilità termica, i ceramici sono inclini allo shock termico: cioè, si criccano se soggetti ad elevati gradienti termici

⇓

$$TSR \cong \frac{\sigma_f k}{E \alpha_l}$$

Meccanismi di Tenacizzazione

- ✓ **L’idea di base è quella di aumentare l’energia necessaria per estendere una cricca**

Tre approcci fondamentali:

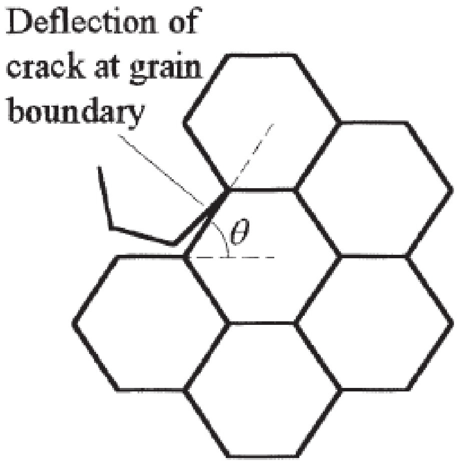
Crack Deflection

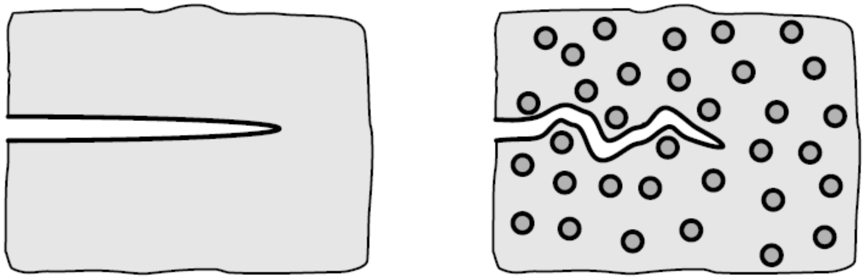
Crack Bridging

Transformation Toughening

Crack Deflection

- ✓ When the crack can be deflected from its straight path, the surface of the crack per advanced distance becomes larger, thus requiring additional energy for crack propagation and increasing the fracture toughness





(a) Without particles (b) With particles

Fig. 7.2. Deflection of a crack by appropriate particles in a ceramic

Stress residui

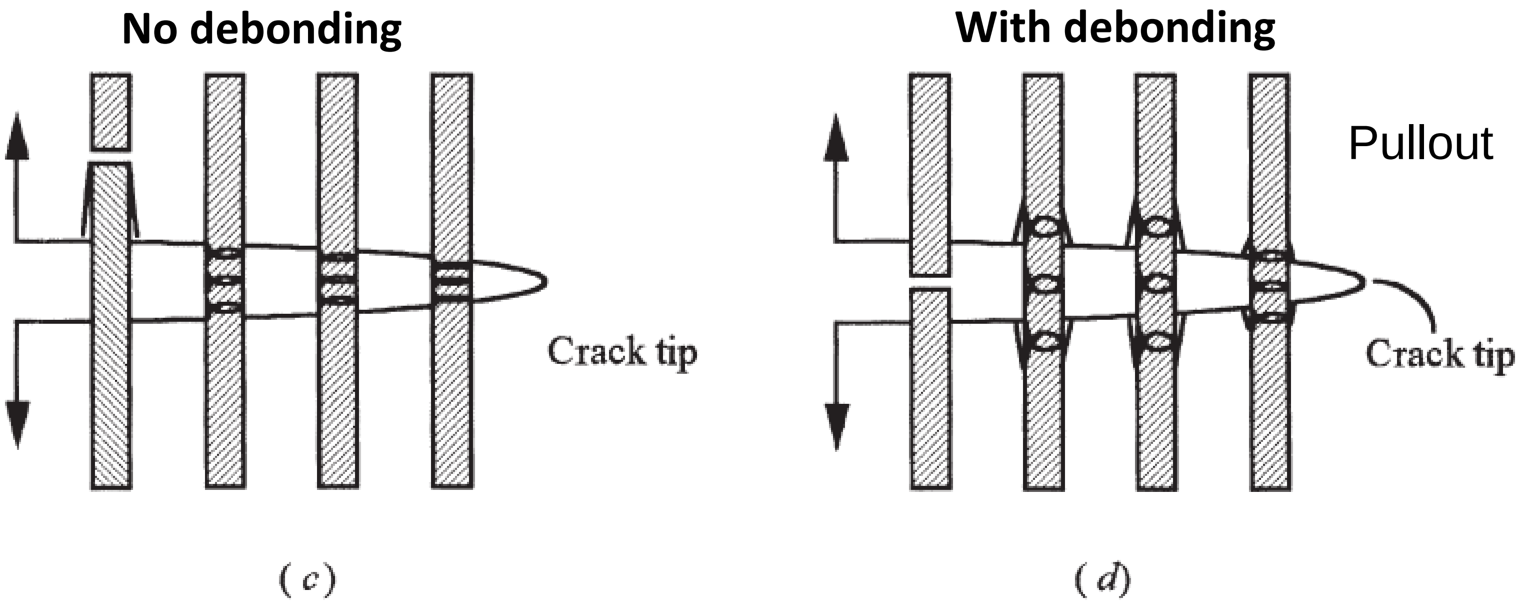
as crack deflects along weak grain boundaries, K_{tip} is reduced, because stress is no longer normal to crack plan

K_{Ic}= 2,2 MPa $m^{1/2}$ per monoscristallo di allumina

$$K_{tip} = \left(\cos^3 \frac{\theta}{2}\right) K_{app}$$

K_{Ic}= 4 MPa $m^{1/2}$ per allumina policristallina

Crack Bridging



(c)

(d)

✓ In this mechanism, the toughening results from bridging of the crack surfaces behind the crack tip by a strong reinforcing phase. These bridging ligaments generate closure forces on the crack face that reduce K_{tip}. In other words, by providing some partial support of the applied load, the bridging constituent reduces the crack-tip stress intensity. The formation of a debonded interface spreads the strain displacement imposed on the bridging reinforcing ligament over a longer gauge length

Fracture toughness of a "composite" *due to elastic stretching of a partially debonded reinforcing phase at crack tip with* ***no interfacial friction:***

$$K_{Ic} = \sqrt{E_c \cdot G_m + \sigma_f^2 \left(\frac{r \cdot V_f}{12} \cdot \frac{E_c}{E_f} \cdot \frac{\gamma_f}{\gamma_i} \right)}$$

P. Becher, J.Am.Ceram.Soc., 74:255-269 (1991)

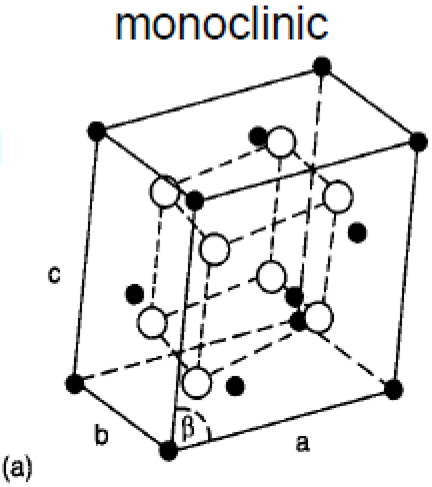
where:	c, m, f , i	composite, matrix, reinforcement, interface
	E, V, r	Young's modulus, volume fraction, radius of bridging ligament
	σ, G	strength of reinforcement phase, toughness of unreinforced ligament
	γ_f/γ_i	ratio of fracture energy of the bridging ligaments to that of the reinforcement/matrix interface

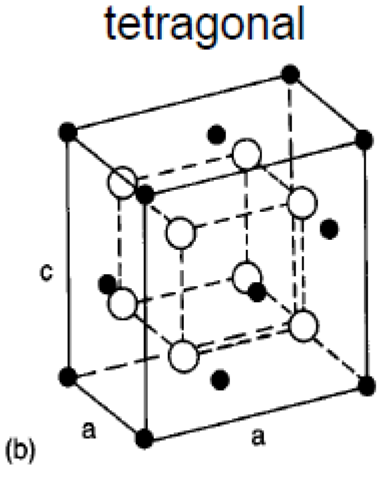
i.e. fracture toughness is increased for

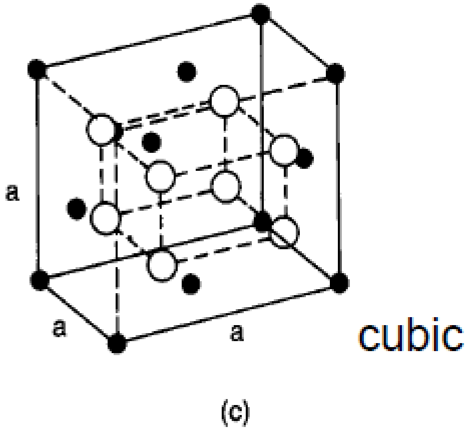
- **"high" reinforcement content,**
- **"weak" reinforcement *(increasing E_c/E_f ratio)* and**
- **"weak" reinforcement / matrix interfaces (increasing γ_f/γ_i ratio)**

Zirconia

- Zirconia exists in 3 different crystal structures based on the fluorite structure
  - a) monoclinic at low temperature
  - b) tetragonal at intermediate temperature
  - c) cubic at high temperature
- Cubic ⇔ tetragonal transformation is diffusional.
- Tetragonal ⇒ monoclinic transformation is martensitic with a 6% increase in volume







- ✓ The *t-m* transformation, which is martensitic, occurs during the sintering and on both heating and cooling
- ✓ The *t-m* transformation is accompanied by a large shear strain and a large volume increase. Together these create large internal stresses on cooling. So large, in fact, that pure zirconia sintered above 1170°C inevitably disintegrates by cracking upon cooling
- ✓ To maintain the integrity of sintered zirconia bodies at room temperature, one can either sinter at low temperature for it to remain monoclinic during sintering—which leads to a low-strength and toughness ceramic—or stabilize the tetragonal or the cubic phases at room temperature by alloying, thereby avoiding the *t-m* transformation during cooling
- ✓ Calcium, magnesium, yttrium, and cerium oxides have been the most widely used stabilizers and lead to a number of different microstructures

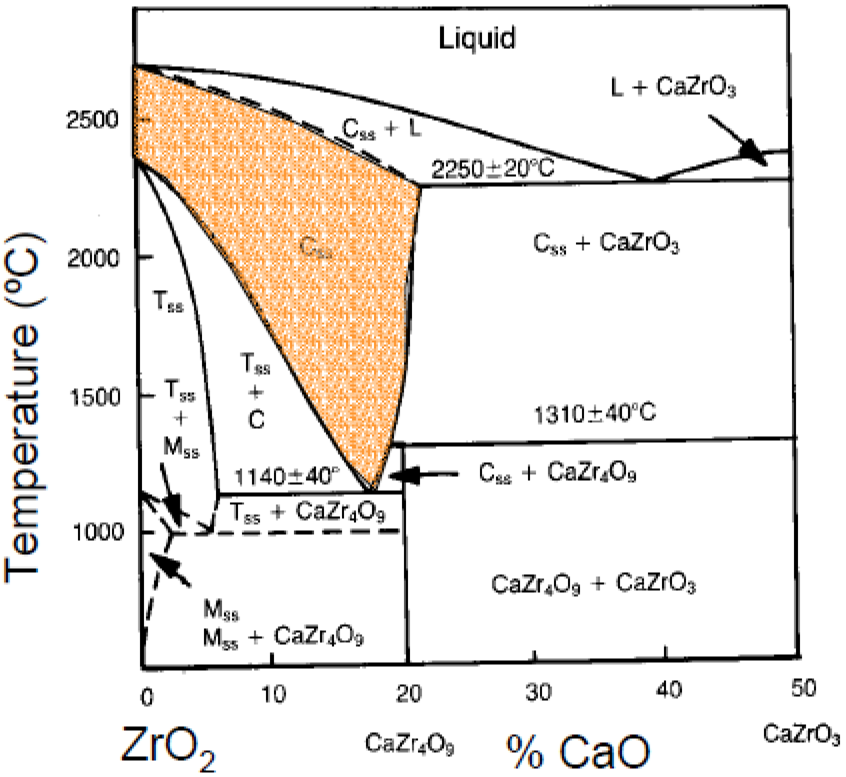
- ✓ In general, zirconia ceramics may conveniently be classified into three major types according to their microstructure:
  FSZ, **PSZ**, and **TZP**, standing, respectively, for *fully stabilized zirconia*, *partially stabilized zirconia*, and *tetragonal zirconia polycrystals*

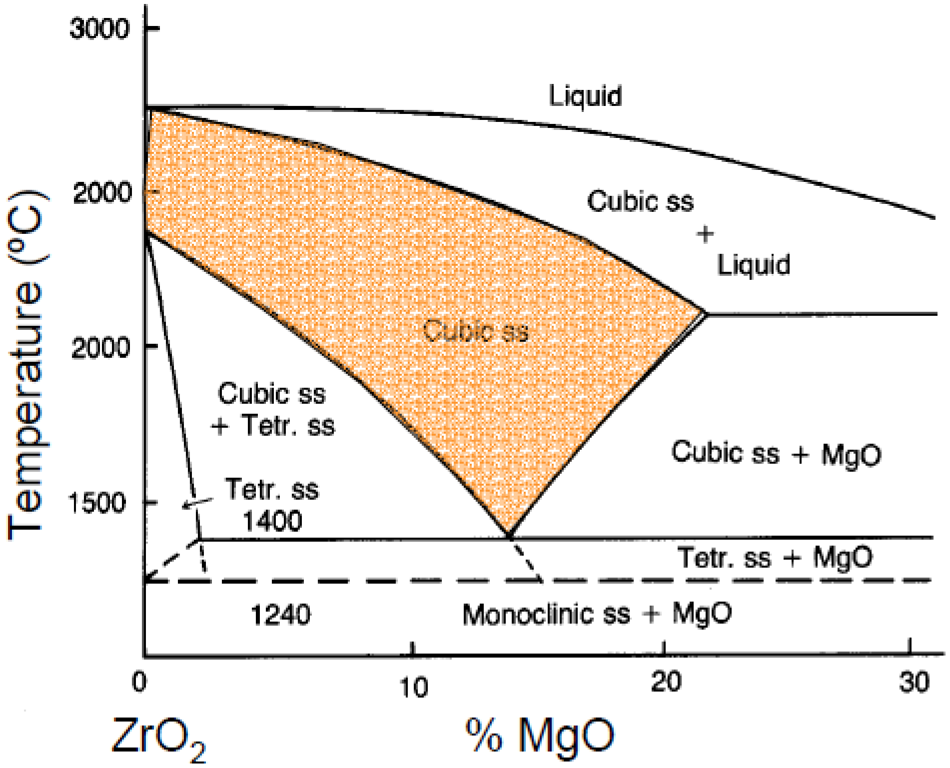
- ✓ In FSZ zirconia is in its cubic form, the form most commonly used in oxygen sensors and fuel cell electrolytes. It is generally obtained with large concentration of stabilizers (i.e., more than 8 mol% Y_2O_3)

- ✓ The PSZ consists of nanosized tetragonal or monoclinic particles that have precipitated out in a cubic matrix

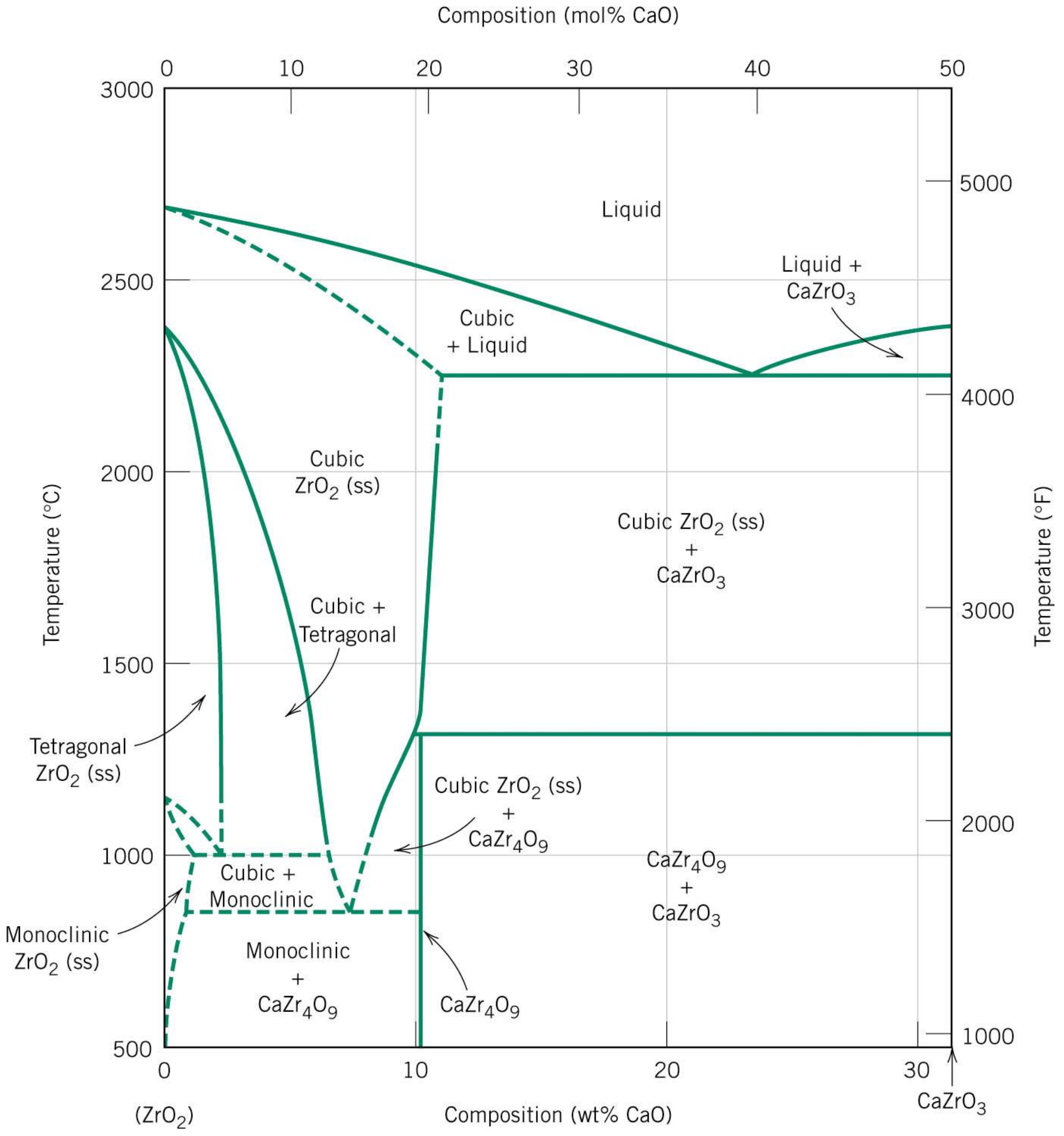
- ✓ TZPs are often considered as monoliths of tetragonal phase, although they may contain a secondary cubic phase. The majority of TZPs that have been investigated are those stabilized with yttria or ceria

Stabilised Zirconia



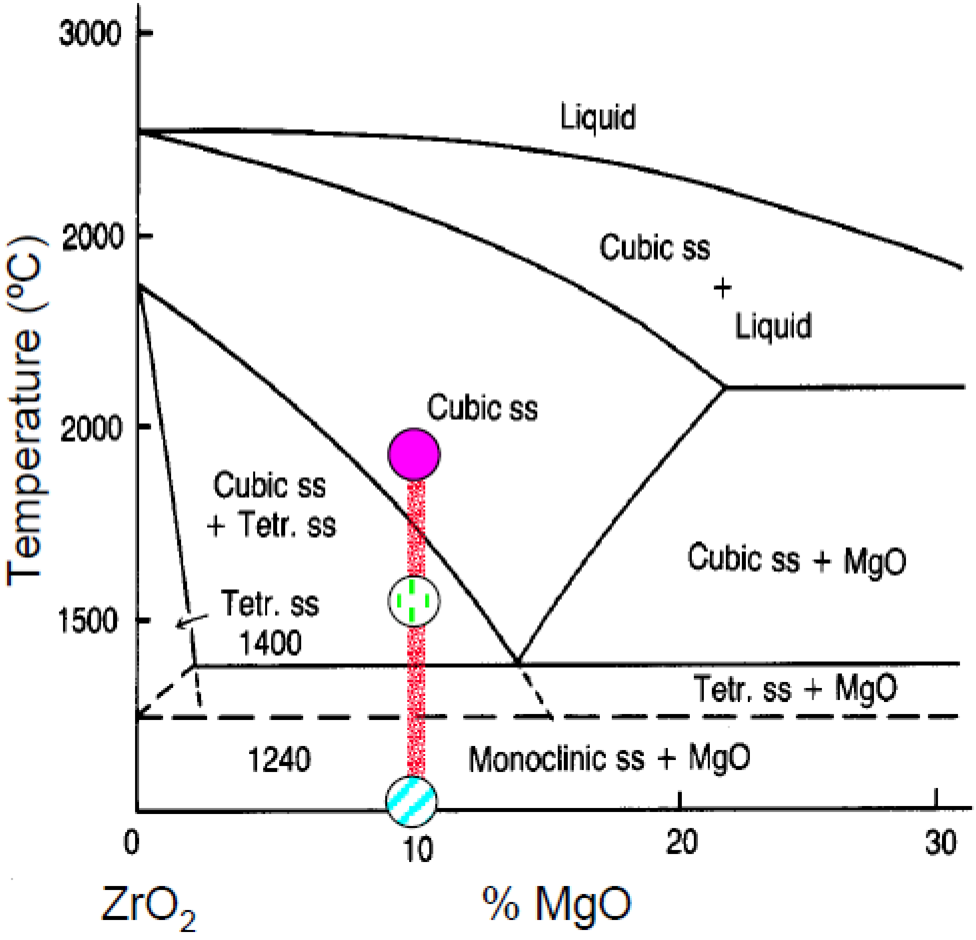


- A number of dopants can be used to stabilise the cubic phase to lower temperatures
- Most important are CaO, MgO, Y_2O_3 and CeO_2


Composition (mol% CaO)
0
10
20
30
40
50
3000
2500
2000
1500
1000
500
5000
4000
3000
2000
1000
Temperature (°C)
Temperature (°F)
Liquid
Liquid + $CaZrO_3$
Cubic + Liquid
Cubic ZrO_2 (ss)
Cubic ZrO_2 (ss) + $CaZrO_3$
Cubic + Tetragonal
Tetragonal ZrO_2 (ss)
Cubic ZrO_2 (ss) + $CaZr_4O_9$
$CaZr_4O_9$ + $CaZrO_3$
Cubic + Monoclinic
Monoclinic ZrO_2 (ss)
Monoclinic + $CaZr_4O_9$
$CaZr_4O_9$
0
10
20
30
(ZrO_2)
Composition (wt% CaO)
$CaZrO_3$

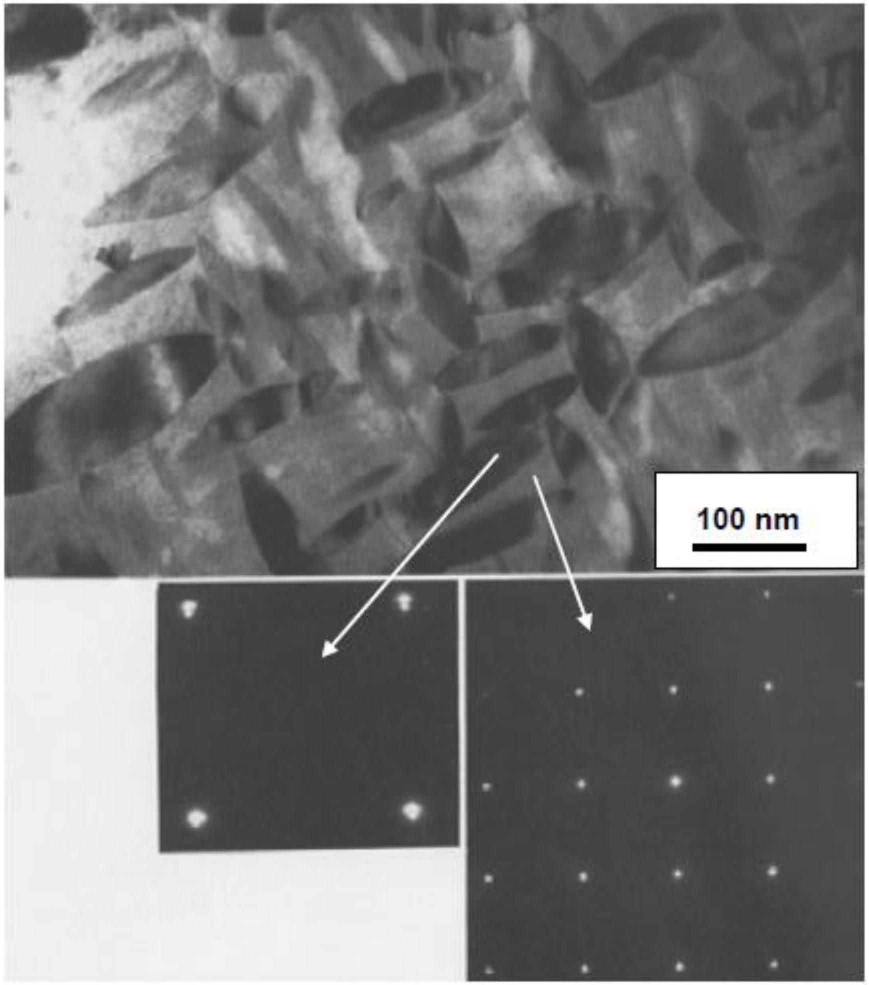
Partially Stabilised Zirconia (PSZ)

- Add about 10% MgO
- Sinter the material in the cubic phase ●
- Lower temperature and heat treat (age) to nucleate small precipitates of t-phase ◍
  - These are grown to below the critical size for t-m transformation
- Cool to room temperature ▨
  - Remaining c-phase does not get time to transform



Mg-PSZ Microstructures

- Age at 1400°C.
  After 4-5 hours tetragonal precipitates form and grow by conventional diffusional processes as coherent spheroids along {001} cube planes.
- Below a well defined critical size of about 200 nm the t-particles are retained on cooling to room temperature.
- Optimum microstructures contain about 25% - 30% by volume of tetragonal phase.

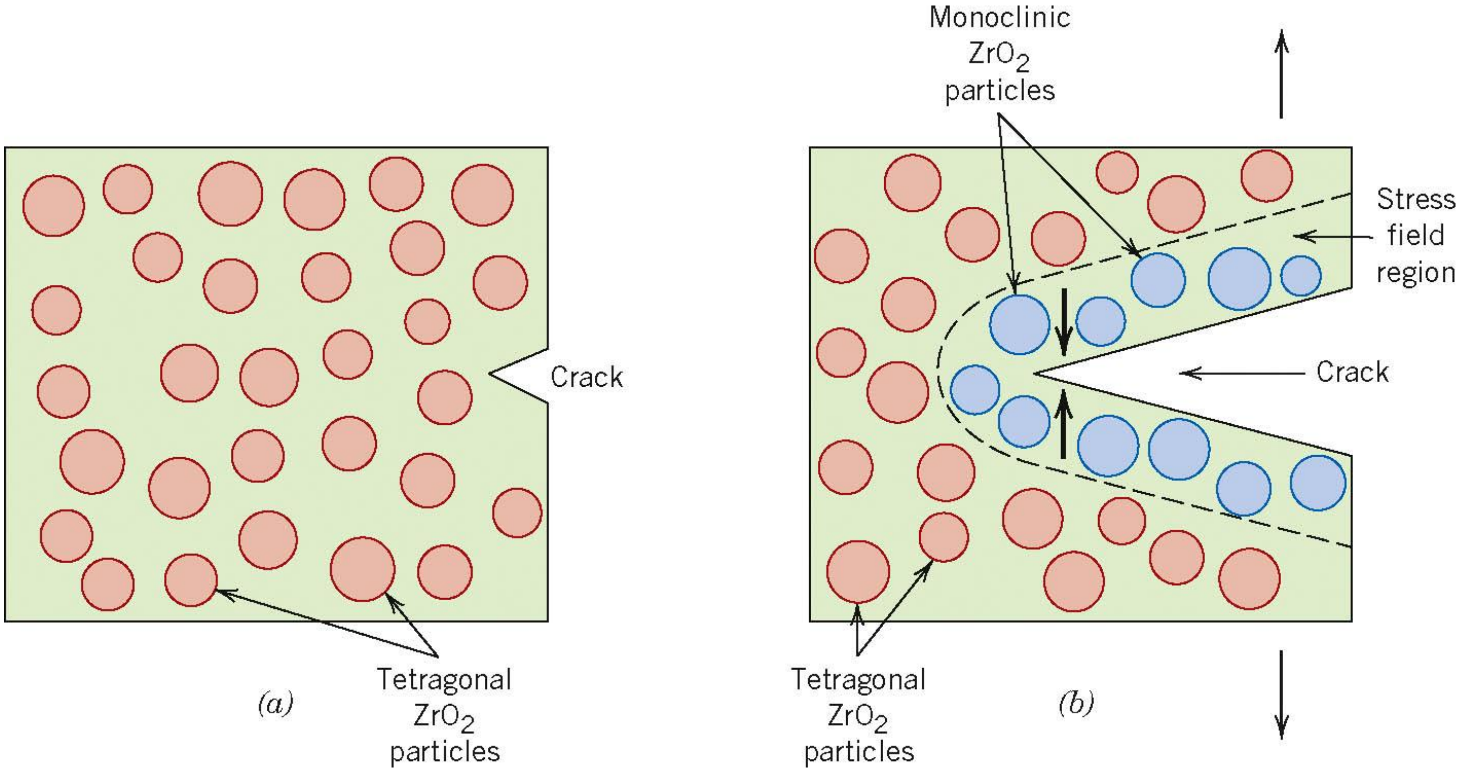


Transformation Toughening

ZrO_2 Zirconia

Al raffreddamento presenta una trasformazione martensitica dalla fase tetragonale a quella monoclina. Controllando opportunamente la composizione, la dimensione delle particelle ed il ciclo termico, si può raffreddare la zirconia in modo tale da mantenere la fase tetragonale come precipitati fino a T ambiente. La fase tetragonale non è in equilibrio a T ambiente e tenderebbe a trasformarsi nella più stabile fase monoclina. Tuttavia, tale trasformazione comporta un aumento di volume. Se la dimensione dei precipitati è sufficientemente piccola (<0,5μm), la resistenza dei grani adiacenti ostacola la trasfomazione impedendo la necessaria espansione di volume. Se viene applicata una sollecitazione ed una cricca tenta di propagarsi, i grani di zirconia tetragonale metastabile adiacenti all’apice della cricca si espandono tasformandosi nella fase monoclina stabile. Tale trasformazione martensitica è accompagnata da un aumento di volume del ~4% dei precipitati adiacenti alla cricca. Tale aumento di volume pone in compressione la cricca e la blocca. La zirconia pura non presenta tale comportamento. Sono necessari degli additivi per stabilizzare tale comportamento: MgO, Y_2O_3, CeO_2

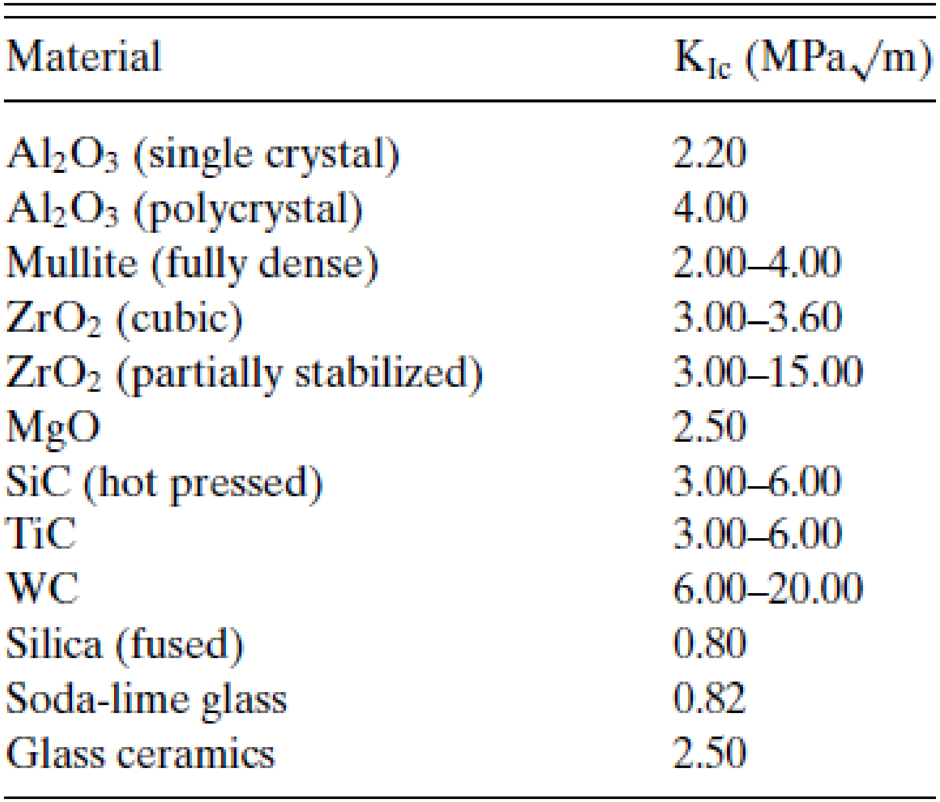
Una eccessiva quantità di stabilizzanti causa la totale stabilizzazione della zirconia nella fase cubica, che non mostra tenacizzazione perché non si può verificare la trasformazione t→m



$$\text{Monoclinic} \xrightarrow[1170°C]{} \text{tetragonal} \xrightarrow[2370°C]{} \text{cubic} \xrightarrow[2680°C]{} \text{liquid}$$

Principale limitazione: la Temperatura

I materiali così tenacizzati mostrano una progressiva riduzione di resistenza e tenacità all’aumentare della T (diventa progressivamente stabile la fase tetragonale)



Material	K_{Ic} (MPa$\sqrt{m}$)
Al_2O_3 (single crystal)	2.20
Al_2O_3 (polycrystal)	4.00
Mullite (fully dense)	2.00–4.00
ZrO_2 (cubic)	3.00–3.60
ZrO_2 (partially stabilized)	3.00–15.00
MgO	2.50
SiC (hot pressed)	3.00–6.00
TiC	3.00–6.00
WC	6.00–20.00
Silica (fused)	0.80
Soda-lime glass	0.82
Glass ceramics	2.50

Trattamenti termici del vetro

- Ricottura:

  --rimuove gli stress interni causati da un raffreddamento disuniforme
- Tempra del vetro:

  --crea degli stress residui di compressione in superficie

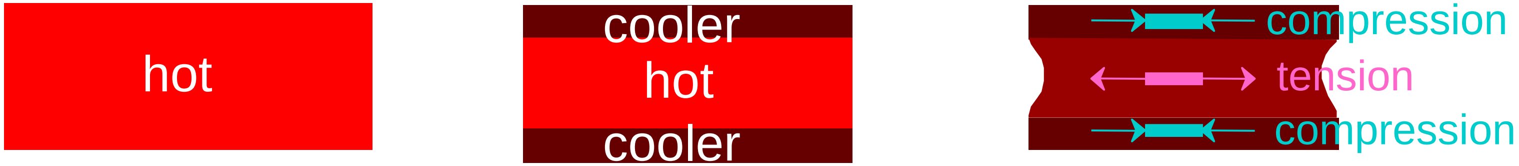
  --migliora la resistenza e la tenacità

  --sequenza:

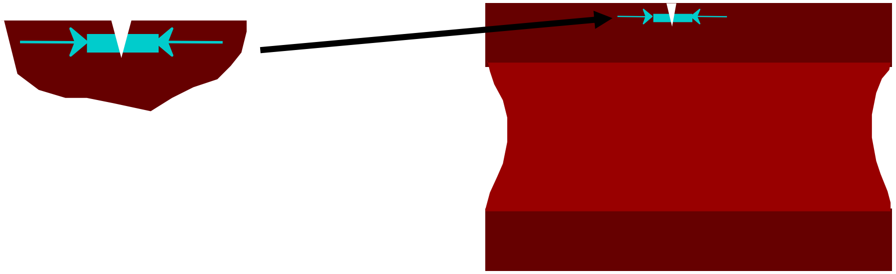
before cooling

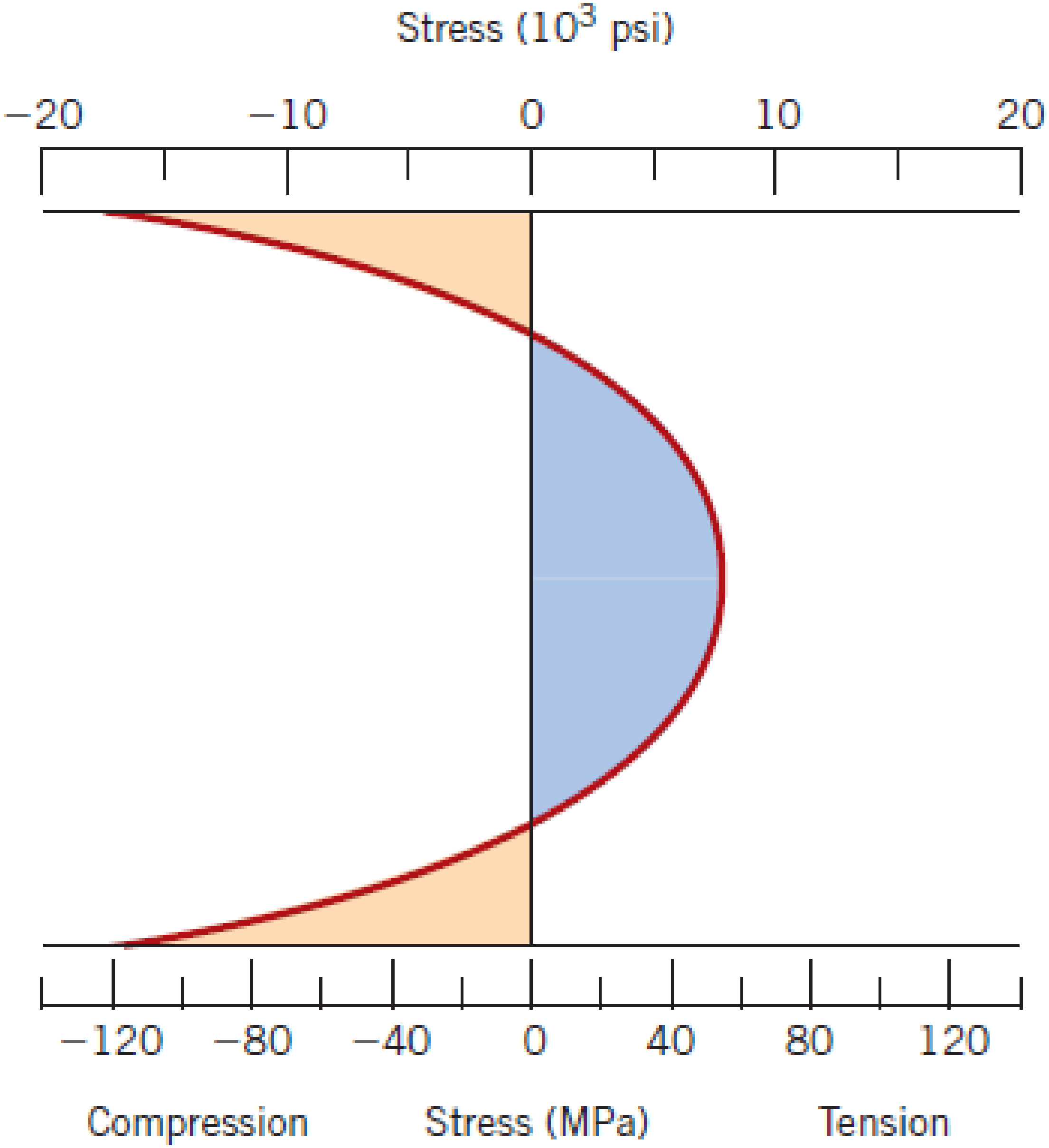
surface cooling

further cooled



--Result: surface crack growth is suppressed.




Stress (10^3 psi)
−20
−10
0
10
20
−120
−80
−40
0
40
80
120
Compression
Stress (MPa)
Tension

Subcritical Crack Growth

- As discussed previously, at low and intermediate temperatures, failure typically emanates from a preexisting flaw formed during processing or surface finishing. The condition for failure is straightforward: Fracture occurs rapidly and catastrophically when $K_I > K_{ic}$

- It was tacitly implied that for conditions where $K_I < K_{Ic}$, the crack was stable, i.e., did not grow with time, and consequently, the material would be able to sustain the load indefinitely

- In reality, the situation is not that simple — preexisting cracks can and do grow slowly under steady loading, even when $K_I < K_{ic}$

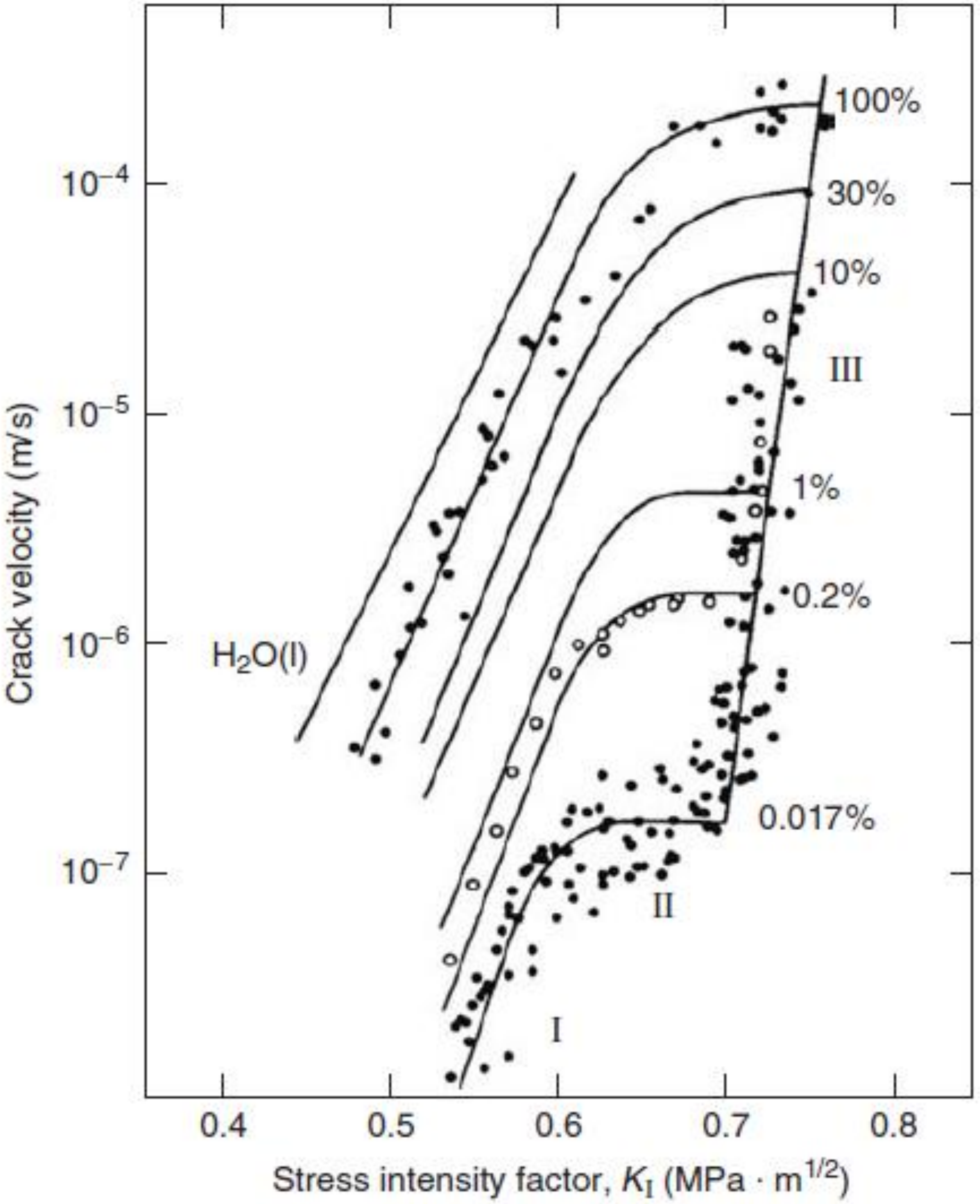
- A phenomenon that has been well appreciated for a long time is that the exposure of a ceramic to the combined effect of a steady stress and a corrosive environment results in slow crack growth

- ✓ In this mode of failure, ***a preexisting subcritical crack, or one that nucleates during service, grows slowly by a stress-enhanced chemical reactivity at the crack tip*** and is referred to as ***subcritical crack growth (SCG)***. Unfortunately, this phenomenon is also sometimes termed *static fatigue*

- ✓ The insidiousness of, and hence the importance of understanding this phenomenon lies in the fact that as the crack tip advances, the material is effectively weakened and eventually can give way suddenly and catastrophically after years of service

- ✓ Slow crack propagation occurs in many ceramics and is especially prevalent in ceramics containing a silica phase and in the presence of an appreciable partial pressure of water vapor

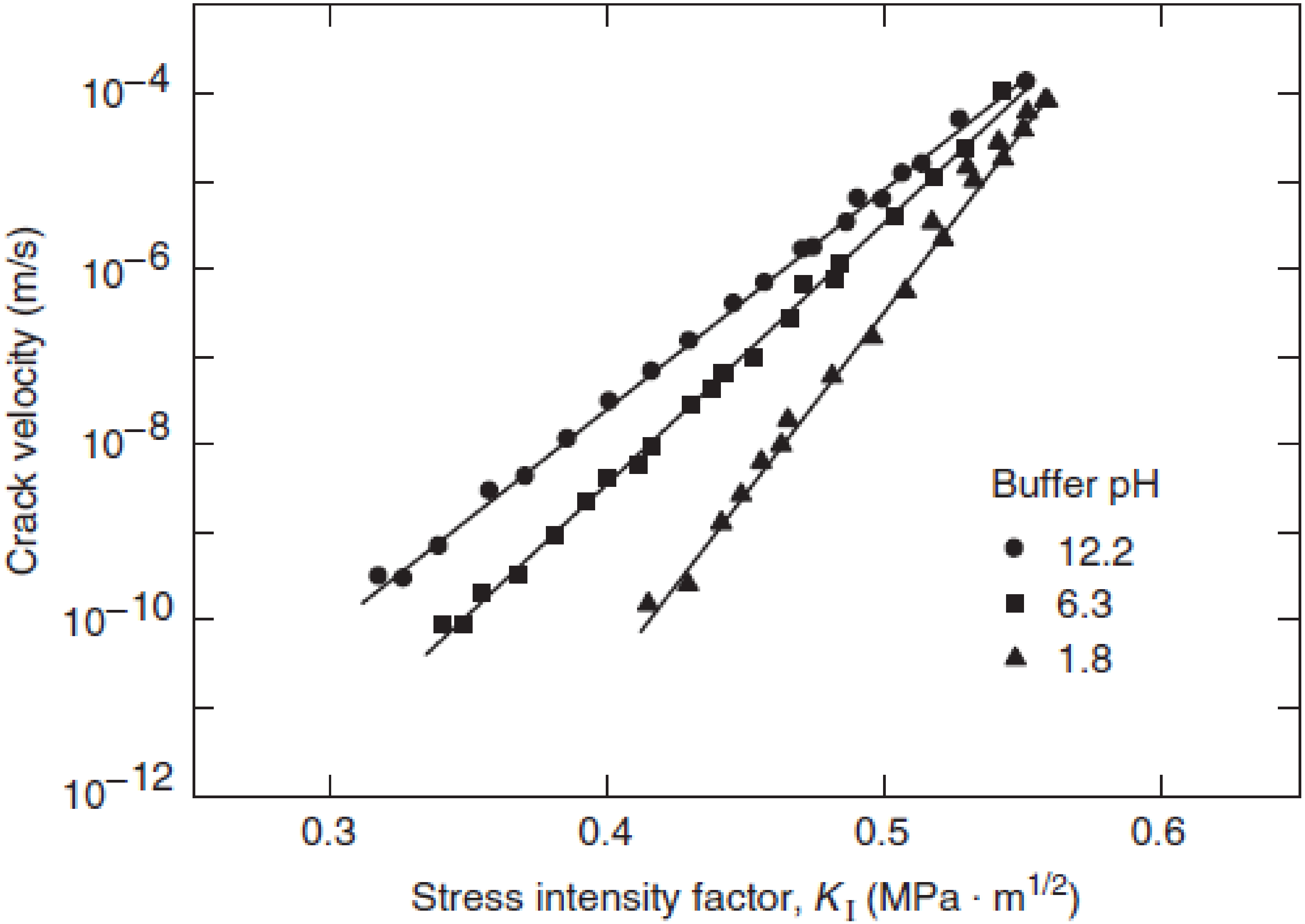
- ✓ For a given material, temperature, and relative humidity, the controlling variable is the ***applied stress intensity factor***



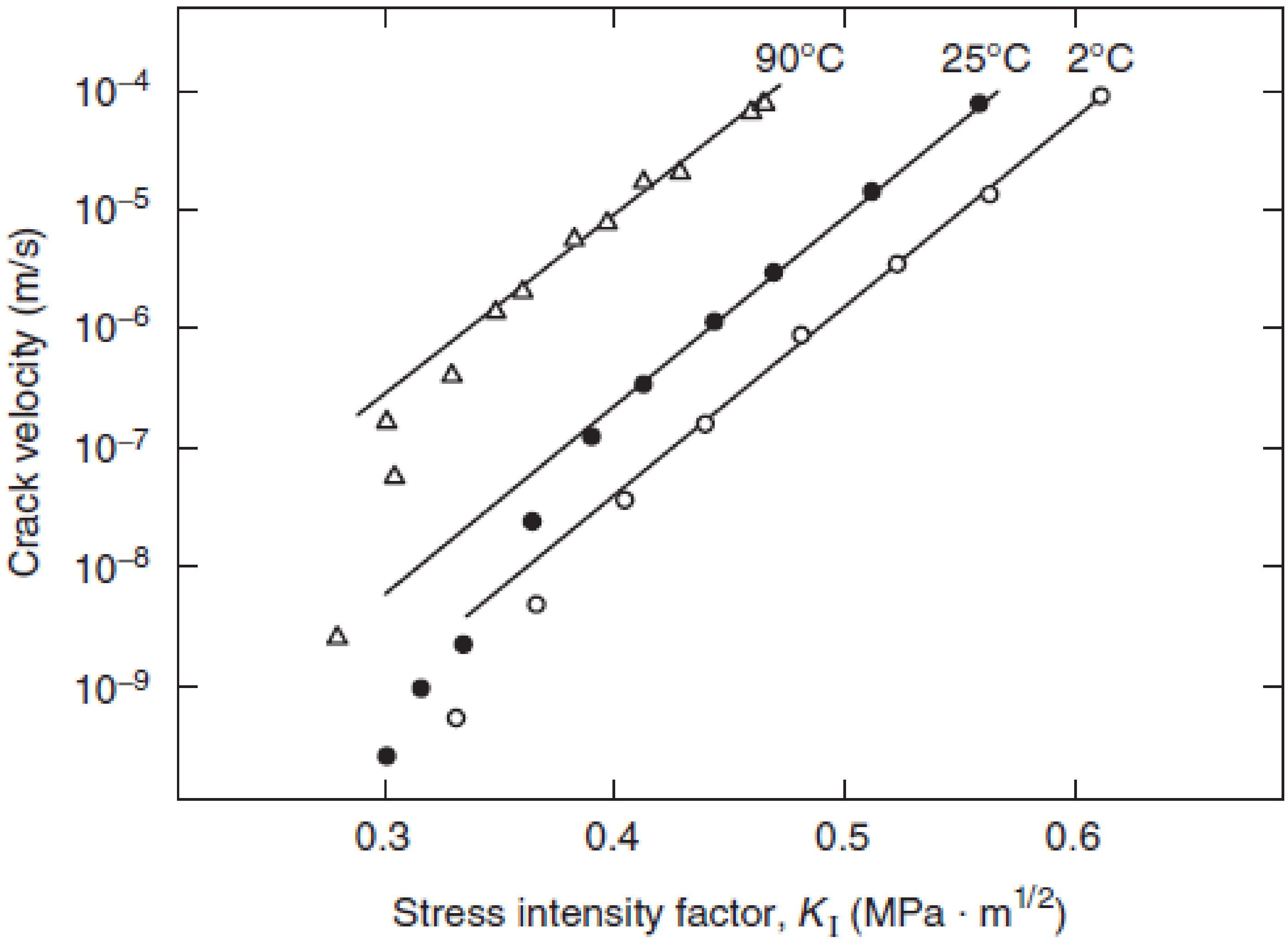
Crack velocity in soda–lime–silica glass as a function of stress intensity factor in nitrogen at various values of relative humidity

- ✓ The stress intensity factor K_I is the controlling factor; all data from many cracks with various combinations of crack length and applied stress fall on the same master curves when expressed in terms of K_I
- ✓ At low values of K_I the semilogarithmic plot is linear. This range of behavior is termed **region I**
- ✓ Within region I the crack velocity for constant K_I is greater for greater values of relative humidity. Crack growth in region I is attributable to a stress-enhanced chemical reaction between water and the glass. The rate of crack growth is reaction rate controlled so that increasing the concentration of the reactant should increase the rate of growth

Further evidence of chemical control in region I. Increasing the pH increases the rate of crack propagation at constant K_I for silica glass in water



Effect of temperature on crack velocity in soda–lime–silica glass in water



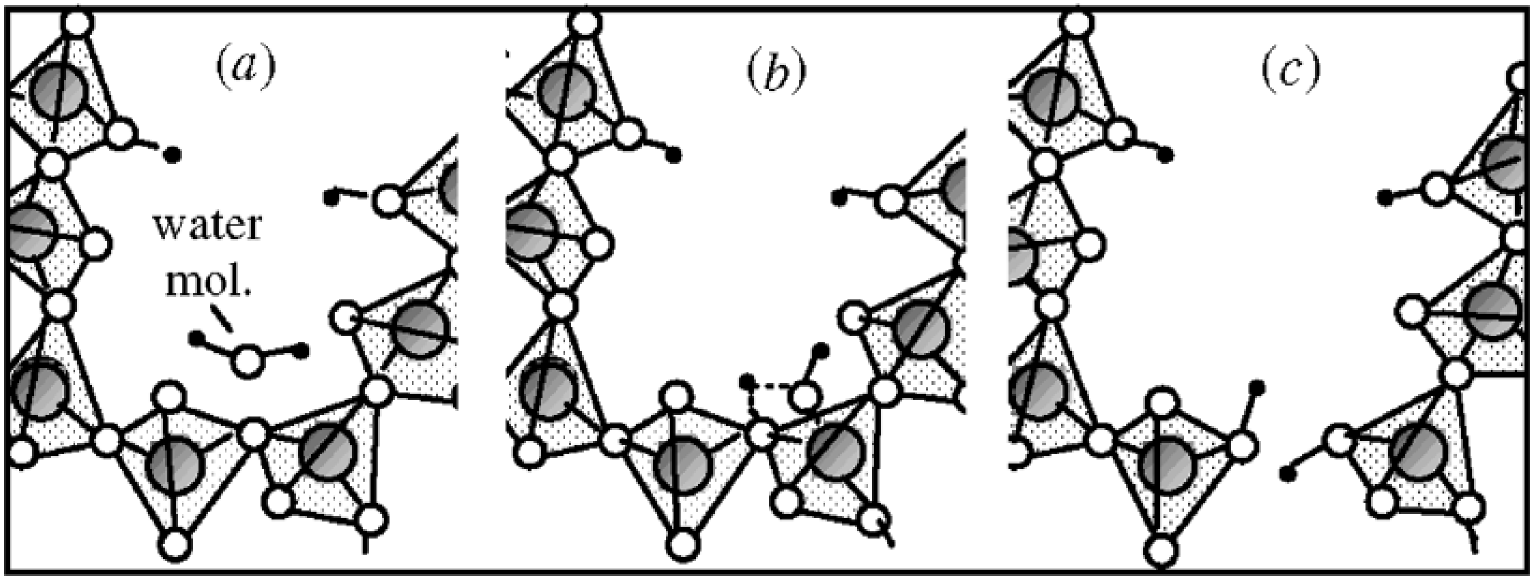
- ✓ There is the existence of **region II** at higher values of K_I, in which the crack velocity is still dependent on the partial pressure of water but substantially independent of K_I. Here crack growth rate is still controlled by a stress-enhanced chemical reaction between water and glass, but now the rate of growth is determined by the rate of transport of water to the crack tip

- ✓ At still higher values of K_I, **region III** occurs, in which crack propagation becomes independent of water in the environment

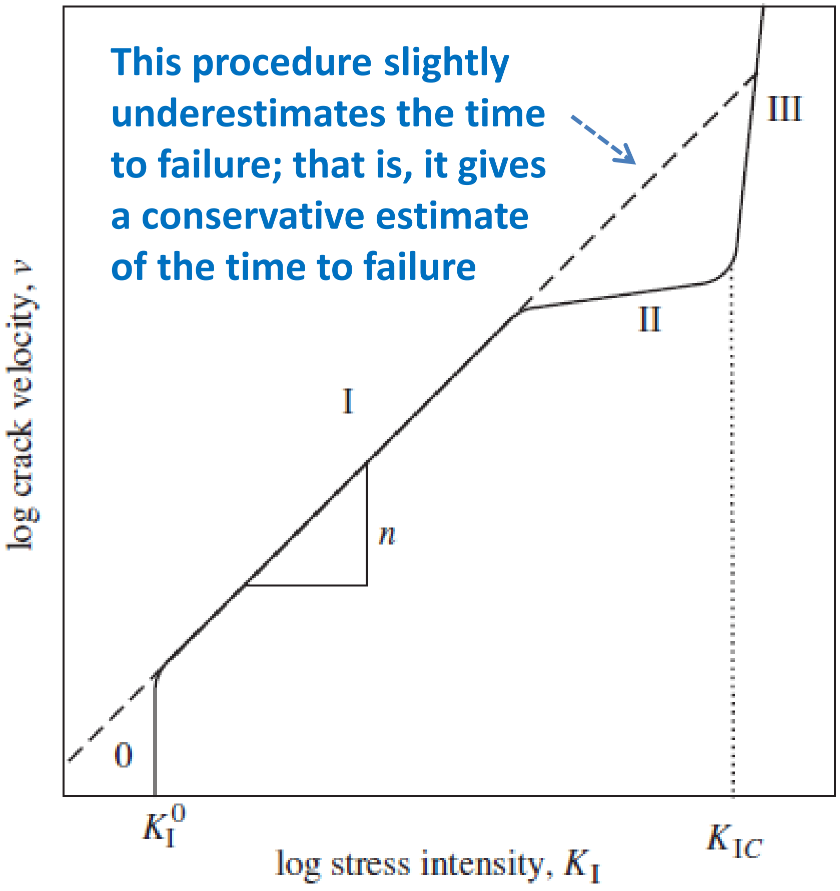
- ✓ Sometimes a **fatigue threshold or fatigue limit** is observed; that is, the crack velocity is zero below some threshold stress intensity K^0_I . This phenomenon is not easy to study since the crack velocity is extremely slow just above the threshold, but the threshold is expected theoretically

- ✓ It is region I that determines the lifetime of a part
- ✓ The model that has been suggested to explain region I for glasses in the presence of moisture is based on chemical-reaction theories
- ✓ It is now generally accepted that a stressed Si–O–Si bond at a crack tip will react with water to form two Si–OH bonds according to the following chemical reaction:

$$\mathrm{Si{-}O{-}Si} + \mathrm{H_2O} = 2\mathrm{Si{-}OH}$$



- ✓ Experimentally, it is now fairly well established that water is not the only agent that causes SCG in glasses; other polar molecules such as methanol and ammonia have also been found to cause SCG, provided that the molecules are small enough to fit into the extending crack (i.e., smaller than about 0.3 nm)



This procedure slightly underestimates the time to failure; that is, it gives a conservative estimate of the time to failure

The data in region I are well described by a straight line on a log–log plot of crack velocity v as a function of K_I. This plot leads to the empirical power law for crack velocity,

$$\boxed{v = AK_I^n}$$

where *n* is the stress corrosion susceptibility parameter. This law is convenient mathematically and is usually used in lifetime calculations

TIME TO FAILURE UNDER CONSTANT STRESS

- ✓ The general fracture mechanics relation for the stress intensity factor K_I for a crack of length c under stress σ is

$$K_{\mathrm{I}} = Y \sigma c^{1/2}$$

When the applied stress σ remains constant, the crack grows slowly until $K_I = K_{IC}$, at which point failure occurs at some time after the stress was applied. While the applied stress is constant, both the crack length and the stress intensity applied to the crack increase with time

- ✓ For constant σ the stress intensity factor will increase at a rate given by differentiating previous equation with time

$$\frac{dK_I}{dt} = \frac{\sigma Y}{2c^{1/2}}\boxed{\frac{dc}{dt}} + \sigma c^{1/2}\boxed{\frac{dY}{dt}}$$

$K_I = Y\sigma c^{1/2}$

v

For cracks that are small compared to the specimen dimensions, the change in Y as the crack grows is small so that the last term may be ignored

$$dt = \frac{2}{\sigma^2 Y^2}\frac{K_I}{v}dK_I$$

$$t_f = \frac{2}{\sigma^2 Y^2}\int_{K_{Ii}}^{K_{IC}}\frac{K_I}{v}dK_I$$

$v = AK_I^n$

$$t_f = \frac{2}{\sigma^2 A Y^2 (n-2)} \left(\frac{1}{K_{\mathrm{I}i}^{n-2}} - \frac{1}{K_{\mathrm{IC}}^{n-2}} \right)$$

If n is large (as it usually is) $K_{\mathrm{I}i}^{n-2} \ll K_{\mathrm{IC}}^{n-2}$

⬇

$$t_f = \frac{2}{\sigma^2 A Y^2 (n-2)} \frac{1}{K_{\mathrm{I}i}^{n-2}}$$

Statistical treatment of strength in ceramics

- All components have **defects** due to fabrication and usage. They have a size from a few µm up to a few 100 µm

- **Strength of a component** is defined by a combination of
  - critical stress intensity factor
  - size of critical defect
  - position of critical defect
  - stress and stress direction the crack sees

- Ceramic materials **fail without warning** even at elevated temperatures
  K_{Ic} is between 1 MPa $\sqrt{m}$ and 20 MPa $\sqrt{m}$

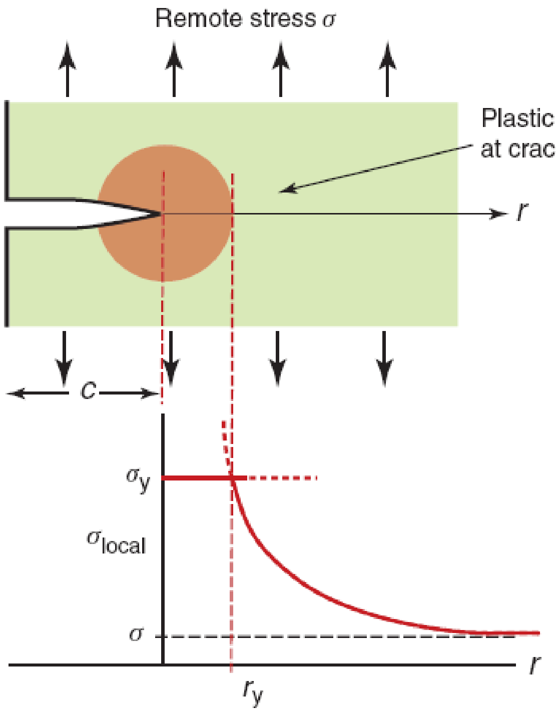
- The aim is always to **improve** both
  - σ_c *by reducing a_c, e.g. by improved processing*
  - K_{Ic} *by increasing fracture energy, e.g. crack bridging*

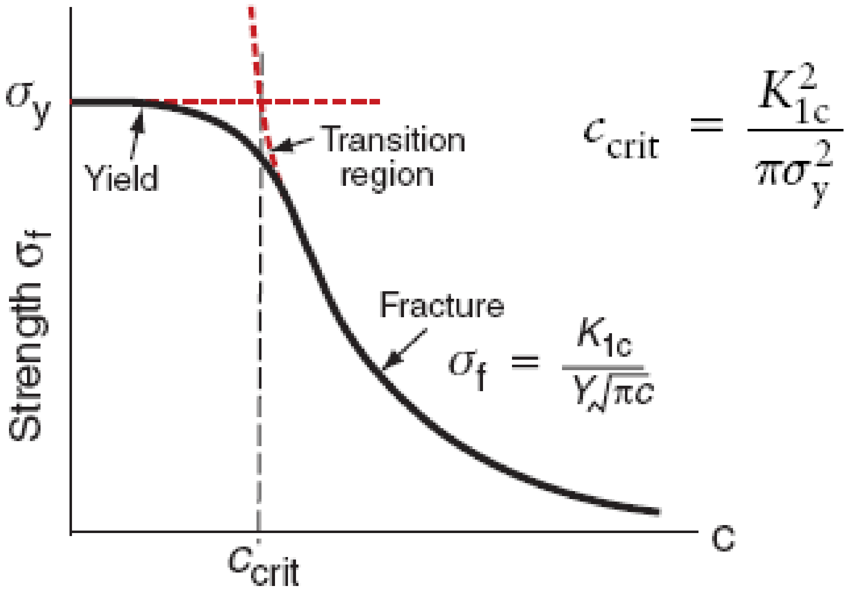
- Strength of ceramics must be described by **statistics** as identical components will not fail at one reproducible strength value.

- ✓ A material will always contain a distributions of flaws

- ✓ The presence of flaws in ductile metals is not very serious, because these metals have the ability to deform plastically and thus attenuate, at least to some extent, the insidious effect of flaws on strength

- ✓ The same cannot be said of brittle materials. Such preexisting flaws are responsible for the phenomenon of catastrophic fracture in these materials. In general, flaws vary in size, shape, and orientation; consequently, the strength of a material will vary from specimen to specimen





When cracks are small, materials yield before they fracture; when they are large, the opposite is true. **But what is ‘small’?**

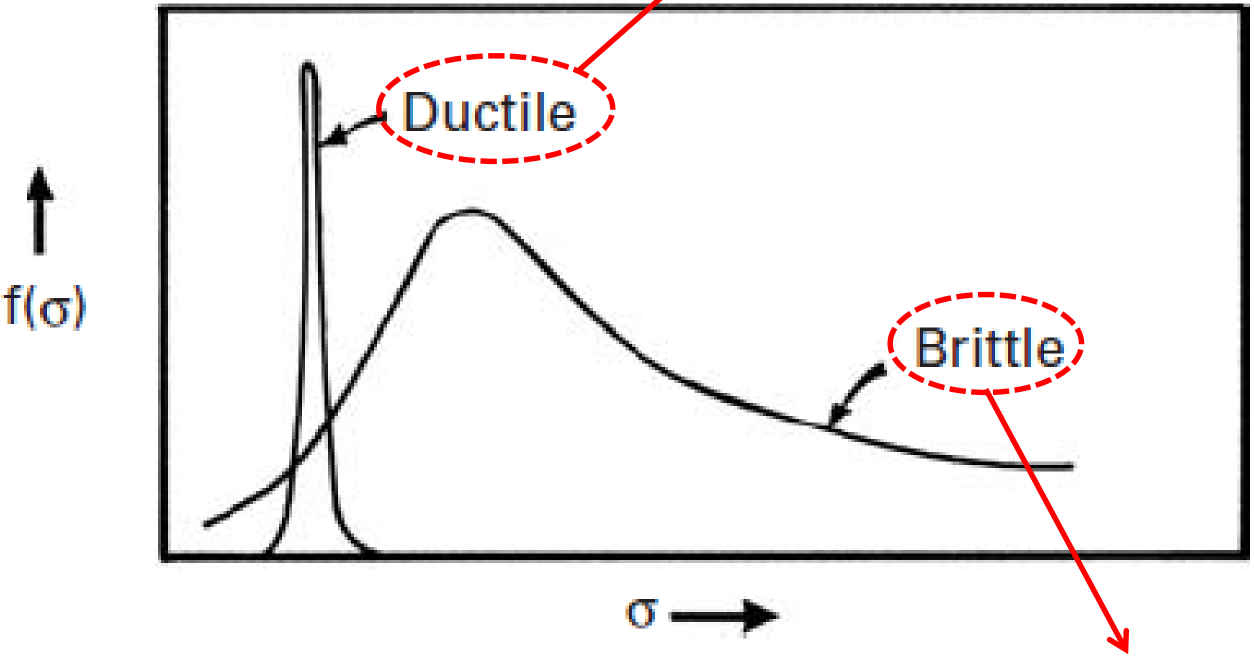

Approximate crack lengths for transition between yield and fracture

Material class	Transition crack length, c_{crit} (mm)
Metals	1–1000
Polymers	0.1–10
Ceramics	0.01–0.1
Composites	0.1–10

These crack lengths are a measure of the *damage tolerance* of the material. Tough metals are able to contain large cracks but still yield in a predictable, ductile, manner. Ceramics (which always contain small cracks) fail in a brittle way at stresses far below their yield strengths.

- ✓ If we were to test a large number of identical samples and plot the strength distribution of a brittle and a ductile solid, we would get the curves

The strength distribution curve for the ductile solid is very narrow and close to a Gaussian or normal distribution



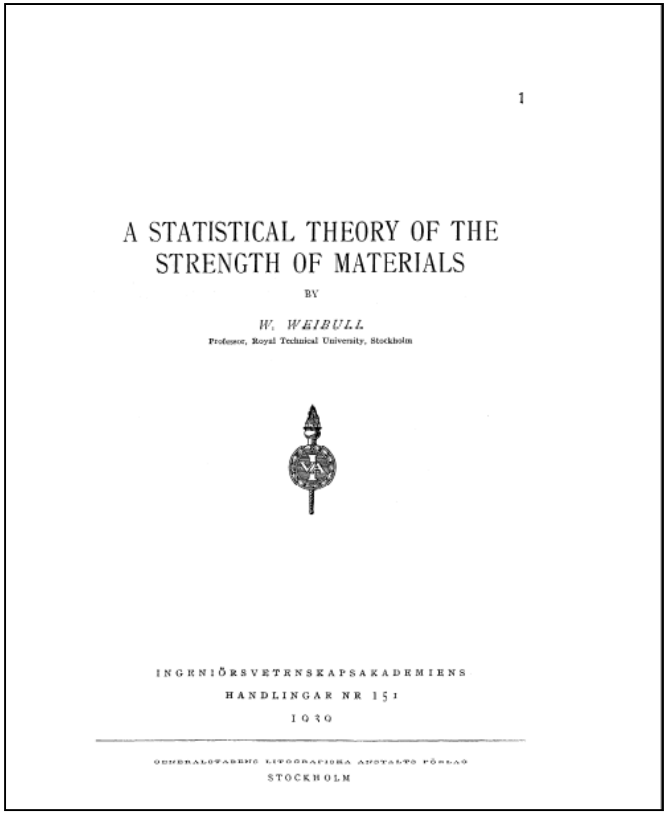
That for the brittle solid is very broad with a large tail on the high-strength side -- that is, a non-Gaussian distribution

Strength distribution of a brittle and a ductile solid

- ✓ It turns out that the strength distribution of a brittle solid can be explained by a statistical distribution called the ***Weibull distribution***, named after the Swedish engineer who first proposed it

Swedish engineer famous for his pioneering work on reliability, providing a statistical treatment of
- fatigue,
- strength and
- lifetime in engineering design.

Waloddi **Weibull: 1887-1979**



1

A STATISTICAL THEORY OF THE
STRENGTH OF MATERIALS

BY

W. WEIBULL

Professor, Royal Technical University, Stockholm

INGENIÖRSVETENSKAPSAKADEMIENS
HANDLINGAR NR 151
1939

GENERALSTABENS LITOGRAFISKA ANSTALTS FÖRLAG
STOCKHOLM

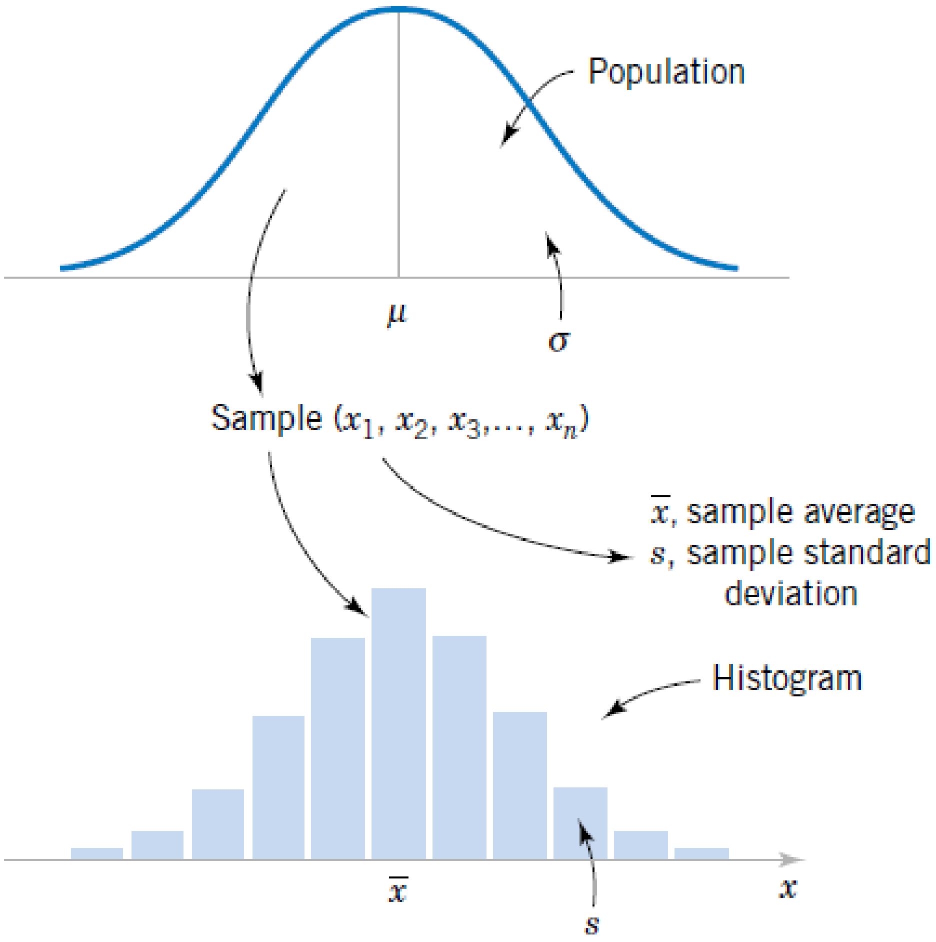
- ✓ Measurement of the strength of a series of nominally identical ceramic specimens typically produces considerable scatter in the results. This behavior is easy to explain qualitatively as resulting from a scatter in the size, position, and orientation of the cracks responsible for failure
- ✓ The existence of this scatter has important engineering consequences
- ✓ First, the strength that can safely be used in design is clearly less than the average measured strength
- ✓ Second, the probability of failure of a large specimen is greater than that of a small specimen under the same stress because of the larger probability of having a serious flaw in a larger volume
- ✓ Third, the measured strength of specimens of the same size depends on the measurement technique since different techniques subject different volumes of the specimen to tensile stress

- It is desirable to have some means of describing these effects quantitatively and incorporating this description into a method of design for safe use

- Weibull analysis provides such a means. It is a form of extreme value statistics dealing with a *weakest link situation* in which the failure of a single element of a specimen causes failure of the whole specimen

Statistical distributions

Il concetto di ***distribuzione di probabilità*** e di ***funzione di densità di probabilità***



- ✓ La curva che interpola i dati può essere ottenuta facendo tendere all'infinito la numerosità del campione e facendo diminuire l'ampiezza degli intervalli dell'istogramma
- ✓ L'istogramma caratterizza il campione (le osservazioni), la distribuzione di probabilità caratterizza la popolazione da cui il campione è estratto
- ✓ Una distribuzione di probabilità è un modello matematico che mette in relazione il valore di una variabile casuale con la probabilità che quel valore si presenti nella popolazione
- ✓ Un istogramma è una approssimazione di una funzione di densità di probabilità

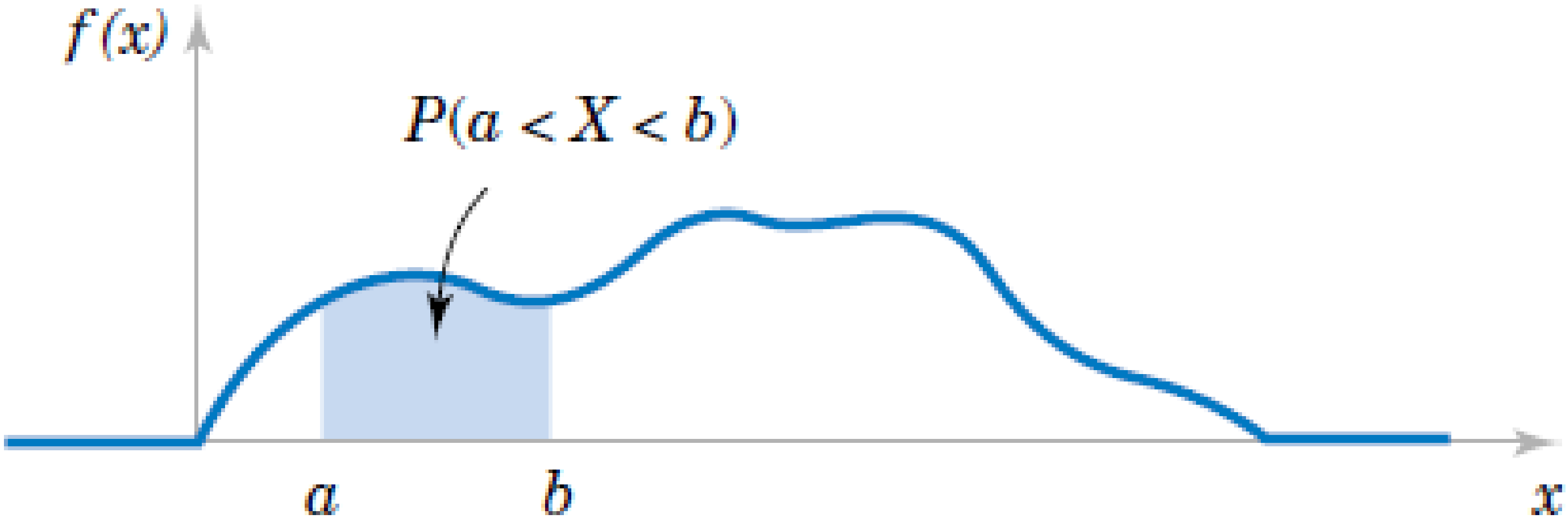
Ci sono due tipi di distribuzioni di probabilità:

- ✓ *Distribuzione di probabilità continua* *(dati quantitativi)*. Quando la variabile da misurare è espressa in una scala continua, la sua distribuzione di probabilità è detta distribuzione di probabilità continua (distribuzione gaussiana, distribuzione di Student, di Fisher, ecc.)

- ✓ *Distribuzione di probabilità discreta* *(dati qualitativi).* Quando il parametro che viene misurato può assumere solo certi valori, la sua distribuzione di probabilità è detta distribuzione di probabilità discreta (ad esempio i risultati di una ispezione, riportati come conformi o non conformi) (distribuzione binomiale, di Poisson, ipergeometrica ecc.)

- ✓ A **probability density function** *f*(*x*) can be used to describe the probability distribution of a **continuous random variable** *X*

- ✓ The probability that *X* is between *a* and *b* is determined as the integral of *f*(*x*) from *a* to *b*



For a continuous random variable *X*, a **probability density function** is a function such that:

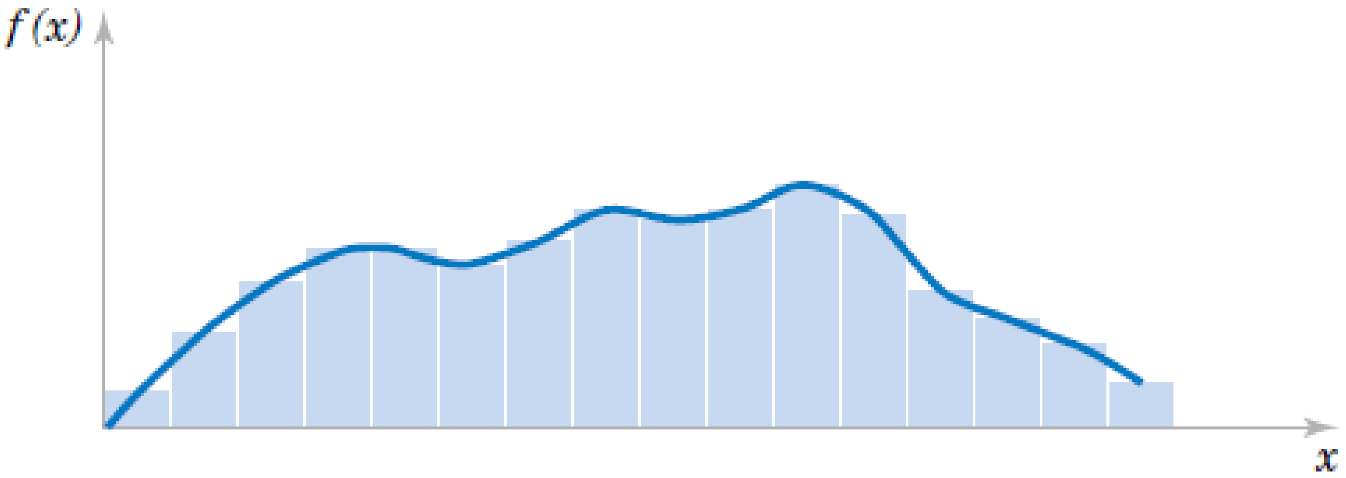
$$f(x) \geq 0$$

$$\int_{-\infty}^{+\infty} f(x)dx = 1$$

$$P(a \leq X \leq b) = \int_{a}^{b} f(x)dx$$

- ✓ A probability density function provides a simple description of the probabilities associated with a random variable. A probability density function is zero for x values that cannot occur and it is assumed to be zero wherever it is not specifically defined

A **histogram** is an approximation to a probability density function. For each interval of the histogram, the area of the bar equals the relative frequency (proportion) of the measurements in the interval. The relative frequency is an estimate of the probability that a measurement falls in the interval. Similarly, the area under $f(x)$ over any interval equals the true probability that a measurement falls in the interval.



Let the continuous random variable X denote the diameter of a hole drilled in a sheet metal component. The target diameter is 12.5 millimeters. Most random disturbances to the process result in larger diameters. Historical data show that the distribution of X can be modeled by a probability density function $f(x) = 20e^{-20(x-12.5)}$, $x \geq 12.5$.

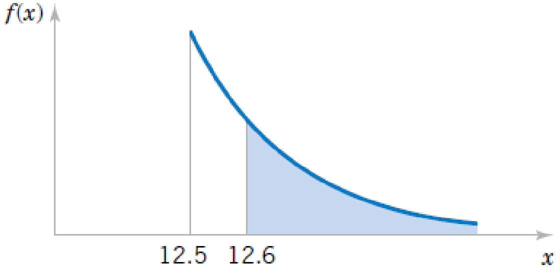
If a part with a diameter larger than 12.60 millimeters is scrapped, what proportion of parts is scrapped? The density function and the requested probability are shown in Fig. 4-5. A part is scrapped if $X > 12.60$. Now,

$$P(X > 12.60) = \int_{12.6}^{\infty} f(x)\,dx = \int_{12.6}^{\infty} 20e^{-20(x-12.5)}\,dx = -e^{-20(x-12.5)}\Big|_{12.6}^{\infty} = 0.135$$

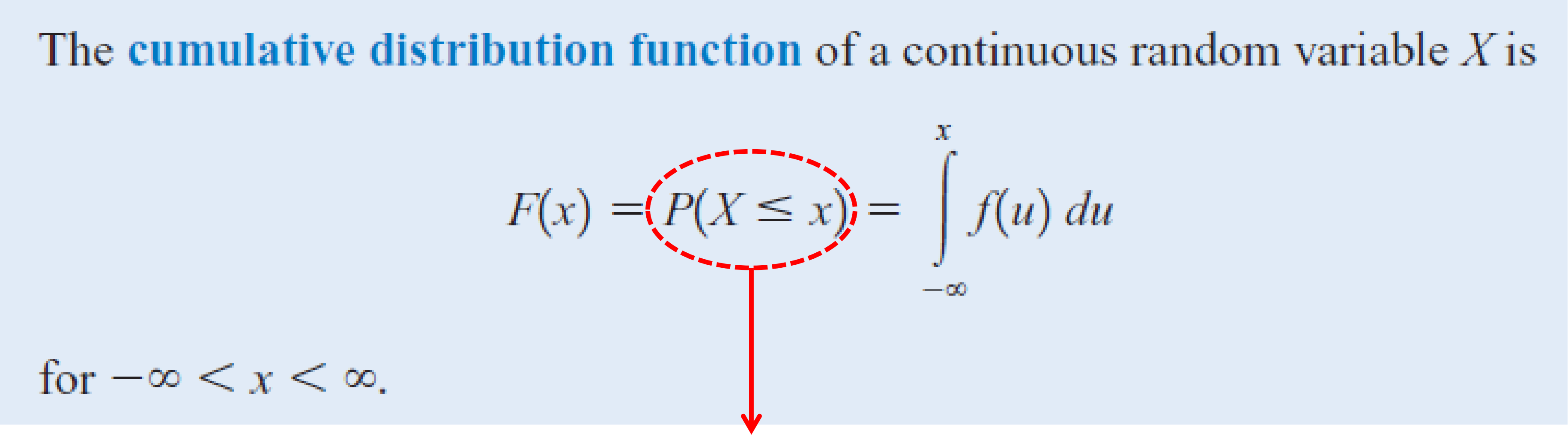
What proportion of parts is between 12.5 and 12.6 millimeters? Now,

$$P(12.5 < X < 12.6) = \int_{12.5}^{12.6} f(x)\,dx = -e^{-20(x-12.5)}\Big|_{12.5}^{12.6} = 0.865$$

Because the total area under $f(x)$ equals 1, we can also calculate $P(12.5 < X < 12.6) = 1 - P(X > 12.6) = 1 - 0.135 = 0.865$.



CUMULATIVE DISTRIBUTION FUNCTIONS



The **cumulative distribution function** of a continuous random variable X is

$$F(x) = P(X \le x) = \int_{-\infty}^{x} f(u)\,du$$

for $-\infty < x < \infty$.

Ovvero è la funzione che associa a ciascun valore x la probabilità che la variabile casuale X assuma valori minori o uguali ad x

The probability density function of a continuous random variable can be determined from the cumulative distribution function by differentiating

$$\frac{d}{dx}\int_{-\infty}^{x} f(u)\,du = f(x) \quad \Longrightarrow \quad f(x) = \frac{dF(x)}{dx}$$

MEAN AND VARIANCE OF A CONTINUOUS RANDOM VARIABLE

Suppose *X* is a continuous random variable with probability density function *f*(*x*). The **mean** or **expected value** of *X*, denoted as or *E*(*X*), is

$$\mu = E\left(X\right) = \int_{-\infty}^{+\infty} xf\left(x\right)dx$$

The **variance** of *X*, denoted as *V*(*X*) or is

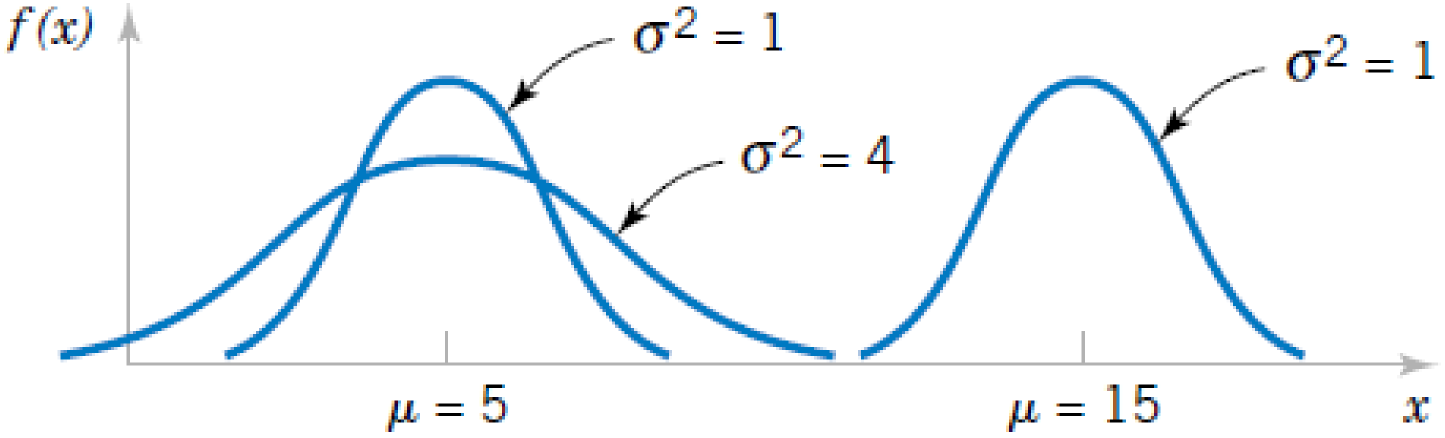
$$\sigma^2 = V\left(X\right) = \int_{-\infty}^{+\infty} \left(x-\mu\right)^2 f\left(x\right)dx$$

The **standard deviation** of X is σ

NORMAL (GAUSSIAN) DISTRIBUTION

- ✓ Undoubtedly, the most widely used model for the distribution of a random variable is a **normal distribution**

- ✓ Random variables with different means and variances can be modeled by normal probability density functions with appropriate choices of the center and width of the curve



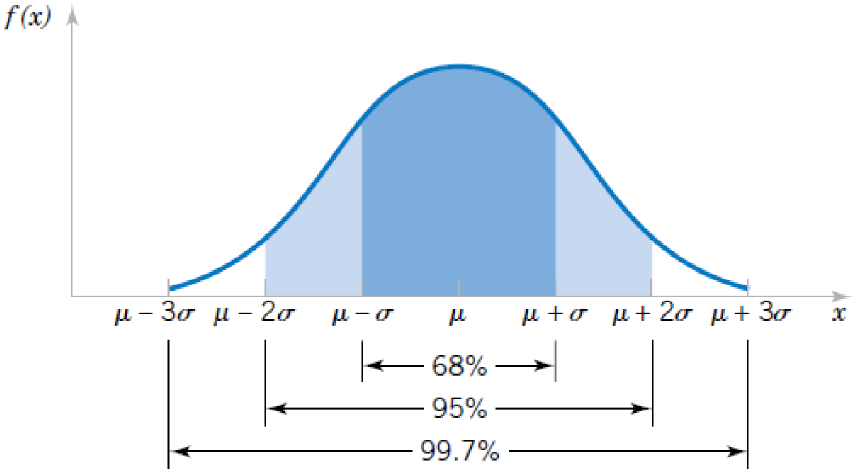
A random variable *X* with probability density function

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \qquad -\infty < x < +\infty$$

is a **normal random variable** with parameters μ, where $-\infty < \mu < +\infty$, and $\sigma > 0$. Also,

$E(X) = \mu$ and $V(X) = \sigma^2$

and the notation $N(\mu, \sigma^2)$ is used to denote the distribution

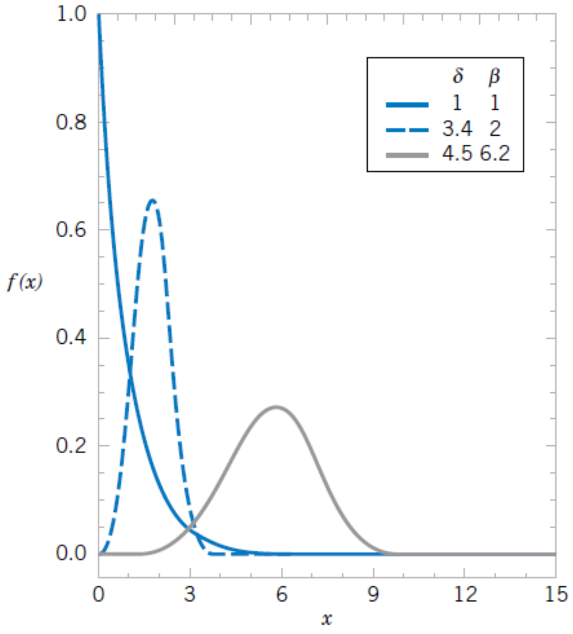


WEIBULL DISTRIBUTION

The random variable *X* with probability density function

$$f(x) = \frac{\beta}{\delta}\left(\frac{x}{\delta}\right)^{\beta-1} \exp\left[-\left(\frac{x}{\delta}\right)^{\beta}\right], \qquad \text{for } x > 0$$

is a **Weibull random variable** with scale parameter $\delta > 0$ and shape parameter $\beta > 0$



- The cumulative distribution function is often used to compute probabilities. The following result can be obtained. If X has a Weibull distribution with parameters δ and β, then the cumulative distribution function of X is

$$F(x) = 1 - e^{-\left(\frac{x}{\delta}\right)^{\beta}}$$

- If X has a Weibull distribution with parameters δ and β,

$$\mu = E(x) = \delta\Gamma\left(1 + \frac{1}{\beta}\right) \quad \text{and} \quad \sigma^2 = V(x) = \delta^2\Gamma\left(1 + \frac{2}{\beta}\right) - \delta^2\left[\Gamma\left(1 + \frac{1}{\beta}\right)\right]^2$$

- ✓ Two forms of the Weibull distribution are frequently used to describe strength data: the two- and three-parameter distributions

- ✓ The two-parameter distribution is

$$P_f(\sigma) = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right]$$

where ***m*** is the Weibull shape parameter or **Weibull modulus**, which is an inverse measure of the distribution width; that is, a high value of m corresponds to a narrow distribution. The Weibull scale parameter σ_0 is a measure of centrality, that is, the center of the distribution. In fact, σ_0 is the 63rd percentile; the probability of failure occurring at or below a stress σ_0 is 0.63, or 63%.

The mean and the standard deviation are given by

$$\bar{\sigma} = \sigma_0 \Gamma\left(1 + \frac{1}{m}\right)$$

$$s^2 = \sigma_0^2 \left[\Gamma\left(1 + \frac{2}{m}\right) - \Gamma^2\left(1 + \frac{1}{m}\right)^2\right]$$

The coefficient of variation **CV** is a dimensionless measure of the dispersion of the data and is defined as the ratio of the standard deviation to the mean:

$$C_V = \frac{s}{\bar{\sigma}} = \left[\frac{\Gamma(1+2/m)}{\Gamma^2(1+1/m)} - 1\right]^{1/2} \approx \frac{1.28}{m}$$

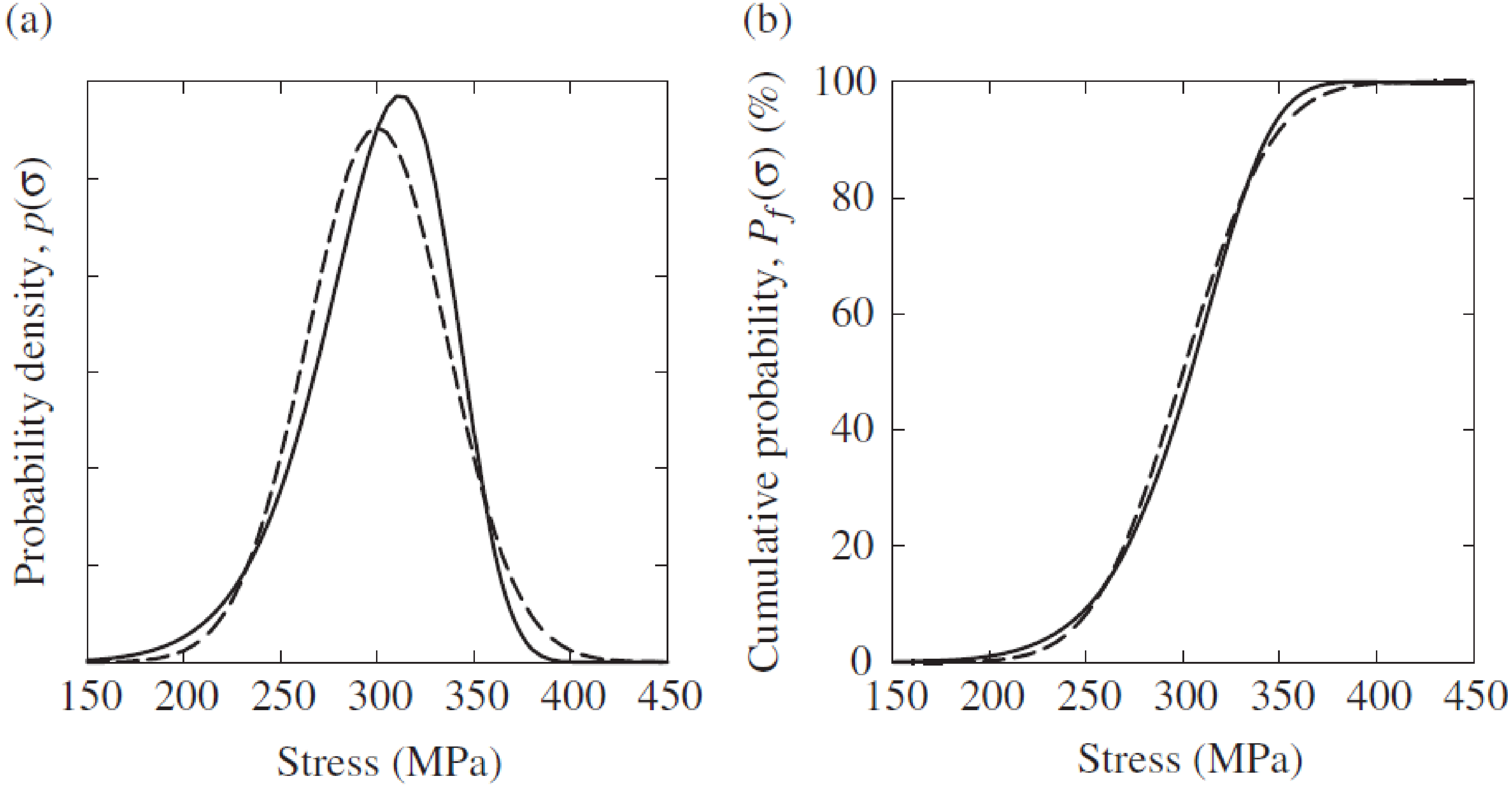
$$\Gamma(x) = \int_0^\infty y^{x-1} e^{-y}\, dy$$

m	$\Gamma(1 + 1/m)$	m	$\Gamma(1 + 1/m)$	m	$\Gamma(1 + 1/m)$	m	$\Gamma(1 + 1/m)$
1	1.00000	6	0.92772	11	0.95508	16	0.96758
2	0.88623	7	0.93544	12	0.95829	17	0.96929
3	0.89298	8	0.94174	13	0.96107	18	0.97084
4	0.90640	9	0.94697	14	0.96351	19	0.97223
5	0.91817	10	0.95135	15	0.96566	20	0.97350

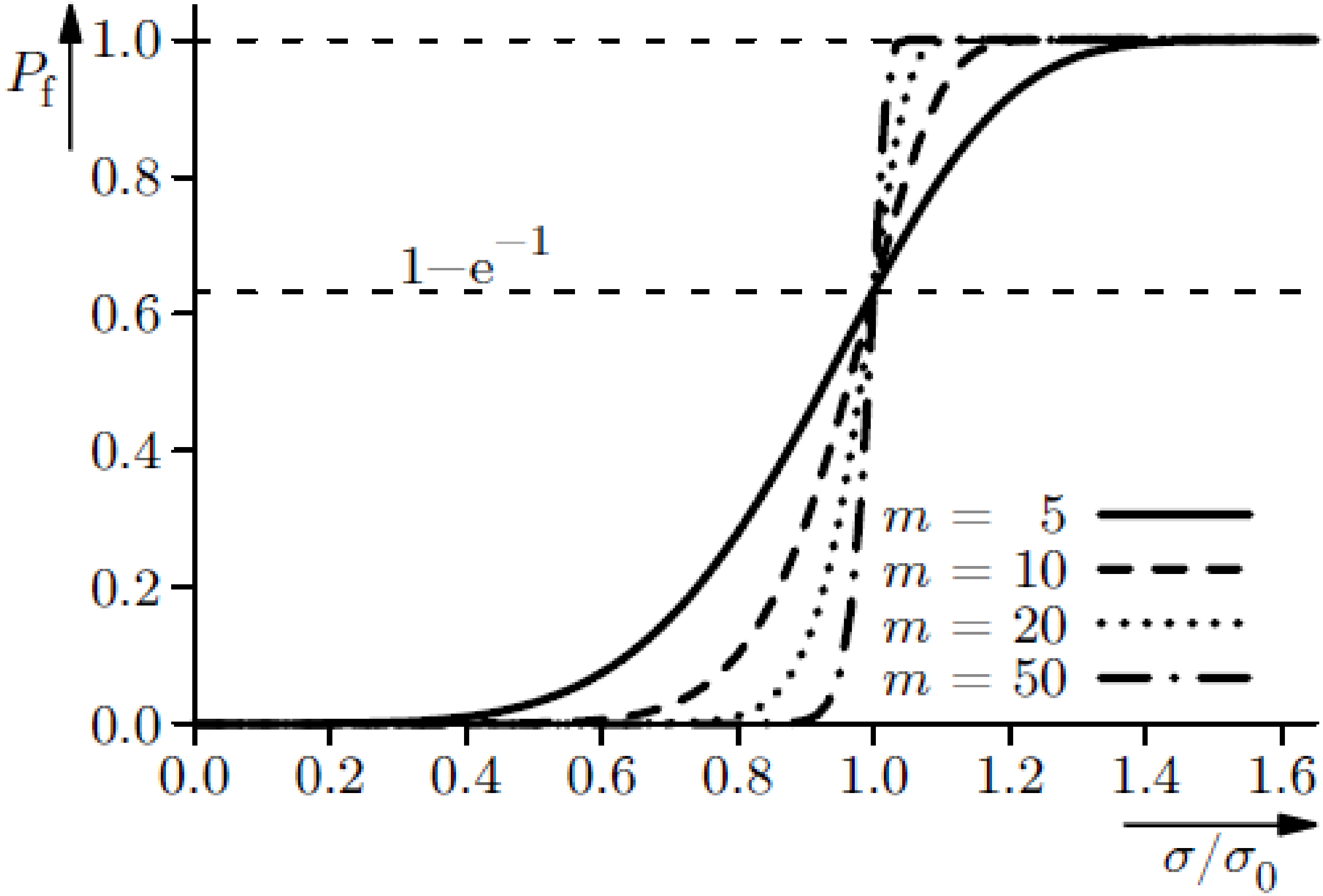
- ✓ The three-parameter Weibull distribution is given by

$$P_f(\sigma) = \begin{cases} 1 - \exp\left\{-\left(\dfrac{\sigma - \sigma_u}{\sigma_0}\right)^m\right\} & \sigma > \sigma_u \\ 0 & \sigma \leq \sigma_u \end{cases}$$

- ✓ The two- and three-parameter distributions are the same except that for the latter the stress is shifted by σ_u. The three parameters m, σ_u, and σ_0 are generally treated as empirical parameters and determined experimentally. The parameter σ_u is a stress level below which there is zero probability of failure. For ceramics the remote possibility exists of having a very large flaw in a specimen so that the safest assumption is to take $\sigma_u = 0$, which is then the two parameter distribution, as is usually done. This gives the most conservative estimate of survival probability



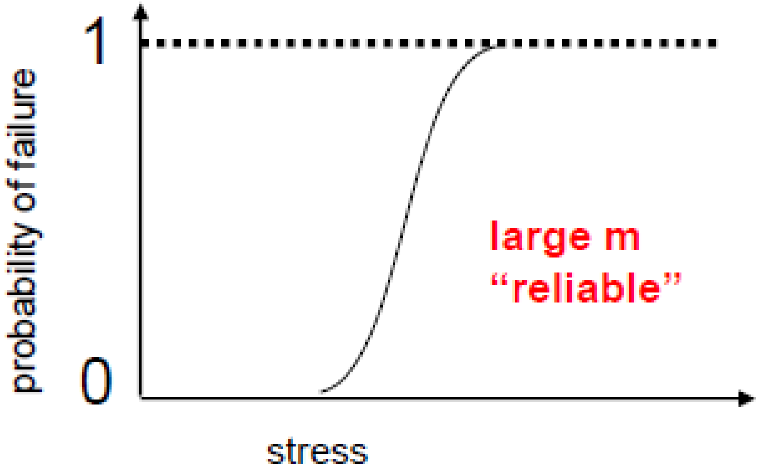
(a) Probability density function and (b) cumulative probability of failure for Weibull (solid lines) and Gaussian (dashed lines) distributions, both calculated for mean strength of 300 MPa and standard deviation of 36.1 MPa.



P_f
1.0
0.8
0.6
0.4
0.2
0.0
$1-e^{-1}$
$m = 5$
$m = 10$
$m = 20$
$m = 50$
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
σ/σ_0

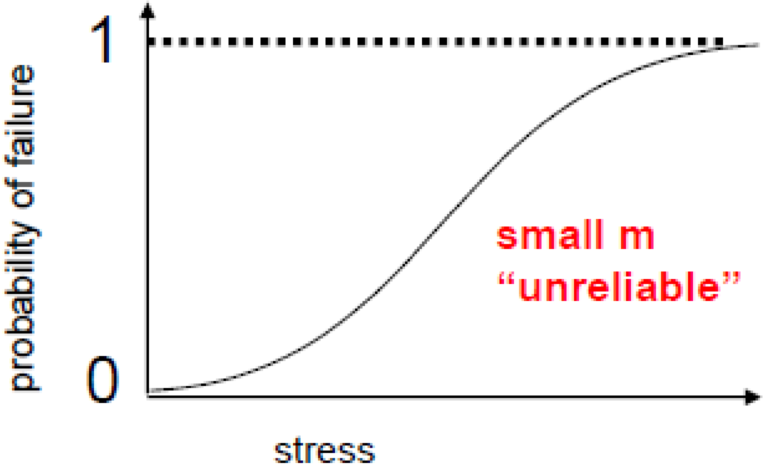
- **large m:**
  narrow distribution, small spread
  ➔ reliable material

- “tough” ceramic components:
  m = 10-40



- **small m:**
  wide distribution, large spread
  ➔ unreliable material

- “bad” ceramic components:
  m = 1-10



WEAKEST LINK THEORY

- ✓ The Weibull treatment of failure is in two parts: **(1)** a weakest link argument leading to a volume dependence for the distribution of strength and **(2)** the assumption of a particular statistical distribution function
- ✓ The weakest link argument is based on the idea that failure at any flaw leads to total failure and the material is homogeneous in the sense that the flaws are distributed throughout the volume (Weibull, 1939)
- ✓ Consider a material divided into a very large number of elements n of equal volume δV under stress σ. Take $P_{f,i}$ $(\sigma, \delta V)$ as the probability of failure from the ith volume element by a stress σ
- ✓ The probability that this element survives σ is therefore $1-P_{f,i}$ $(\sigma, \delta V)$. Since the stress is taken to be the same for all volume elements and the specimen is assumed to be homogeneous, all $P_{f,i}$ $(\sigma, \delta V)$ can be taken the same, P_f $(\sigma, \delta V)$

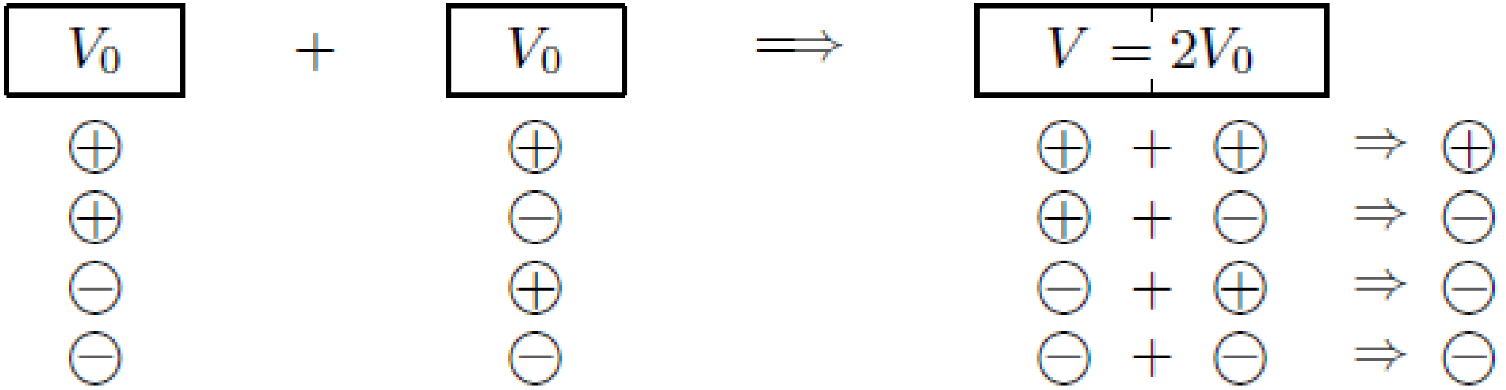
- ✓ For the entire specimen to survive the stress, all the volume elements must survive so that the total probability of survival, 1-P_f (σ, V), of a specimen of volume V = n δV under ***uniform stress*** is given by

$$1 - P_f(\sigma, V) = [1 - P_f(\sigma, \delta V)]^n = \left[1 - \frac{V}{n}\frac{P_f(\sigma, \delta V)}{\delta V}\right]^n$$

$$= \left[1 - \frac{V}{n}\varphi(\sigma)\right]^n$$

where we have assumed that as *n* increases P_f (σ, δV)/δV approaches a limit φ(σ). As the specimen is subdivided into larger numbers of smaller volumes, *n* approaches infinity and δV approaches zero. Then

$$\lim_{n\to\infty}\left(1 - \frac{x}{n}\right)^n = \exp(-x)$$



$P_{s,1}(V_0) = 0.5$ $\quad$ $P_{s,2}(V_0) = 0.5$ $\quad$ $P_s(V = 2V_0) = 0.25$

Volume dependence of the survival probability.
The circled symbols denote the chances for survival and failure of the component

so that

$$P_f(\sigma, V) = 1 - \exp[-V\varphi(\sigma)]$$

This line of argument shows that the probability of failure of the specimen depends exponentially on the specimen volume times a **risk function** φ(σ) that characterizes the stress dependence of cumulative failure probability per unit volume at the limit of small volume. This weakest link argument does not give a specific form for φ(σ), but clearly it must be a monotonically increasing function of σ. Weibull assumed the form

$$\varphi(\sigma) = \left(\frac{\sigma}{\Sigma_0}\right)^m$$

This gives the probability of failure of the whole specimen, P_f, as

$$P_f = 1 - \exp\left[-V\left(\frac{\sigma}{\Sigma_0}\right)^m\right]$$

This is the two-parameter Weibull distribution with scale parameter

$$\sigma_0 = \Sigma_0 \, V^{-1/m}$$

Note Σ_0 has the rather odd dimensions of stress x (volume)$^{1/m}$, which results from the definition of φ(σ) being the probability per unit volume. In the literature σ_0 is widely used for both the distribution parameter σ_0 and the Weibull scale parameter that incorporates weakest link theory. Here we define the latter as Σ_0 to clearly distinguish between the two parameters

- ✓ The parameter σ_0 is more straightforward to calculate for any given set of data but it does depend on the size of the specimen; that size must always be reported together with σ_0. The parameter Σ_0 is more fundamental since it does not depend on the size of the specimen; it is the Weibull scale parameter for specimens of unit volume

- ✓ The **mean strength** now becomes

$$\bar{\sigma} = \sigma_0 \Gamma\left(1 + \frac{1}{m}\right) = \frac{\Sigma_0}{V^{1/m}} \Gamma\left(1 + \frac{1}{m}\right)$$

- ✓ The above analysis assumes the stress is ***uniform*** but frequently the applied stress is ***not uniform and varies with position***, that is, $\sigma = \sigma(\mathbf{r})$.

Consider a body of volume V+δV which can be thought of as two pieces, one of volume V and the other of volume δV. The body will only survive if both parts survive, that is,

$$P_s(V+\delta V) = P_s(V)\cdot P_s(\delta V)$$

As defined above, φ(σ) is the probability per unit (small) volume that the material fails by a stress *σ* so that

$$P_s(\delta V) = 1 - P_f(\delta V) = 1 - \varphi(\sigma)\,\delta V$$

$$\frac{P_s(V+\delta V) - P_s(V)}{\delta V} = -\varphi(\sigma)\cdot P_s(V)$$

As δV becomes small, the left-hand side of this equation approaches the derivative of P_s:

$$\frac{dP_s}{dV} = -\varphi(\sigma) \cdot P_s$$

Integrating over the entire specimen volume

$$P_f = 1 - P_s = 1 - \exp\left\{-\int_V \boxed{\varphi[\sigma(\underline{\mathbf{r}})]}\, dV\right\}$$

$$\varphi(\sigma) = \left(\frac{\sigma}{\Sigma_0}\right)^m$$

$$P_f = 1 - \exp\left[-\int_V \left(\frac{\sigma(\underline{\mathbf{r}})}{\Sigma_0}\right)^m dV\right]$$

General form

If the applied stress is uniform, σ is a constant inside the integral and the earlier result is recovered

- ✓ The complexity and power of the method should not obscure the fact that it rests on the assumption of the Weibull form for the distribution of strength and that this distribution is only an assumption that gives a reasonable fit to the data in many cases

EFFECT OF SPECIMEN SIZE

If the strength corresponding to the same failure probability P_f is σ_1 for a specimen of volume V_1 and σ_2 for a specimen of volume V_2, then

$$\ln \ln \left(\frac{1}{1 - P_f} \right) = \left\{ \begin{array}{l} \ln V_1 + m \ln \sigma_1 - m \ln \Sigma_0 \\ \ln V_2 + m \ln \sigma_2 - m \ln \Sigma_0 \end{array} \right\}$$

Since Σ_0 is independent of the specimen size, subtracting these two equations gives

$$\frac{\sigma_1}{\sigma_2} = \left(\frac{V_2}{V_1}\right)^{1/m}$$

This equation is true for any failure probability so it is also true for the mean strength, giving

$$\frac{\bar{\sigma}_1}{\bar{\sigma}_2} = \left(\frac{V_2}{V_1}\right)^{1/m} \qquad (*)$$

This proves the expected result that **the mean strength is lower for larger specimens** and the effect is more pronounced for lower values of *m*. This result was derived for a uniform tensile stress, but a more general analysis can show it to be correct for a variety of loading schemes

ADAPTATION TO BEND TESTING

- ✓ To adapt the two-parameter Weibull distribution to tests in which the stress varies with position, the general form of the Weibull distribution must be used
- ✓ For most bend-testing methods, while the stresses increase with increased loading, the shape of the stress field is invariant. Under these conditions the maximum stress anywhere in the specimen, σ_{max}, can be factored out:

$$\sigma(\underline{\mathbf{r}}) = \sigma_{\max}\, g(\underline{\mathbf{r}})$$

where g(**r**) is a function of position only. As an example, considering the stress on the outer, tensile surface of a three-point bend specimen, g(**r**) rises linearly from zero at each outer loading point to unity at the inner loading point

$$P_f = 1 - \exp\left[-\int_V \left(\frac{\sigma(\underline{\mathbf{r}})}{\Sigma_0} \right)^m dV \right]$$

$$\Downarrow$$

$$P_f = 1 - \exp\left[-\left(\frac{\sigma_{\max}}{\Sigma_0} \right)^m \int_V g^m(\underline{\mathbf{r}})\, dV \right]$$

It is convenient to define **k**, the **loading factor** for the test method, by

$$k = \frac{1}{V} \int_V g^m(\underline{\mathbf{r}})\, dV \qquad \text{or} \qquad k = \frac{1}{V} \int_V \left(\frac{\sigma(\underline{\mathbf{r}})}{\sigma_{\max}} \right)^m dV$$

$$\Downarrow$$

$$P_f = 1 - \exp\left[-kV \left(\frac{\sigma_{\max}}{\Sigma_0} \right)^m \right] \qquad (**)$$

where **k** is a dimensionless function of *m* characteristic of the test method and specimen geometry

- ✓ For a given failure probability for any test, a specimen of volume V will have the same strength as a tensile specimen of volume kV, where kV can be interpreted as the *effective volume* of the specimen under test; that is, *it is a measure of how much of the volume of the specimen is under a significant tensile stress*
- ✓ Typically, the strength of a specimen, σ, is taken as the value of the maximum stress at failure, σ_{max}. Therefore the mean strength is given by

$$\bar{\sigma} = \frac{\Sigma_0}{(kV)^{1/m}} \Gamma\left(1 + \frac{1}{m}\right) \qquad (***)$$

which clearly shows how the mean strength depends on specimen volume and test technique

To explore this dependence further, consider two test methods; for method 1 with loading factor k_1 and specimen volume V_1, the cumulative probability of failure is P_{f1} when the maximum stress is σ_{max1}; similarly for method 2 the corresponding parameters are k_2, V_2, P_{f2}, and σ_{max2}

$$\ln \ln\left(\frac{1}{1-P_{f1}}\right) = m \ln \sigma_{\max 1} - m \ln \Sigma_0 + \ln(k_1 V_1)$$

$$\ln \ln\left(\frac{1}{1-P_{f2}}\right) = m \ln \sigma_{\max 2} - m \ln \Sigma_0 + \ln(k_2 V_2)$$

(Here we implicitly assume that the material in both tests is the same, that is, has the same distribution of flaws and so *m* and Σ_0 are the same). Considering the stresses that give the same probability of failure in the two methods, $P_{f1}=P_{f2}$, gives

$$\ln \sigma_{\max 1} - \ln \sigma_{\max 2} = \frac{1}{m} \ln \left(\frac{k_2 V_2}{k_1 V_1} \right)$$

$$\frac{\sigma_{\max 1}}{\sigma_{\max 2}} = \left(\frac{k_2 V_2}{k_1 V_1} \right)^{1/m}$$

This result is derived for any value of Pf and so gives the ratio of strengths for any failure probability. For the mean strength:

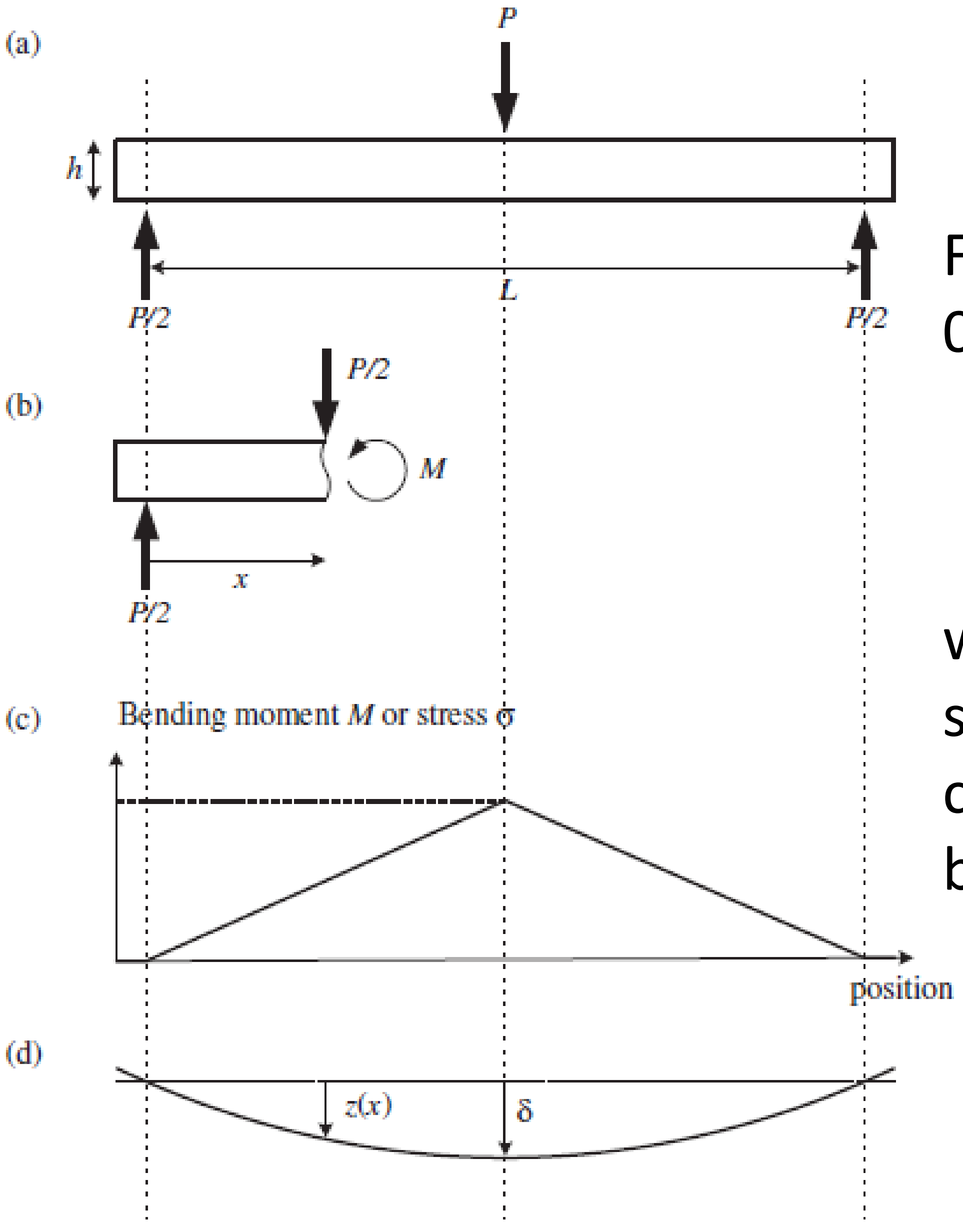
$$\frac{\bar{\sigma}_{\max 1}}{\bar{\sigma}_{\max 2}} = \left(\frac{k_2 V_2}{k_1 V_1} \right)^{1/m}$$

If the two test techniques are actually the same, then $k_1=k_2$ and the previous equation (*) is recovered

- ✓ Once the loading factor **k** is known, the strength distribution for any test method is given by Eq. (**) and the mean strength by (***)
- ✓ Now k will be evaluated for two test methods, namely uniaxial tension and three-point bending

- ✓ Considering first uniform uniaxial tension, the maximum stress is the applied tensile stress which is uniform throughout the specimen, that is, g(**r**) = 1, giving the loading factor for uniform tension k_t as equal to one ($k_t = 1$)

- ✓ In three-point bending, it is noted that the stress varies in proportion to the distance y from the neutral axis and in proportion to the distance x from the outer support point



For the left half of the specimen, 0<x<L/2

$$\sigma(\underline{\mathbf{r}}) = \sigma_{3b,\max} \frac{2x}{L} \frac{2y}{h} \qquad g(\underline{\mathbf{r}}) = \frac{4xy}{Lh}$$

where $\sigma_{3b,\max}$ is the maximum stress in the tensile surface and so corresponds to the measured breaking strength

By symmetry, the contribution to the integral for *k* from each half of the specimen is the same so the loading factor in three-point bending, k_3, can be evaluated by doubling the integration for one half:

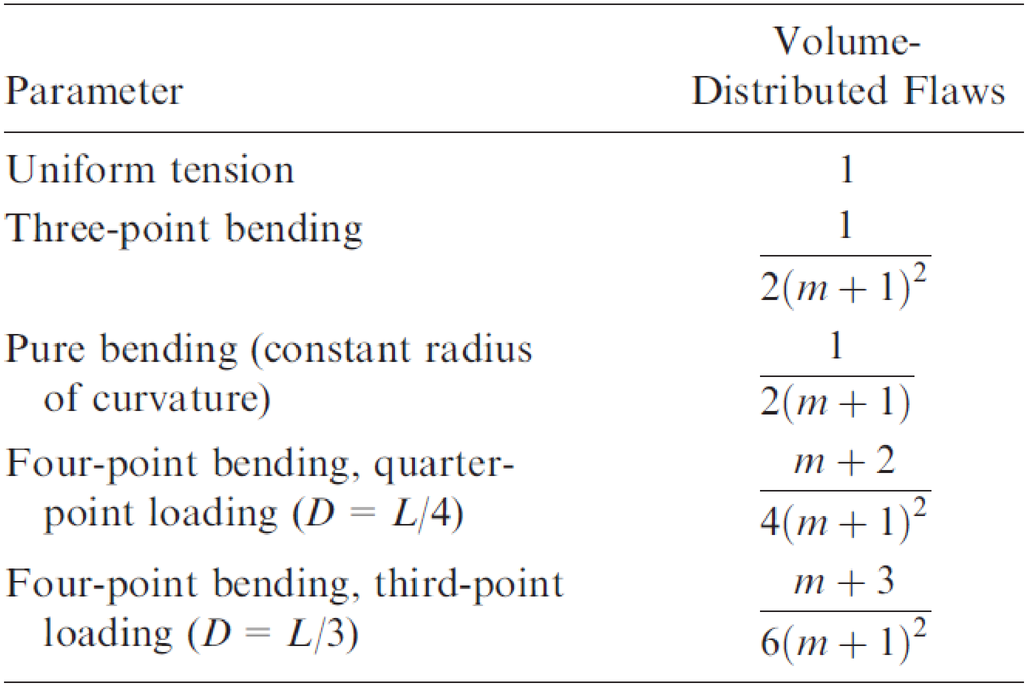
$$k_{3b} = \frac{2}{V}\int_0^{L/2}\left(\frac{2x}{L}\right)^m dx \int_0^{h/2}\left(\frac{2y}{h}\right)^m dy \int_0^{d} dz = \frac{1}{2(m+1)^2}$$

where the volume V=Lhd, which is the volume of the specimen between the outer loading points, not the total volume of the specimen, which is usually longer than L. Note that the integration over y is only over the tensile half of the thickness of the specimen since only the tensile side (y>0) contributes to the risk of failure

These results can now be used to give the ratio of the strengths of specimens of equal volume measured in three-point bending and tension:

$$\frac{\bar{\sigma}_{3b,\max}}{\bar{\sigma}_t} = \left(\frac{k_t}{k_{3b}}\right)^{1/m} = [2(m+1)^2]^{1/m}$$

Since m>0, the bending strength is expected to be greater than the tensile strength, as is usually observed in practice



Parameter	Volume-Distributed Flaws
Uniform tension	1
Three-point bending	$\frac{1}{2(m+1)^2}$
Pure bending (constant radius of curvature)	$\frac{1}{2(m+1)}$
Four-point bending, quarter-point loading ($D = L/4$)	$\frac{m+2}{4(m+1)^2}$
Four-point bending, third-point loading ($D = L/3$)	$\frac{m+3}{6(m+1)^2}$

The strengths of 10 nominally identical ceramic bars were measured and found to be 387, 350, 300, 420, 400, 367, 410, 340, 345, and 310 MPa. (*a*) Determine m and σ_0 for this material. (*b*) Calculate the design stress that would ensure a survival probability higher than 0.999.

(*a*) To determine m and σ_0, the Weibull plot for this set of data has to be made. Do as follows:

- Rank the specimens in order of increasing strength, $1, 2, 3, \ldots, j, j+1, \ldots, N$, where N is the total number of samples.
- Determine the survival probability for the jth specimen. As a first approximation, the probability of survival of the first specimen is $1 - 1/(N+1)$; for the second, $1 - 2/(N+1)$, for the jth specimen $1 - j/(N+1)$, etc. This expression is adequate for most applications. However, an alternate and more accurate expression deduced from a more detailed statistical analysis yields

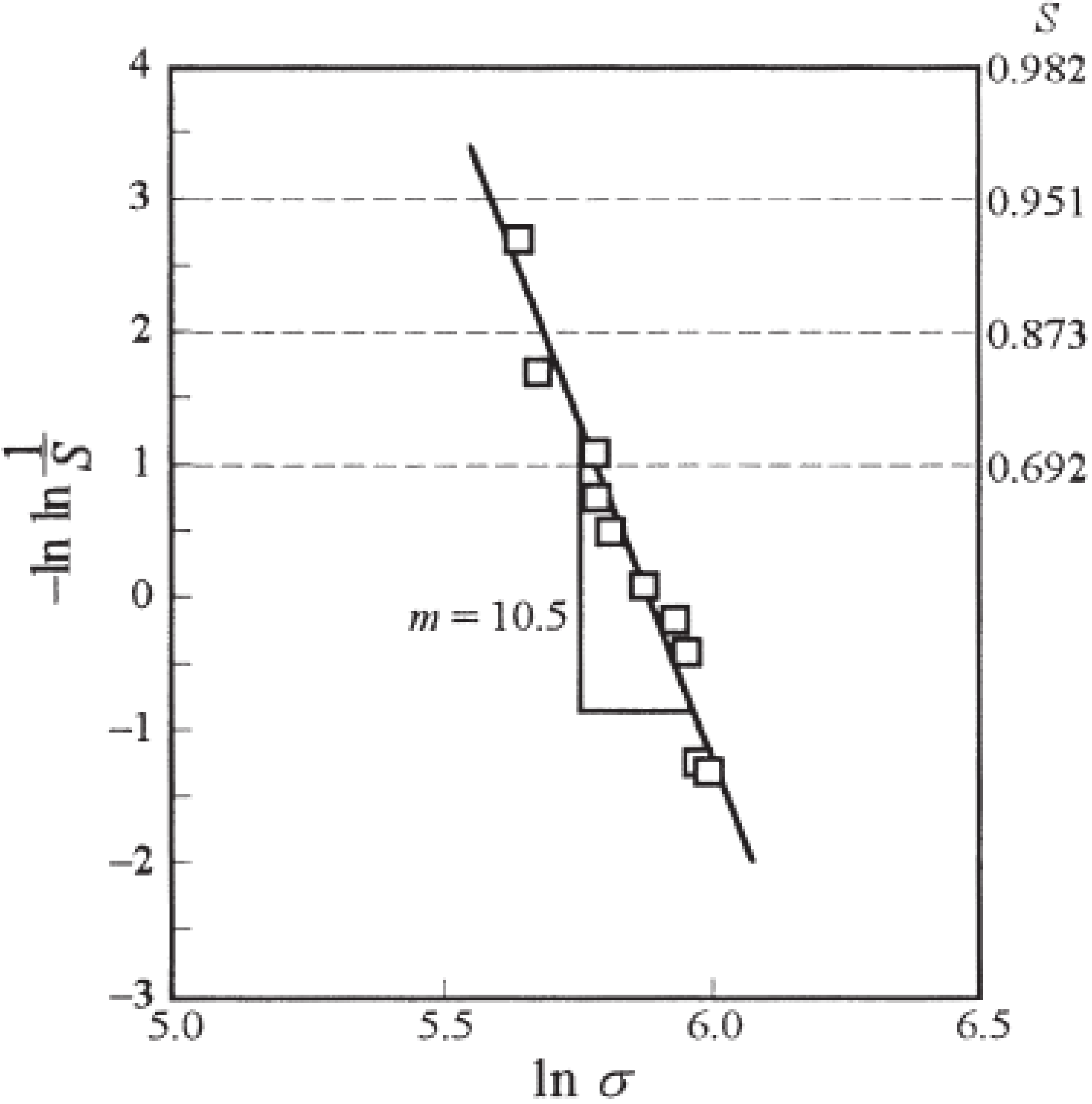
$$S_j = 1 - \frac{j - 0.3}{N + 0.4} \qquad (11.25)$$

- Plot $-\ln\ln(1/S)$ versus $\ln\sigma$. The least-squares fit to the resulting line is the Weibull modulus.

The last two columns in Table 11.2 are plotted in Fig. 11.21. A least-squares fit of the data yields a slope of 10.5, which is typical of many conventional as-finished ceramics. From the table, $\sigma_0 \approx 385\,\text{MPa}$ (i.e. when $-\ln\ln 1/S = 0$).

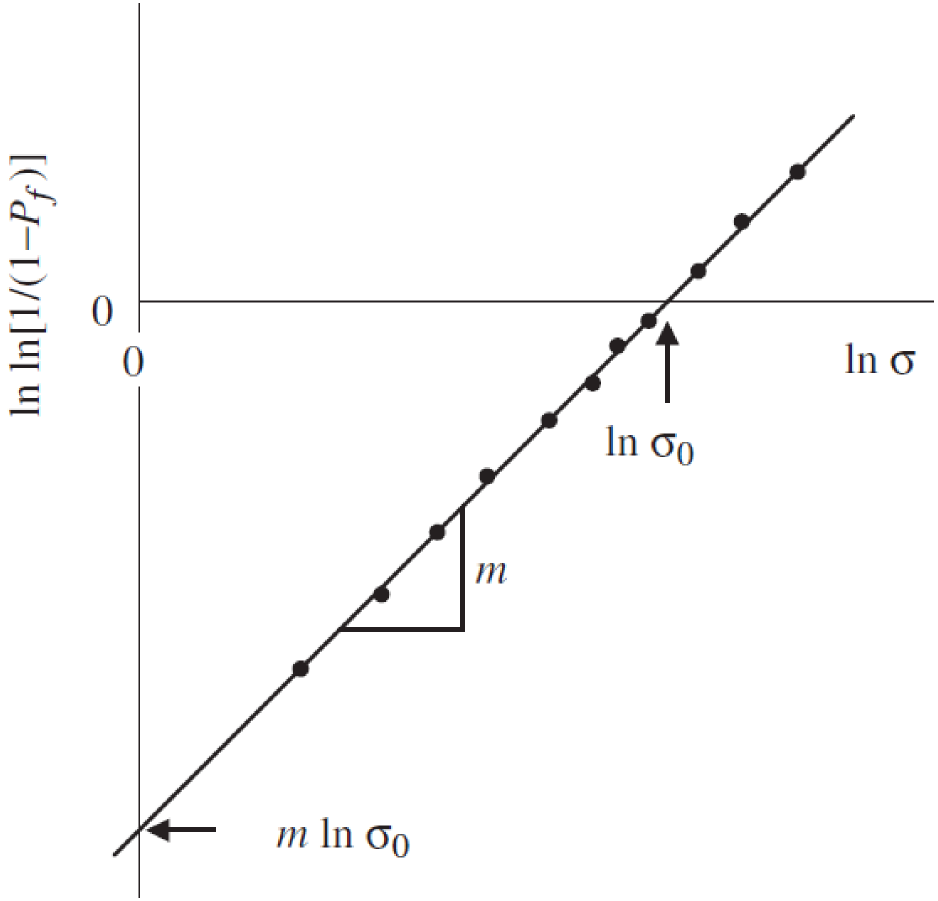
Table 11.2 Summary of data needed to find *m* from a set of experimental results

Rank *j*	S_j	σ_j	$\ln\sigma_j$	$-\ln\ln(1\sigma_j)$
1	0.932	300	5.700	2.6532
2	0.837	310	5.734	1.7260
3	0.740	340	5.823	1.2000
4	0.644	345	5.840	0.8200
5	0.548	350	5.860	0.5080
6	0.452	367	5.905	0.2310
7	0.356	387	5.960	–0.0320
8	0.260	400	5.990	–0.2980
9	0.160	410	6.016	–0.6060
10	0.070	420	6.040	–0.9780


S
4
3
2
1
0
−1
−2
−3
0.982
0.951
0.873
0.692
$-\ln \ln \frac{1}{S}$
$m = 10.5$
5.0
5.5
6.0
6.5
$\ln \sigma$

$$\ln\ln\left(\frac{1}{1-P_f}\right) = \ln V + m\ln\sigma - m\ln\Sigma_0 = m\ln\sigma - m\ln\sigma_0$$

$$\ln V - m\ln\Sigma_0 = -m\ln\sigma_0 = \text{intercept}$$



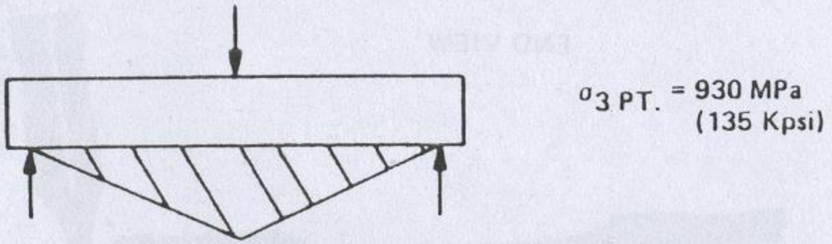
SAFETY FACTORS

- ✓ Another important concept is that of the safety factor, which is the mean strength divided by the value of the maximum allowable design stress that has been chosen
- ✓ Within the bounds of a statistical treatment of strength, it is not possible to have absolute safety. One can at best choose the working stress as a fraction of the mean stress to provide a calculated low probability of failure
- ✓ One can choose some value of P_s considered adequate for safety and solve for the **safety factor *sf*** defined as the ratio of the mean strength to the working stress ($\sigma_{\text{allowable}}$) necessary to achieve this value of P_s. The result is

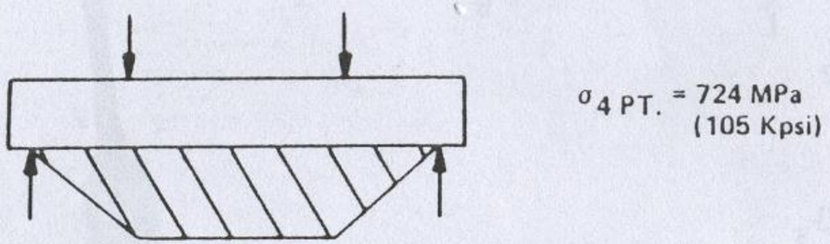
$$\mathrm{sf} = \frac{\bar{\sigma}}{\sigma_{\text{allowable}}} = \frac{\Gamma(1 + 1/m)}{(-\ln P_s)^{1/m}}$$

- ✓ Typical allowable failure probabilities range from, say, 10^{-3} for cases where there is no serious consequence of failure to perhaps 10^{-7} or lower where loss of life or other very serious consequences might result from failure. For the former case and m values of 10 and 15, the required safety factors predicted by the Weibull theory are 1.90 and 1.53, respectively. For the latter case the predicted safety factors are 4.77 and 2.83, respectively

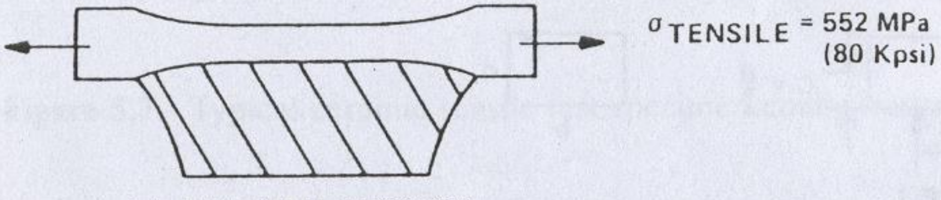
- ✓ A larger value of *m* permits the use of a working stress much nearer to the mean strength. The reason for striving to achieve high values of m through good processing is evident



(a) 3-POINT BENDING



(b) 4-POINT BENDING



(c) UNIAXIAL TENSION

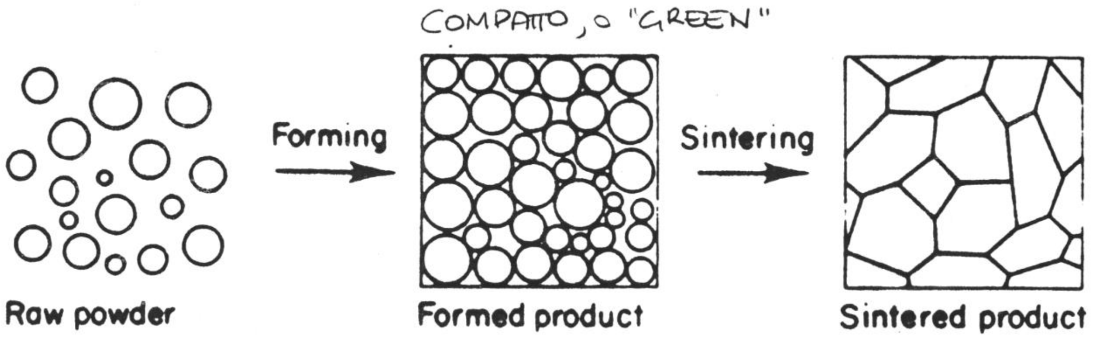
Figure 5.9 Comparison of the tensile stress distributions for three-point, four-point, and uniaxial tensile test specimens along with typical average strengths as measured by each technique for Norton NC-132 hot-pressed Si_3N_4. Shaded area represents the tensile stress, ranging from zero at the supports of the bend specimens to maximum at midspan, and being uniformly maximum along the whole gauge length of the tensile specimen.

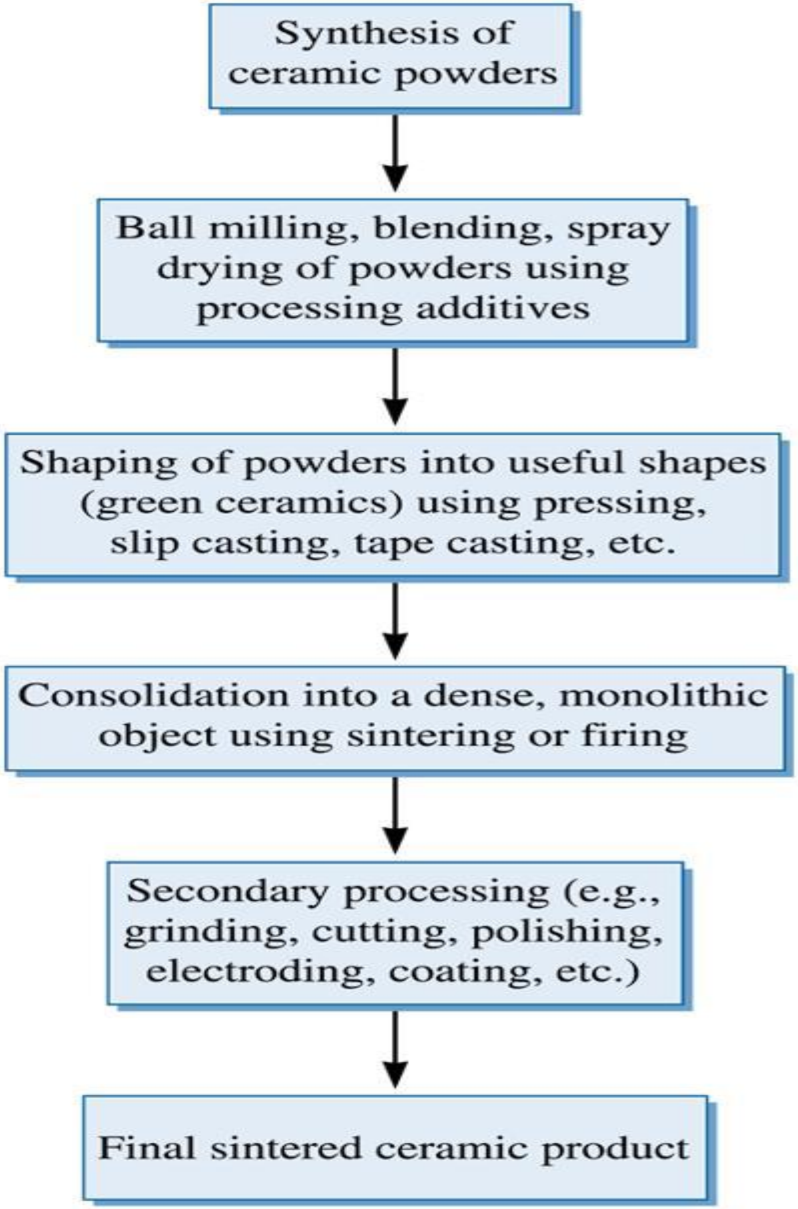
Produzione materiali ceramici

La maggior parte dei processi di produzione di componenti ceramici parte da *polveri* finemente macinate.

Tipiche fasi del processo di produzione:

1. Produzione e selezione delle polveri;
2. Formatura e preconsolidamento (compatto o "green");
3. Densificazione.





Synthesis of ceramic powders

Ball milling, blending, spray drying of powders using processing additives

Shaping of powders into useful shapes (green ceramics) using pressing, slip casting, tape casting, etc.

Consolidation into a dense, monolithic object using sintering or firing

Secondary processing (e.g., grinding, cutting, polishing, electroding, coating, etc.)

Final sintered ceramic product

Sequenza base

I criteri di selezione delle polveri ceramiche di partenza dipendono dalle proprietà finali richieste.

1) Purezza
   Influenza fortemente le proprietà meccaniche (soprattutto ad alta temperatura), ottiche, magnetiche ed elettriche. L'effetto delle impurezze dipende dalla natura chimica della matrice e dell'impurezza stessa, dalla distribuzione delle impurezze e dalle condizioni operative del componente;

2) Distribuzione dimensionale
   In molti casi l'obiettivo della fase di consolidamento è quello di raggiungere il massimo "impacchettamento" particellare e la massima uniformità → minore ritiro e porosità durante la successiva fase di densificazione. Per avere la massima compattazione particellare è necessario avere una determinata distribuzione dimensionale.

3) Reattività
   La "driving force" primaria per la densificazione di un "compatto" ad alta temperatura è la variazione di energia superficiale. Particelle molto piccole con una elevata area superficiale hanno una elevata energia superficiale e, di conseguenza, possiedono una elevata forza guida che tende a far diminuire l'estensione superficiale mediante "fusione" con altre particelle.

Controllo dimensionale delle polveri

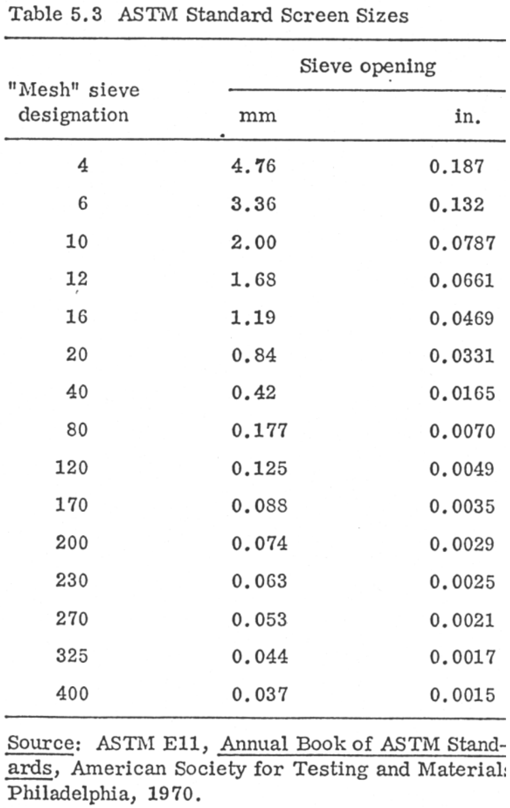


Table 5.3 ASTM Standard Screen Sizes

"Mesh" sieve designation	Sieve opening mm	in.
4	4.76	0.187
6	3.36	0.132
10	2.00	0.0787
12	1.68	0.0661
16	1.19	0.0469
20	0.84	0.0331
40	0.42	0.0165
80	0.177	0.0070
120	0.125	0.0049
170	0.088	0.0035
200	0.074	0.0029
230	0.063	0.0025
270	0.053	0.0021
325	0.044	0.0017
400	0.037	0.0015

Source: ASTM E11, Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, 1970.

SETACCIATURA: la polvere viene fatta passare attraverso più setacci posti in cascata, da quelli con apertura di diametro maggiore a quelli di diametro minore. La polvere si separa in intervalli dimensionali, tanto più ristretti quanto maggiore è il numero di setacci impiegato.

I setacci sono classificati in funzione del numero di aperture uguali presenti in un pollice lineare, indicati come *mesh*.

Es.: Una polvere che è passata tutta attraverso un setaccio 325 mesh (indicata come - **325 mesh**) non contiene particelle al di sopra di 44 µm.
Una polvere indicata come - **120 mesh + 170 mesh** ha particelle comprese fra 88 µm e 0.125 mm.

Preconsolidamento delle polveri

Prima della formatura e della successiva densificazione, la maggior parte delle polveri necessita di una fase di preconsolidamento consistente nella miscelazione con additivi di natura e funzione diversa, e in procedimenti volti a migliorare la qualità del compatto.

Additivi

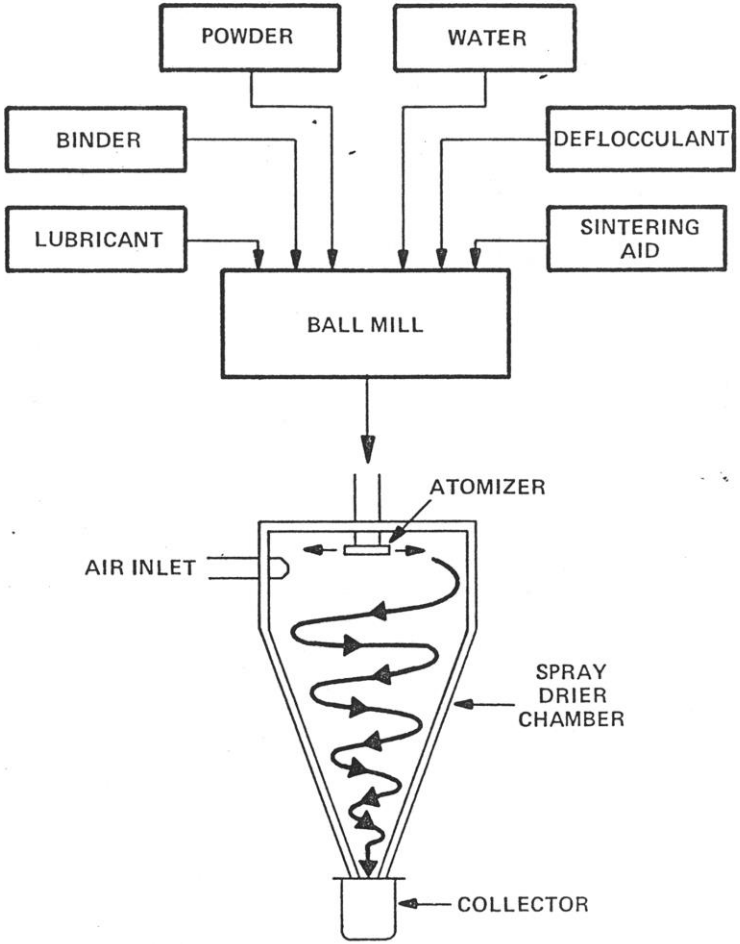
Leganti (binders) – Sono aggiunti per impartire adeguata resistenza al “green” prima delle successiva densificazione;

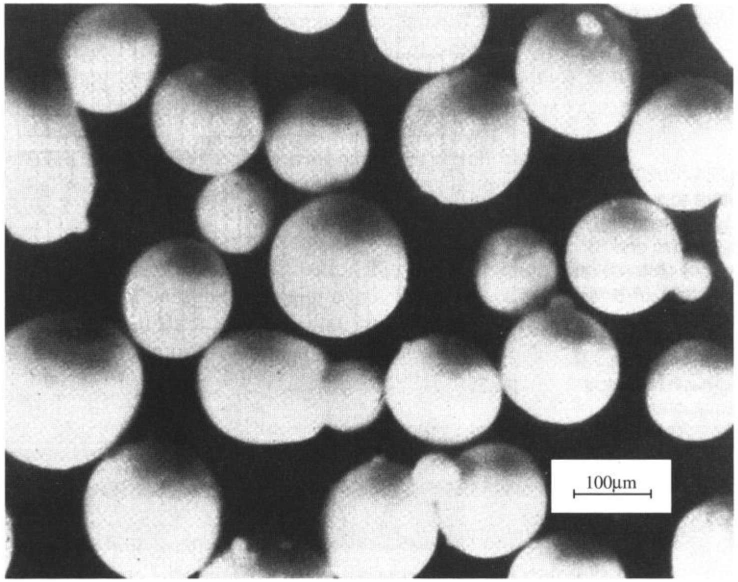
Lubrificanti (lubricants) – Sono aggiunti per diminuire l’attrito tra particelle e quello tra particelle e stampo;

Agenti di sinterizzazione (sintering aids) – Sono aggiunti per attivare la densificazione;

Plastificanti (plasticizers), promotori di bagnabilità (wetting agents) – Sono aggiunti per ottenere le desiderate proprietà reologiche necessarie per il particolare processo di formatura.

Esiste anche la possibilità di aumentare la scorrevolezza e la fluidità delle polveri mediante **spray drying.** Lo slurry viene spruzzato in un flusso ad alta pressione/velocità di aria calda che essicca e atomizza finemente il contenuto solido dello slurry

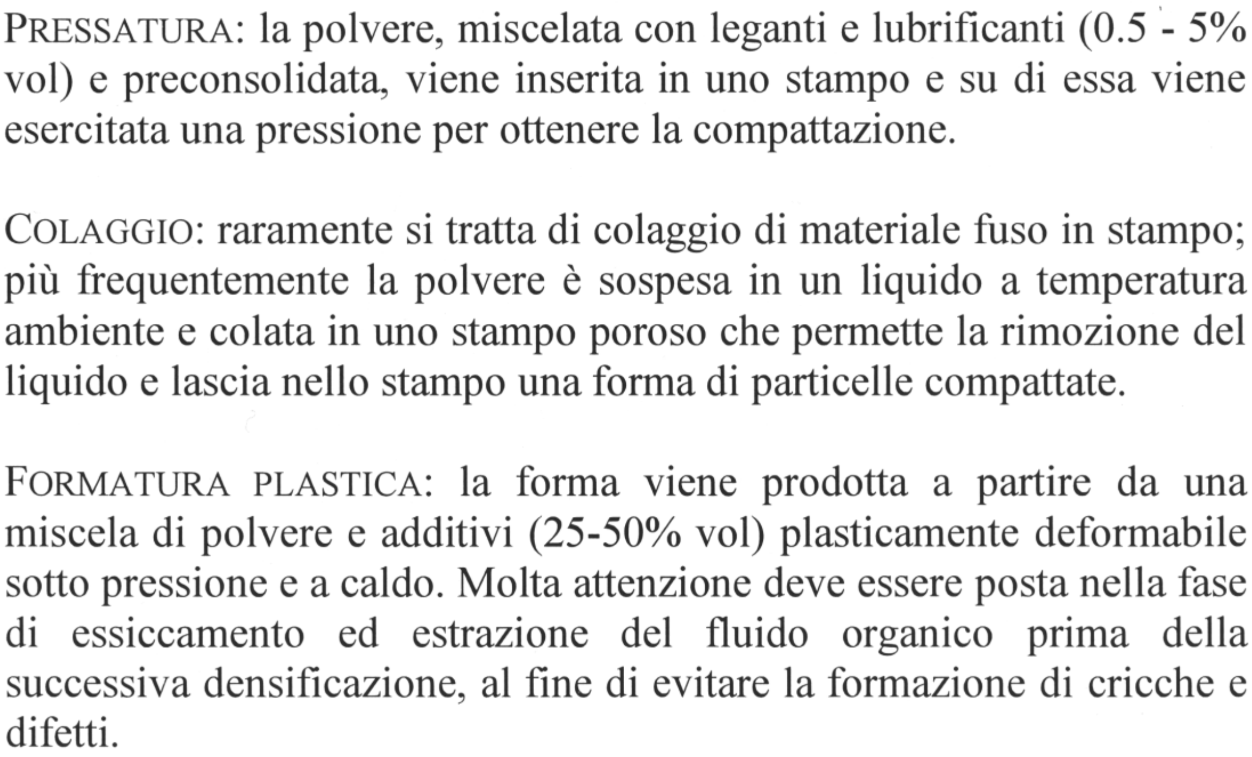




Processi di formatura

Formatura = operazione con la quale si dà forma ad un impasto ceramico prima della densificazione. Il materiale formato ("verde") deve possedere sufficiente consistenza meccanica per le manipolazioni successive.
Criticità: i difetti che condizionano le proprietà meccaniche dei pezzi ceramici hanno spesso la loro origine nel processo di formatura.

I principali processi di formatura sono:

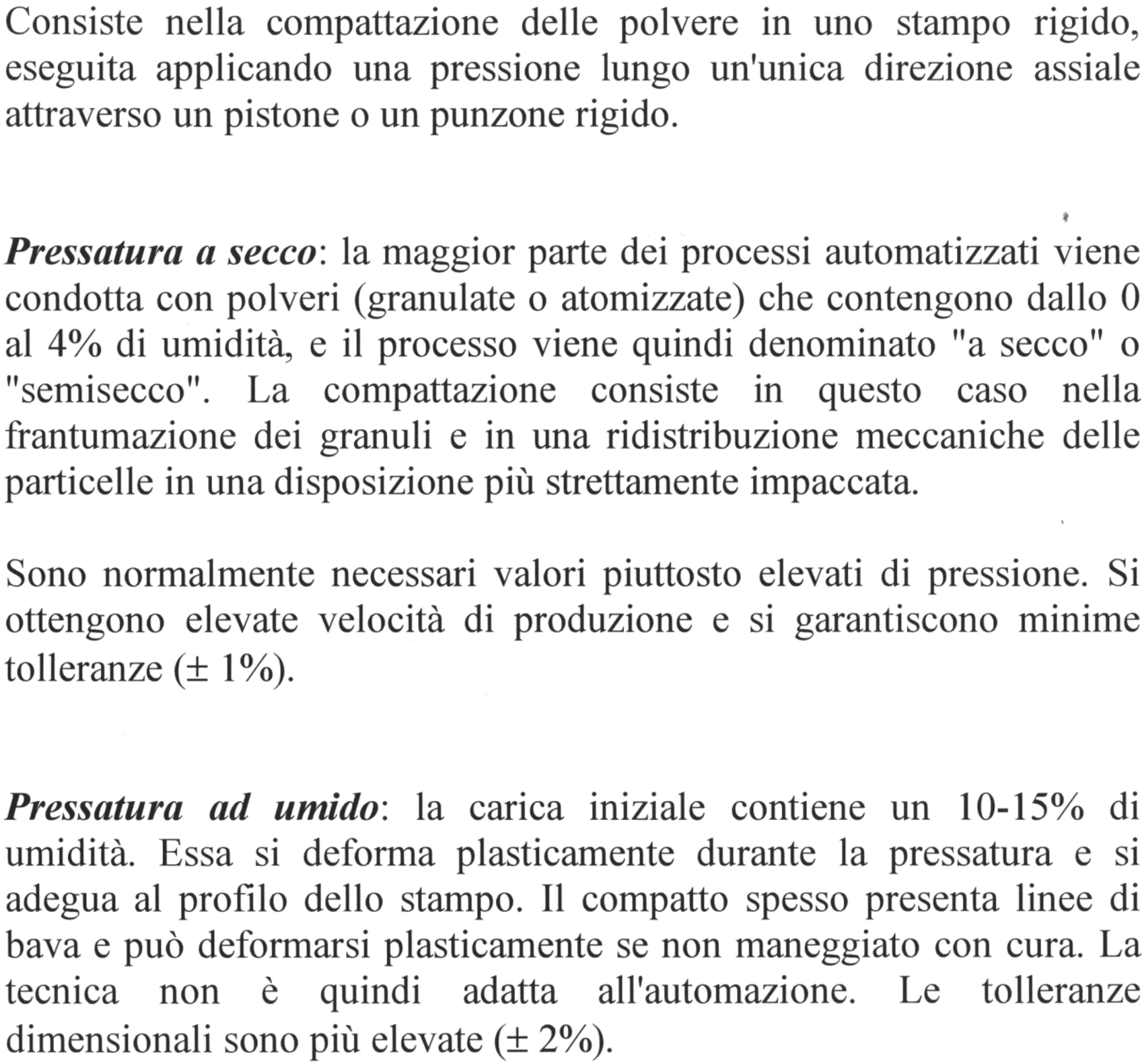


PRESSATURA: la polvere, miscelata con leganti e lubrificanti (0.5 - 5% vol) e preconsolidata, viene inserita in uno stampo e su di essa viene esercitata una pressione per ottenere la compattazione.

COLAGGIO: raramente si tratta di colaggio di materiale fuso in stampo; più frequentemente la polvere è sospesa in un liquido a temperatura ambiente e colata in uno stampo poroso che permette la rimozione del liquido e lascia nello stampo una forma di particelle compattate.

FORMATURA PLASTICA: la forma viene prodotta a partire da una miscela di polvere e additivi (25-50% vol) plasticamente deformabile sotto pressione e a caldo. Molta attenzione deve essere posta nella fase di essiccamento ed estrazione del fluido organico prima della successiva densificazione, al fine di evitare la formazione di cricche e difetti.

Pressatura uniassiale



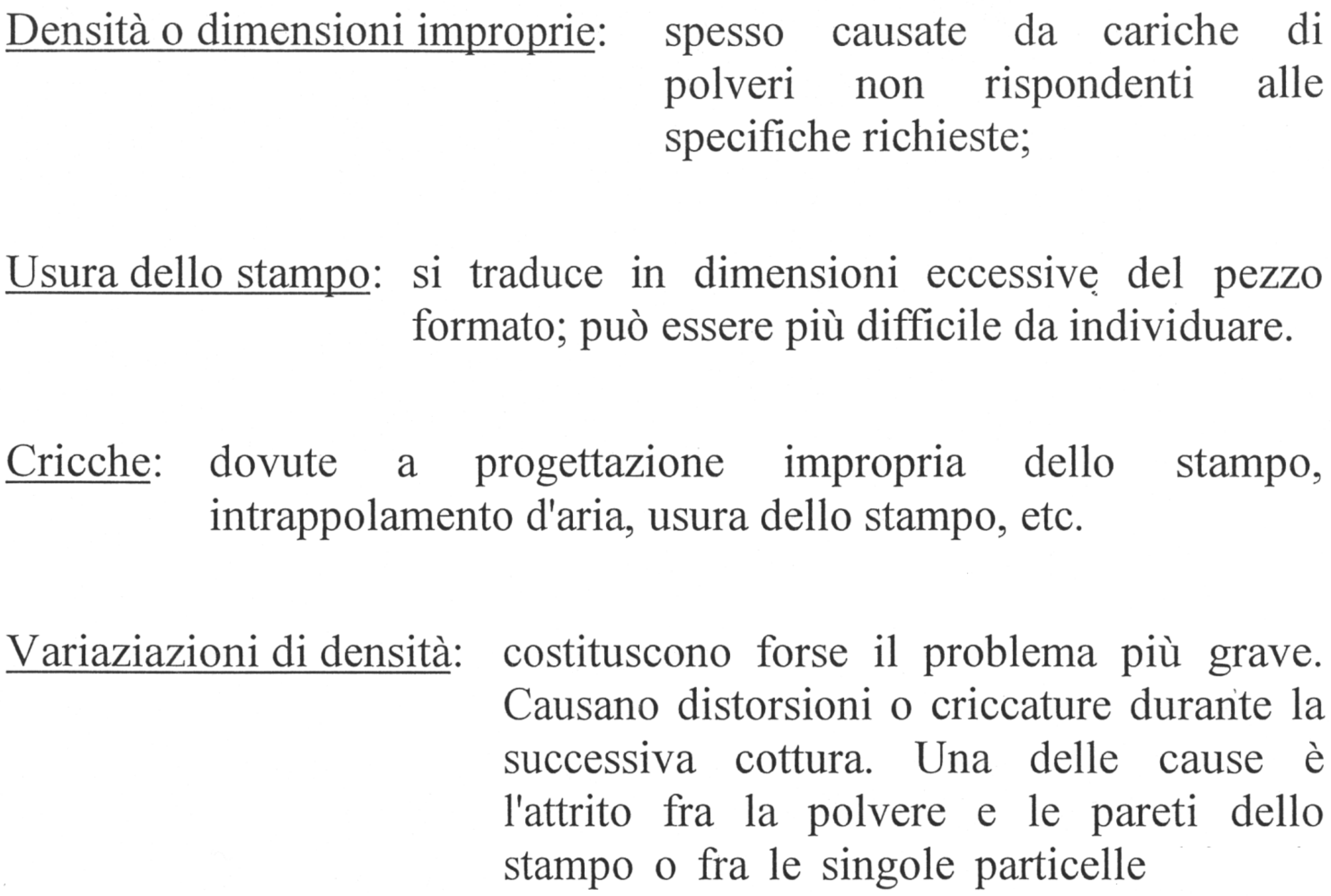
Consiste nella compattazione delle polvere in uno stampo rigido, eseguita applicando una pressione lungo un'unica direzione assiale attraverso un pistone o un punzone rigido.

Pressatura a secco: la maggior parte dei processi automatizzati viene condotta con polveri (granulate o atomizzate) che contengono dallo 0 al 4% di umidità, e il processo viene quindi denominato "a secco" o "semisecco". La compattazione consiste in questo caso nella frantumazione dei granuli e in una ridistribuzione meccaniche delle particelle in una disposizione più strettamente impaccata.

Sono normalmente necessari valori piuttosto elevati di pressione. Si ottengono elevate velocità di produzione e si garantiscono minime tolleranze (± 1%).

Pressatura ad umido: la carica iniziale contiene un 10-15% di umidità. Essa si deforma plasticamente durante la pressatura e si adegua al profilo dello stampo. Il compatto spesso presenta linee di bava e può deformarsi plasticamente se non maneggiato con cura. La tecnica non è quindi adatta all'automazione. Le tolleranze dimensionali sono più elevate (± 2%).

Problemi della pressatura uniassiale



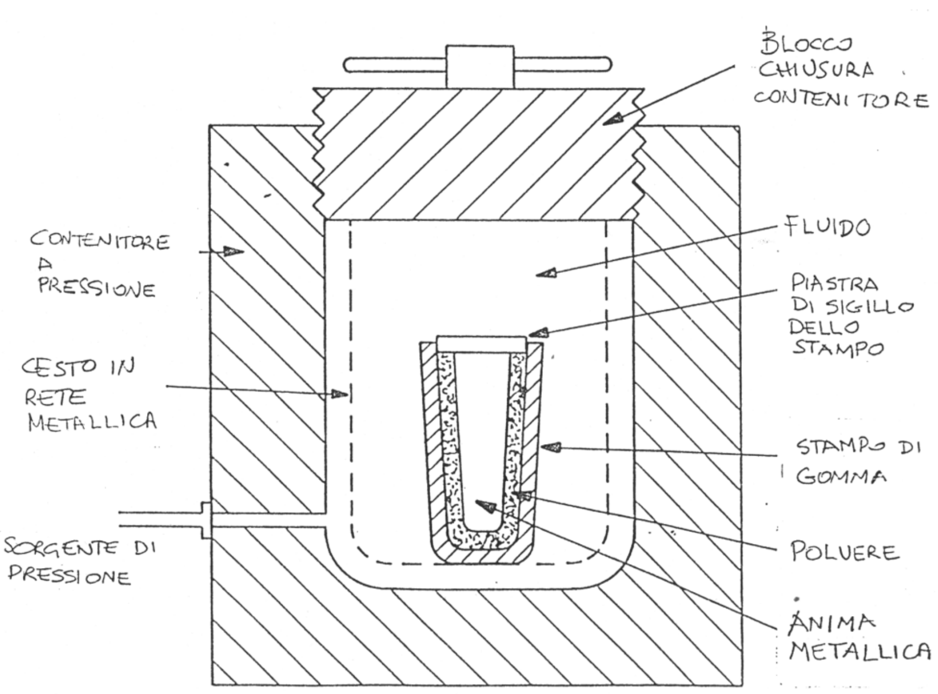
Densità o dimensioni improprie: spesso causate da cariche di polveri non rispondenti alle specifiche richieste;

Usura dello stampo: si traduce in dimensioni eccessive del pezzo formato; può essere più difficile da individuare.

Cricche: dovute a progettazione impropria dello stampo, intrappolamento d'aria, usura dello stampo, etc.

Variaziazioni di densità: costituscono forse il problema più grave. Causano distorsioni o criccature durante la successiva cottura. Una delle cause è l'attrito fra la polvere e le pareti dello stampo o fra le singole particelle

Pressatura isostatica



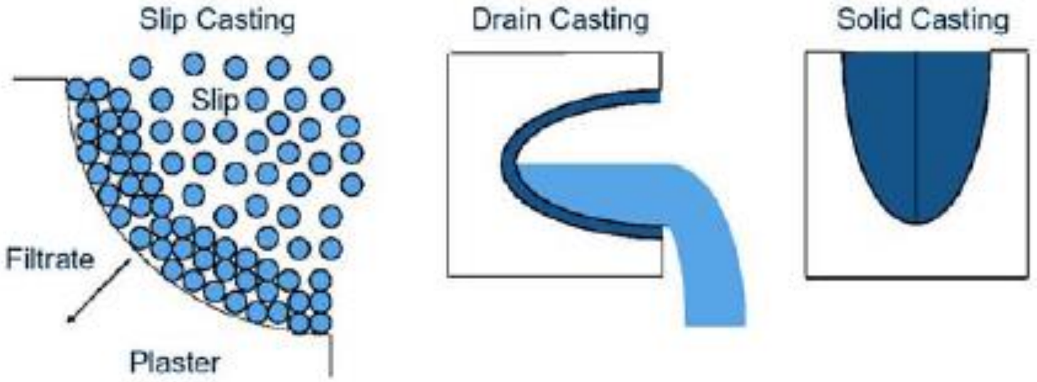
-La pressione è applicata uniformemente

-Si possono compattare volumi maggiori di polveri

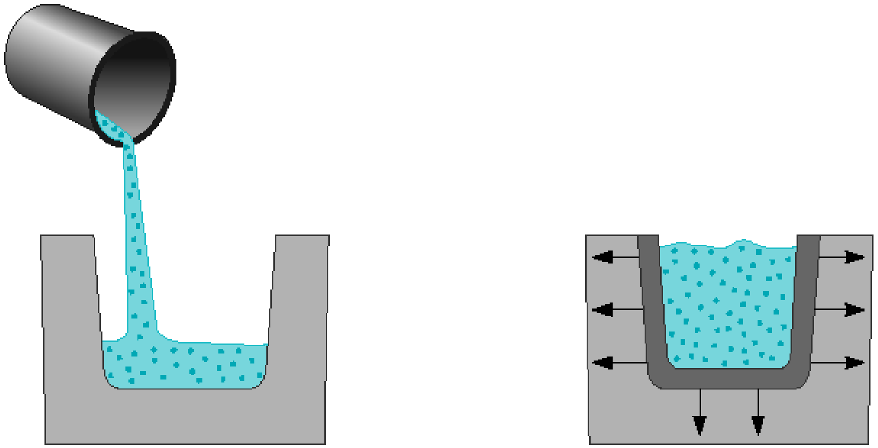
La polvere viene inserita in uno *stampo* in gomma, a sua volta immerso in un fluido incomprimibile e posto in un contenitore a pressione in acciaio. Si manda in pressione il fluido che comprime uniformemente (isostaticamente) la superficie dello stampo. Al momento della decompressione lo stampo si distacca dal compatto

Slip casting

Slip casting è un processo di formatura per colaggio di una sospensione ceramica che consiste nel riempire uno stampo poroso, tipicamente in gesso, con uno sospensione (slip o slurry) ceramica. L'acqua è rimossa dalla sospensione attraverso l'azione capillare esercitata dallo stampo poroso, le particelle ceramiche sono compattate sulla superficie dello stampo per formare un oggetto solido. Se si vuole realizzare un oggetto pieno è necessario rabboccare lo slip nello stampo, man mano che l'acqua è drenata, fino ad ottenere il completo riempimento dello stesso con un materiale che è tutto solido e pieno. Il green, durante l'essiccazione, subisce un piccolo ritiro che lo rende facilmente staccabile dallo stampo.

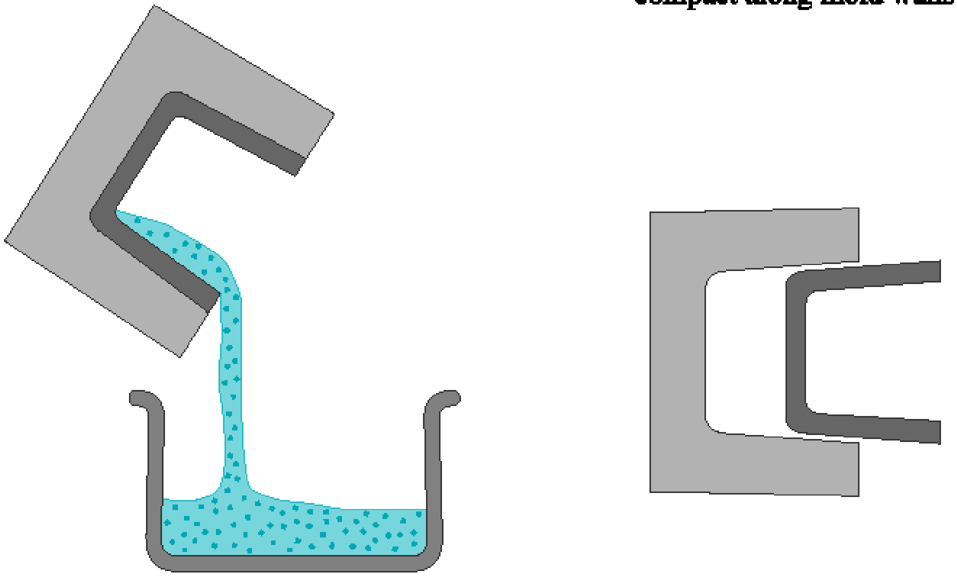


Slip casting



(a)
Fill mold with slip

(b)
Mold extracts liquid, forms compact along mold walls

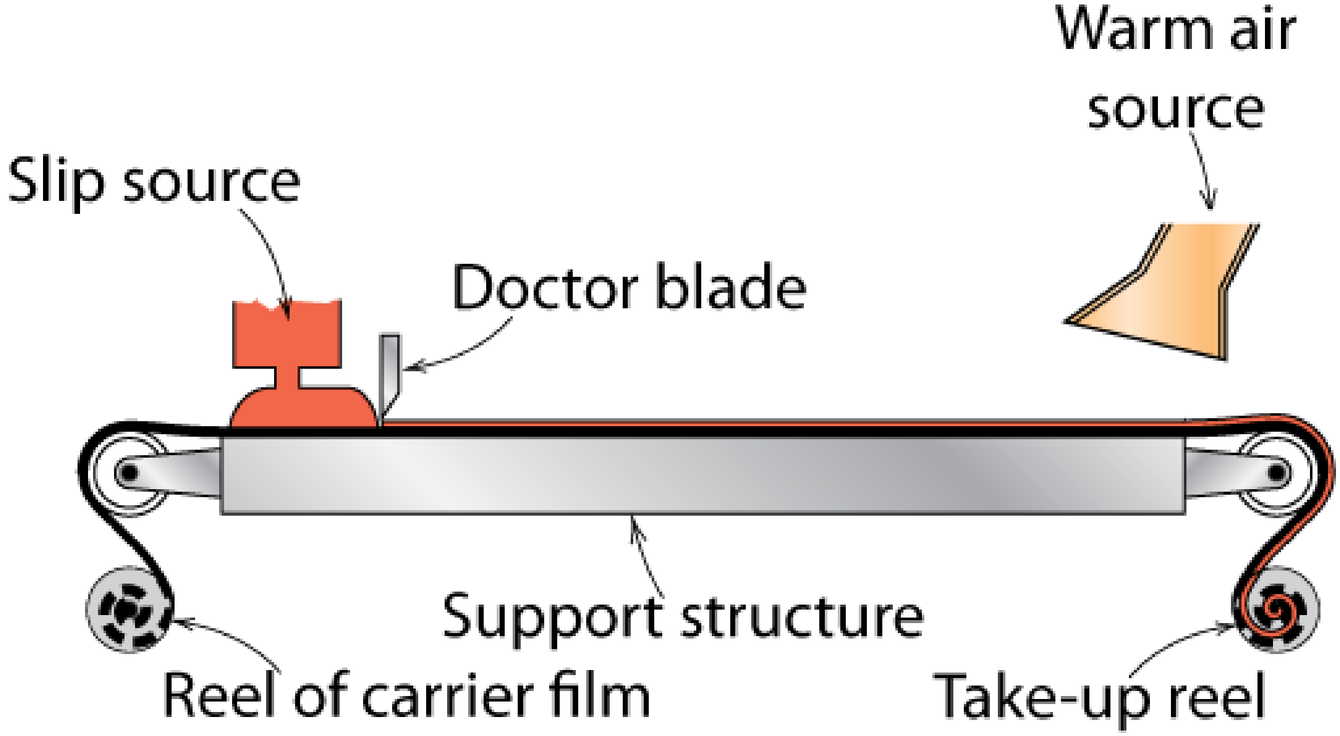


(c)
Excess slip drained

(d)
Casting removed after partial drying

Tape Casting

Il colaggio su nastro (tape casting) è il processo di formatura più idoneo per la produzione di componenti ceramici di superficie ampia, sottili e piani ed è importante nel settore dei materiali piezoelettrici, dei substrati per l’elettronica e dei materiali dielettrici. Attraverso il movimento di un nastro lo slip viene estruso dalla fenditura (doctor blade) e asciugato. La presenza di leganti organici o inorganici consente al green una sufficiente resistenza meccanica per i successivi processi di lavorazione.

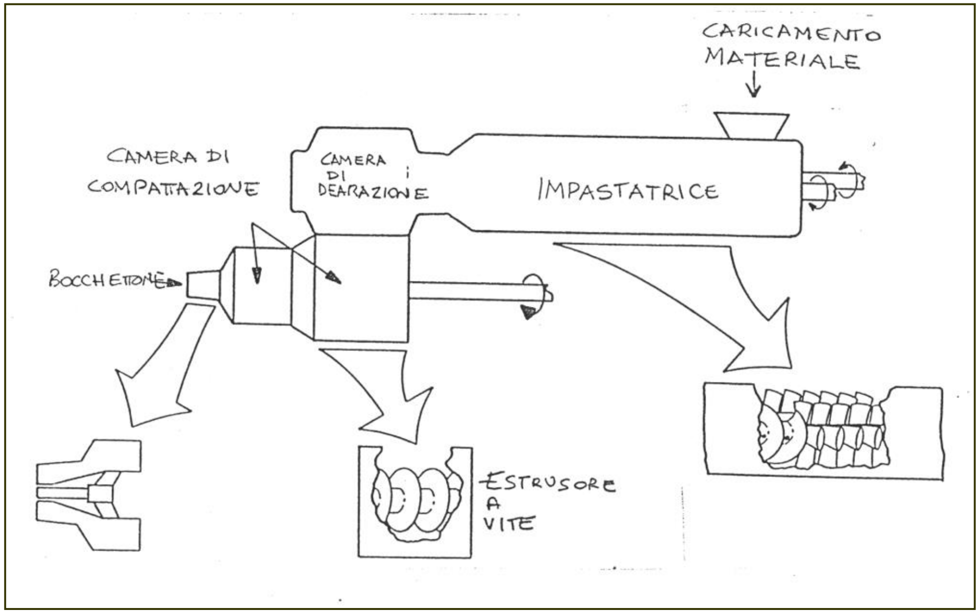


Estrusione

Si utilizza per la formatura di pezzi caratterizzati da forma allungata e sezione costante.

Si parte da una miscela di argilla ed acqua per i ceramici tradizionali, o di ceramico e additivo polimerico per i ceramici avanzati.

La miscela caricata dalla tramoggia passa in un cilindro evacuato dove viene deaerata, omogeneizzata e forzata, con una vite, attraverso una trafila della forma desiderata. Il pezzo in uscita viene sostenuto, tagliato ed essiccato.



Densificazione del compatto: Sinterizzazione

Sintering is the process by which a powder compact is transformed to a strong, dense ceramic body upon heating.

The following criteria must be met before sintering can occur:

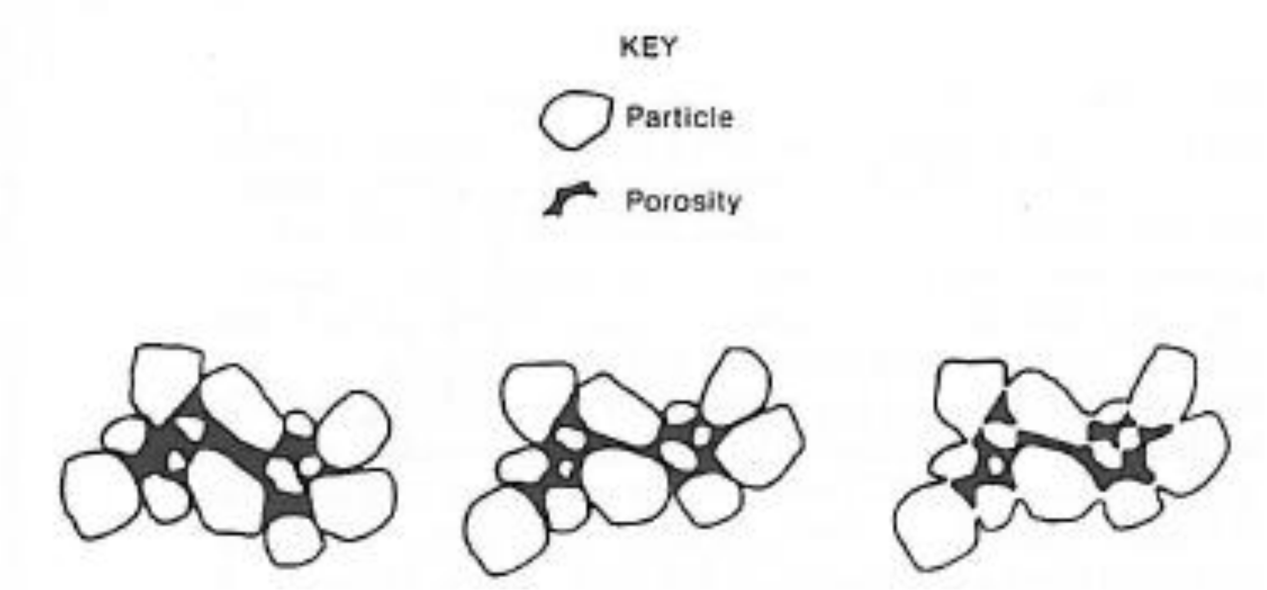
1) ***a mechanism for material transport must be present***

2) ***a source of energy to activate and sustain this material transport must be present***

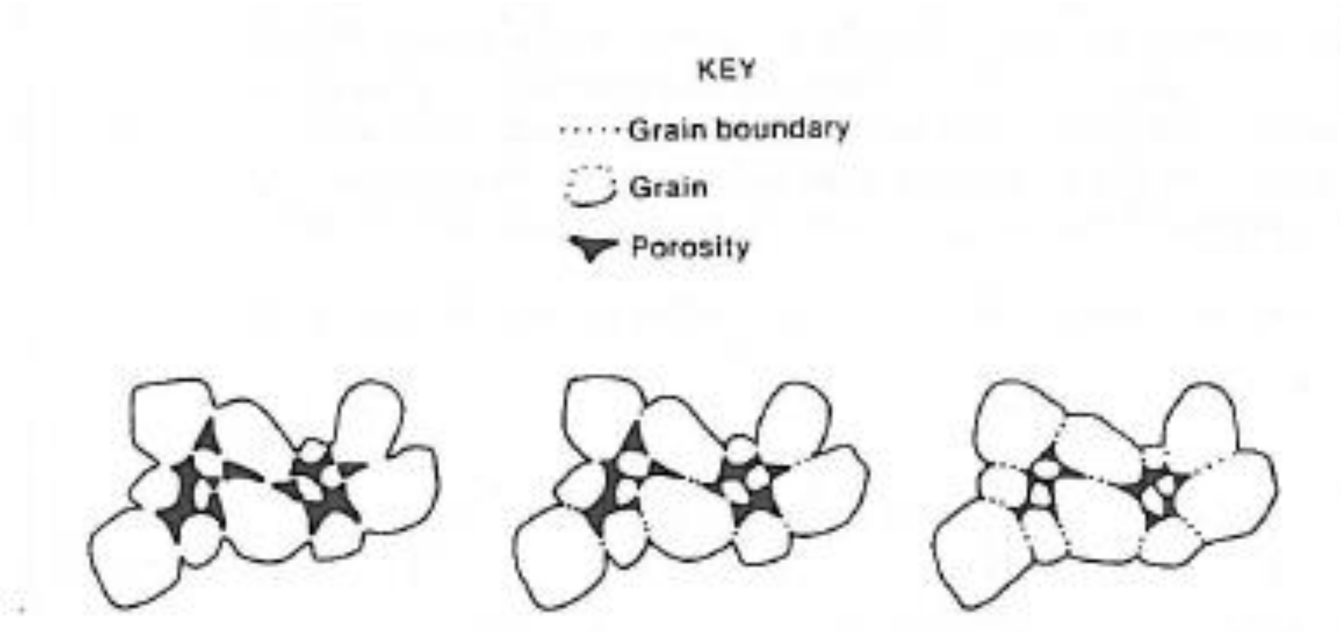
Stages of sintering

Three stages are identified, according to the sequence in physical changes that occur as the particles bond together and the porosity disappears.

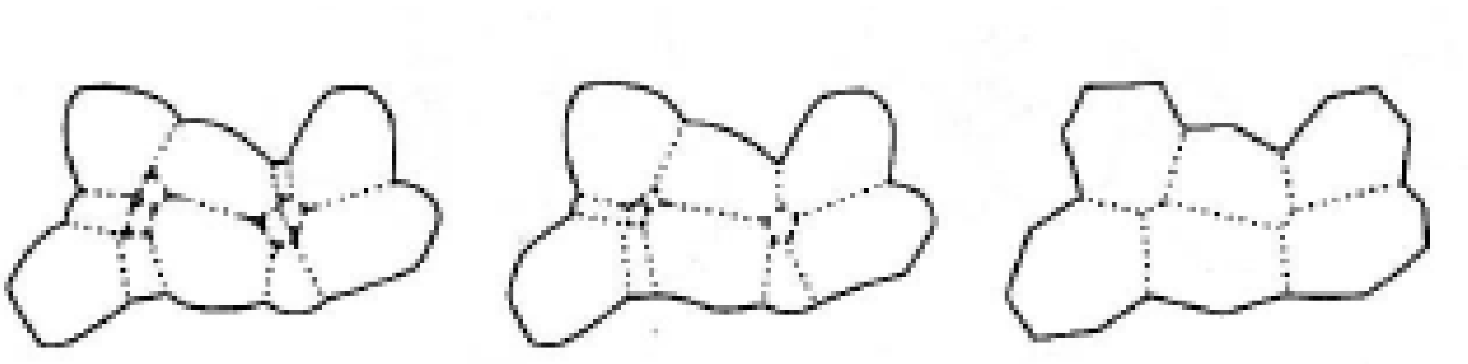
The initial stage involves rearrangement of particles and initial neck formation at the contact point between each particle. The rearrangement consists of slight movement or rotation of adjacent particles to increase the number of points of contact.



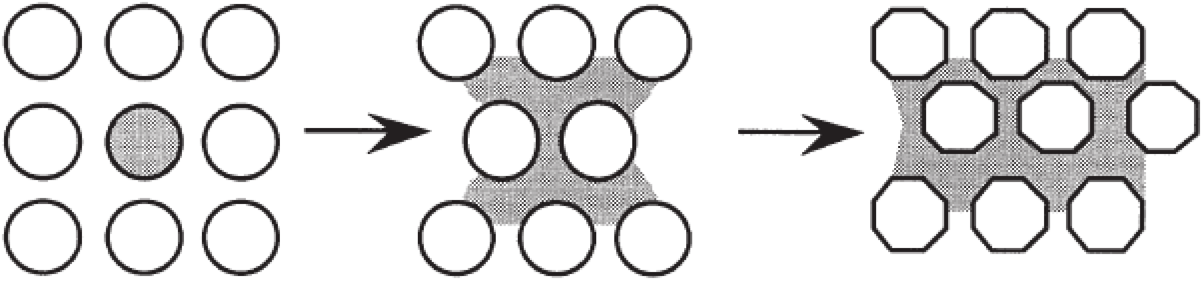
The second stage of sintering is referred to as intermediate sintering. The size of the necks between particles grow. Porosity decreases and the centers of the original particles move closer together. This results in shrinkage equivalent to the amount of porosity decrease. The grain boundaries begin to move so that one particle (a *grain*) begins to grow while the adjacent grain is consumed. Intermediate sintering continues as long as pore channels are interconnected and ends when pores become isolated. Most of the shrinkage occurs during this second stage.



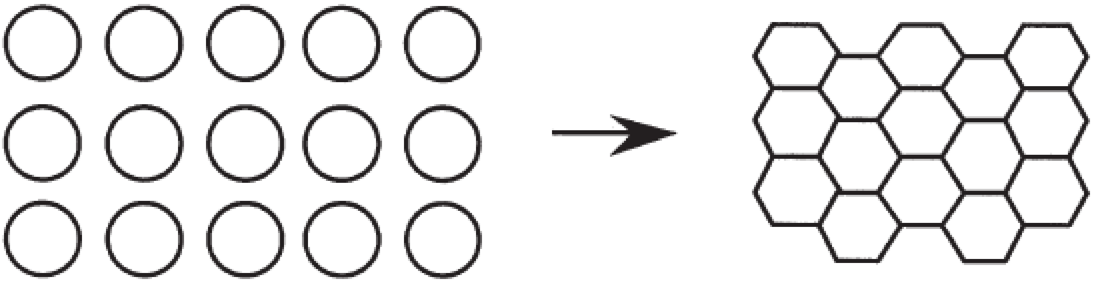
The third stage of sintering is referred to as final sintering. It involves the final removal of porosity. The porosity is removed by vacancy diffusion along grain boundaries. Therefore the pore must remain close to the grain boundaries. Pore removal and vacancy diffusion are aided by movement of grain boundaries and controlled grain growth (which is driven by surface energy).



Sintering can occur in the presence or absence of a liquid phase. In the former case, it is called *liquid-phase sintering*, where the compositions and firing temperatures are chosen such that some liquid is formed during processing



In the absence of a liquid phase, the process is referred to as *solid-state sintering*

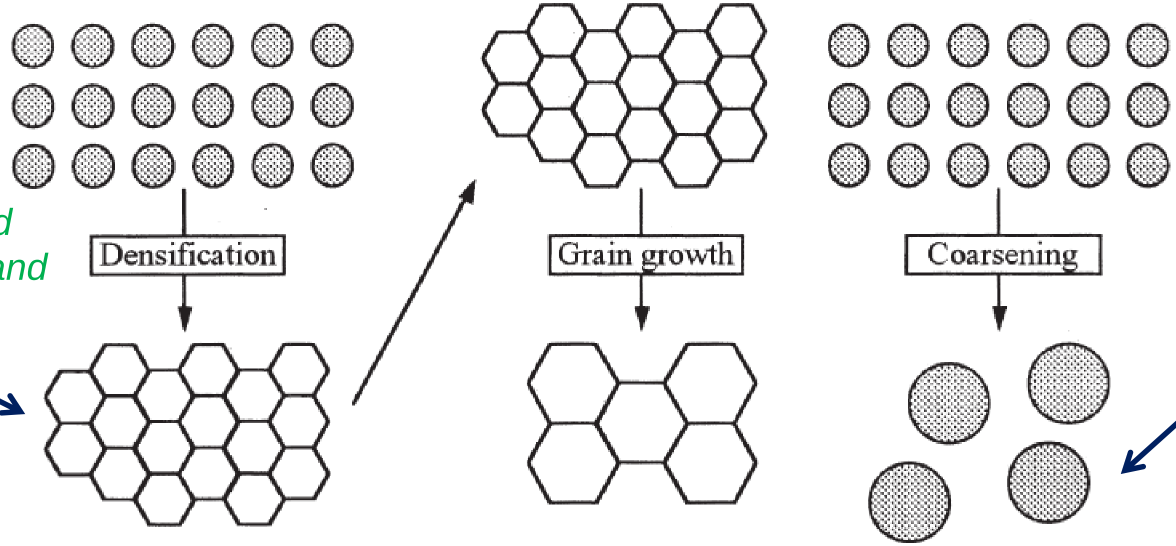


Solid-State Sintering

The macroscopic driving force operative during sintering is the reduction of the excess energy associated with surfaces. This can happen by:

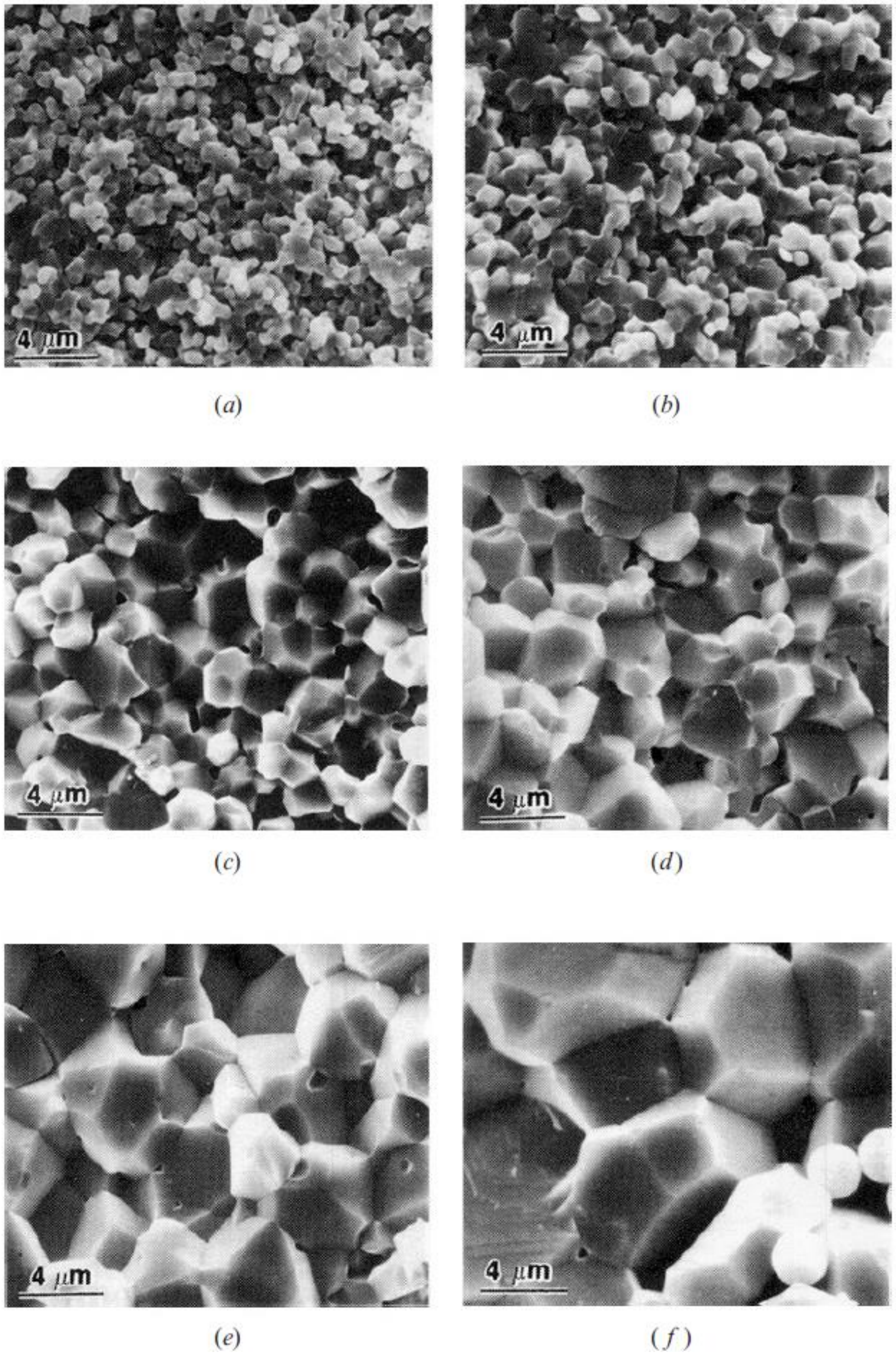
1. reduction of the total surface area by an increase in the average size of the particles which leads to *coarsening*;
2. the elimination of solid/vapor interfaces and the creation of grain boundary area, followed by grain growth, which leads to *densification.*

These two mechanisms are usually in competition



pores get smaller and disappear with time and the compact shrinks

pores and grains get larger with time



(a) (b)

(c) (d)

(e) (f)

the average grain size increases whereas the average pore size decreases

Local Driving Force for Sintering

The global driving force operating during sintering is the reduction in surface energy, which manifests itself locally as curvature differences.

Effect of curvature on

Partial pressure

$$\boxed{P_{\mathrm{curv}} = P_{\mathrm{flat}}\left(1 + \frac{2\Omega_{\mathrm{MX}}\gamma_{\mathrm{sv}}}{\rho kT}\right)}$$

the pressure of a material above a convex surface is greater than that over a flat surface, and vice versa for a concave surface.

Per una superficie curva la tensione di vapore in equilibrio con il solido varia in funzione della curvatura

Vacancy concentration

$$\boxed{\Delta C_{\mathrm{vac}} = C_{\mathrm{curv}} - C_0 = -C_0\frac{\kappa\,\Omega_{\mathrm{MX}}\gamma_{\mathrm{sv}}}{kT}}$$

vacancy concentration under a concave surface is greater than that under a flat surface, which in turn is greater than that under a convex surface

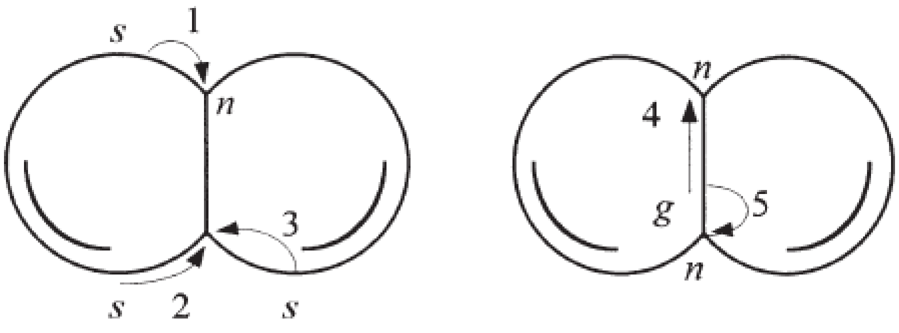
It costs less energy to create a vacancy in the vicinity of a concave surface than a convex one

Riassumendo:

Curvature causes local variations in partial pressures and vacancy concentrations. The partial pressure over a convex surface is higher than that over a concave surface. Conversely, the vacancy concentration under a concave surface is higher than that below a convex surface. ***In either case, a driving force is present that induces the atoms to migrate from the convex to the concave areas***

There are basically *five atomic mechanisms* by which mass can be transferred in a powder compact

coarsening and change in pore shape



(a) (b)

densification

1 Evaporation–condensation

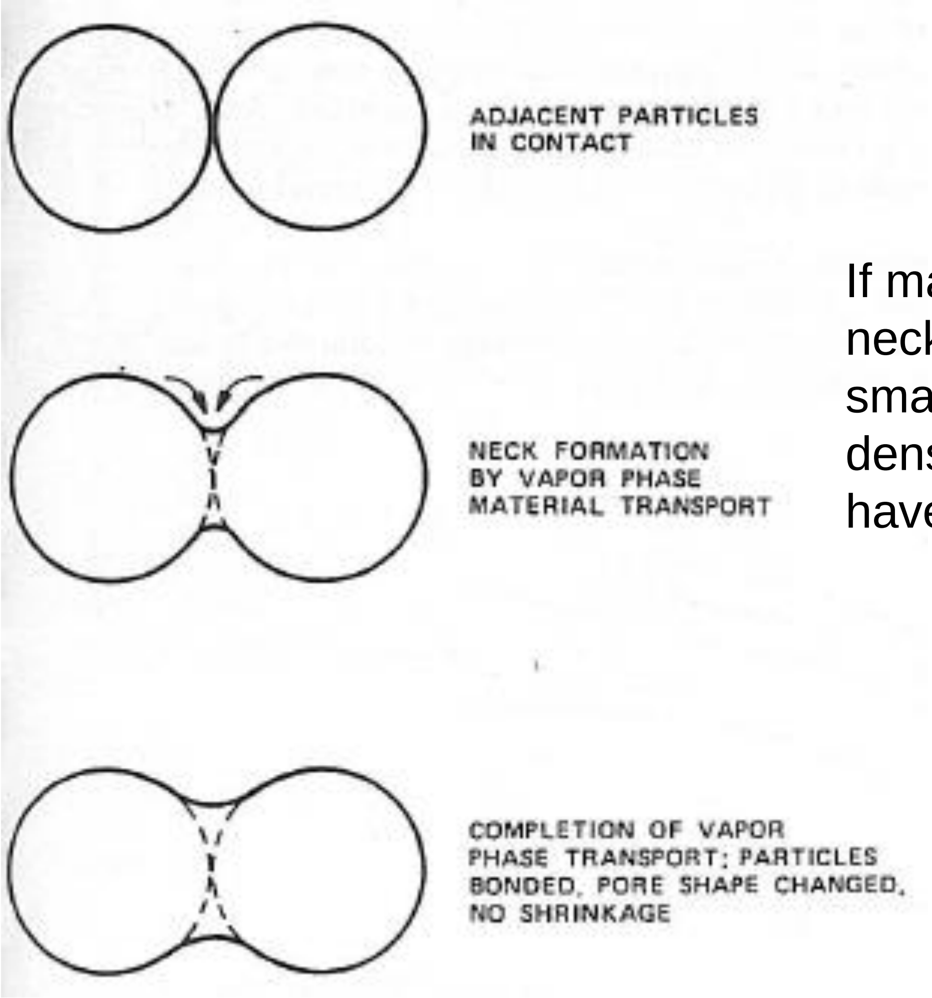
2 Surface diffusion

Volume diffusion. Mass can be transferred → 3 from the surface to the neck area
→ 5 from the grain boundary area to the neck area

4 Grain boundary diffusion from the grain boundary area to the neck area

Any mechanism in which the source of material is the surface of the particles and the sink is the neck area cannot lead to densification, because such a mechanism does not allow the particle centers to move closer together.

The driving force in all cases is the partial pressure differential associated with the local variations in curvature. For instance, the partial pressure at point *s* is greater than that at point *n*, which in turn results in mass transfer from the convex to the concave surfaces. The actual path taken will depend on the kinetics of the various paths. At a given temperature, the fastest one will dominate.



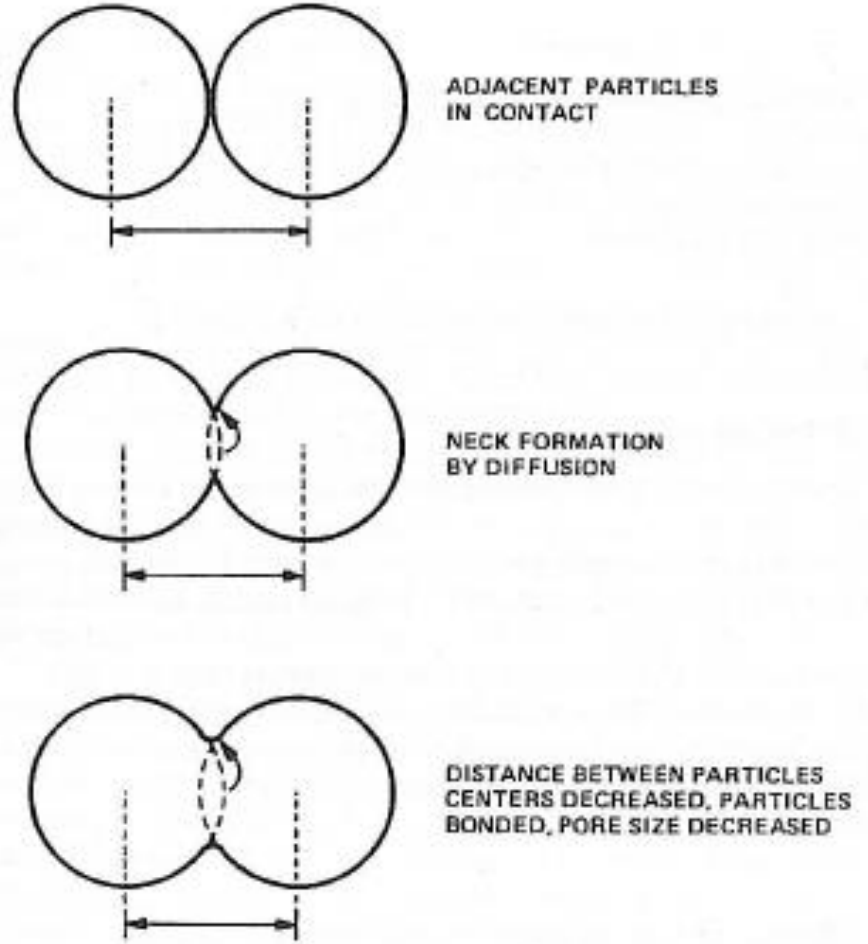
If mass transfer from the surface to the neck area or from the surface of smaller to larger grains does not lead to densification, other mechanisms have to be invoked to explain the latter!!

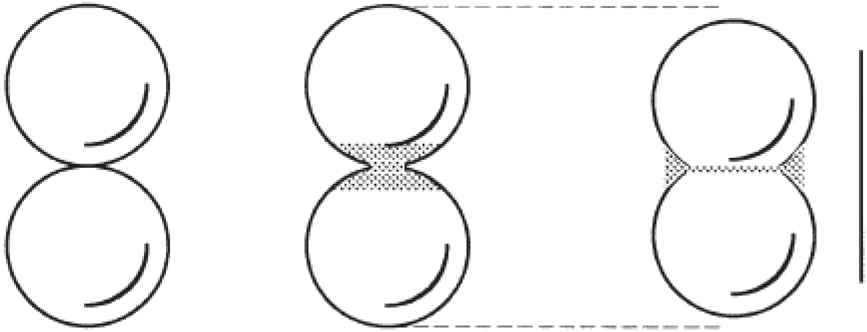
For densification to occur, the source of material has to be the grain boundary or region between powder particles, and the sink has to be the neck or pore region.

↓

The only mechanisms, that can lead to densification are grain boundary diffusion and bulk diffusion from the grain boundary area to the neck area

Both mechanisms entail the diffusion of ions from the grain boundary region toward the neck area, for which the driving force is the curvature-induced vacancy concentration. Because there are more vacancies in the neck area than in the region between the grains, a vacancy flux develops away from the pore surface into the grain boundary area, where the vacancies are eventually annihilated. Needless to say, an equal atomic flux will diffuse in the opposite direction, filling the pores.





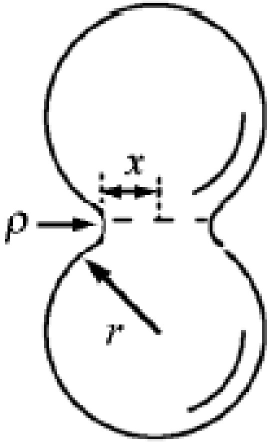
Note shrinkage

A powder compact can reduce its energy by following various paths, some of which can lead to coarsening, others to densification. This brings up the central and critical question in sintering:

What governs whether a collection of particles will densify or coarsen?

To answer the question, models for each of the paths considered above must be developed and compared, with the fastest path determining the behavior of the compact. For instance, a compact in which surface diffusion is much faster than bulk diffusivity would tend to coarsen rather than densify.

In practice, the question is much more difficult to answer, however, because the kinetics of sintering are dependent on many variables, including particle size and packing, sintering atmosphere, degree of agglomeration, temperature, and presence of impurities.



linear shrinkage

$$\frac{\Delta L}{L_0} = \left(\frac{K\gamma a^3 D^* t}{kTd^n} \right)^m$$

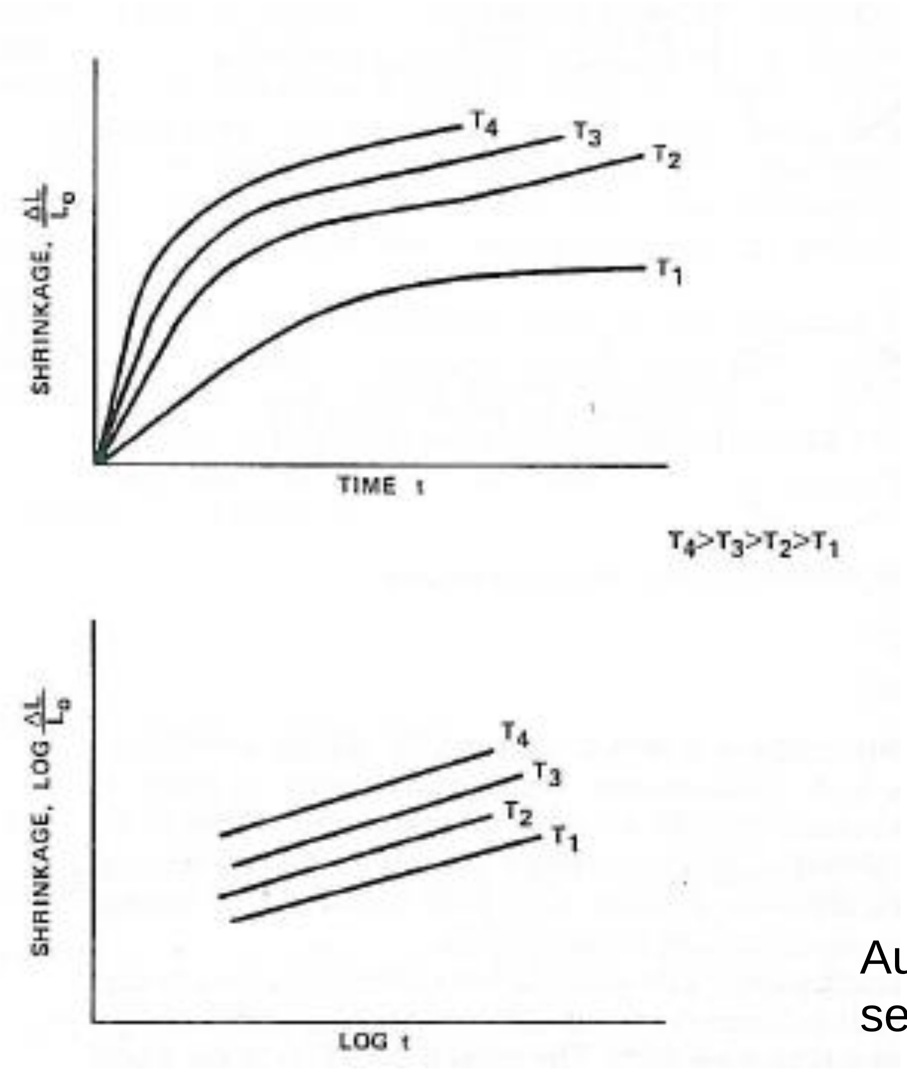
~ 0,3 – 0,5

~ 3

Per il primo stadio di sinterizzazione

K = cost dipendente dalla geometria
γ = energia superficiale
a^3 = volume atomico della vacanza che diffonde
D^* = coeff. di autodiffusione
t = tempo
d = diametro della particella
k = cost di Boltzmann

Effetto della T e del tempo



Aumentando la temperatura aumenta sempre la velocità di sinterizzazione

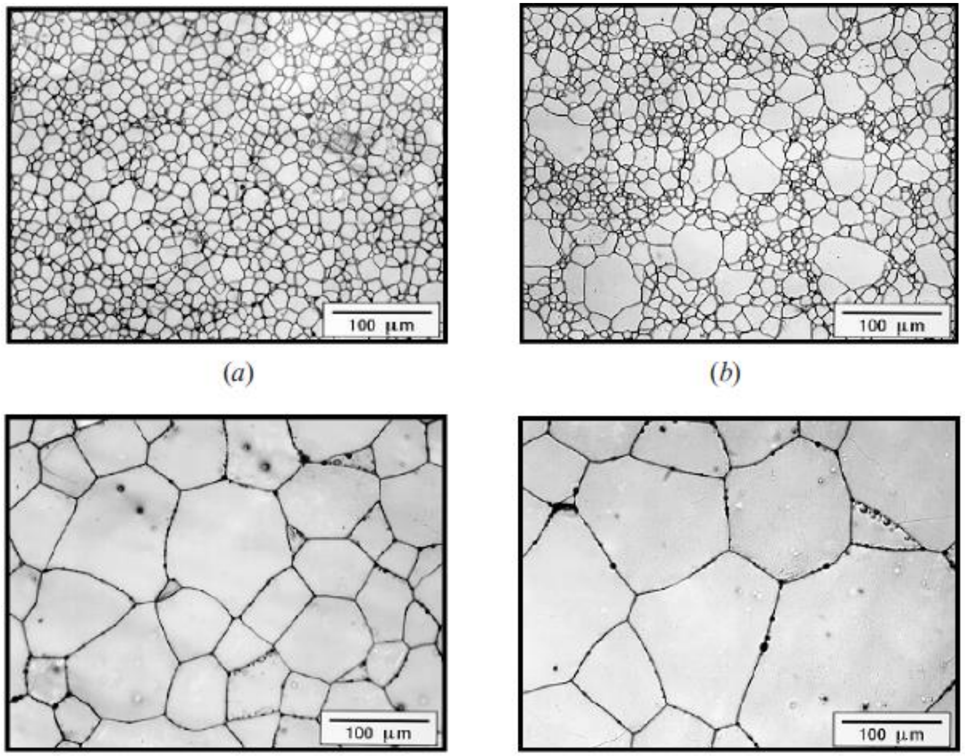
I parametri controllanti la sinterizzazione sono pertanto:

- ***Temperatura***: attiva i processi diffusivi favorendo i meccanismi di trasporto;
- ***Dimensione delle particelle***: la forza motrice è tanto maggiore quanto minore è il raggio della particella (elevata energia superficiale);
- ***Tempo;***
- ***Distribuzione granulometrica:*** polveri della stessa dimensione hanno basso fattore di impacchettamento e formano compatti molto porosi.

Temperatura e raggio delle particelle hanno un'influenza maggiore rispetto al tempo

Ingrossamento dei grani cristallini

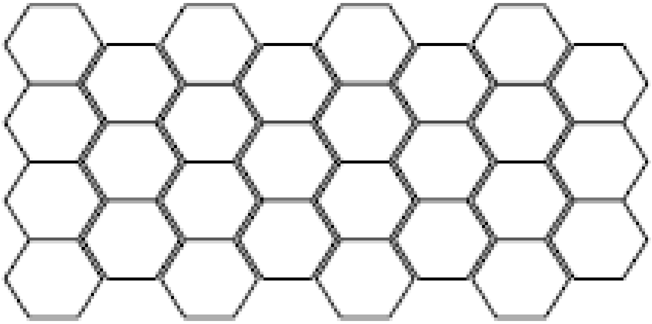
Any collection of particles will coarsen with time, where coarsening implies an increase in the ensemble's average particle size with time.
During the final stages of sintering, in addition to the elimination of pores, a general coarsening of the microstructure by grain growth occurs. During this process the average grain size increases with time as the smaller grains are consumed by larger grains.

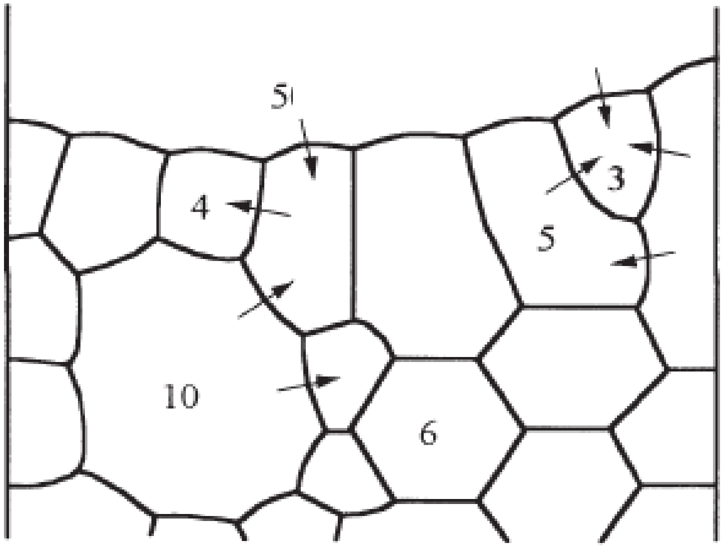


(*a*) (*b*)

(*c*) (*d*)

La forza motrice è dovuta alle diverse dimensioni e quindi al diverso raggio di curvatura dei grani.

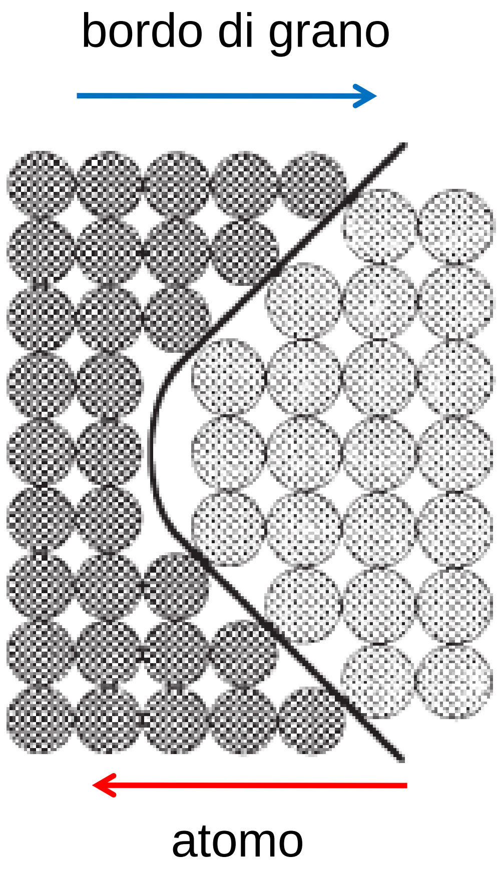




Geometricamente un poliedro di 6 lati piani rappresenta un policristallo a livello minimo di energia. I grani con 6 lati hanno bordi di grano “piatti” che formano angoli di 120° fra di loro. I grano con meno di 6 lati sono delimitati da bordi di grano concavi, mentre quelli con più di 6 lati sono delimitati da bordi di grano convessi. Per ridurre l’area e l’energia superficiale, i bordi di grano tenderanno a muoversi verso il proprio centro di curvatura e quindi:

- grani con meno di 6 lati tenderanno a rimpicciolire;
- grani con più di 6 lati tenderanno a crescere

Ostwald ripening

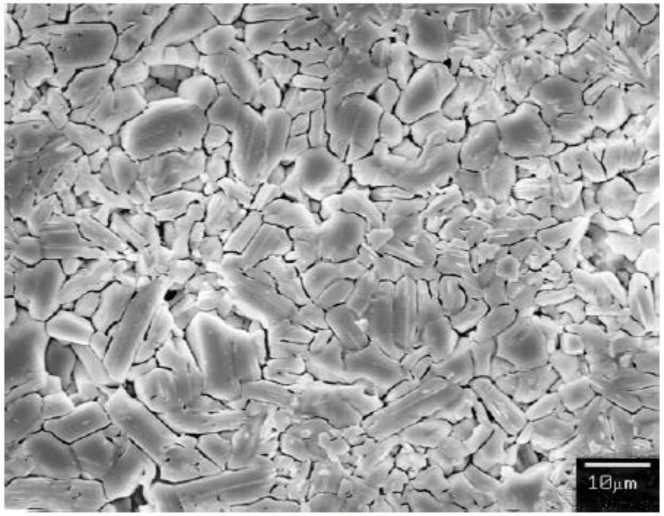


$$d_{av}^{2} - d_{av,0}^{2} = Kt$$

diametro iniziale

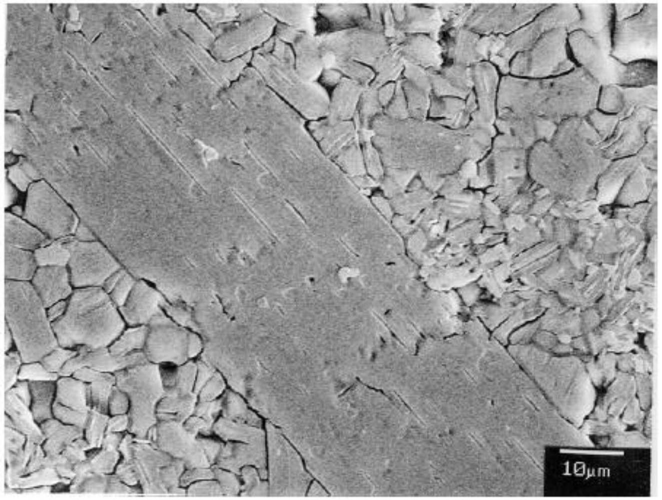
As the grains get larger and the pores fewer, the grain mobility increases accordingly. In some cases, at a combination of grain size and density, the mobility of the grain boundaries becomes large enough that the pores can no longer keep up with them; the boundaries simply move too fast for the pores to follow and consequently unpin themselves.

In some systems, it has been observed that a small number of grains in the population grow rapidly to very large sizes relative to the average size of the population → abnormal grain growth



(*a*)

normal



(*b*)

abnormal

Sinterizzazione in fase liquida

Si divide in sinterizzazione viscosa, o *Vetrificazione*, e *Sinterizzazione con fase liquida*.

Nella *vetrificazione* la composizione chimica del sistema e la temperatura producono una quantità di fase liquida di composizione chimica propria sufficiente ad eliminare la fase gassosa (pori) inizialmente presente fra le particelle. Basta circa il 20% di fase liquida.

Il consolidamento delle polveri avviene con formazione e scorrimento viscoso del liq. sotto le **forze di capilllarità** durante il trattamento termico e con vetrificazione (formazione di **fase solida amorfa**) durante il raffreddamento.

Questo processo è quello utilizzato per es. per la sinterizzazione dei ceramici tradizionali (porcellana e grès)

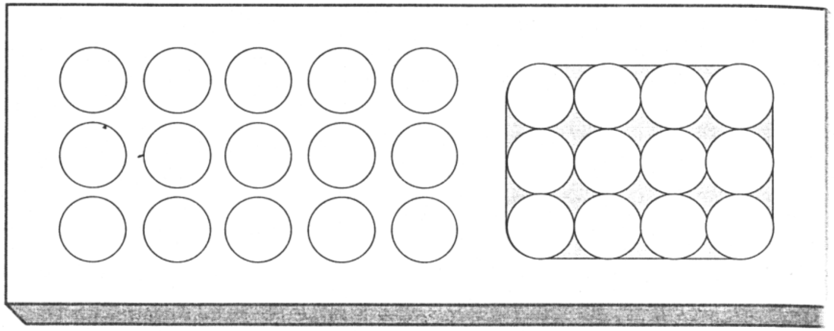


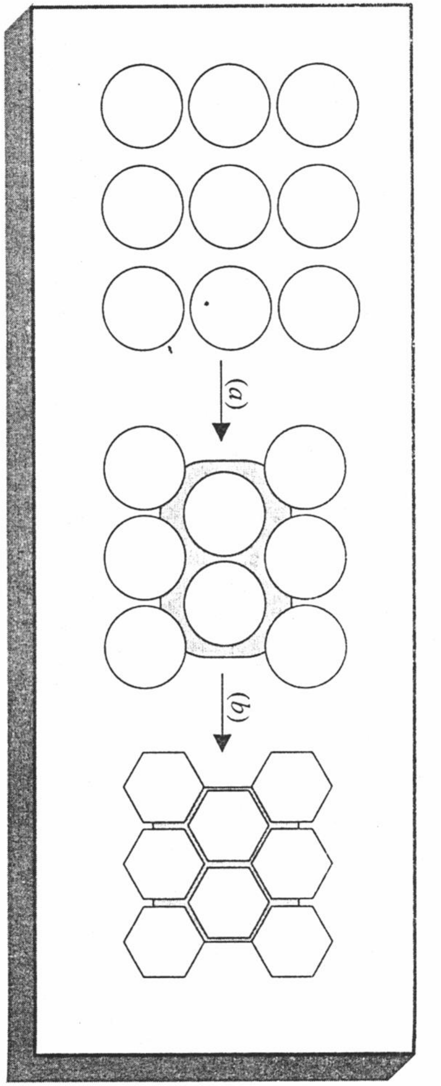
FIGURA [redacted] Rappresentazione schematica del fenomeno di formazione di una fase liquida derivata dalla fusione della fase scura che bagna e "sinterizza" la fase chiara con una conseguente riduzione di volume, cioè densificazione.

Nella *sinterizzazione con fase liquida* la quantità di fase liquida presente (formata mediante l'introduzione di opportuni additivi) non è sufficiente ad eliminare interamente la fase gassosa; per ottenere la densificazione completa è quindi necessario che il sistema subisca anche una variazione nella forma e dimensione dei grani.

La tecnica è importante per quei materiali per i quali la sinterizzazione allo stato solido risulterebbe tecnologicamente troppo gravosa (per es. per temperature troppo elevate).

Es. MgO (add.= CaO-SiO_2), Al_2O_3 (add.= MgO-SiO_2), Si_3N_4 (add.= MgO).

E' necessario che la fase liquida si formi a temperature non troppo elevate e che il film liq. che si forma sia continuo e bagni tutta la fase solida, e sia percorribile prima dal gas intrappolato in uscita e poi dal flusso di materia necessario a rimodellare i grani ed eliminare la porosità residua.



Il meccanismo prevede due stadi successivi:

- ricoprimento delle particelle e loro aggregazione sotto la spinta delle forze di capillarità in un impacchettamento più efficace;
- dissoluzione e riprecipitazione del materiale solido nel film liquido, scorrimento viscoso e deformazione plastica, trasporto in fase vapore e crescita dei grani.

Le forze capillari possono essere dell'ordine dei 7 MPa (1000 psi). Particelle più piccole risultano in pressione capillare più elevata, ed hanno inoltre una energia superficiale più elevata a causa del minor raggio di curvatura ⇒ maggiore energia per la densificazione. Materiali per i quali si richiedono minima porosità e massima resistenza sono ottenuti a partire da particelle < 5 µm.

I principali svantaggi sono legati alla permanenza dell'additivo di sinterizzazione nella microstruttura. La fase, spesso vetrosa, può alle temperature di esercizio, diventare fluida e favorire lo scorrimento viscoso, determinando perdita di resistenza meccanica e di stabilità dimensionale.

Pressatura uniassiale ed isostatica a caldo

Applicazione contemporanea di calore e pressione ad un materiale ceramico in polvere contenuto in uno stampo

Rispetto alla sinterizzazione tradizionale la pressatura a caldo permette di usare temperature più basse e di avere tempi di processo più brevi, minori dimensioni dei grani cristallini e minore porosità.

L’effetto sinergico dell’alta temperatura e pressione porta ad un notevole aumento della velocità di densificazione.

L’impiego della pressatura a caldo è indispensabile in tutti i casi in cui la sola temperatura non consenta di ottenere una soddisfacente densificazione

Pressatura uniassiale a caldo

- Possono essere realizzati soltanto pezzi di forma semplice;
- La pressione è disomogenea: si possono avere zone a differente densificazione.

Pressatura isostatica a caldo (HIP)

E’ possibile realizzare pezzi con geometria complessa

La pressione (70 – 300 MPa) è trasmessa da un gas (Argon solitamente) alla polvere grazie ad uno stampo deformabile che la contiene.

Lo stampo serve a dare la forma al pezzo, ma anche ad evitare che il gas penetri nelle porosità aperte ed equilibri quindi la pressione interna al materiale con quella esterna

La HIP permette di ottenere prodotti praticamente privi di porosità con temperature inferiori del 25-50% rispetto alla sinterizzazione tradizionale.