24-25 Ottobre: Seminario dei Corsi Ordinari
"Leghe a memoria di forma"

Leghe a memoria di forma: un esempio di materiale intelligente dalle 1001 applicazioni...con una tecnologia tutta italiana:

- Il Sistema Ni-Ti e tecniche di caratterizzazione
- Tecniche di produzione ed educazione del NiTi

Relatore: Ausonio Tuissi

Consiglio Nazionale delle Ricerche
Istituto per L'Energetica e le Interfasi
Unità di Lecco

Riassunto I

- Leghe a Memoria di Forma
- Il Sistema NiTi : Effetti SME and Superelasticità SE, Caratteristiche
- Analisi: DSC, DMA, Meccaniche, Strutturali, Elettriche Funzionali

Riassunto II

- Il Processo Produttivo
- Fusione e Lavorazioni a Caldo
- Laminazione e Trafilatura a Freddo
- Shape Setting
- Ciclaggio

Leghe a Memoria di Forma

Leghe base NiTi

- NiTi (Nitinol- Nickel Titanium Naval Ordinance Laboratory - after W.J. Buehler, J.W.Gilfrich and R.C.Wiley J.Appl.Phys., 34 (1963) 1475)
- NiTiX (X=Cu,Fe,Pd,Pt,Hf, Cr, Co,V, Zr, Nb,W).

Leghe base Cu

•CuZnX (X= Al,Si,Sn,Ga,Mn)

•CuAlX * (X=Ni,Be,Zn;Mn)

•CuSn

Base Ferro *

•FeMnSi

•FeMnSiCrNi

•FeNiCoTi

•FeNiC

Leghe commerciali

•NiTi – NiTiCu - CuZnAl

* Possibili sviluppi industriali

Altre leghe

•AuCd

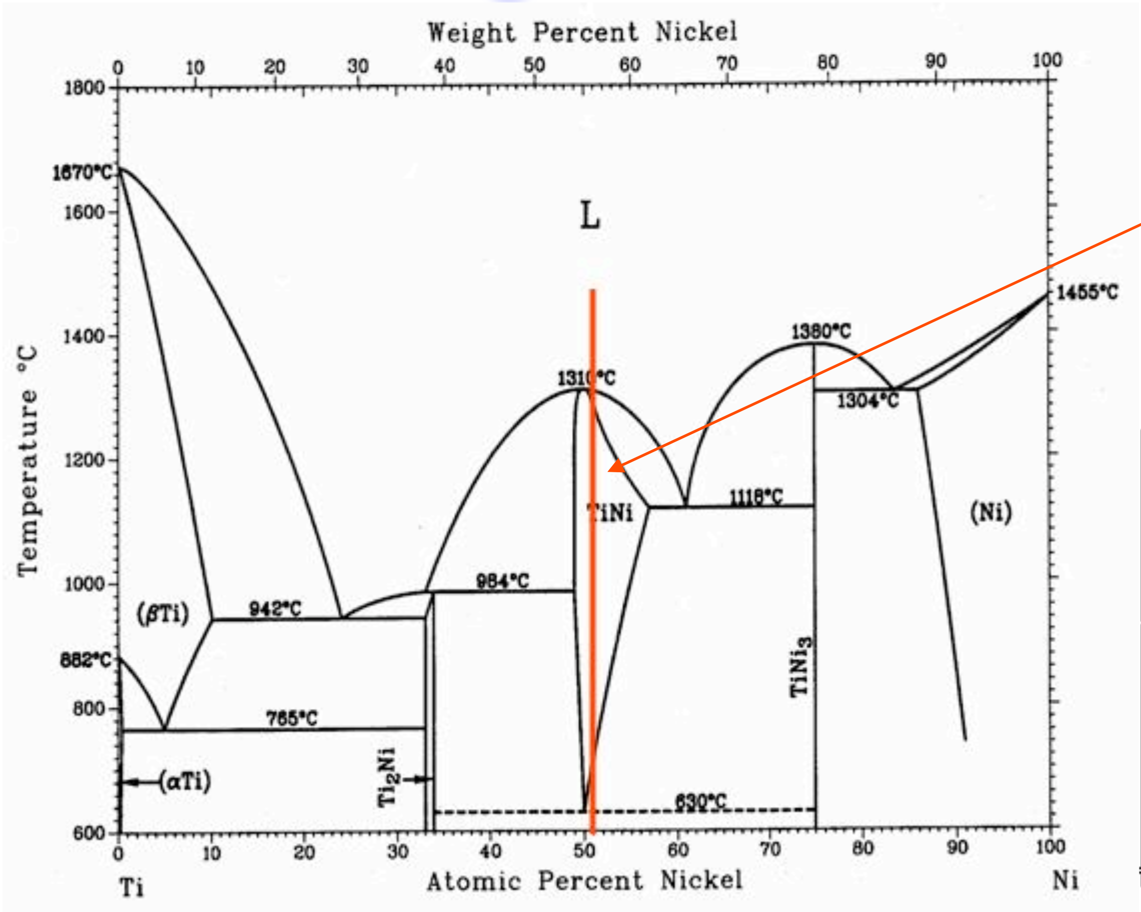
•NiAl

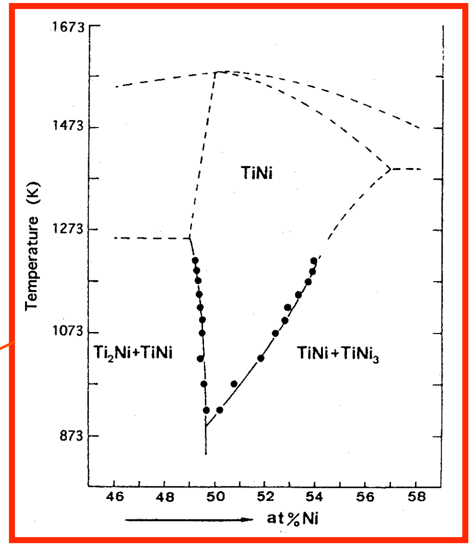
Leghe attivazione magnetica *

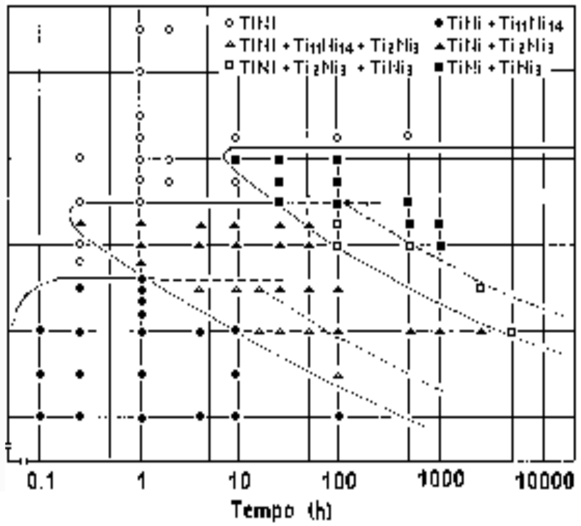
- Ni-Mn-Ga

•Ni-Mn- X (X=Al,In,Sn,Sb).

Ni-Ti: Diagramma di Fase







Effetto Pseudoelastico

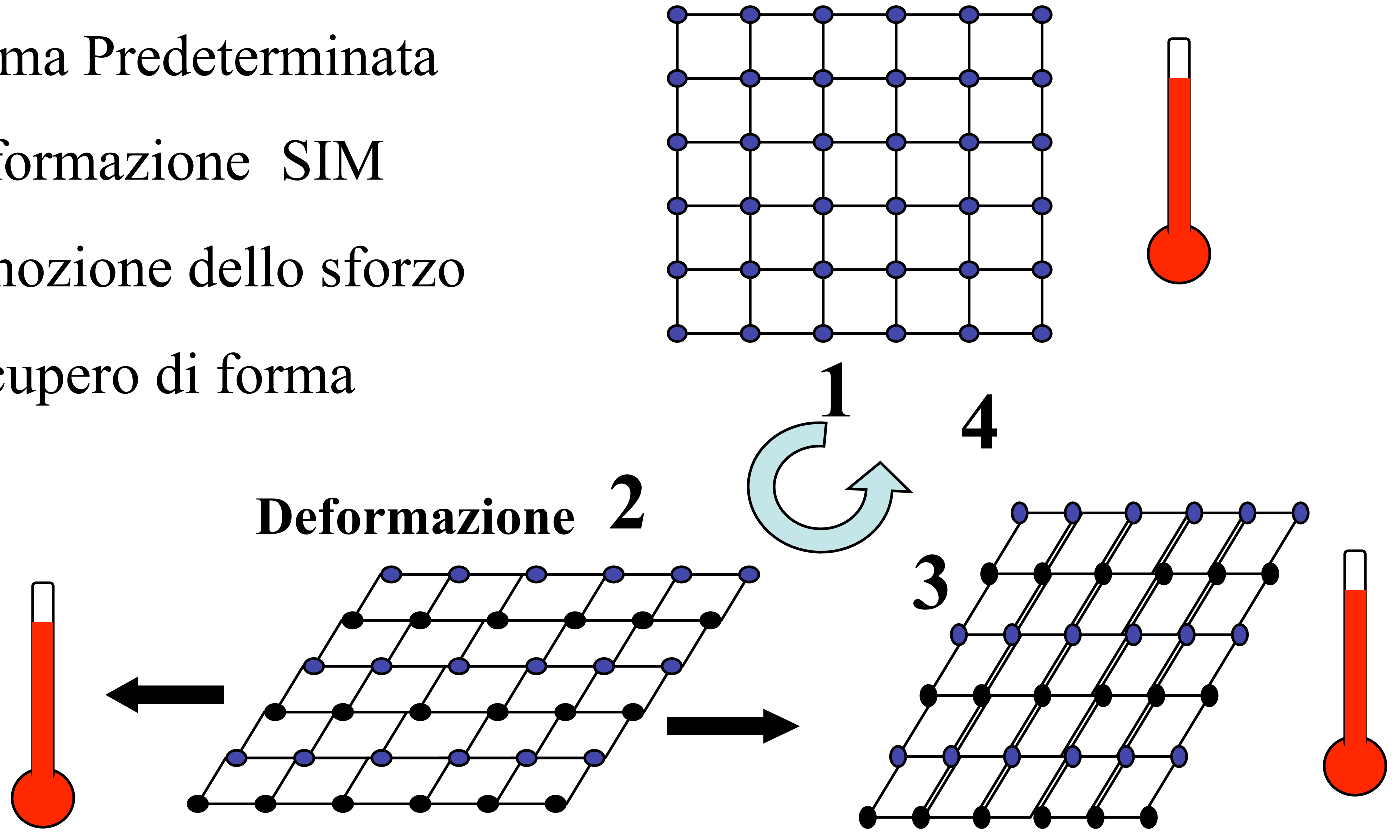
Recupero di una forma macroscopica predeterminata
mediante rimozione della sollecitazione a temperatura costante

1 Forma Predeterminata

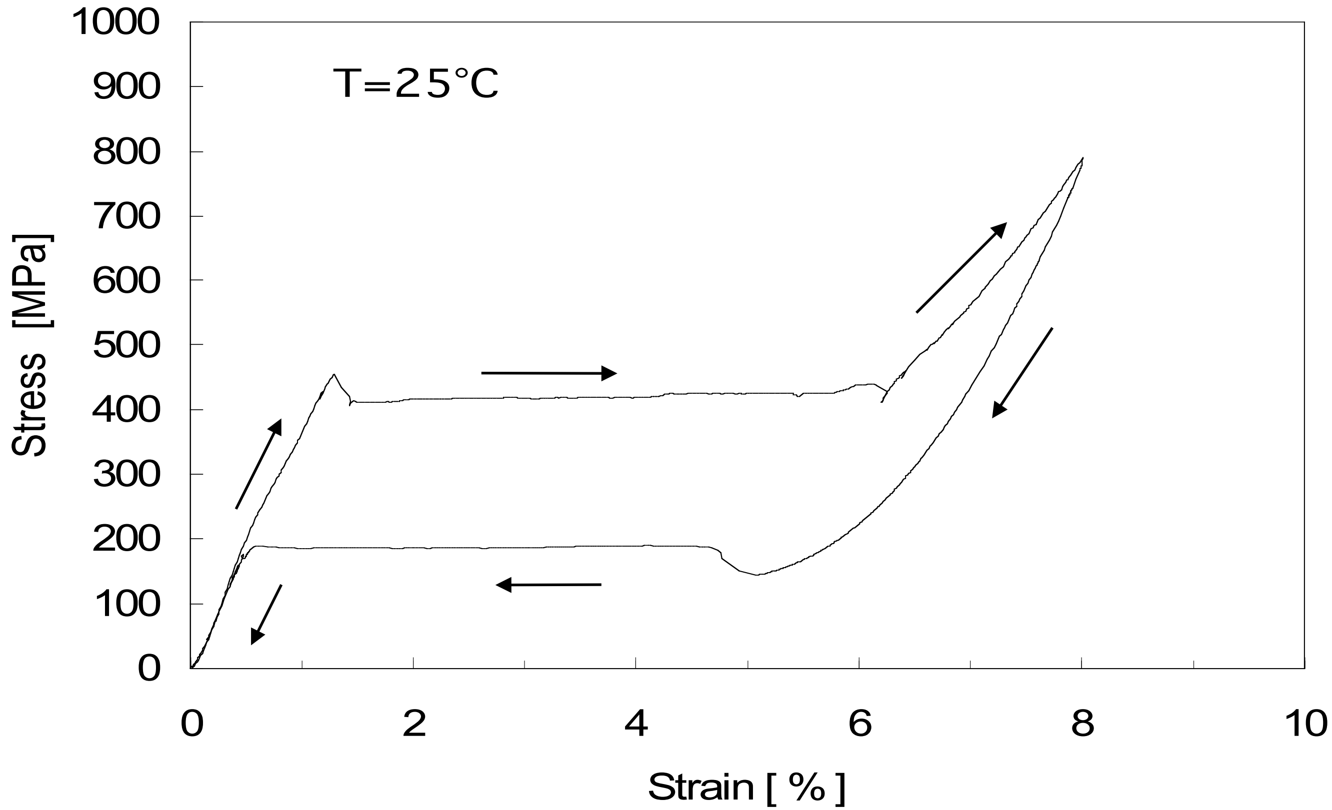
2 Deformazione SIM

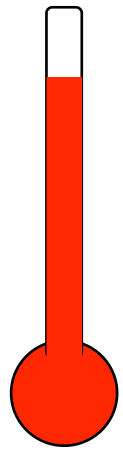
3 Rimozione dello sforzo

4 Recupero di forma



Pseudoelasticità NiTi: 10-12%





Pseudoelasticità è un fenomeno che avviene a temeperatura costante - SIM (stress induced martensite)

Effetto: Memoria di Forma

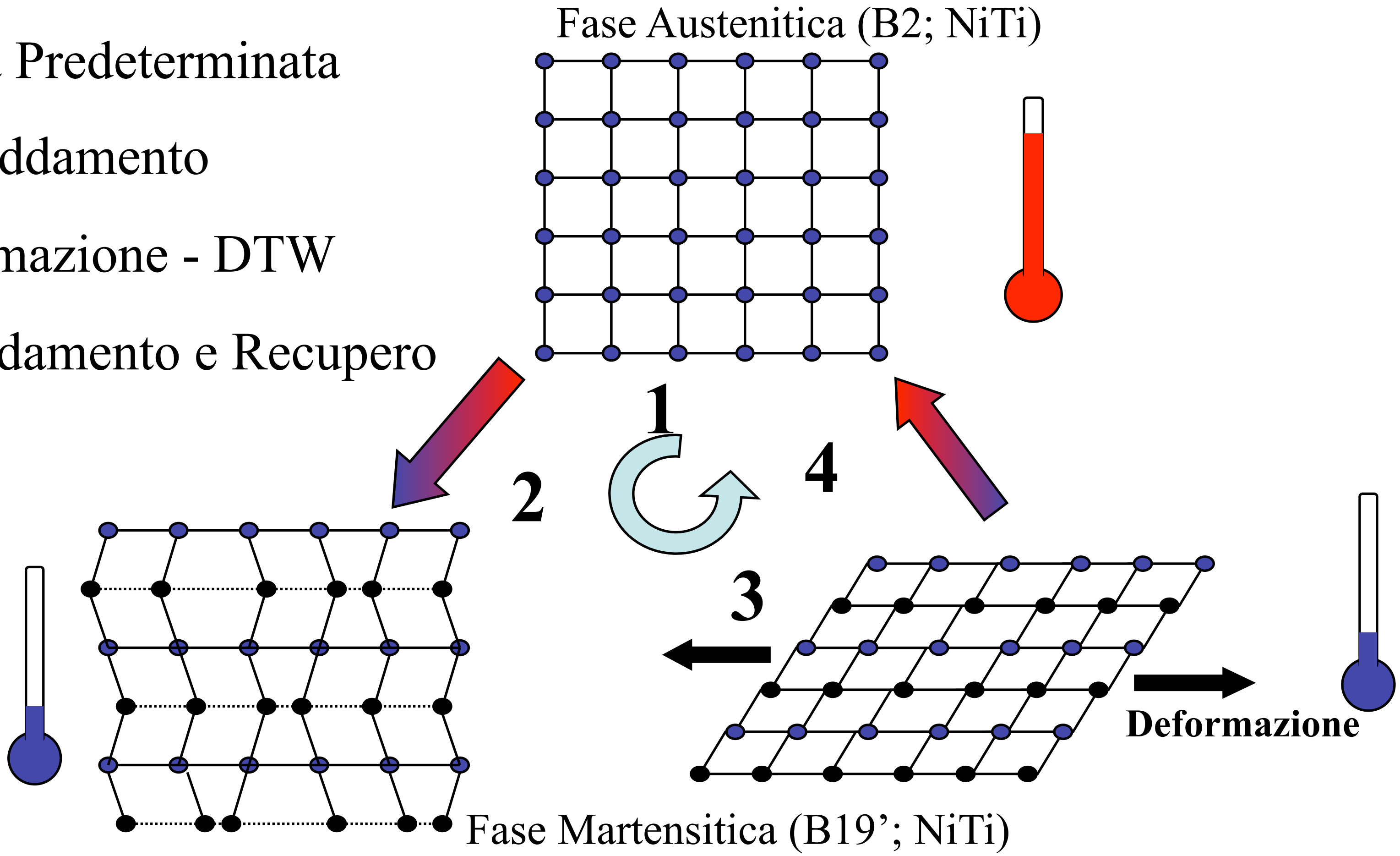
Recupero di una forma macroscopica predeterminata per riscaldamento

1 Forma Predeterminata

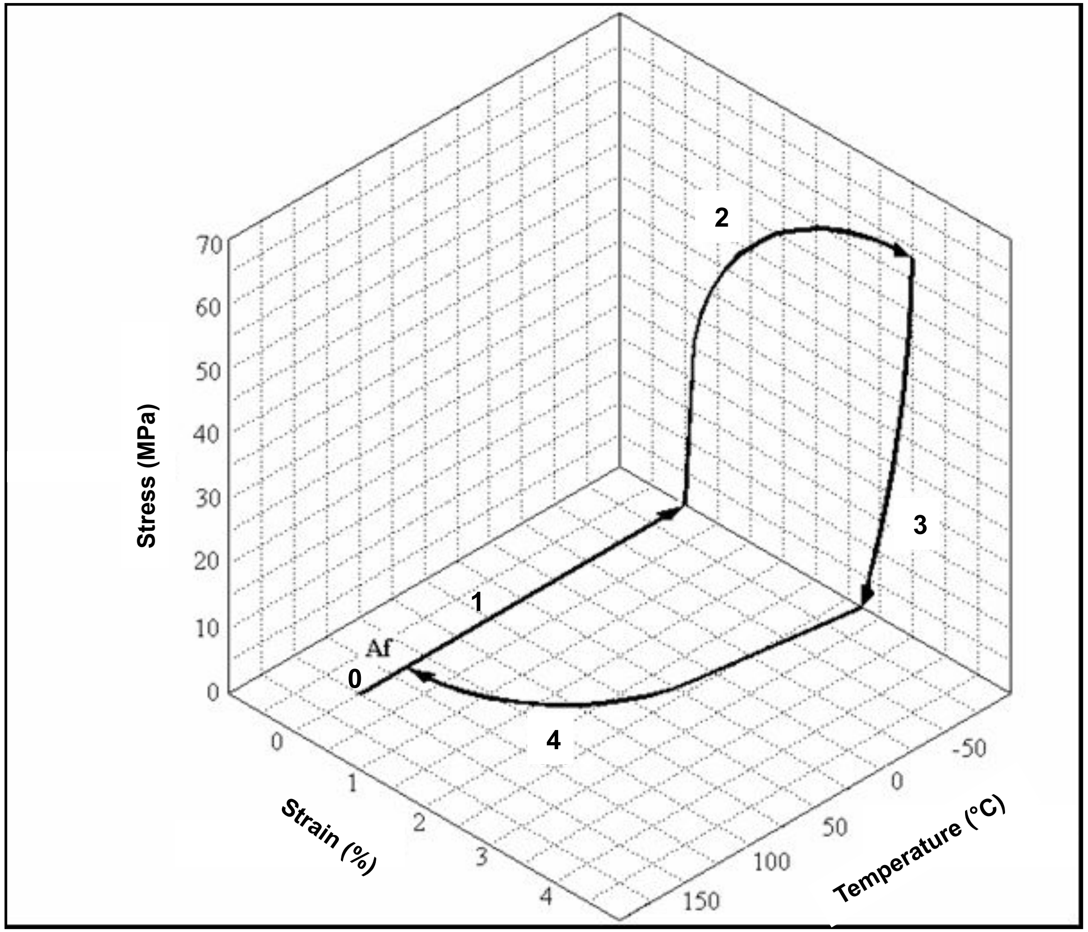
2 Raffreddamento

3 Deformazione - DTW

4 Riscaldamento e Recupero

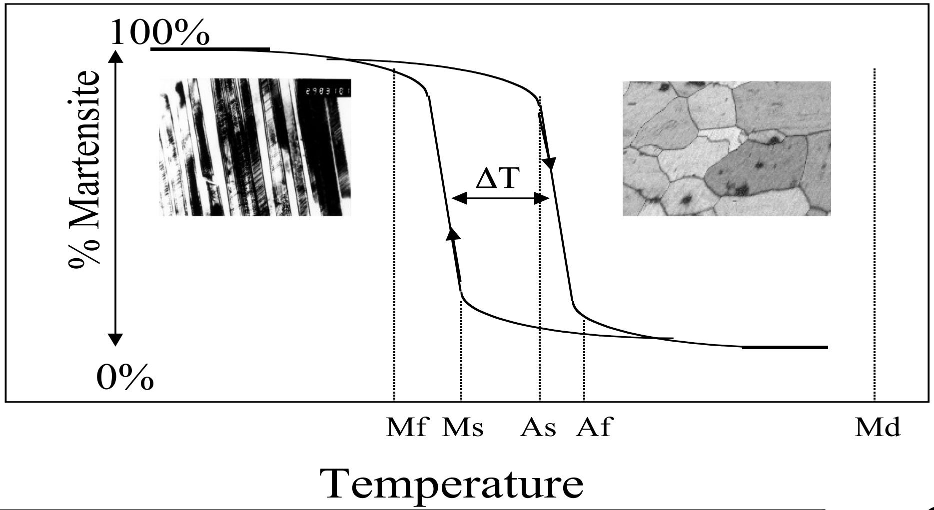


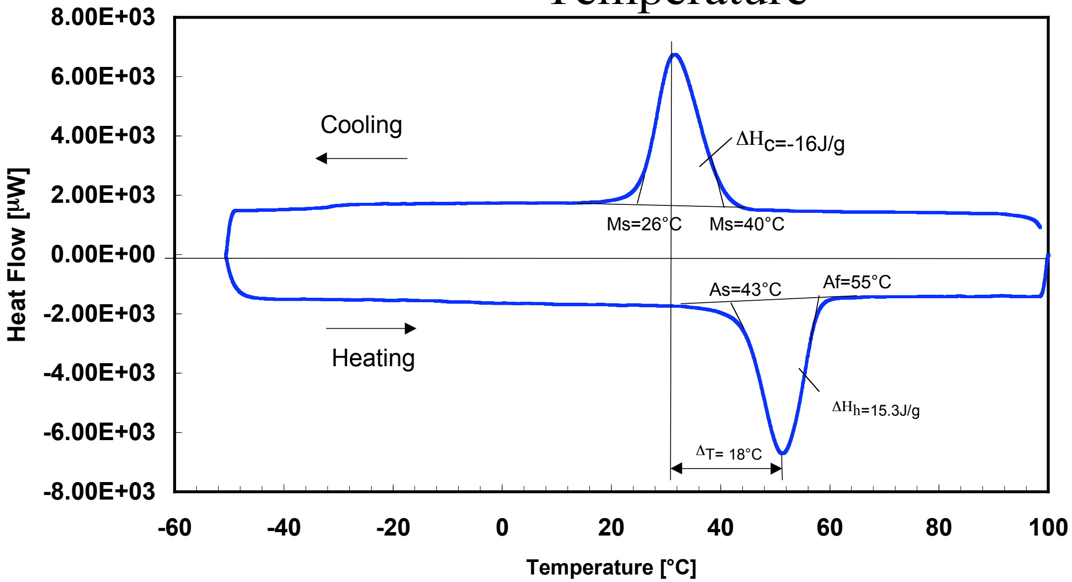
Effetto di Memoria di forma NiTi: 8%



L’effetto di memoria di forma richiede una variazione di temperatura

Trasformazione Martensitica NiTi- B2-B19'





<u>Cooling: Direct Transformation B2-B19'</u>

Ms Martensite Start

Mf Martensite Finish

<u>Heating: Reverse Trasformation B19'-B2</u>

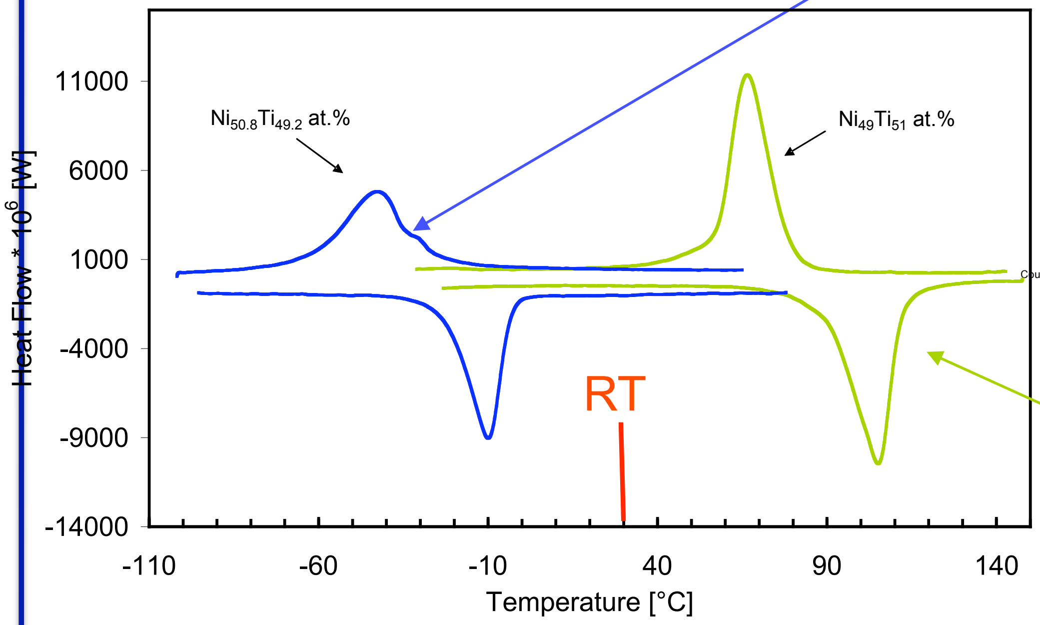
As Austenite Start

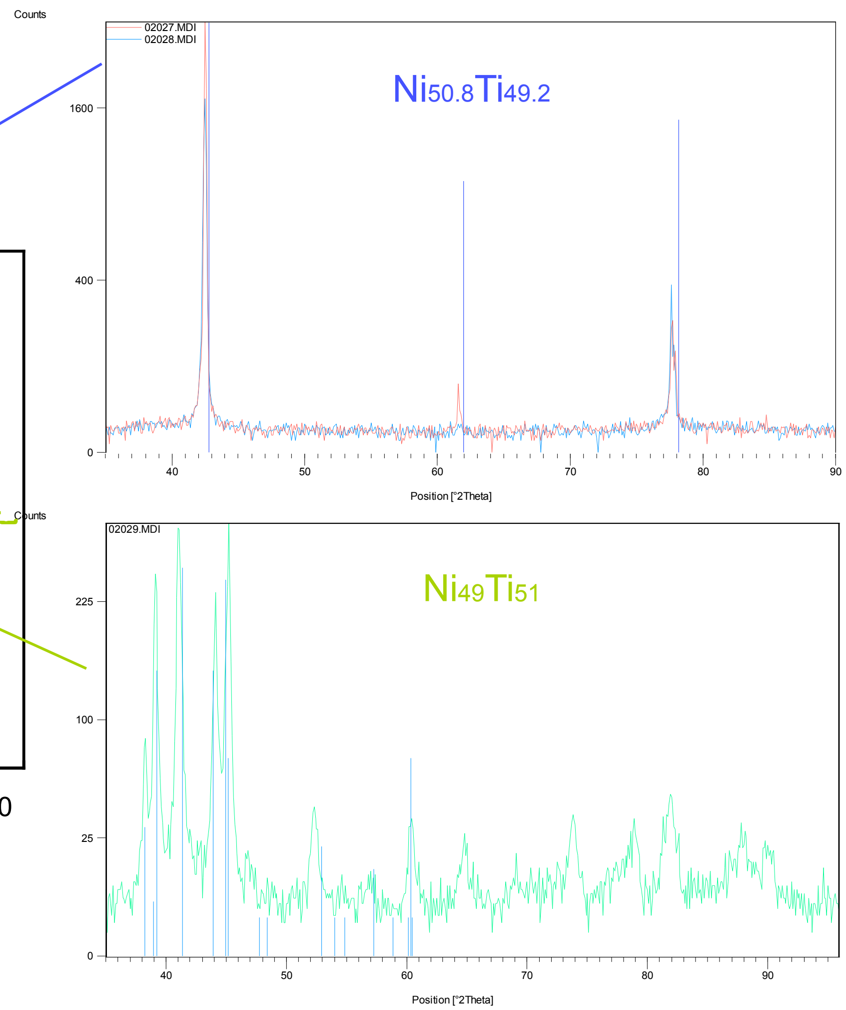
Af Austenite Finish

Trasformazione Martensitica NiTi- B2-B19'

$Ni_{50.8}Ti_{49.2}$ and $Ni_{49}Ti_{51}$ at.% alloys preparati mediante VIM

θ-2θ X-ray diffraction pattern at RT



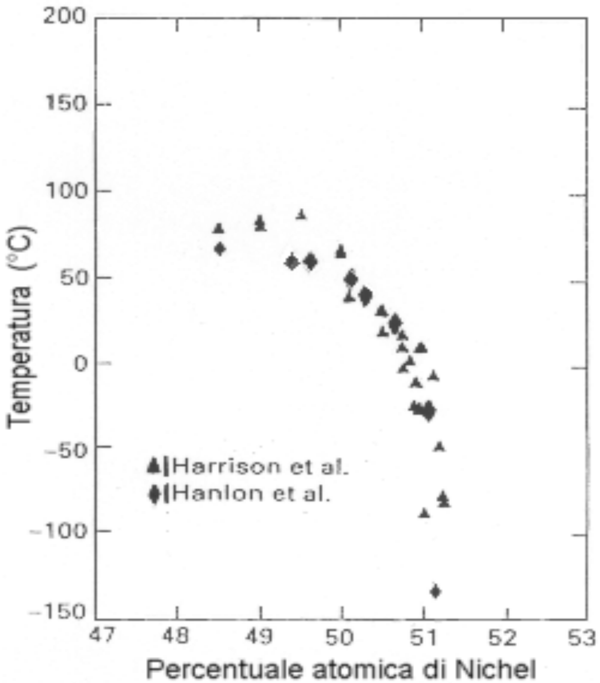


After TT at 850°C for 2 h

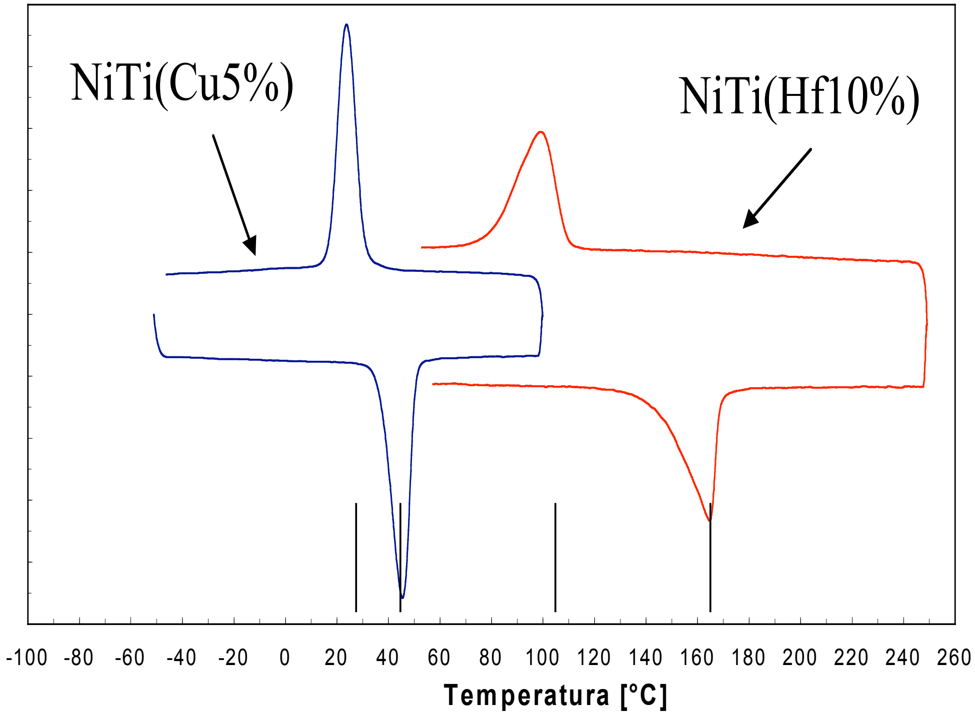
NiTi – Effetto composizione e drogaggio su TT

Temperature di Trasforazione dipendono sensibilmente da : rapporto Ni/Ti e dall'aggiunta di un terzo elemento NiTiX (X= Fe, Cu, Nb, Pt, Pd, Hf, Zr, Hf, Co, Cr, W, terre rare)

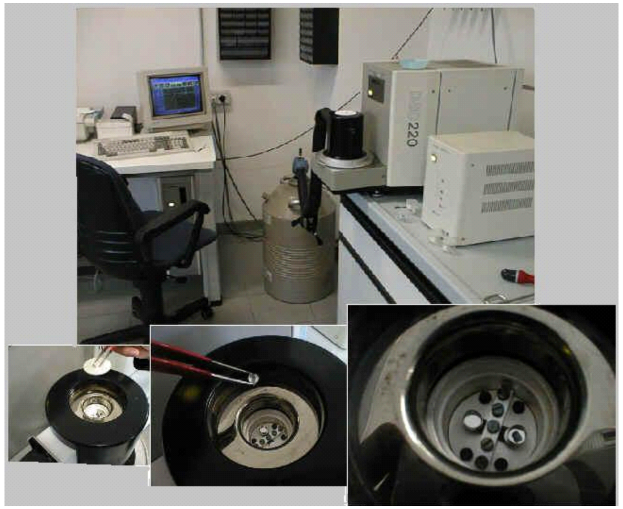
NiTi: (Ms - % Ni)



NiTiX (x=Cu;Hf)



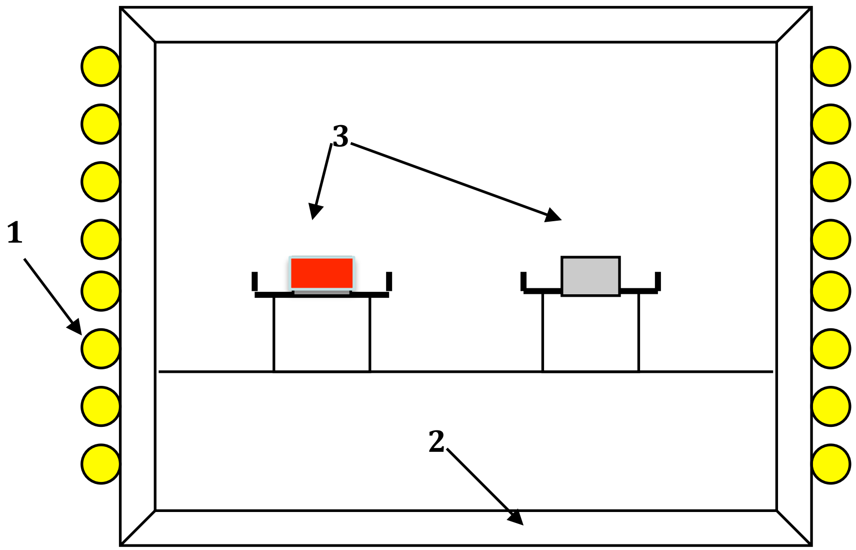
Analisi DSC/DMA



- DSC Seiko 220C
- Temperature range: -130 to 725 °C
- Atmosphere: static or fluxed
- Liquid nitrogen cooling

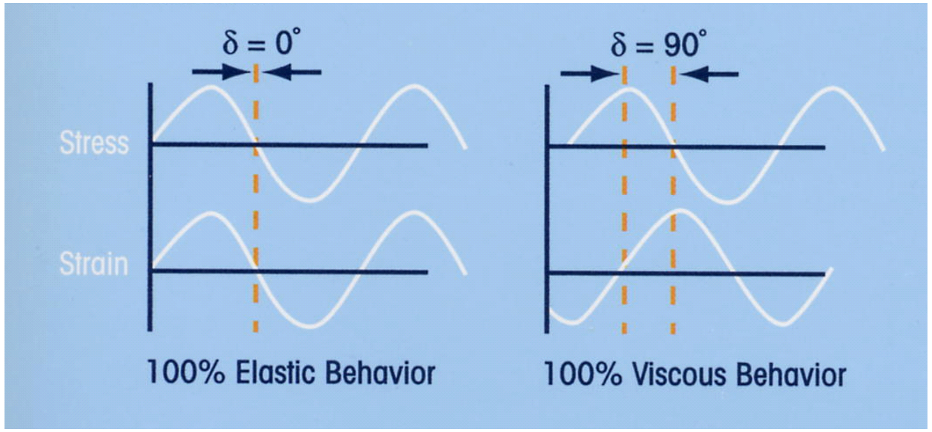
- DMA Q800 TA Instruments
- Temperature range: -150 °C to 600 °C
- Liquid nitrogen cooling
- 18 N load cell
- Frequency range: 0.01-200 Hz
- Sheet, film and fiber clamps
- Tensile clamp and single/dual cantilever clamp

Calorimetro Differenziale a Scansione - DSC



1 Elementi Riscaldanti – 2 Camera - 3 Porta campione/riferimento

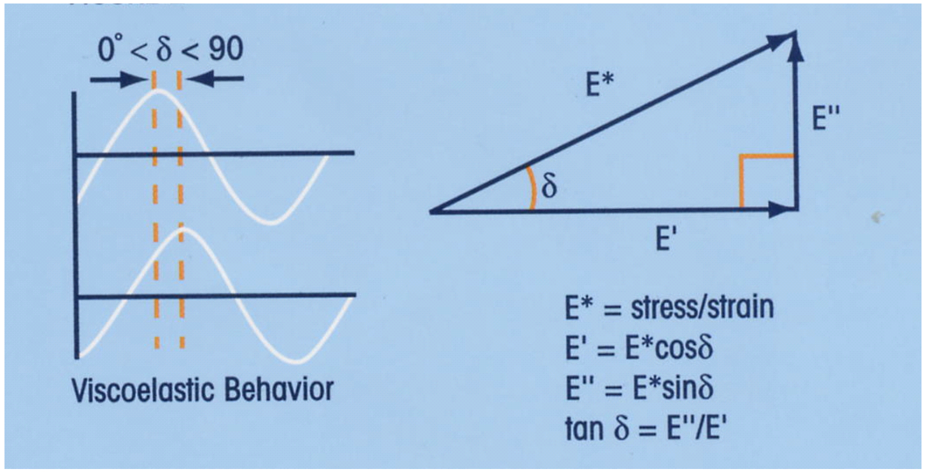
Analisi DMA



Sollecitazione meccanica variabile nel t

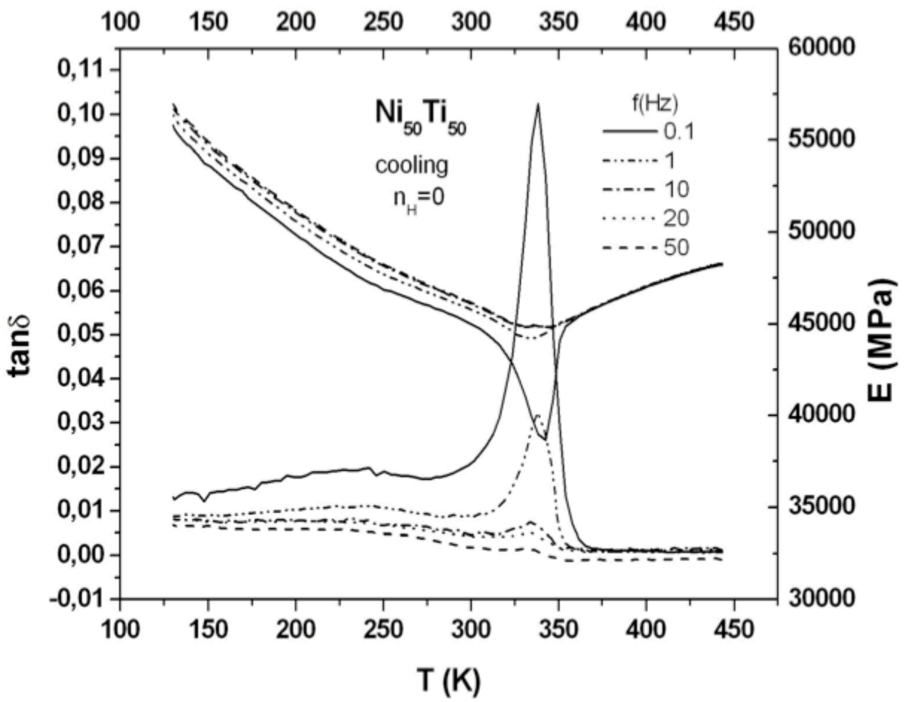
Analisi delle proprietà meccaniche al variare della T

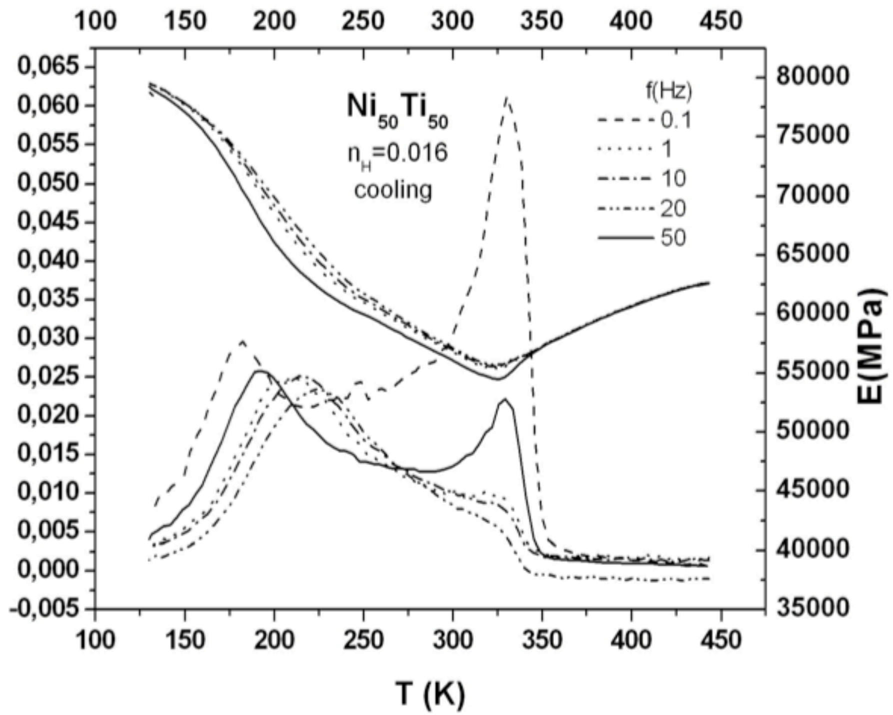
Variabili σ, ε, **T** , ν



$$Q^{-1} = \tan\delta = 1/2\pi \;\; \Delta W/W$$

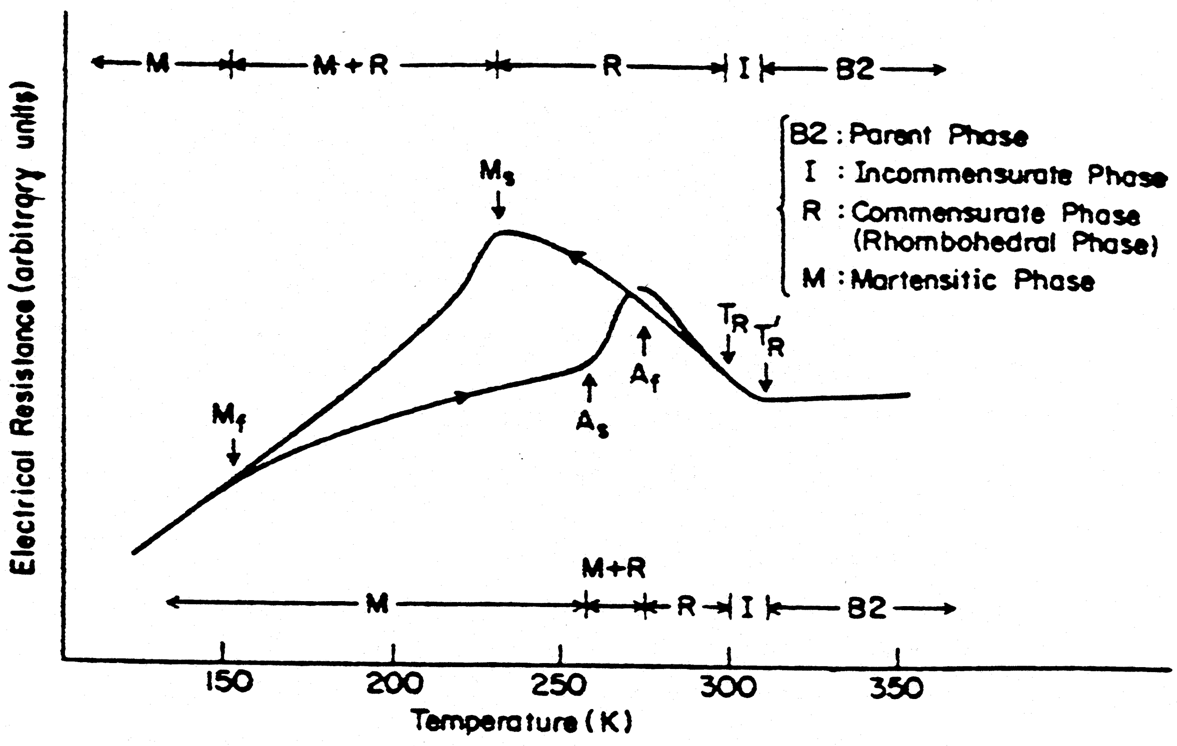
Analisi DMA: effetto dell'H



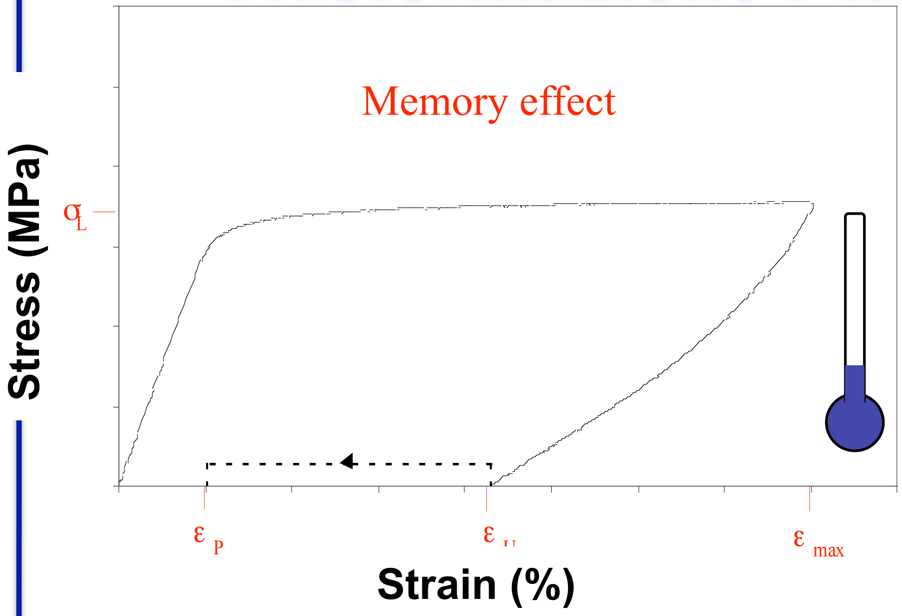


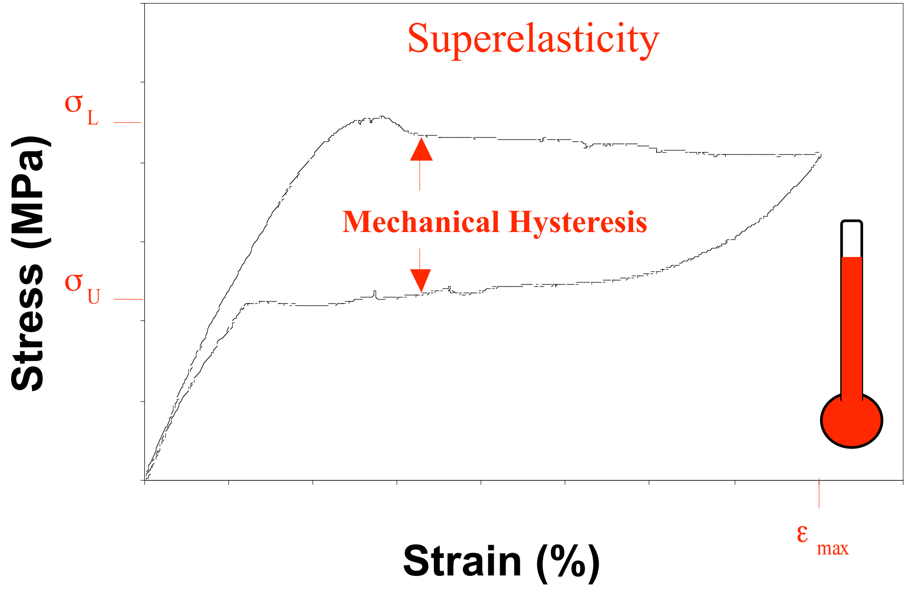
Trasformazione di Fase

Resistenza Elettrica in leghe di NiTi in funzione della temperatura



Trasformazione Martensitica – Misure SS





σ_L = Loading Plateau Stress

ε_U = Unloading Strain

ε_P = Plastic Strain after heating

σ_U = Unloading Plateau Stress

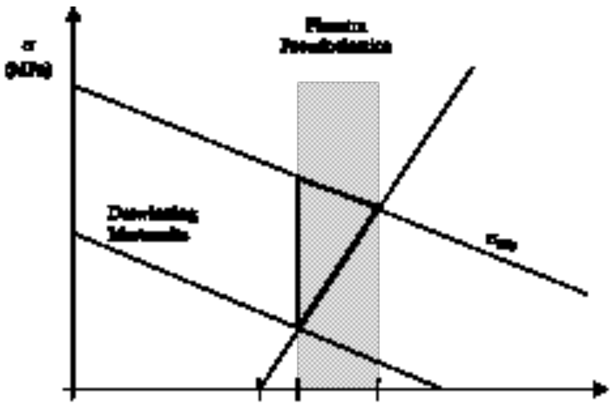
ε_{max} = Max Strain

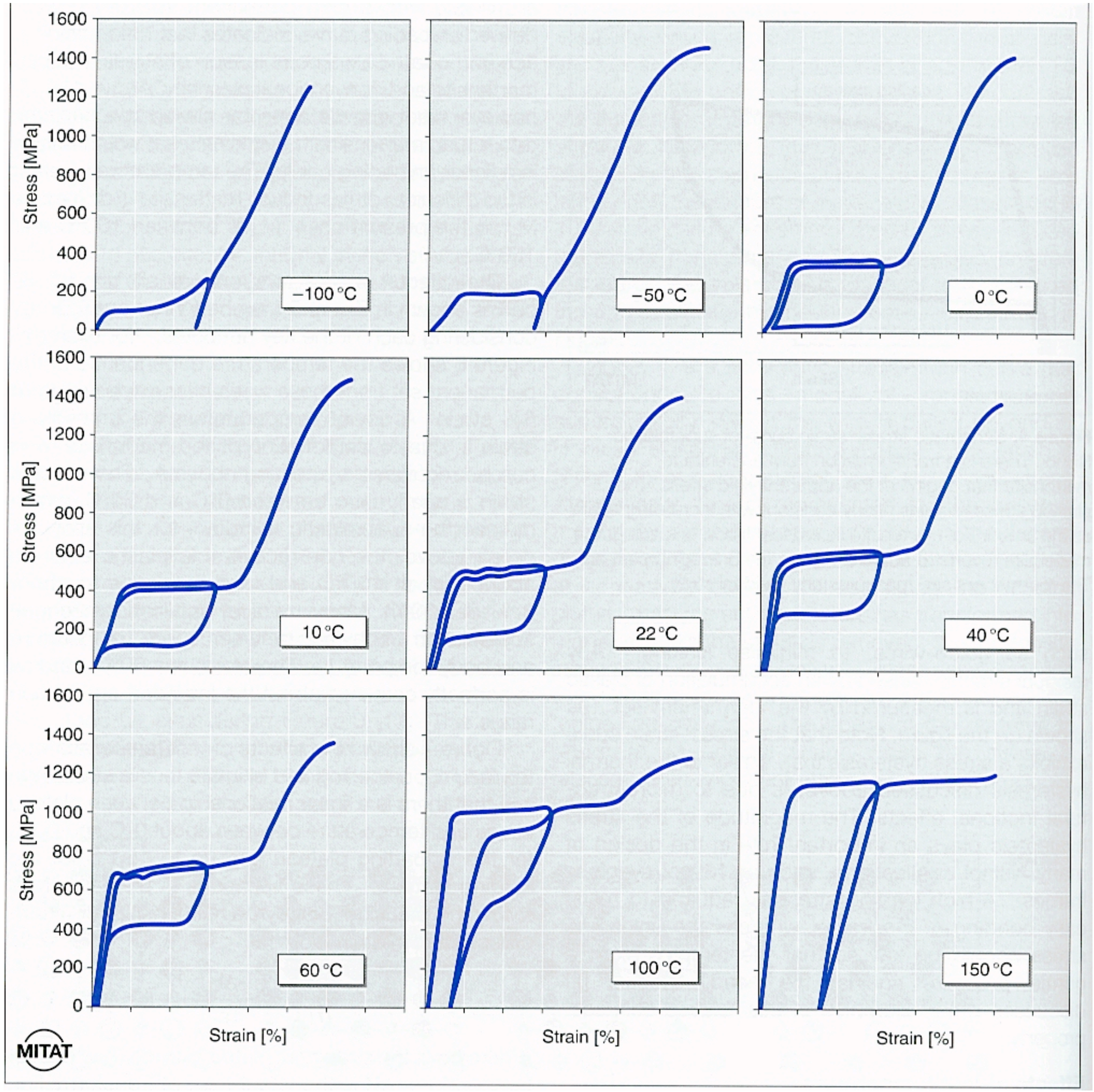
Prove Termomeccaniche statiche

Prove meccaniche condotte a temperatura costante.

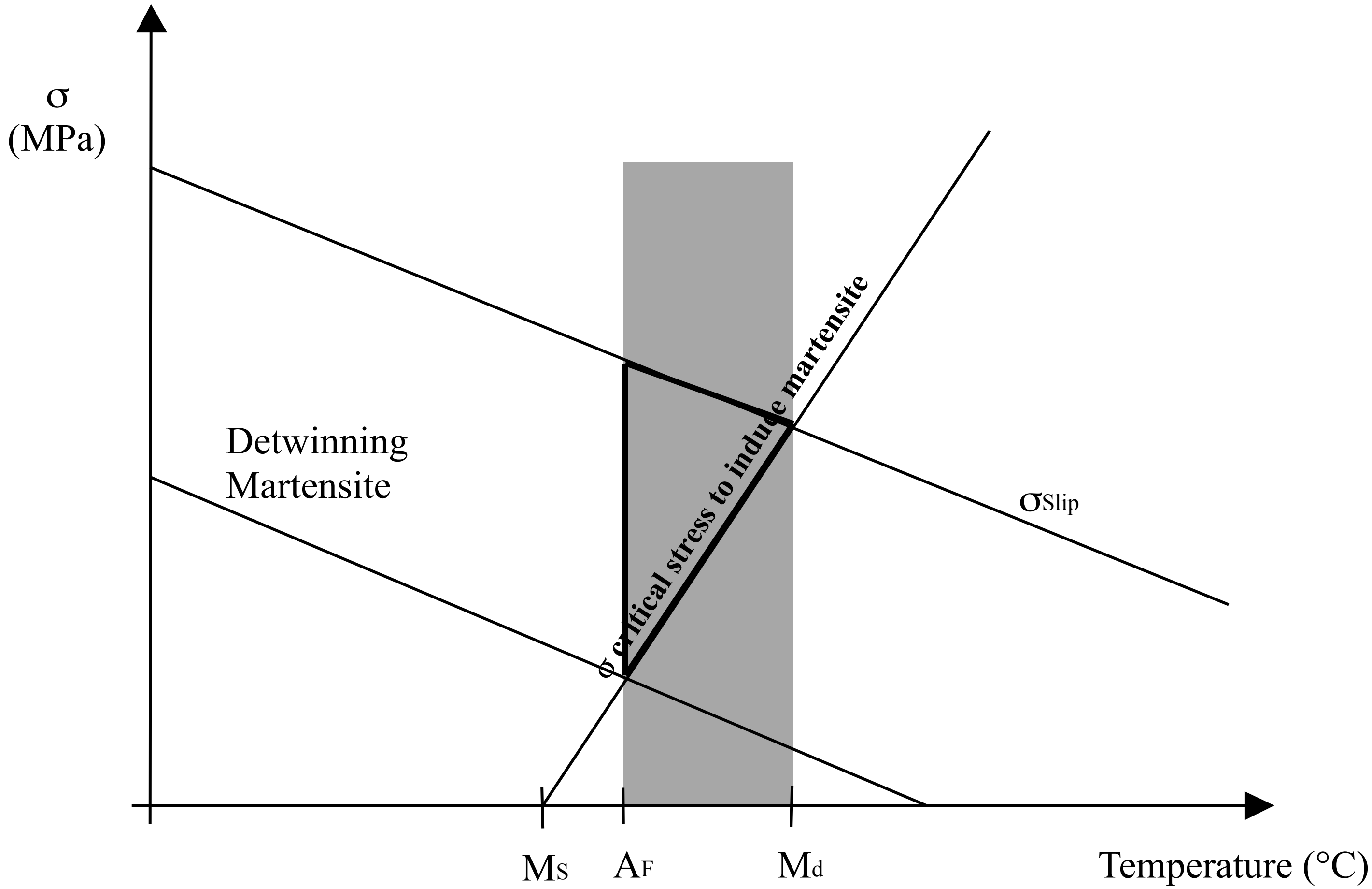
Si possono individuare le seguenti fasi:

- Deformazione fino a ε prefissata.
- Scarico: il campione manifesta comportamento elastico o 'plastico' a seconda della temperatura di prova
- La prova viene completata portando a rottura il campione.

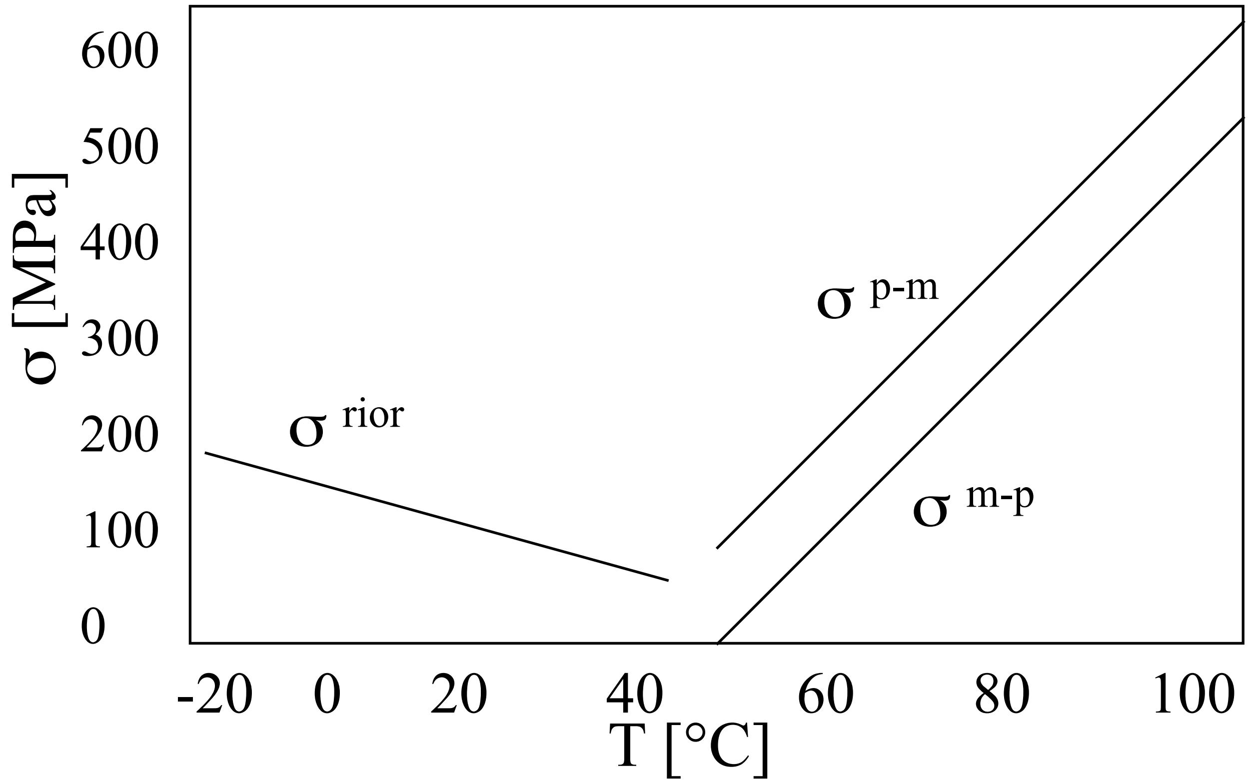




Pseudoelasticità



Linearità Sfrorzo-Temperatura



NiTi

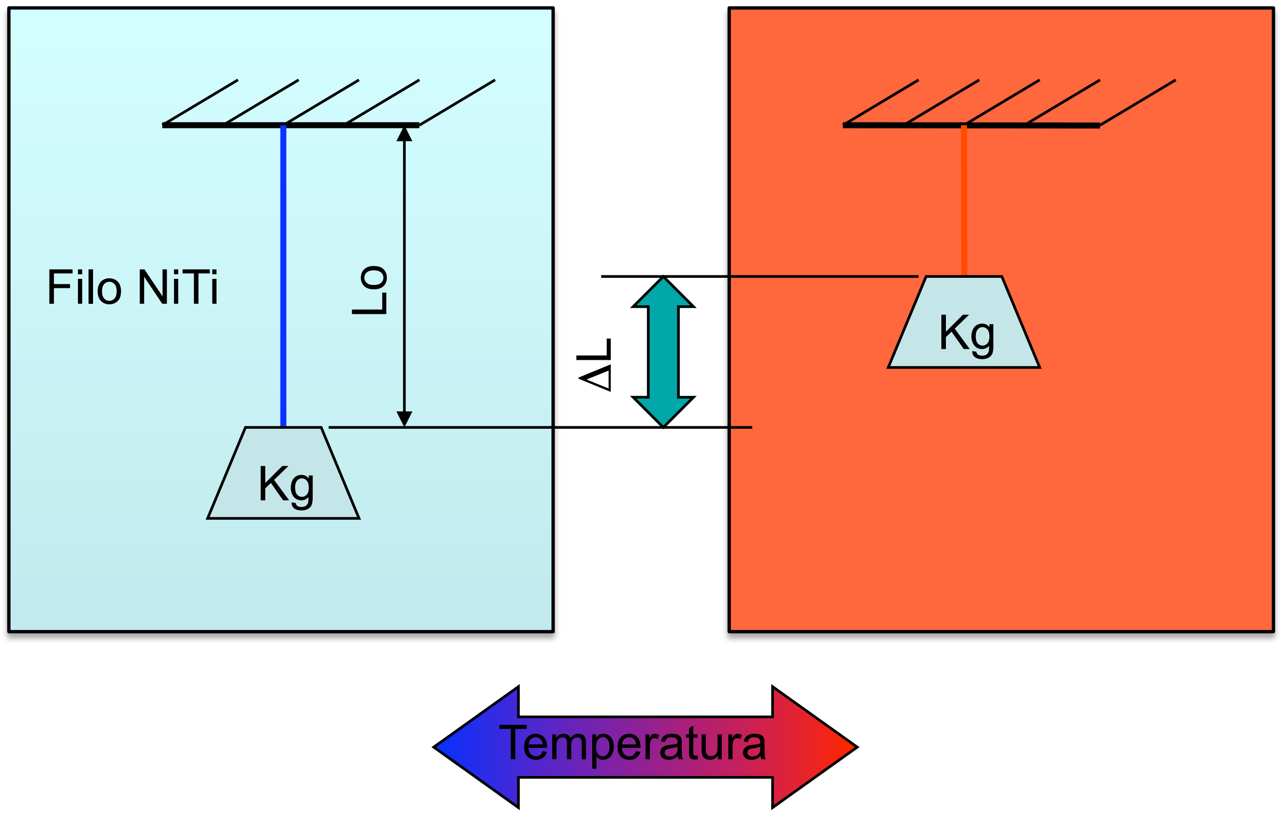
σ^{rior}/dT (1MPa/°C)

$\sigma^{p\text{-}m}/dT$ (8-10 MPa/°C)

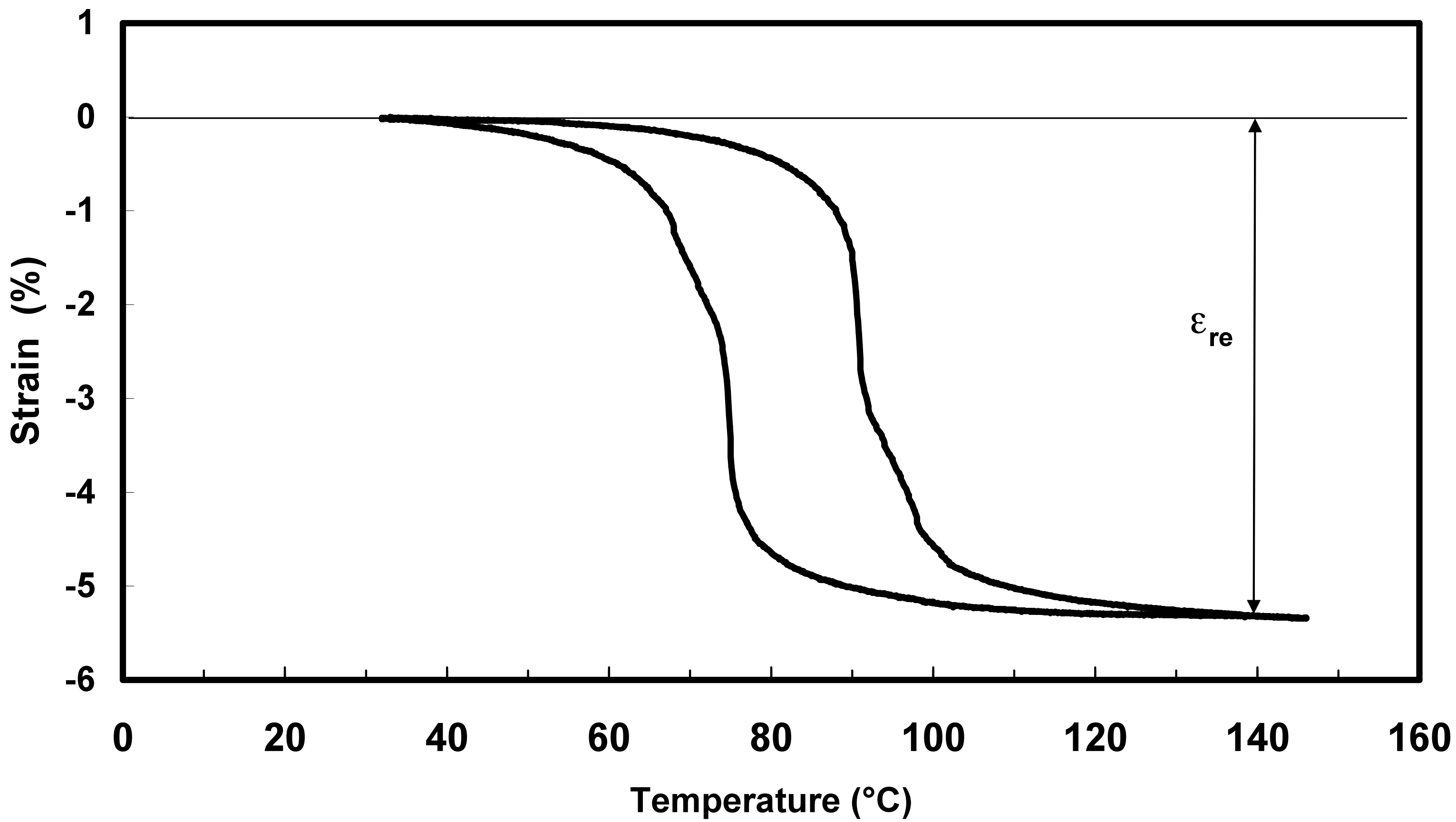
Clausius-Clapeyron: $dP/dT=\Delta H/T\Delta V$

(Versione meccanica): $d\sigma/dMs=-\Delta H/T\varepsilon$

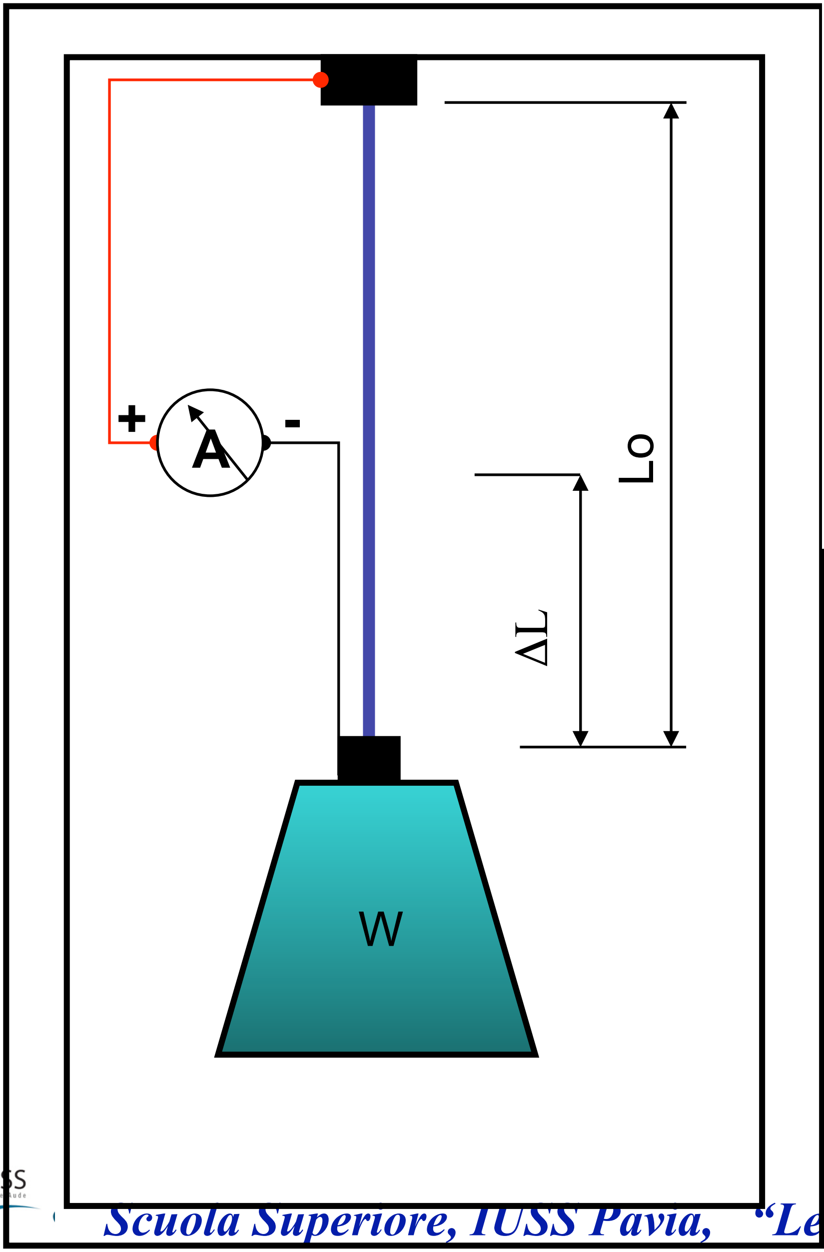
Misura Isteresi Termica

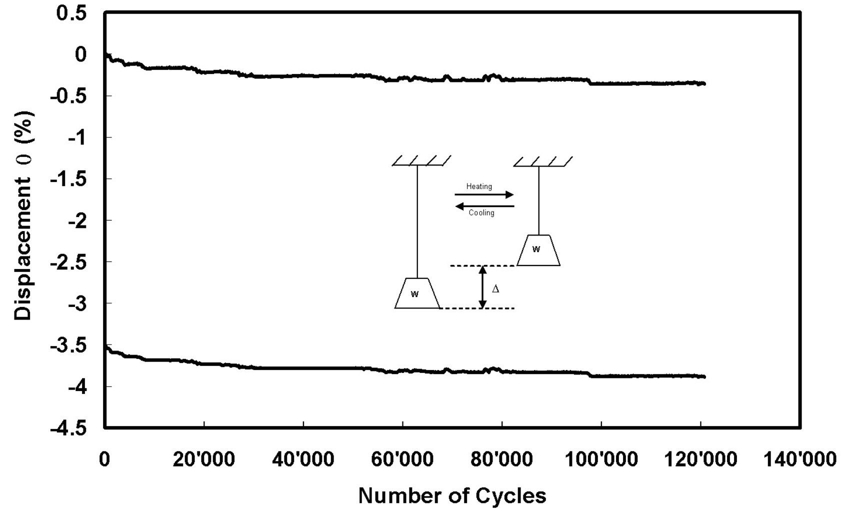


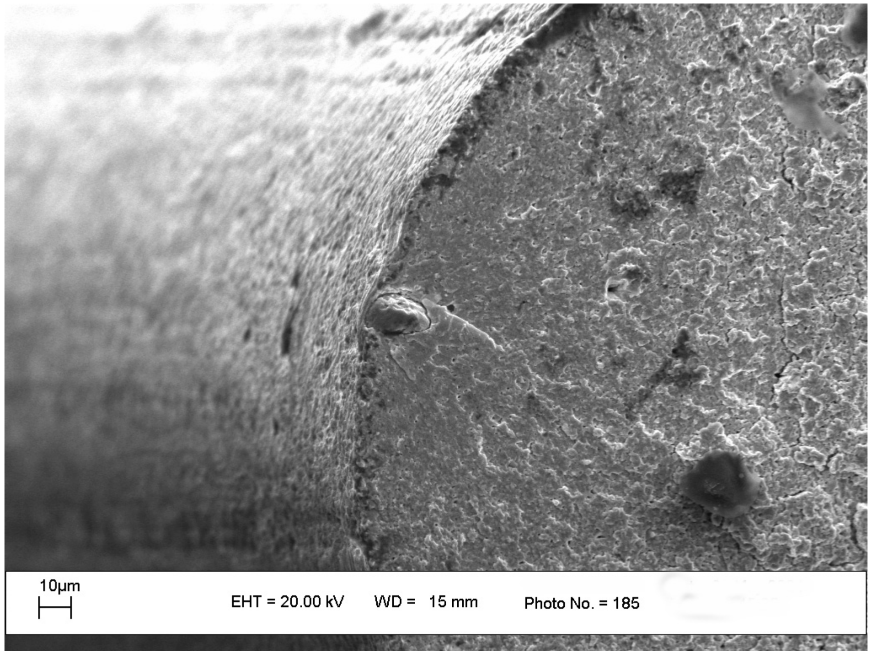
Misura Isteresi Termica: Grafici ε –T



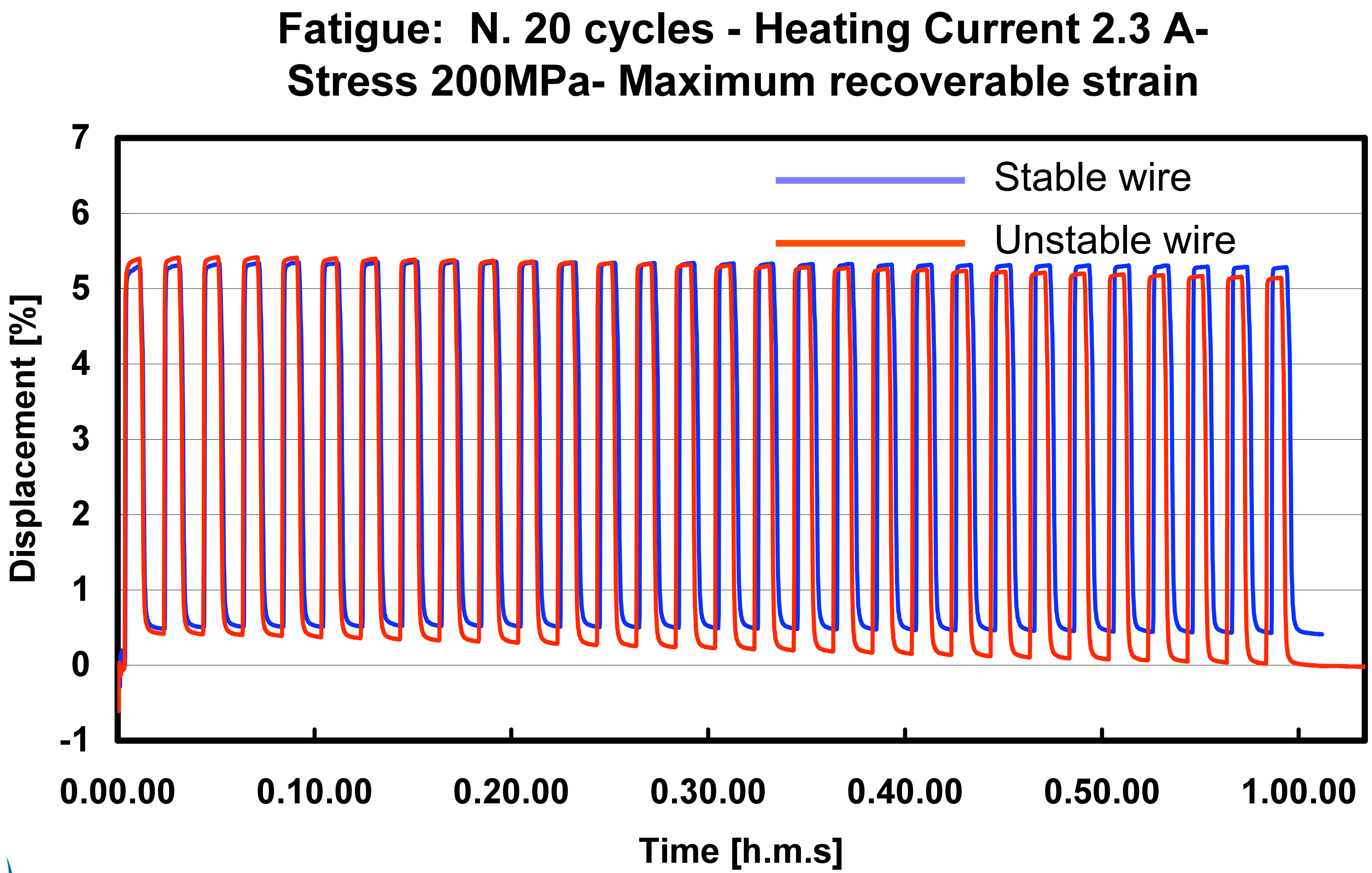
Test Fatica


+
A
-
Lo
ΔL
W


Displacement δ (%)
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
20'000
40'000
60'000
80'000
100'000
120'000
140'000
Number of Cycles
Heating
Cooling
w
w
Δ


10µm
EHT = 20.00 kV
WD = 15 mm
Photo No. = 185

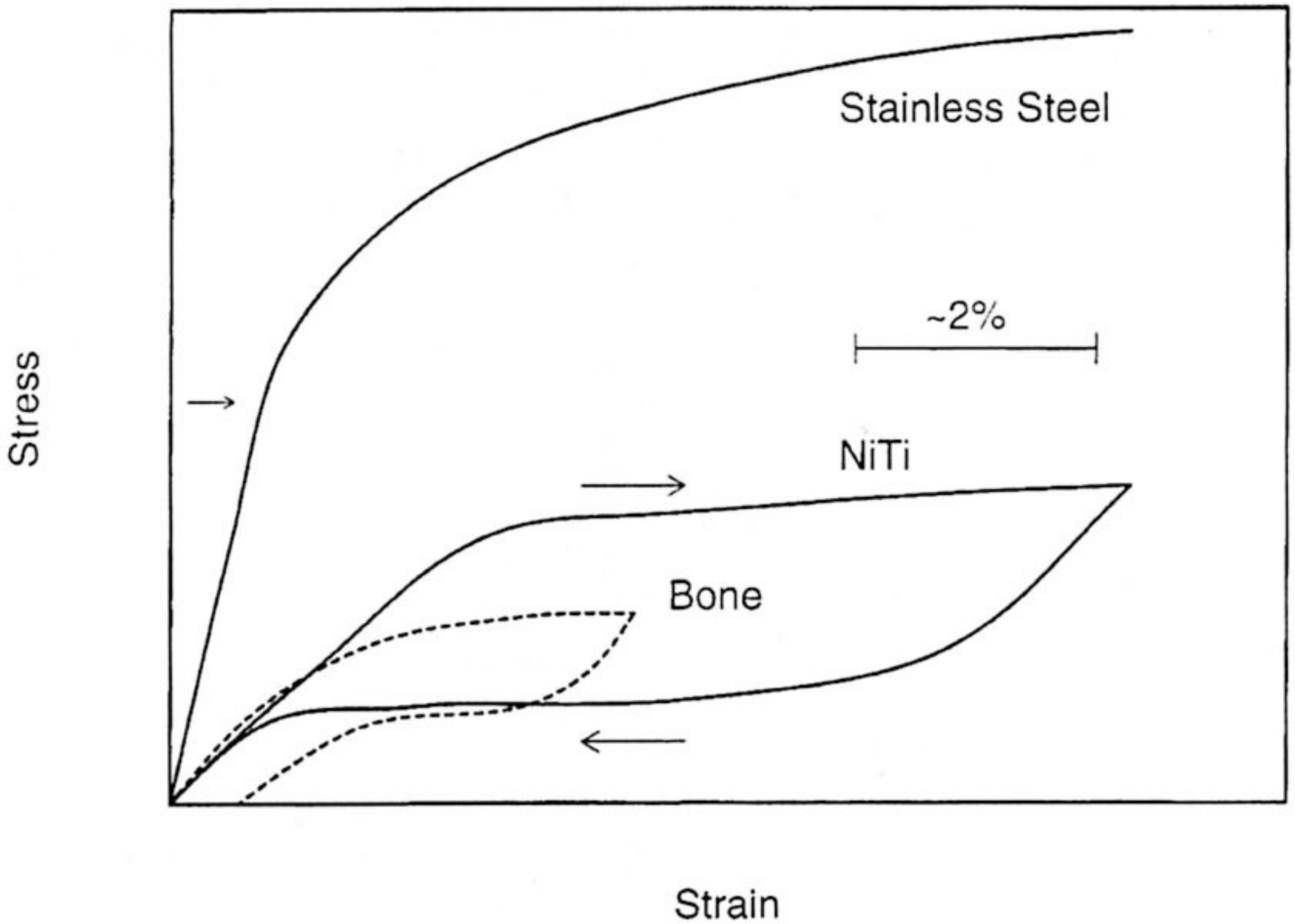
Fatica


Fatigue: N. 20 cycles - Heating Current 2.3 A-
Stress 200MPa- Maximum recoverable strain
Stable wire
Unstable wire
Displacement [%]
7
6
5
4
3
2
1
0
-1
0.00.00
0.10.00
0.20.00
0.30.00
0.40.00
0.50.00
1.00.00
Time [h.m.s]

Caratteristiche NiTi

Melting temperature [°C]	1310
Density [g/cm^3]	6,45
Electrical resistivity austenite [μΩcm]	100
Electrical resistivity martensite [μΩcm]	80
Thermal conductivity austenite at 293 K [W/(m K)]	18
Thermal conductivity martensite at 2 93 K [W/(m K)]	8,5
Thermal expansion austenite [10^{-6}/K]	11
Thermal expansion martensite [10^{-6}/K]	6,6
Corrosion resistance	similar to Ti alloys
Modulus of Elasticity austenite [GPa]	75
Modulus of Elasticity martensite [GPa]	40
Yield strength austenite [MPa]	195 - 690
Yield strength martensite [MPa]	70 - 140
Ultimate tensile strength [MPa]	895-1000(cold deformed)
Transformation temperatures [°C]	-200 100
Shape memory strain [%]	8,5 maximum (Cycling)

Confronto NiTi con altri materiali



Confronto NiTi con altri materiali

	Density (g/cm^3)		Resistance (MPa)		Modulus (GPa)	
	Min	Max	Min	Max	Min	Max
Material						
Glass	2,5	2,62	3200	4500	70	70
Carbon	1,76	2,1	2000	7000	240	700
SiC	2,55	3,5	2000	3700	200	420
Oxides	3,9	3,9	1200	1400	340	400
Polyester	1,2	1,8	600	700	11	13
Aramidic	1,45		3000		70	130
NiTi	6,45		890	1000	40	75

ASTM Standard Specifications

F2633-07 Standard Specification for Wrought Seamless Nickel-Titanium Shape Memory Alloy Tube for Medical Devices and Surgical Implants

F2004-05 Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analys

F2063-05 Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants

F2005-05 Standard Terminology for Nickel-Titanium Shape Memory Alloys

F2516-07°2 Standard Test Method for Tension Testing of Nickel-Titanium Superelastic Materials

F2082-06 Standard Test Method for Determination of Transformation Temperature of Nickel-Titanium Shape Memory Alloys by Bend and Free Recovery

Il Processo Produttivo

Fusione e Colata

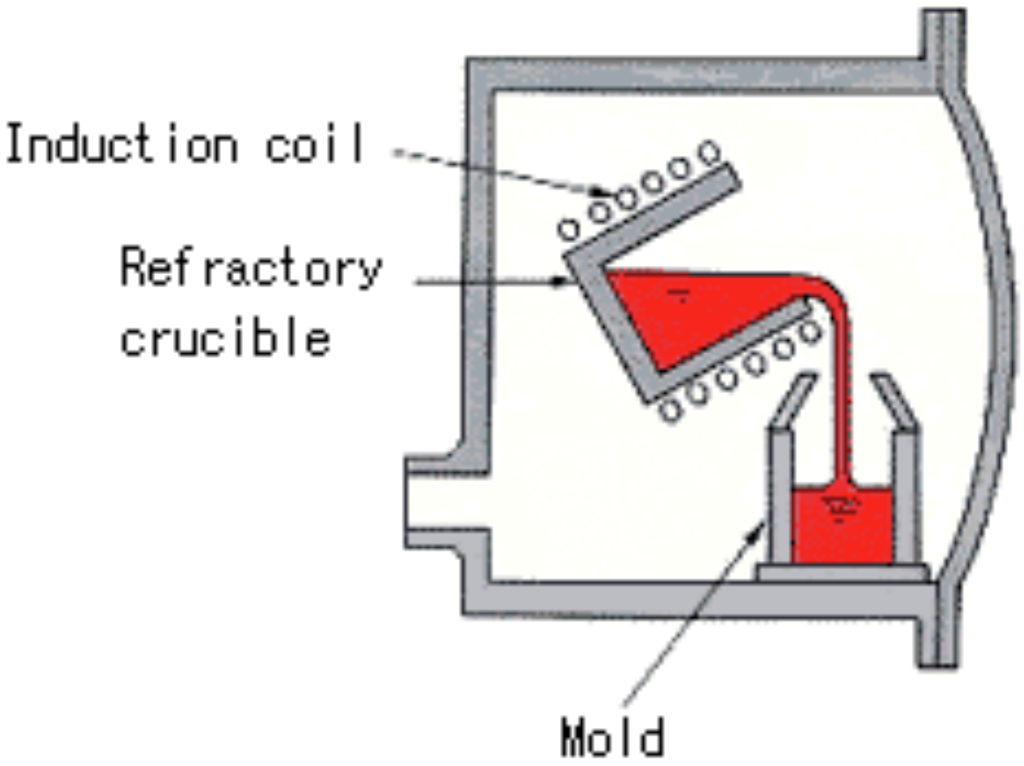
Forgiatura/ Estrusione a Caldo

Laminazione/Trafilatura a freddo

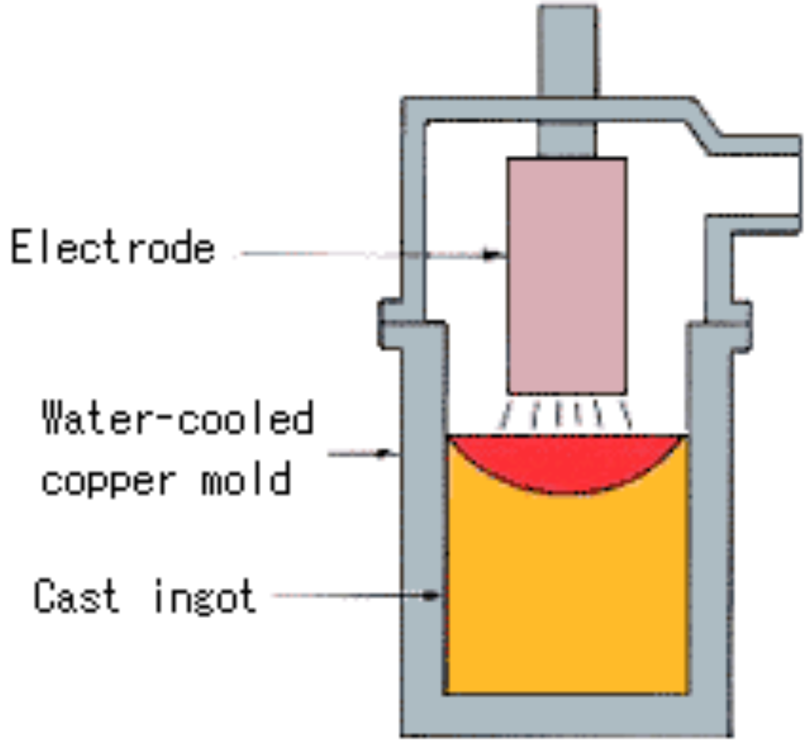
Formatura del dispositvo SMA

Educazione del Materiale

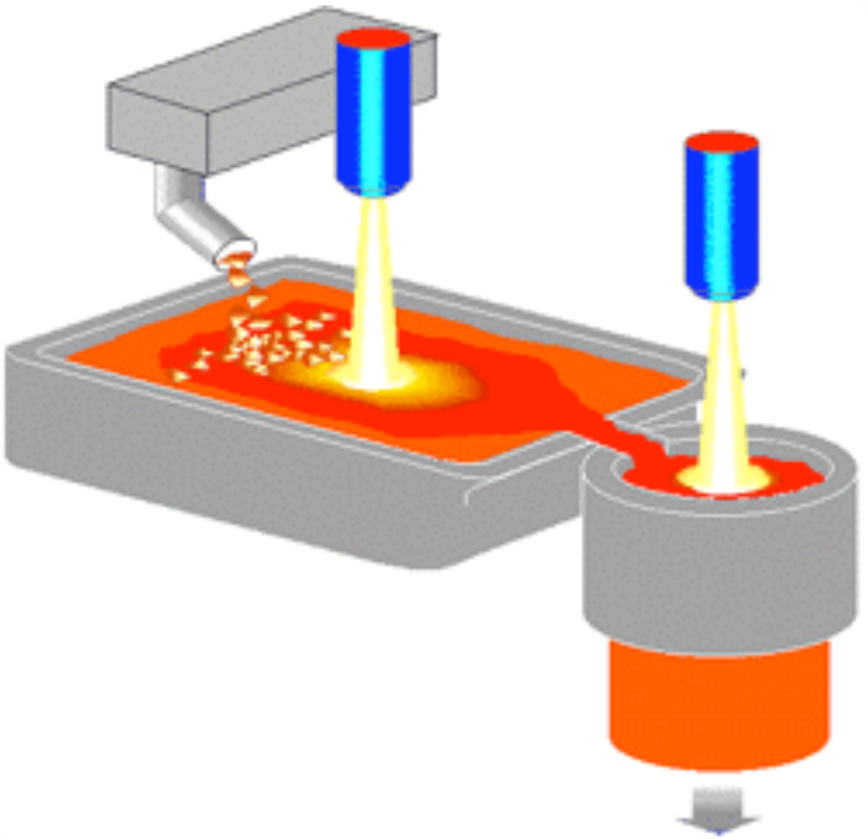
Fusione e Colata : VIM



Fusione e Colata : VAR

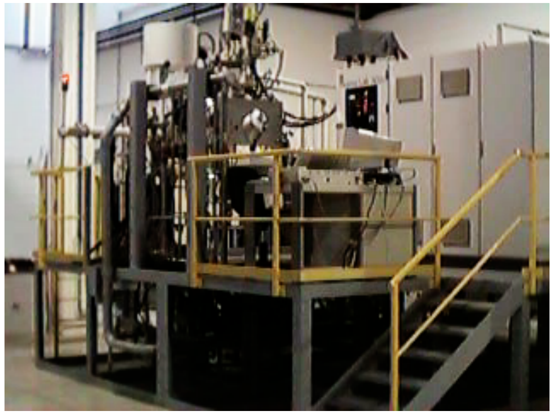


Fusione e Colata : PAM



Tecnologie Fusorie al CNR IENI

Vacuum Arc

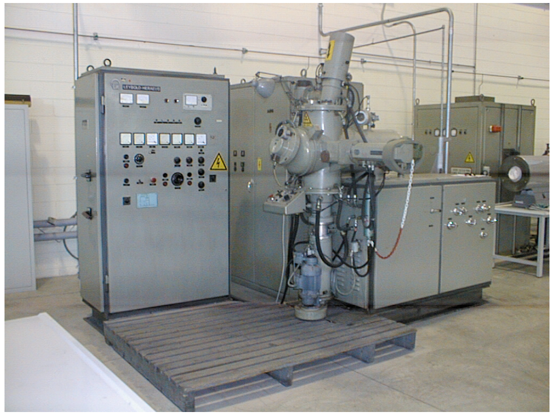


Plasma Arc

Vacuum Induction HF

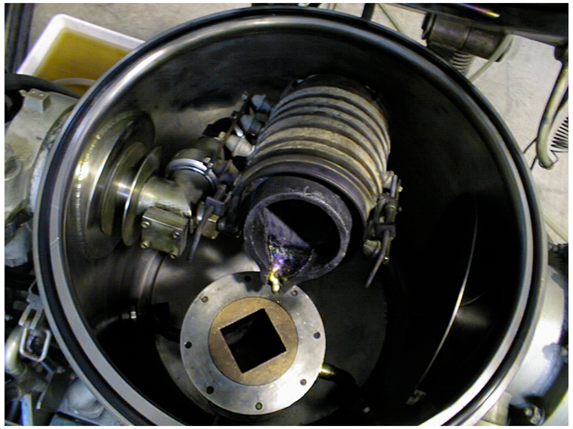
Vacuum Induction MF

Plasma Console



Electron Beam

Fusione e Colata : VIM



Metals: Ni Electrolytic, Ti (< grade 1)

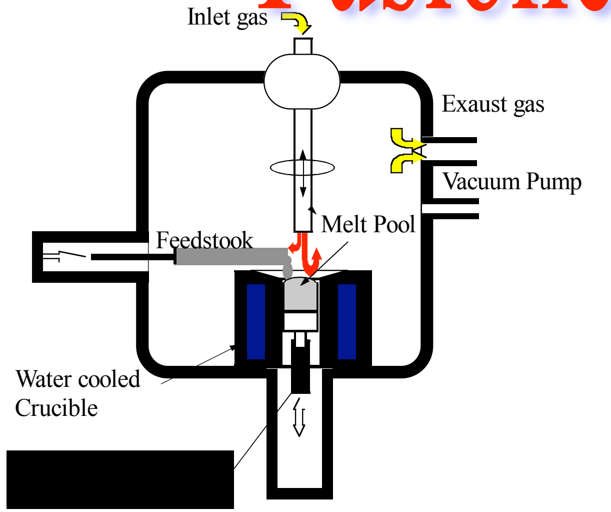
Furnace: Vacuum Induction Melting + Vacuum Arc Remelting

Crucible: Carbon

Mould : Copper

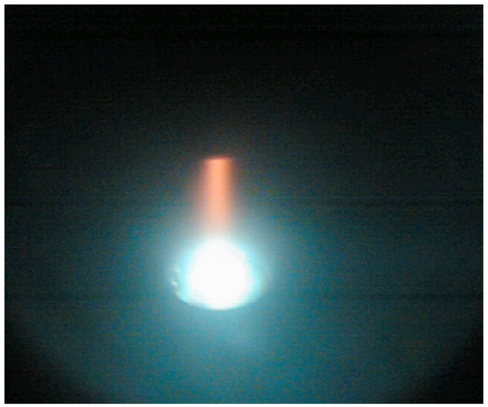
Impurity : O< 500ppm C< 500ppm

Fusione e Colata : PAM

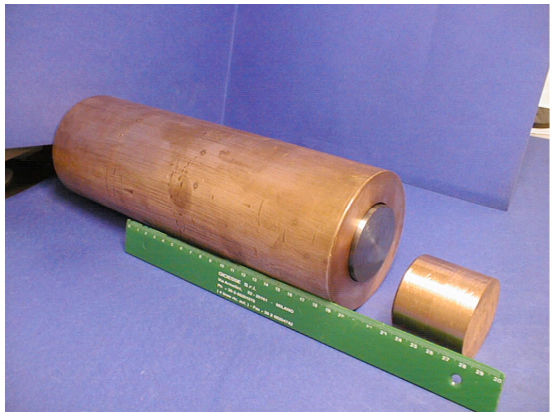


Scheme Drip Melting

As cast ingots



PAM torch



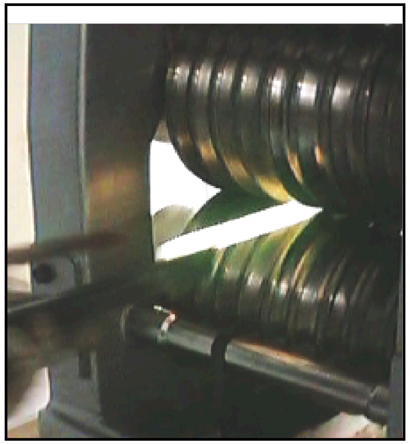
Canned ingot for extrusion

Forgiatura a Caldo

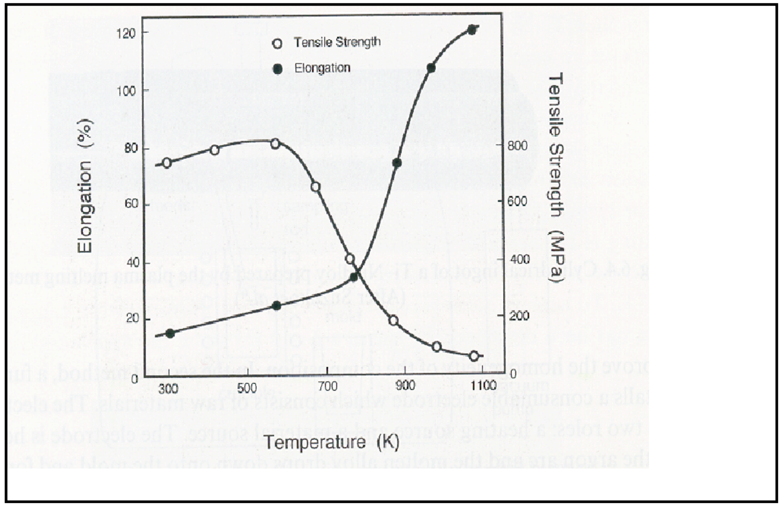
Forgiatura, Laminazione

- Temperatura= T> 800°C

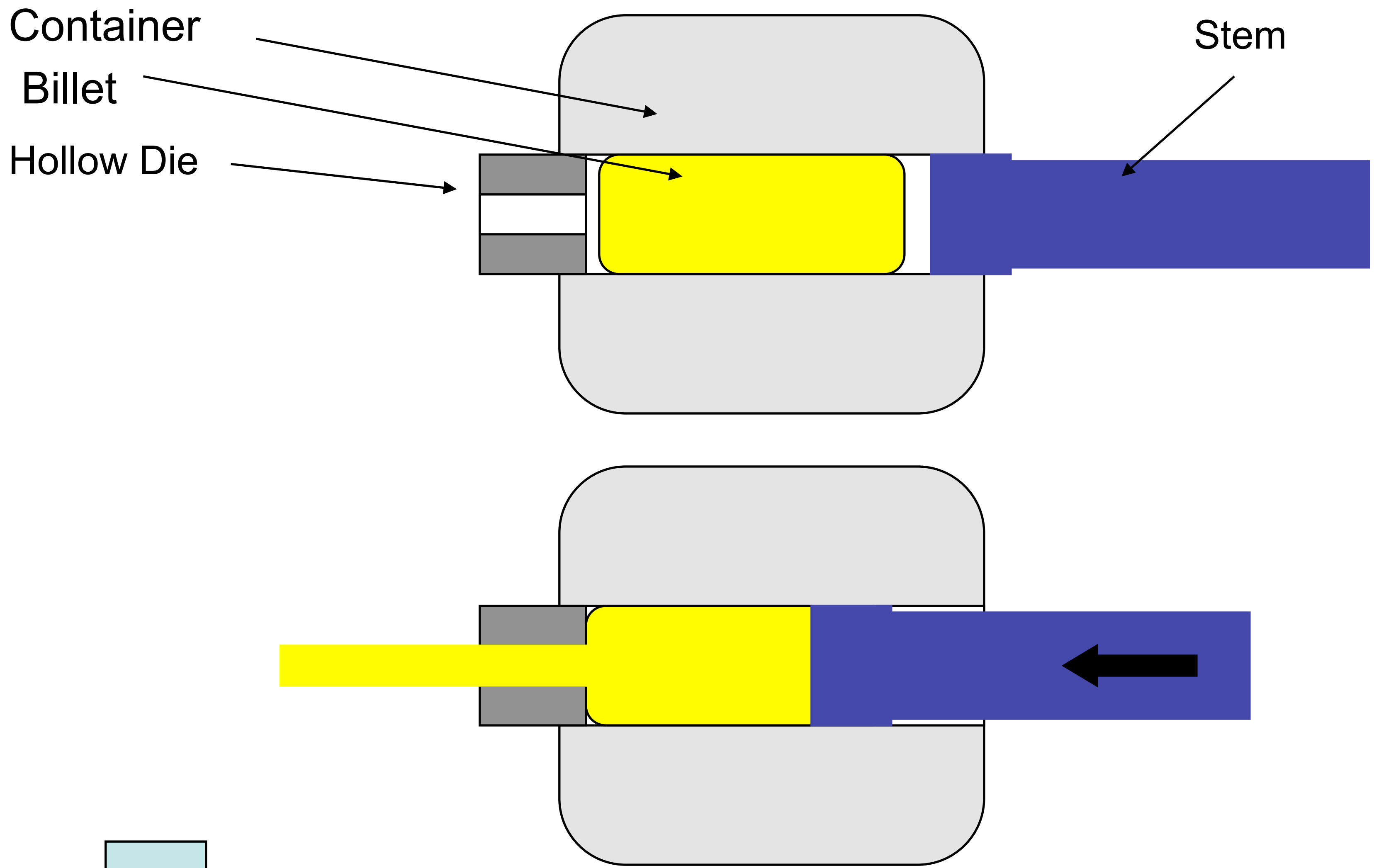
- Rimozione Ossido



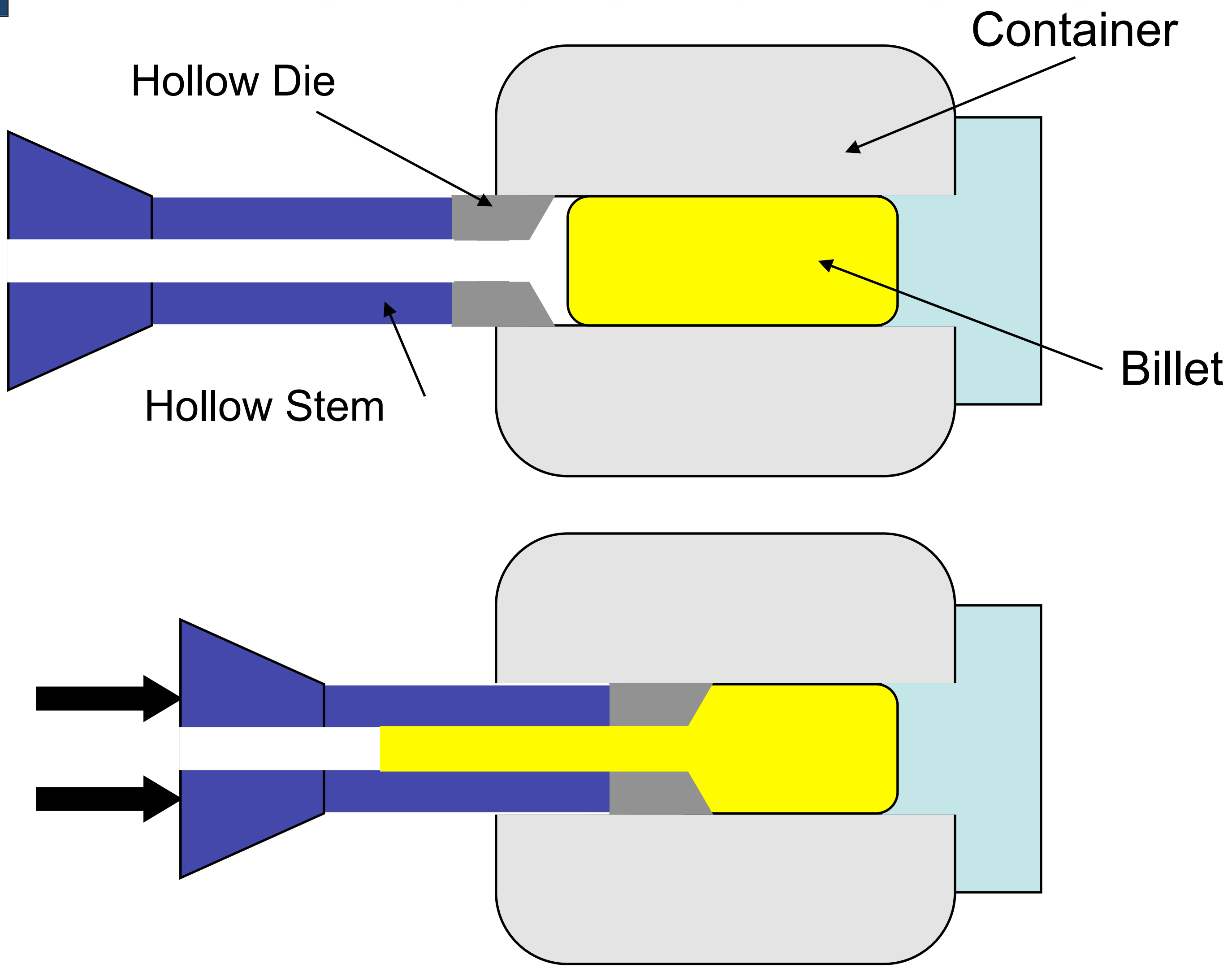
Estrusione (Camicia Protettiva)



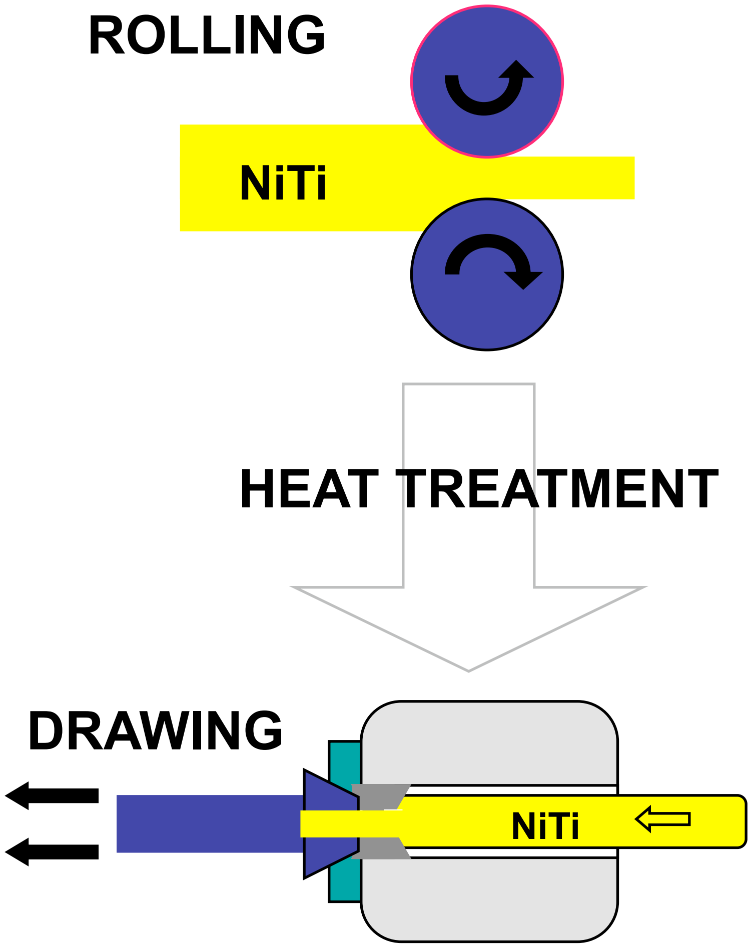
Estrusione Diretta



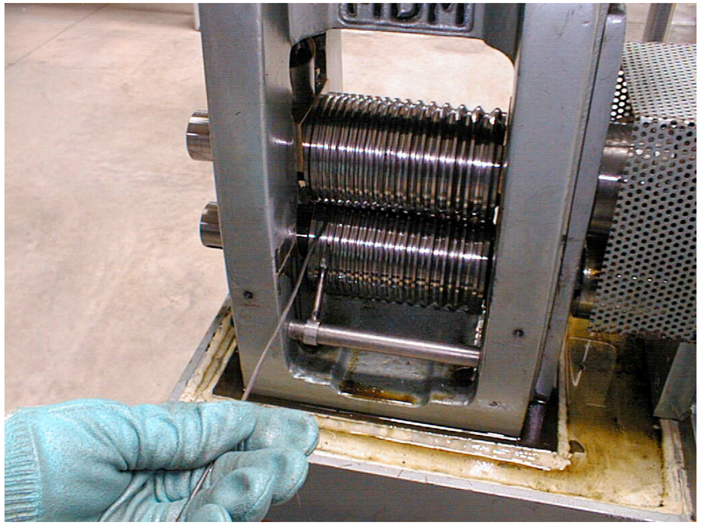
Estrusione Indiretta



Laminazione e Trafilatura



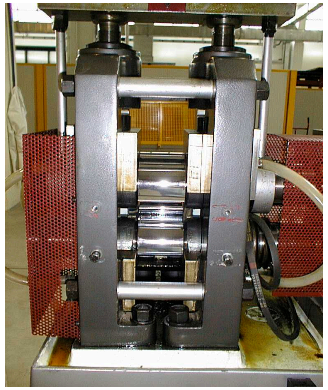
Laminazione a Freddo



Lam. Filo

Lam. Sbozzatore

Lam. Lastra

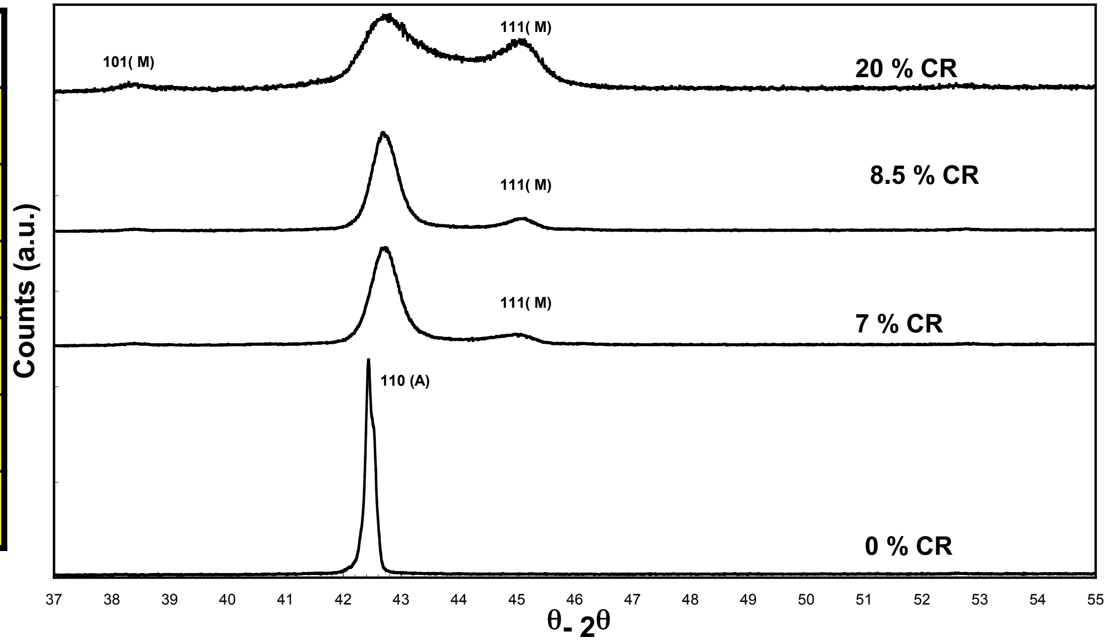


Cilintri Lucidati

Effetto della Laminazione a Freddo

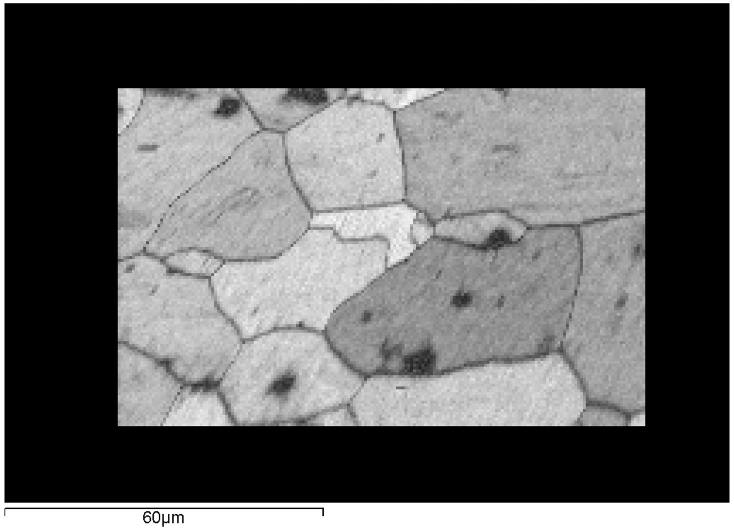
cr %	B2	B19’
0	98,5	1,5
3	98,0	2,0
7	75,8	24,2
10	66,3	33,7
15	38,8	61,1
20	26,3	73,6

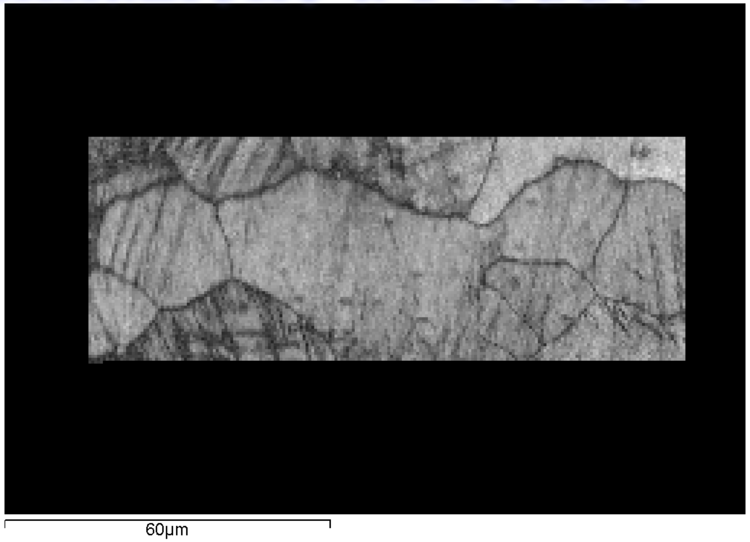
EBSD: B2 and B19’ %

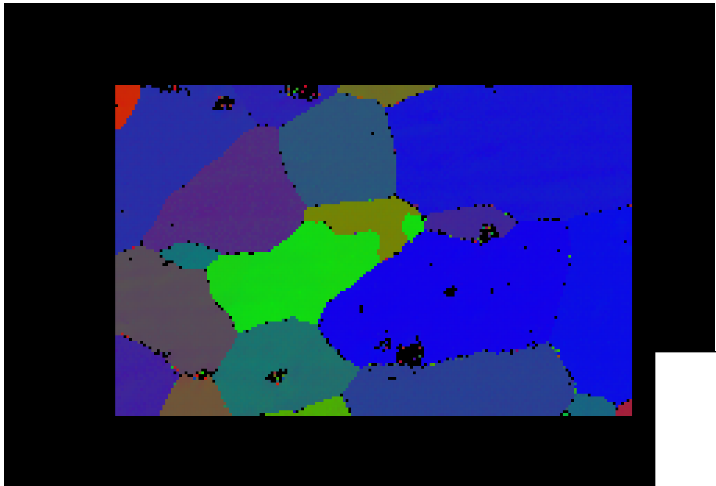


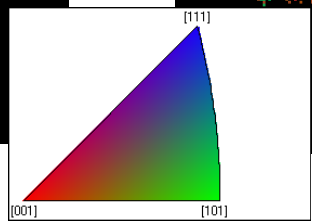
XRPD

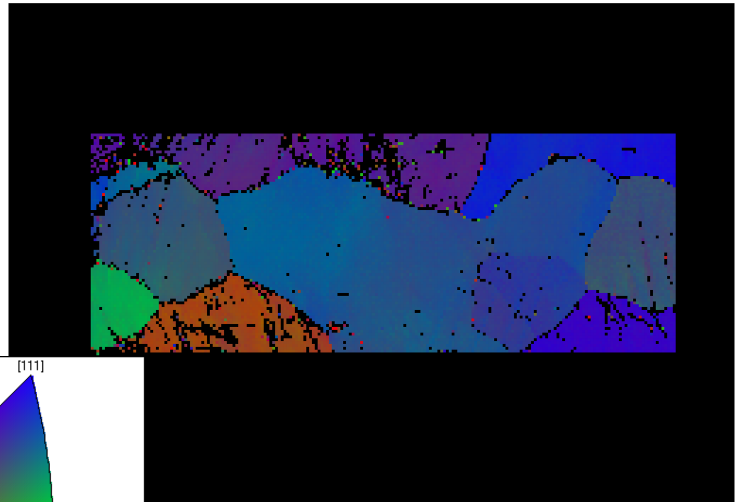
Effetto della Laminazione a Freddo







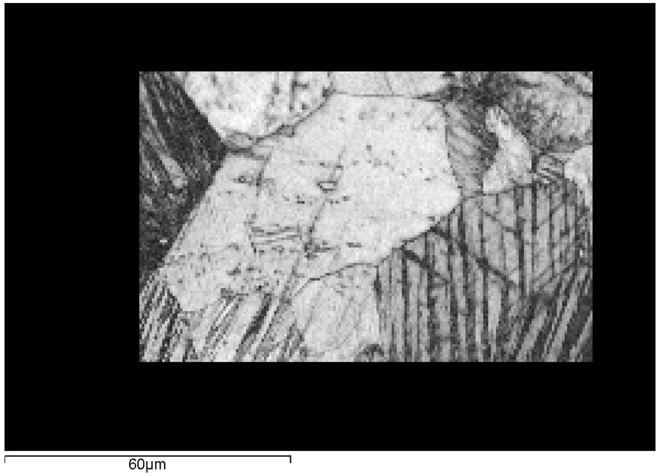


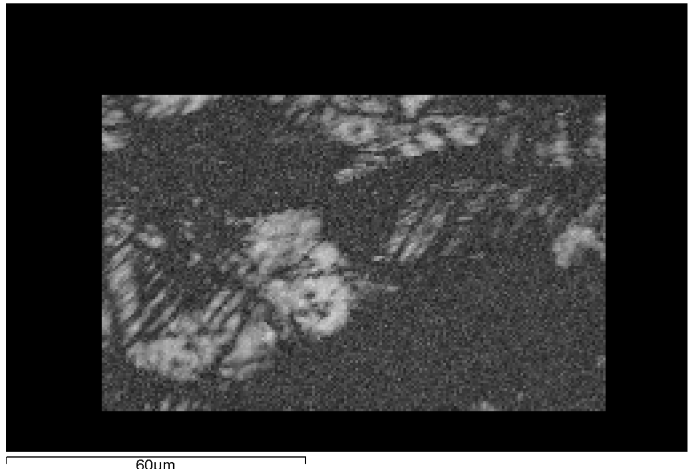


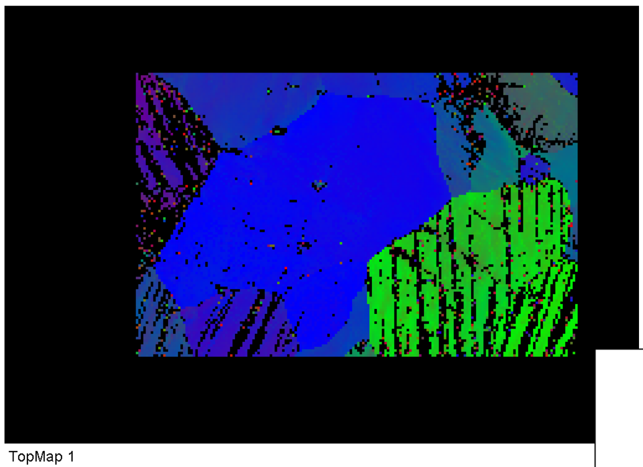
0%

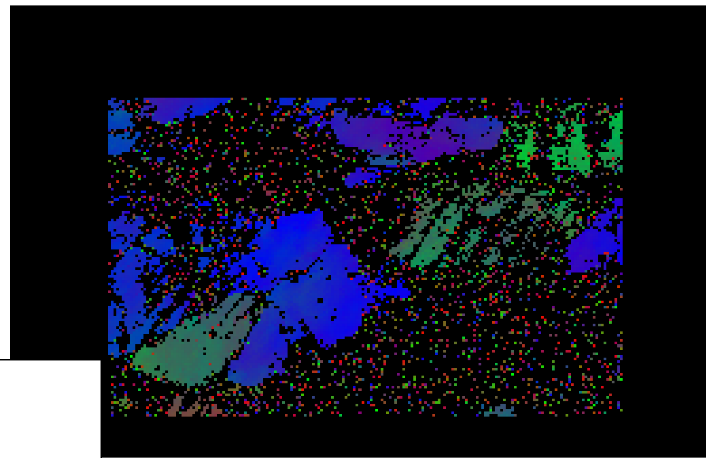
7%

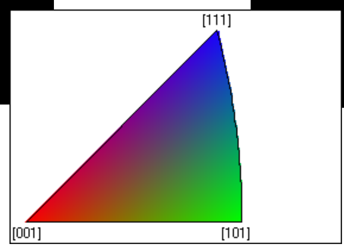
Effetto della Laminazione a Freddo







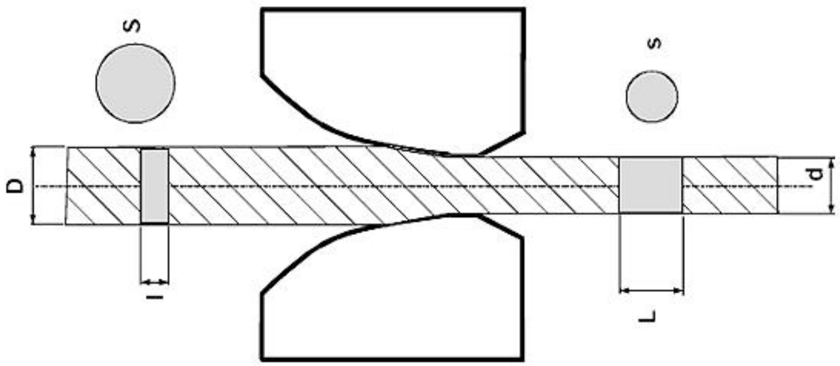




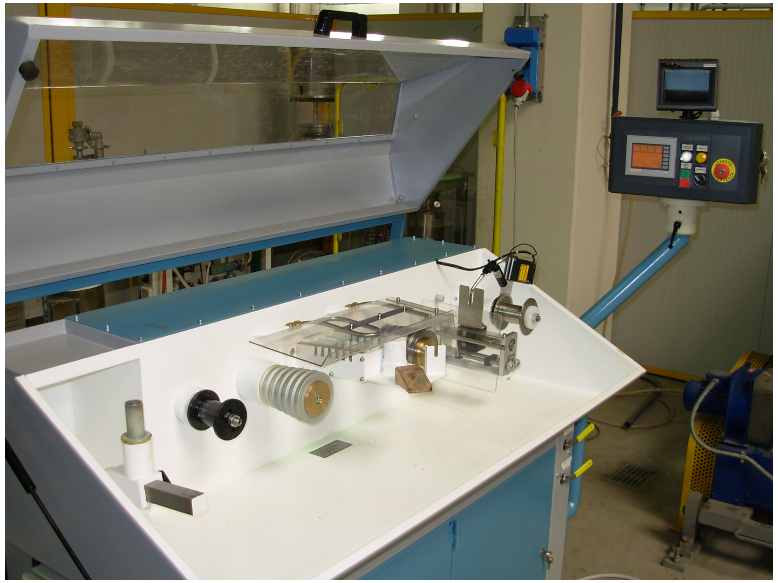
10%

20%

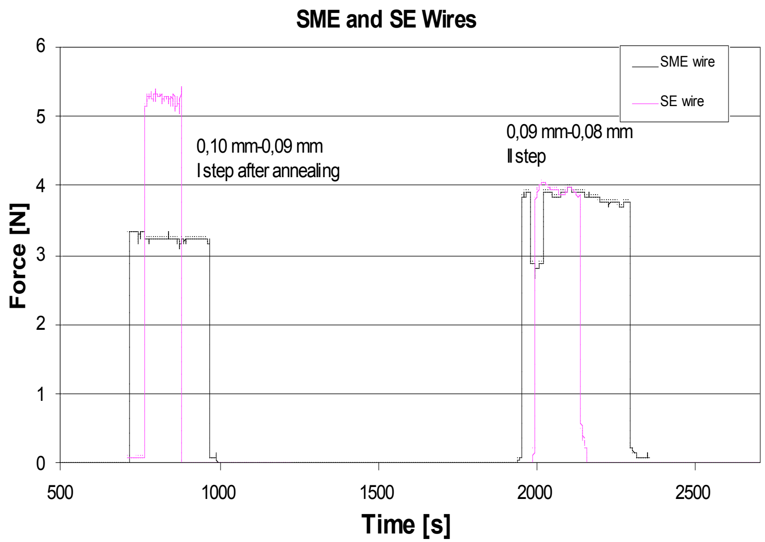
Trafilatura Fili Sottili

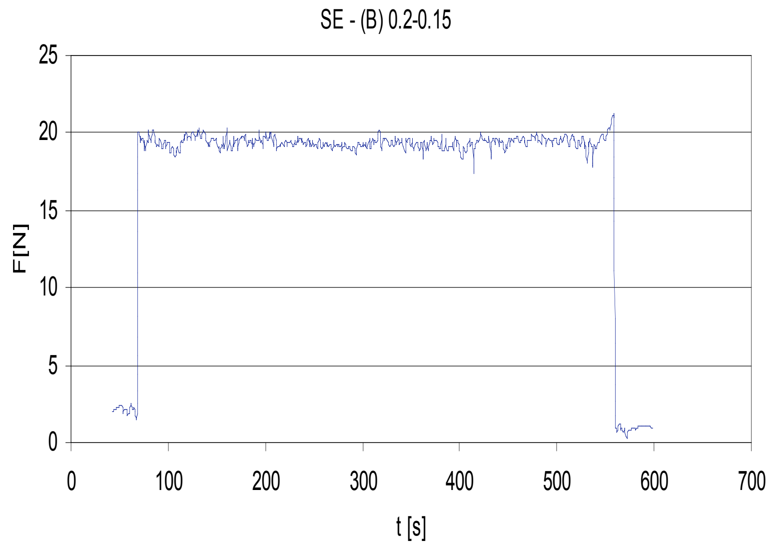


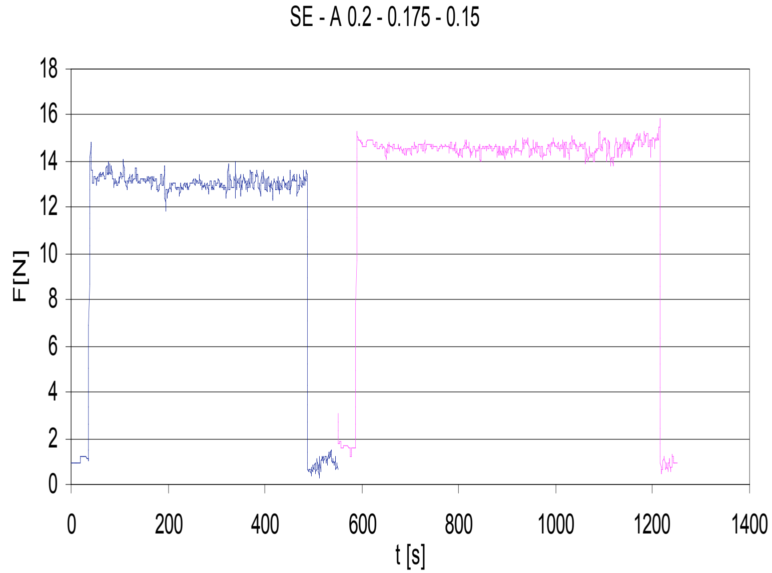
- **Special diamond dies, adequate pay-off and pay-on spooling systems, special load cells were considered in order to realize an equipment with high flexibility for the optimization of the NiTi drawing procedures.**



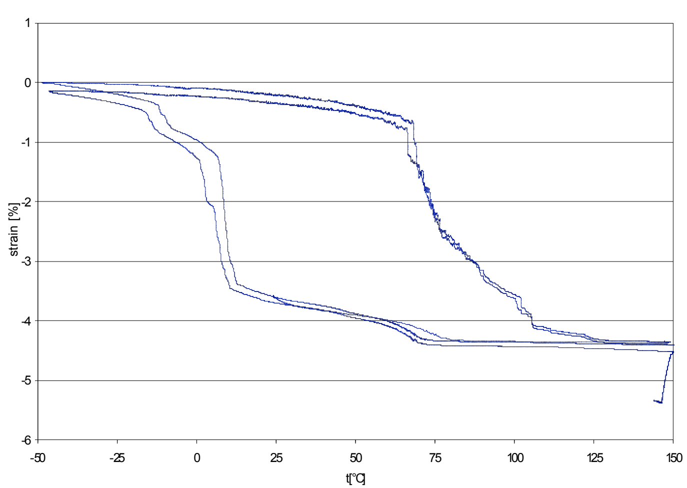
Trafilatura Fili Sottili

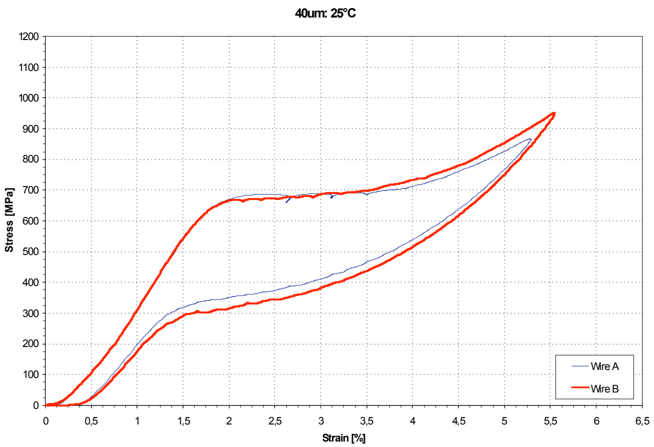


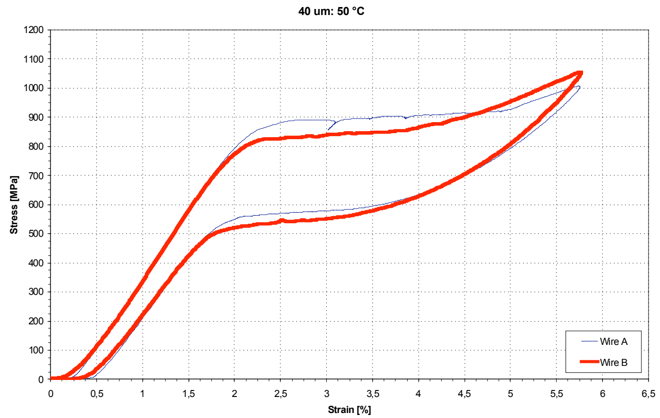




Caratterizzazione Funzionale di Fili Sottili

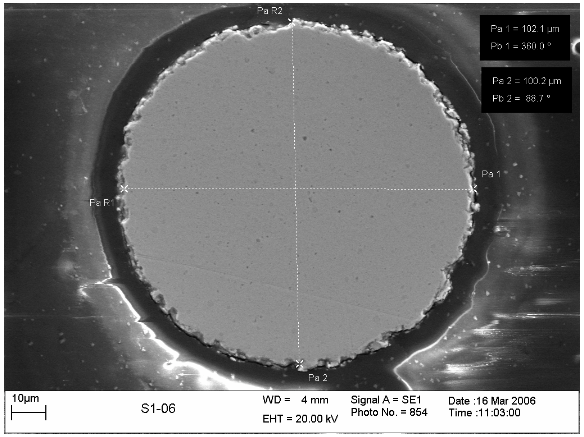




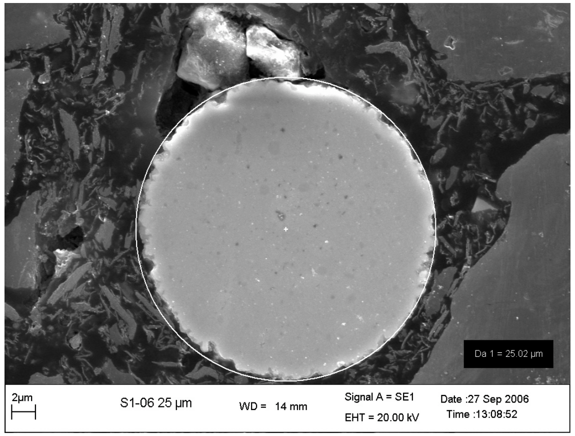


A and B; 40 μm; TT350°C; 30'

Caratterizzazione di Fili Sottili



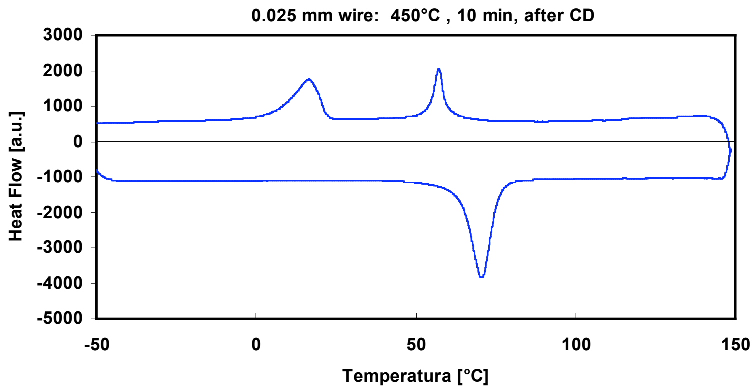
ϕ 100 µm wire



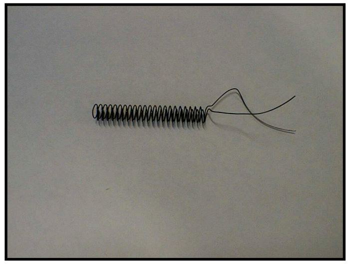
ϕ 25 µm wire

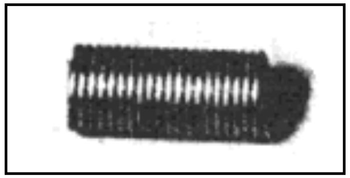
SEM – NiTi wire cross sections

DSC SEIKO 220C



Shape Setting and Training





I Deformazione a Freddo

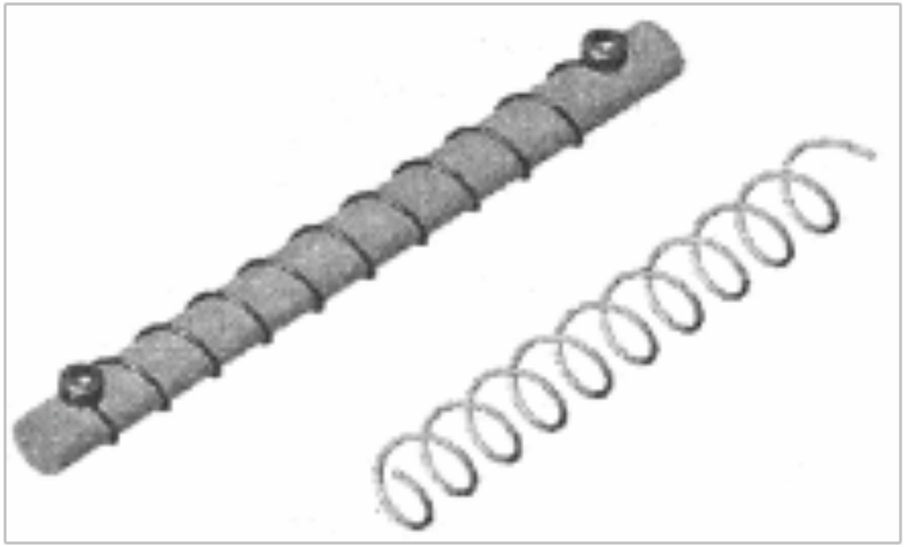
II Fissaggio del materiale nella forma desiderata

III Trattamento termico (basse temperature 550°C; 1-20 min)

Shape setting

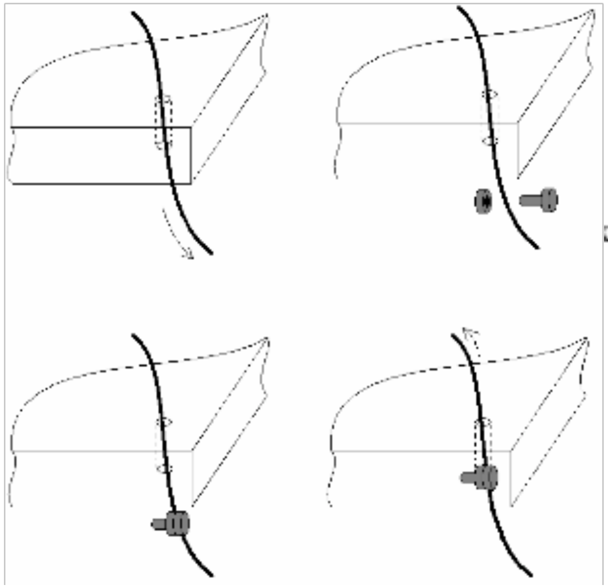
IV Ciclaggio termomeccanico

Shape Setting



Trattamento termico in forno

Shape Setting



ct and tighten around the pegs.

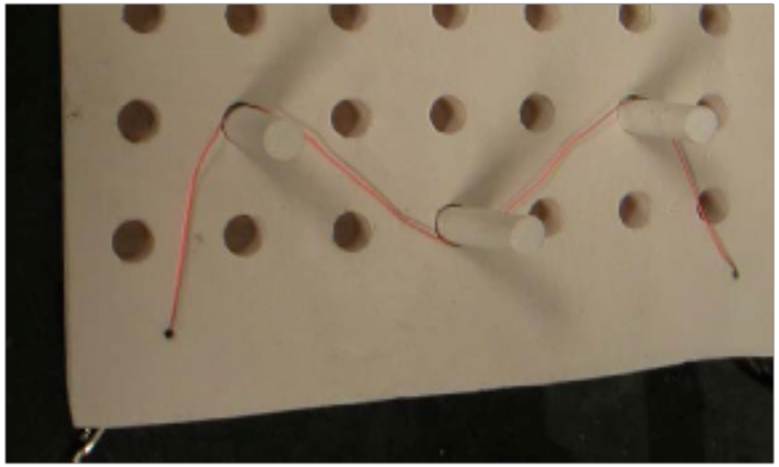
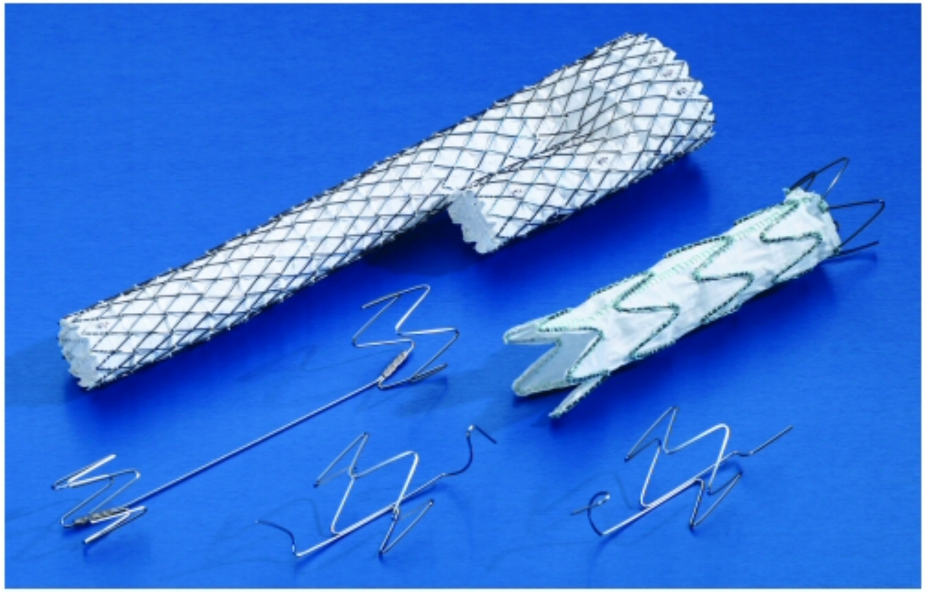
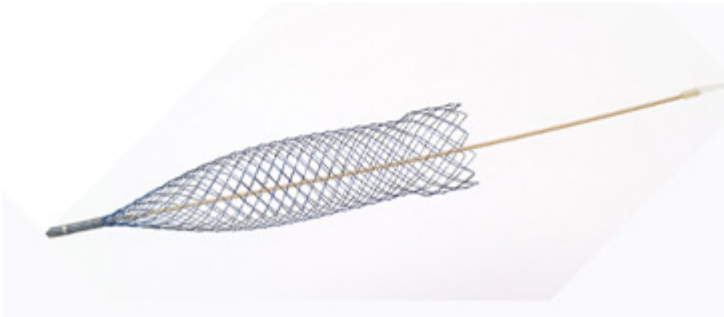


Figure 4: *Example of wire being shape-trained via electric heating.*

Trattamento termico, Effetto Joule

Shape Setting





Wire Training

Sequence of heat treatments and thermo-mechanical cycles

Control of training parameters

Cold deformation degrees

(Pre/ post) deformation Annealing Temperatures

Annealing **Times**

Annealing **Applied Stress**

Type of thermo-mechanical cycling

N. of thermo-mechanical cycles

All the Parameter of thermo-mechanical cycling