2017 Spring

“Calculation and Applications Phase Equilibria”

Principles *of* Solidification

04.12.2017

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Contents for previous class

- **Undercooling ΔT**
- **Interfacial energy**
  γ_{SL} / $S(\theta)$ wetting angle

Solidification: Liquid → Solid

< Nucleation in Pure Metals>

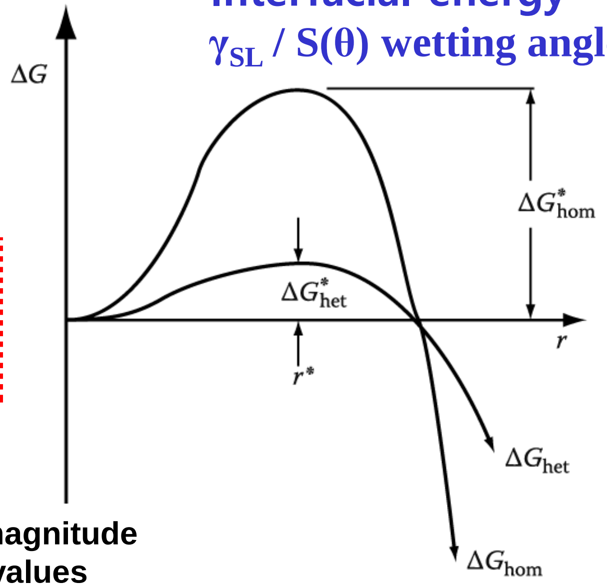
* Homogeneous Nucleation

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \qquad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

r* & ΔG* ↓ as ΔT ↑

$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\}$$

changes by orders of magnitude from zero to very high values over a very narrow temp. range



* Heterogeneous Nucleation

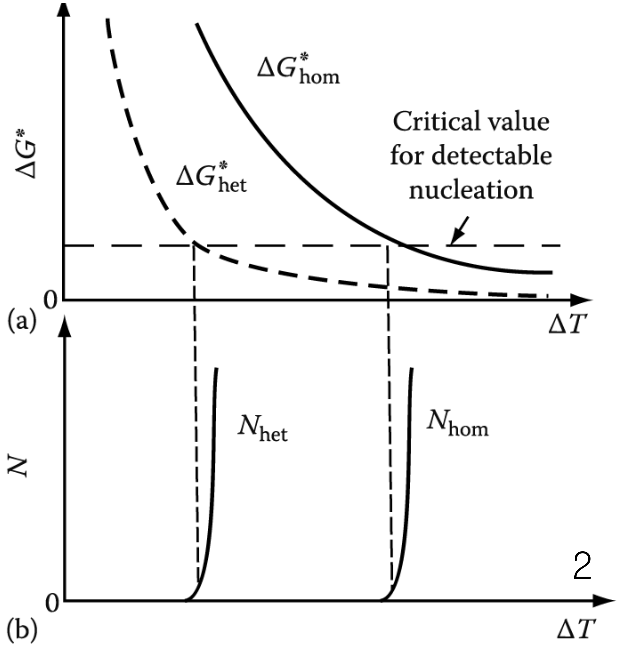
$$\Delta G^*_{het} = S(\theta)\Delta G^*_{\text{hom}}$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

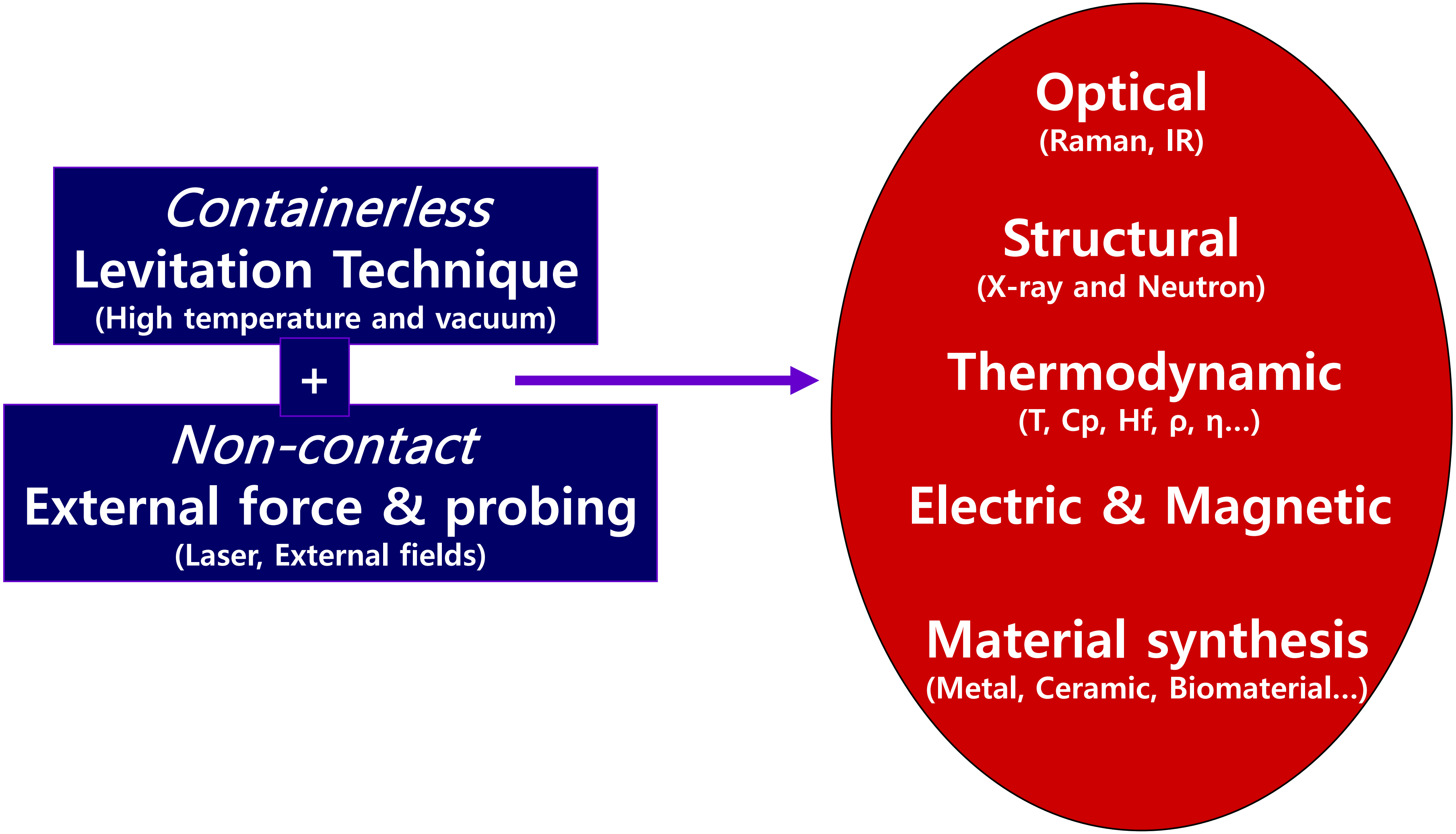
* Nucleation of melting

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

(commonly)



Containerless and Contactless Measurement System



Containerless
Levitation Technique
(High temperature and vacuum)

+

Non-contact
External force & probing
(Laser, External fields)

Optical
(Raman, IR)

Structural
(X-ray and Neutron)

Thermodynamic
(T, Cp, Hf, ρ, η…)

Electric & Magnetic

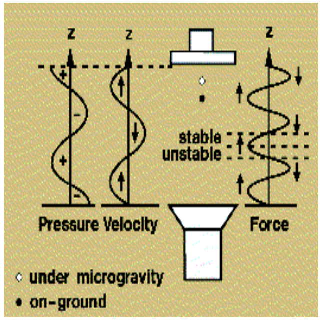
Material synthesis
(Metal, Ceramic, Biomaterial…)

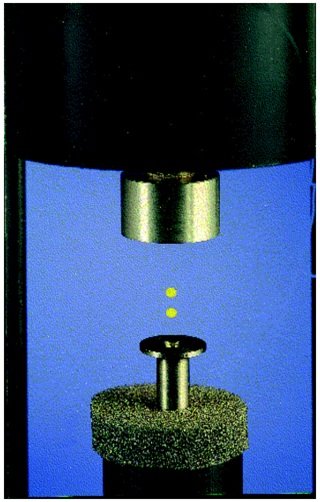
High Temperature Levitation

Ultra-high temperature > 3000 ºC

* Magnetic/diamagnetic/superconducting levitation → Only magnetic sample, below T_c

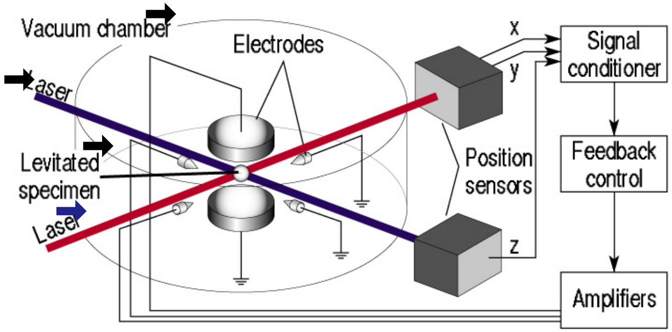
Acoustic

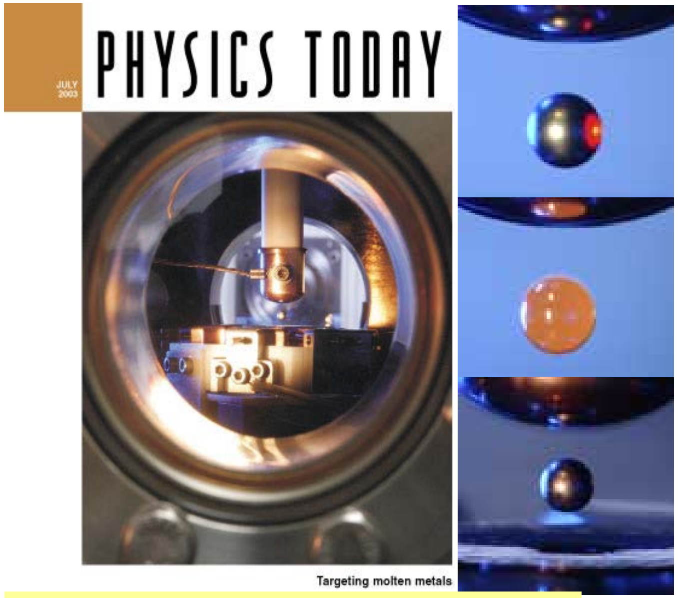




Requirement of acoustic media, Unstable at high T

Electrostatic





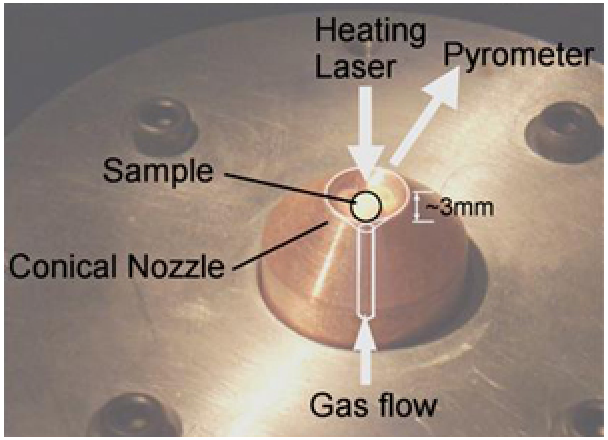
Physics Today, v56, p22, July 2003

All types of samples,
Suitable for sample heating

Electromagnetic

Only metallic & large mass sample

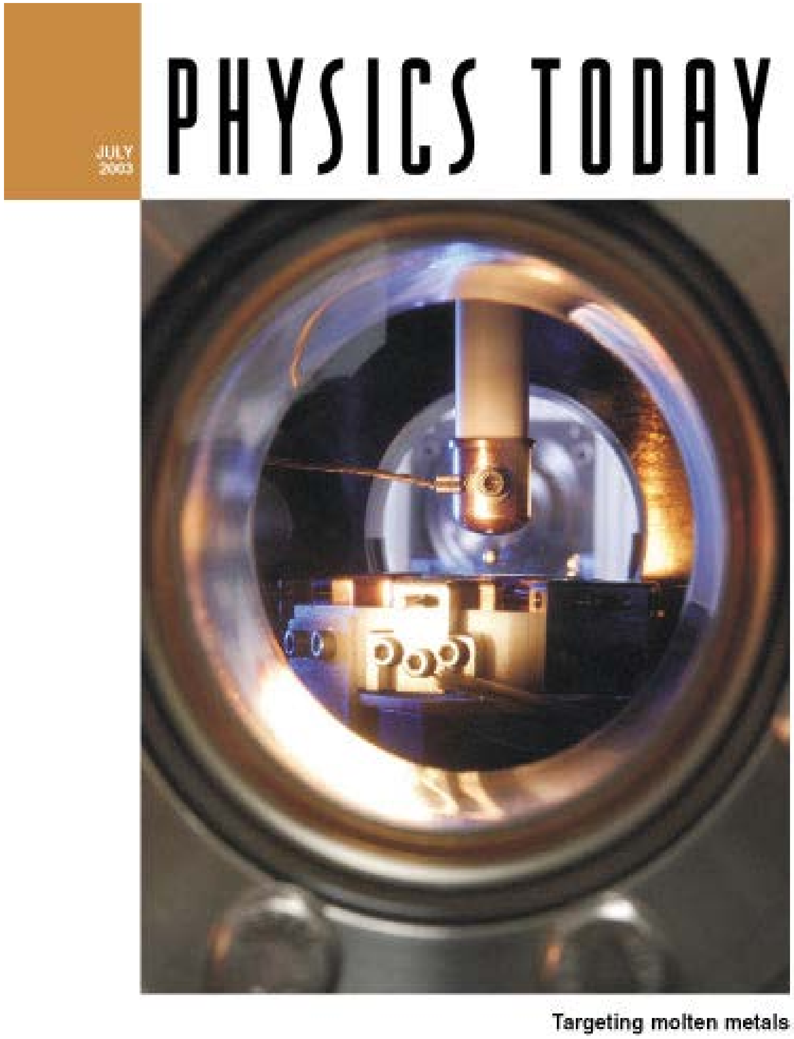
Aerodynamic



http://ec.europa.eu/research/industrial_technologies/articles/article_2288_en.html

Difficult to control rotation of sample,
Gas-sample reaction

Electrostatic Levitation (NASA, MSFC (Huntsville))

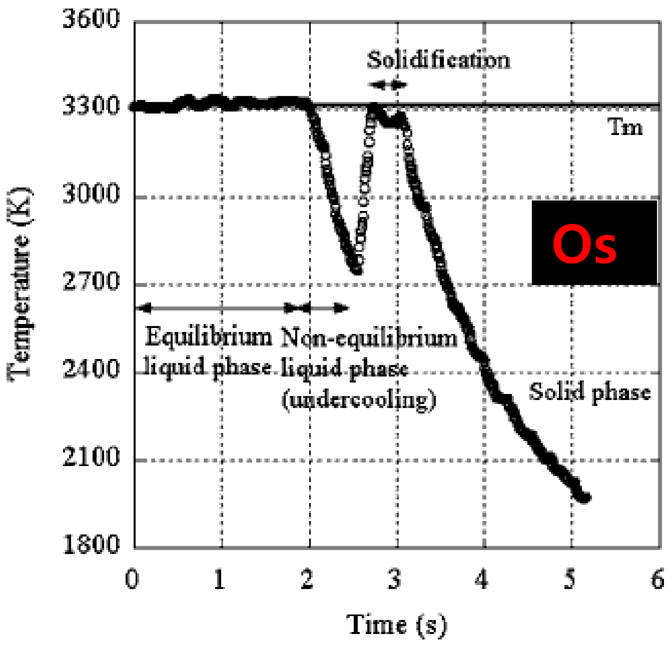


JULY 2003

PHYSICS TODAY

Targeting molten metals

Physics Today, v56, p22, July 2003



P.–F. Paradisa, et.al., JOURNAL OF APPLIED PHYSICS 100, 103523 2006

- **Specific heat,**
- **Emissivity,**
- **Density,**
- **Viscosity,**
- **Surface tension…**

Beam-ESL; High-energy synchrotron x-ray scattering experiment

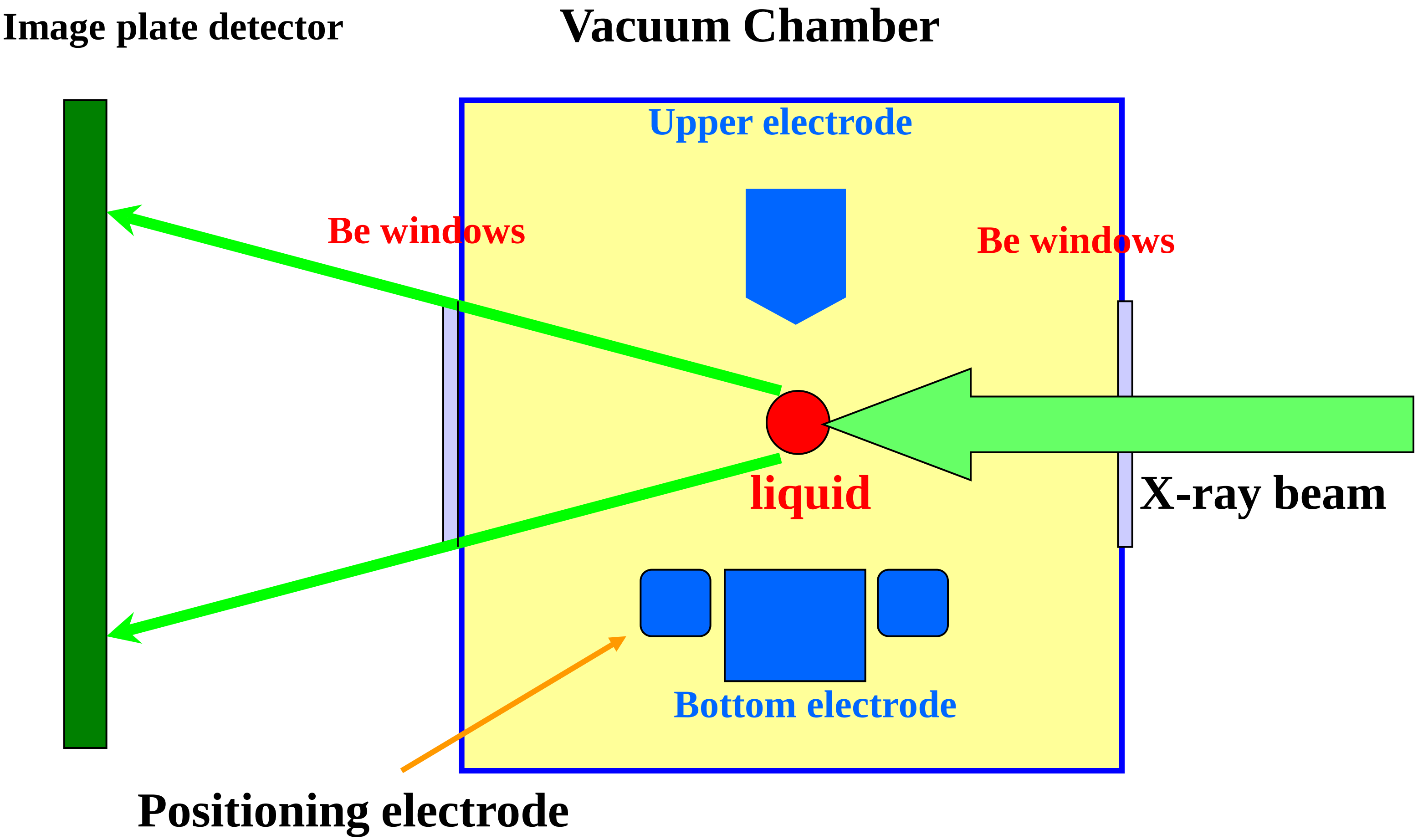


Image plate detector

Vacuum Chamber

Upper electrode

Be windows

Be windows

liquid

X-ray beam

Bottom electrode

Positioning electrode

Sample size : 30-100 mg,
Temperature : 300-2200 K,

X-ray Energy : 125 keV,
Vacuum :10^{-7} torr

Wavelength : 0.0988 ^{o}A
Exposure time : 1 sec.

東亞日報

2009년 08월 07일
23면

인공우주장치로 '건담 합금'도 가능할까

"적 전차를 한 방에 꿰뚫는 강력한 탄환을 만든다. 노트북이나 휴대전화의 배터리 사용시간을 수십 배 늘린다."
지구에 자연적으로 존재하는 물질로는 이런 소재를 개발하기 어렵다.
지금보다 몇 배나 단단한 초금속,
전기저장량을 30배나 높인 물질이 있어야 하기 때문이다.
과학자들이 대신 찾은 곳은 우주 공간이다.
정확히 말하면 진짜 우주를 본뜬 '인공 우주'다.

1979년 소개된 만화영화 '기동전사 건담'의 주인공 로봇 'RX-78-2'. 이 로봇은 달에서만 제련할 수 있는 특수합금 '루나티타늄'으로 만든다. 동아일보 자료 사진

세계 8번째 '진공-무중력 공간' 구현
우주와 환경 유사해 각종 실험 가능

안깨지는 금속-저장량 늘린 배터리 등
'만화영화 같은' 신소재 개발 기대

● 국내 첫 인공우주실험실

국내에서 첫 인공우주실험실이 등장했다. 한국표준과학연구원 이근우 연구원은 2년간 4억 원을 들여 인공우주를 구현한 '정전기식 공중부양장치'를 국내 최초로 개발했다. 우주공간과 비슷하게 '진공과 무중력의 공간'을 만드는 장치다. 세계에서는 8번째로 개발됐다.

진공을 만드는 것은 어렵지 않다. 펌프로 공기를 뽑아내면 된다. 그럼 어떻게 중력을 없앨까. 이 장치는 지구의 중력과 똑같은 힘을 내는 전기장을 중력 반대 방향으로 걸어준다. 중력과 전기장이 상쇄되면서 장치 안에 물체를 놓으면 우주인처럼 공중에 붕 떠오른다. 50mg의 시료라면 0.00005N(뉴턴)의 전기적인 힘을 위로 쏴준다. 이 장치는 고출력 레이저로 공중에 뜬 물질을 섭씨 4000도까지 가열할 수도 있다. 이근우 연구원은 "장치를 거의 완성했을 때 실험용 물체가 제자리에 떠 있지 않고 엉뚱한 곳으로 튀어나가거나 마구 날아다녀 고생했다"며 "물체에 실을 매달고 한 달 동안 미세하게 조정한 끝에 장치를 완성했다"고 말했다.

로켓용 신소재를 연구하고 있는 한국항공우주연구원 이호성 책임연구원은 "중력은 재료과학 연구자들에게 가장 큰 걸림돌"이라며 이 장치를 반겼다. 중력이 있는 지구에선 실험물질을 꼭 어딘가에 '올려' 두어야 하며, 액체는 용기에 담아야 한다. 다른 물질이 닿아 있으니 당연히 실험결과에 오차가 생긴다. 녹는점이 섭씨 3033도에 달하는 오스뮴(Os) 같은 물질은 담아둘 용기조차 없다. 연구팀이 개발한 공중부양장치는 이런 한계를 극복해 '꿈의 실험'을 가능하게 한다. 주로 우주연구기관이 이 장치를 사용할 것으로 전망된다.

● '메이드 인 스페이스' 신소재

1979년 처음 방영된 일본 애니메이션 '기동전사 건담'의 주인공 로봇은 달에서만 제련할 수 있는 '루나티타늄'이라는 금속으로 만든다는 설정을 갖고 있다. 대포보다 큰 120mm 포탄을 맞아도 끄떡없고, 고열이나 방사능도 차단한다. 우주에서는 지구보다 더 뛰어난 소재를 만들 수 있을 거라는 상상력이 만들어 낸 가상의 물질이다. 과학자들은 인공우주실험실에서도 '만화영화 같은' 신소재를 만들 수 있을 거라고 기대한다.

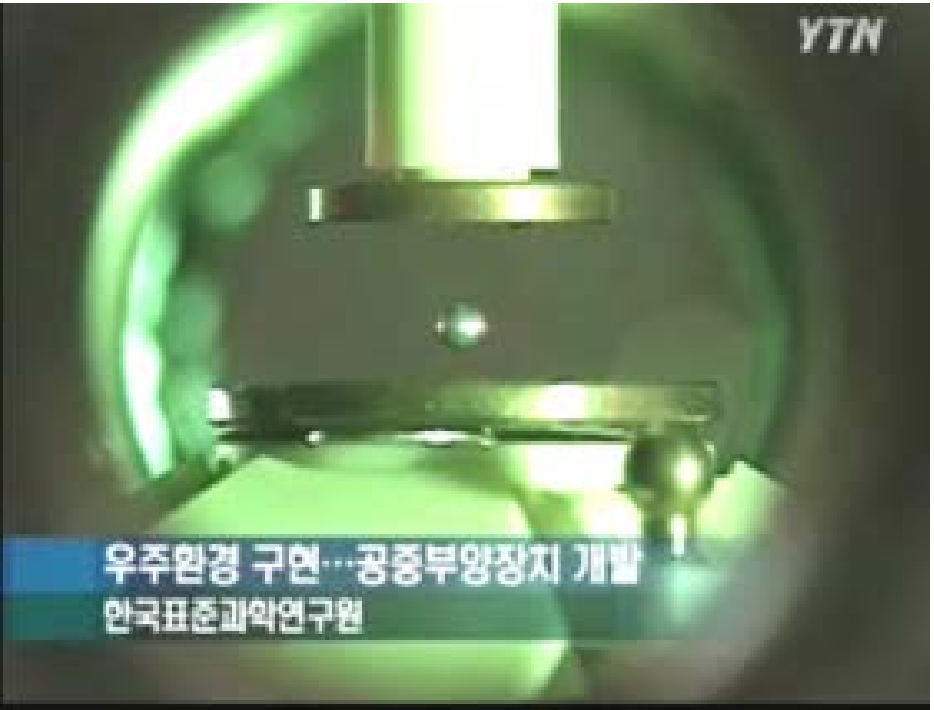
공중부양장치는 전기장을 이용해 물체를 공중에 띄울 수 있다. 알루미늄 금속이 떠 있는 모습. 사진 제공 한국표준과학연구원

미국항공우주국(NASA)은 1992년 인공우주실험실에서 '비결정질 금속'이라는 신소재를 개발했다. 금속이 깨지는 이유는 물질이 결정 형태로 굳어 있기 때문인데 비결정 금속은 결정을 이루지 않아 잘 깨지지 않는다. 이 기술은 현재 전차의 장갑판, 대포알의 탄두, 고탄력 테니스 라켓 등 다양한 첨단물질을 만드는 데 응용되고 있다. 일본우주항공연구개발기구(JAXA) 연구진도 2006년 비슷한 실험장치를 이용해 전기저장량을 30배나 늘린 배터리용 신물질을 개발했다.

아무리 인공 우주라도 진짜 우주만 할 수는 없다. 그래서 국제우주정거장(ISS)을 거대한 우주실험실로 활용하는 방법도 모색되고 있다. NASA는 이미 우주정거장에 소재 개발을 위한 실험장치를 운영하고 있으며 일본도 곧 비슷한 장치를 설치할 예정이다. 이근우 연구원은 "처음에는 국내에 이 장치를 아는 사람이 없어 일부에선 '쓸모없는 일을 한다'는 냉소도 많았다"며 "앞으로 이 장치를 활용해 나노미터 크기의 초미세 반도체 소자를 연구할 계획"이라고 말했다.

대전=전승민 동아사이언스 기자 enhanced@donga.com

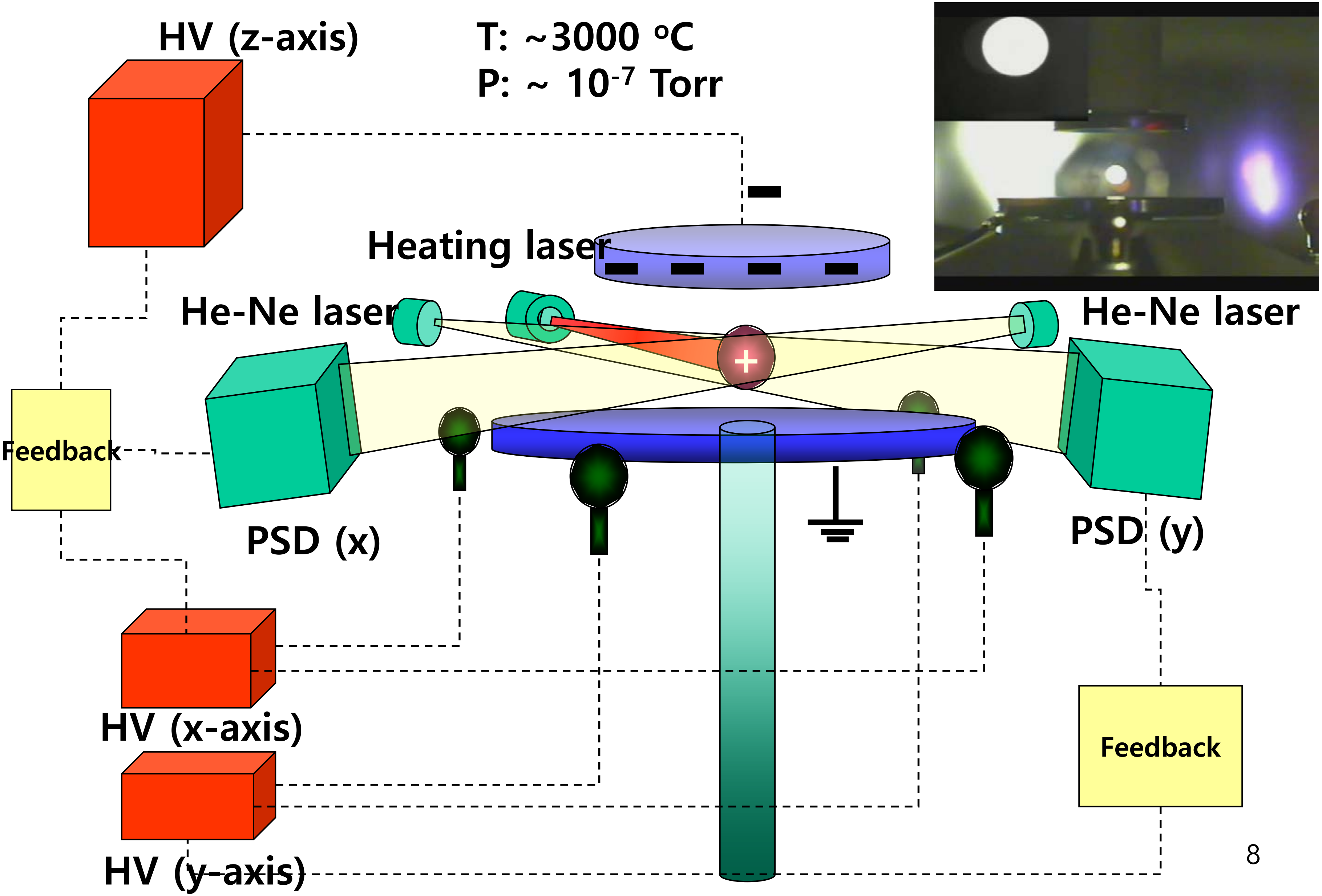
(25.7*27.6)cm

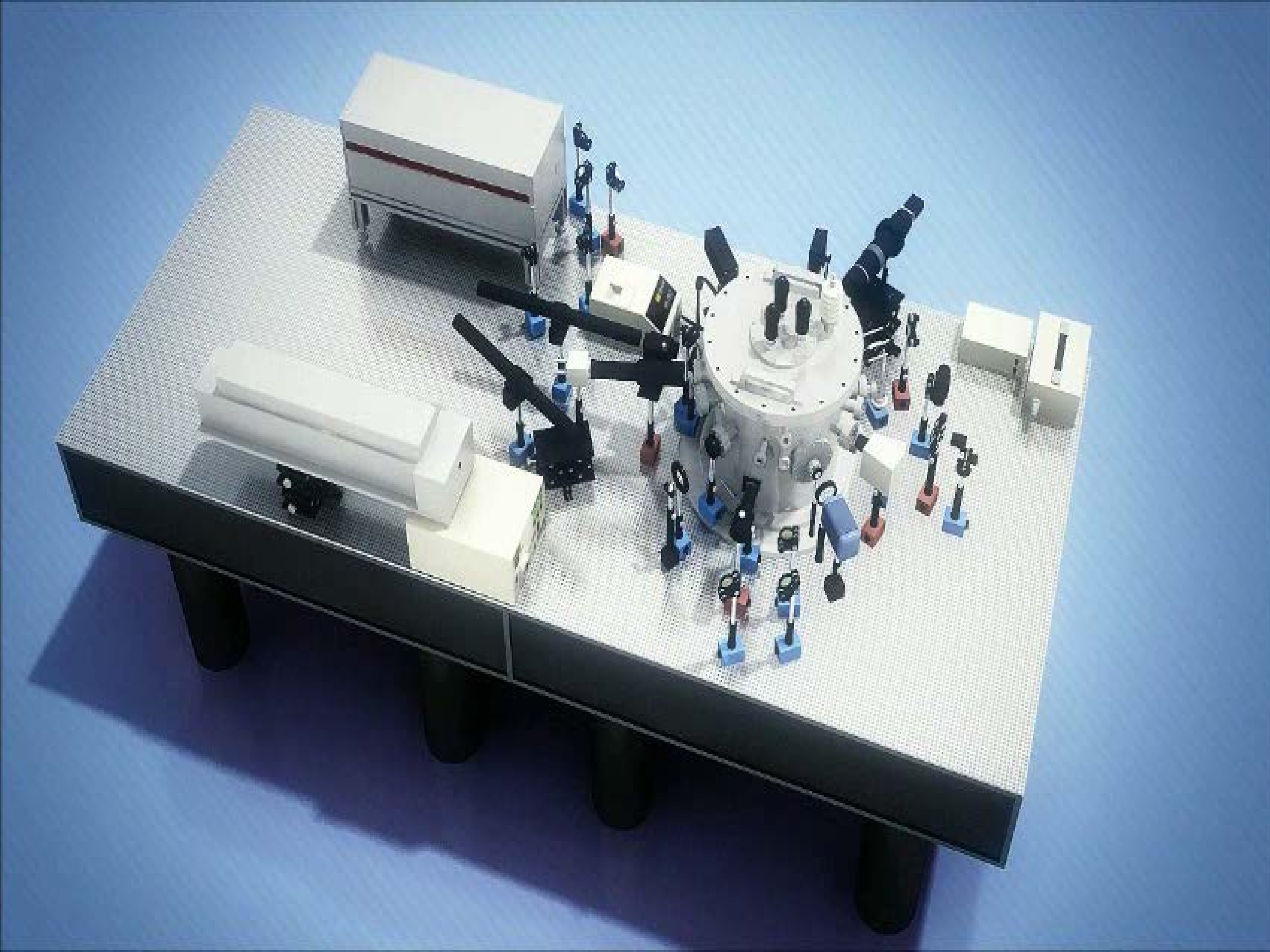


Electrostatic Levitation in KRISS

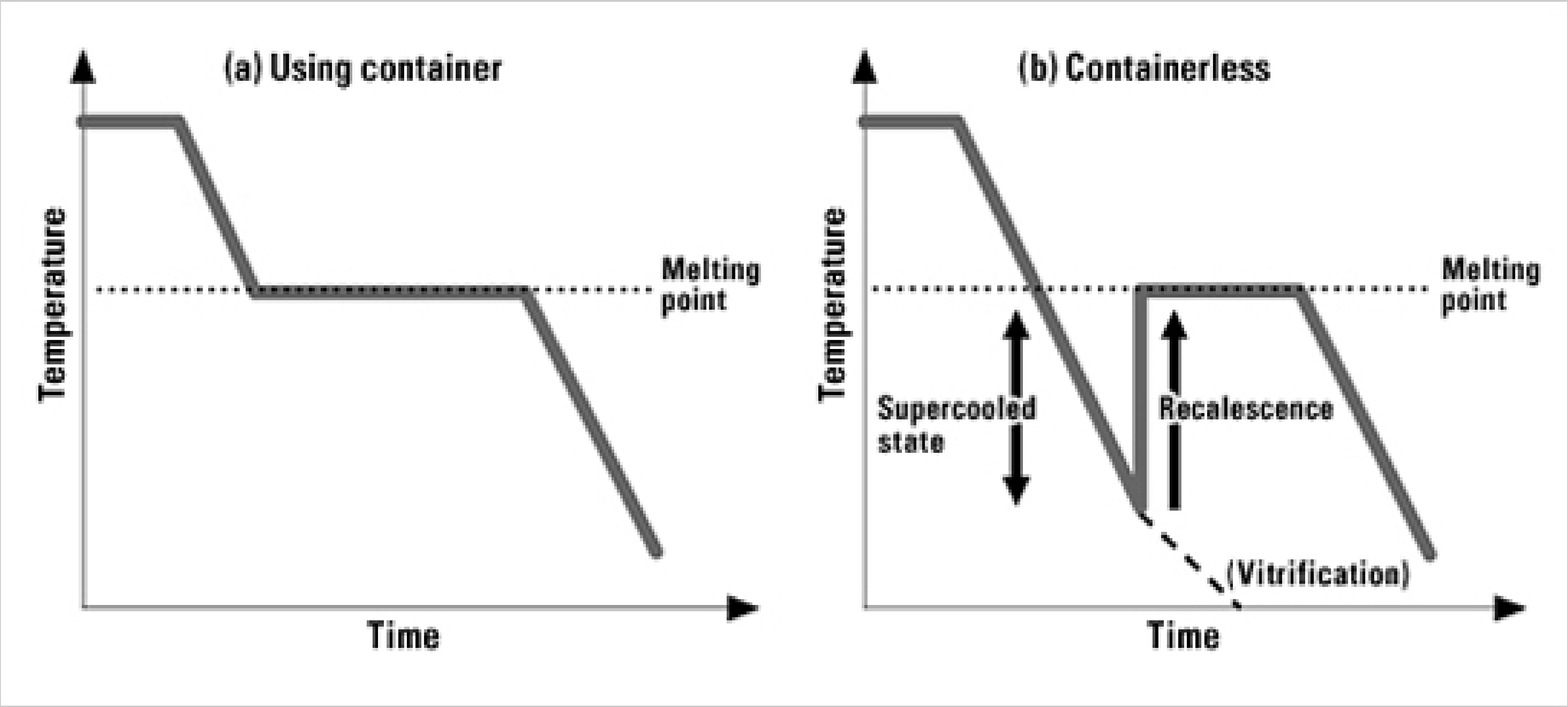
Containerless equipment: close to homogeneous nucleation

T: ~3000 °C
P: ~ 10^{-7} Torr

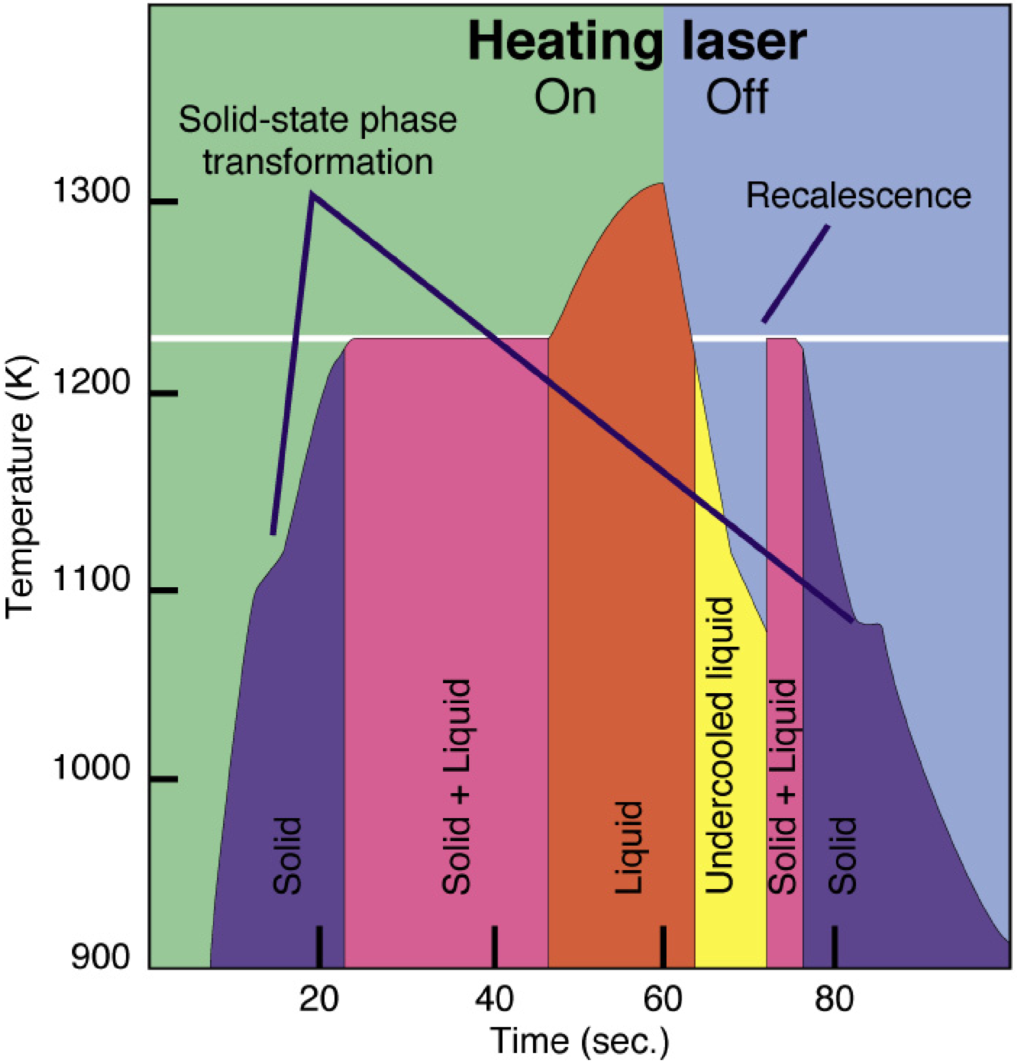


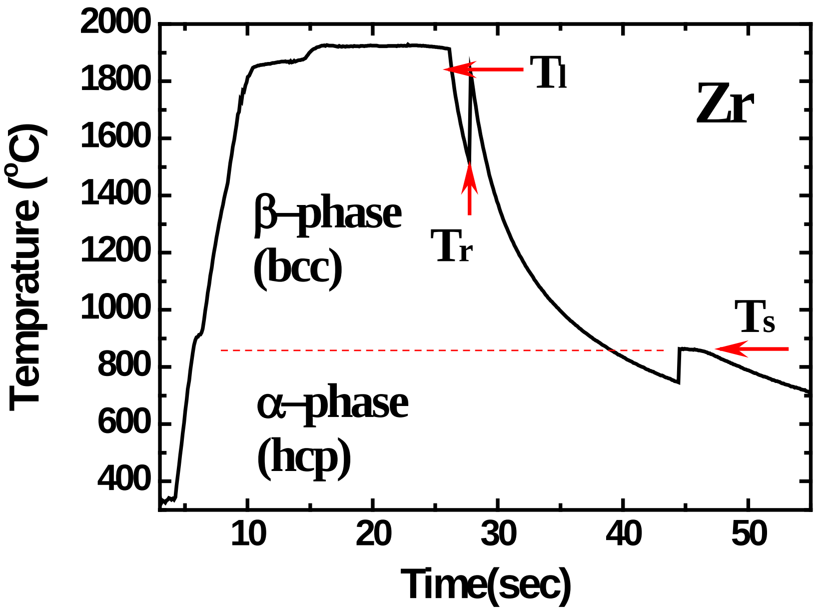


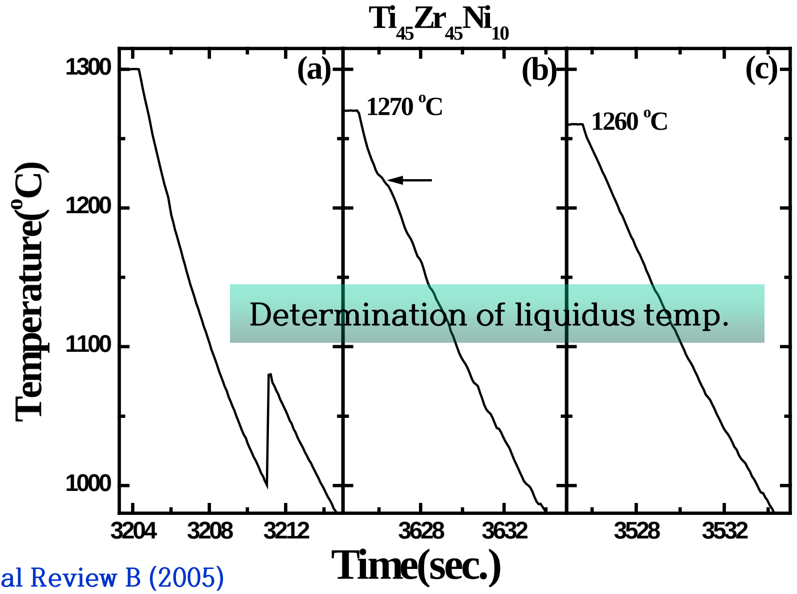
- No solid containers, No impurities from container
  - No heterogeneous nucleation site
    - Extremely large supercooling can be obtained (~ 100 ℃), clear recalescence
      - Metallic glass can be formed through free cooling



Melting and Freezing Using ESL



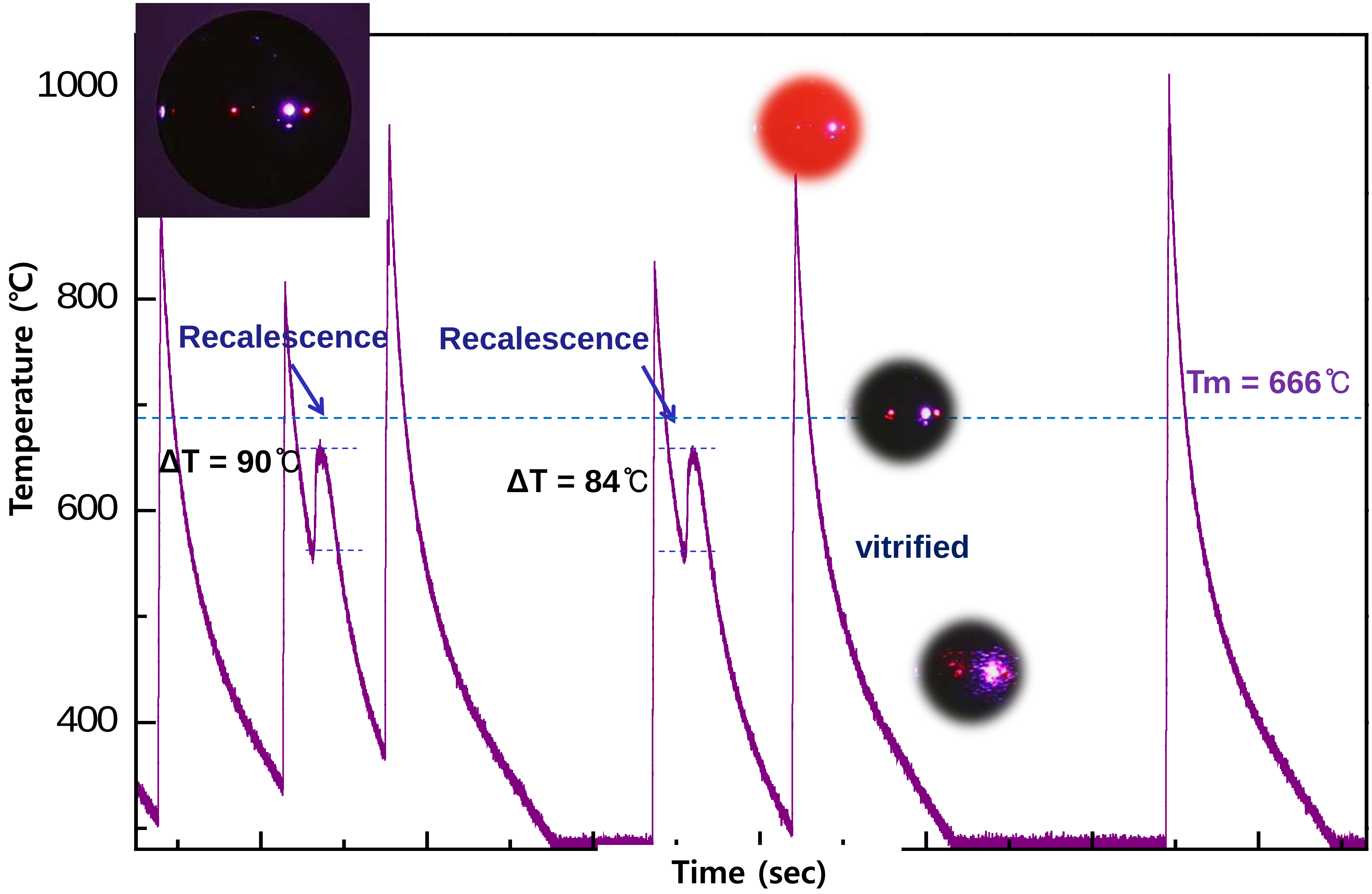




Determination of liquidus temp.

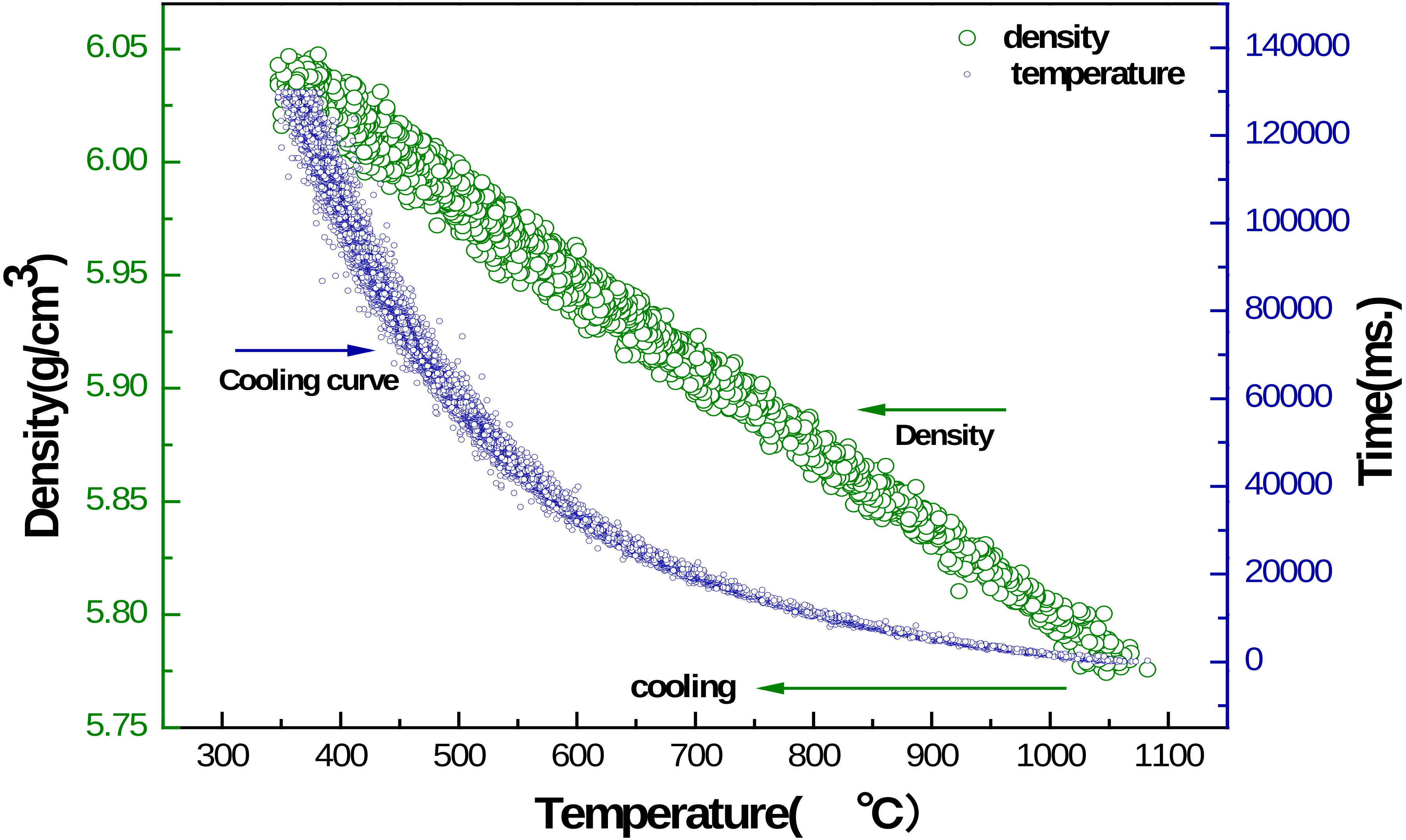
Lee, Gangopadhyay, Kelton, et.al., Physical Review B (2005)

Cyclic cooling curves of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

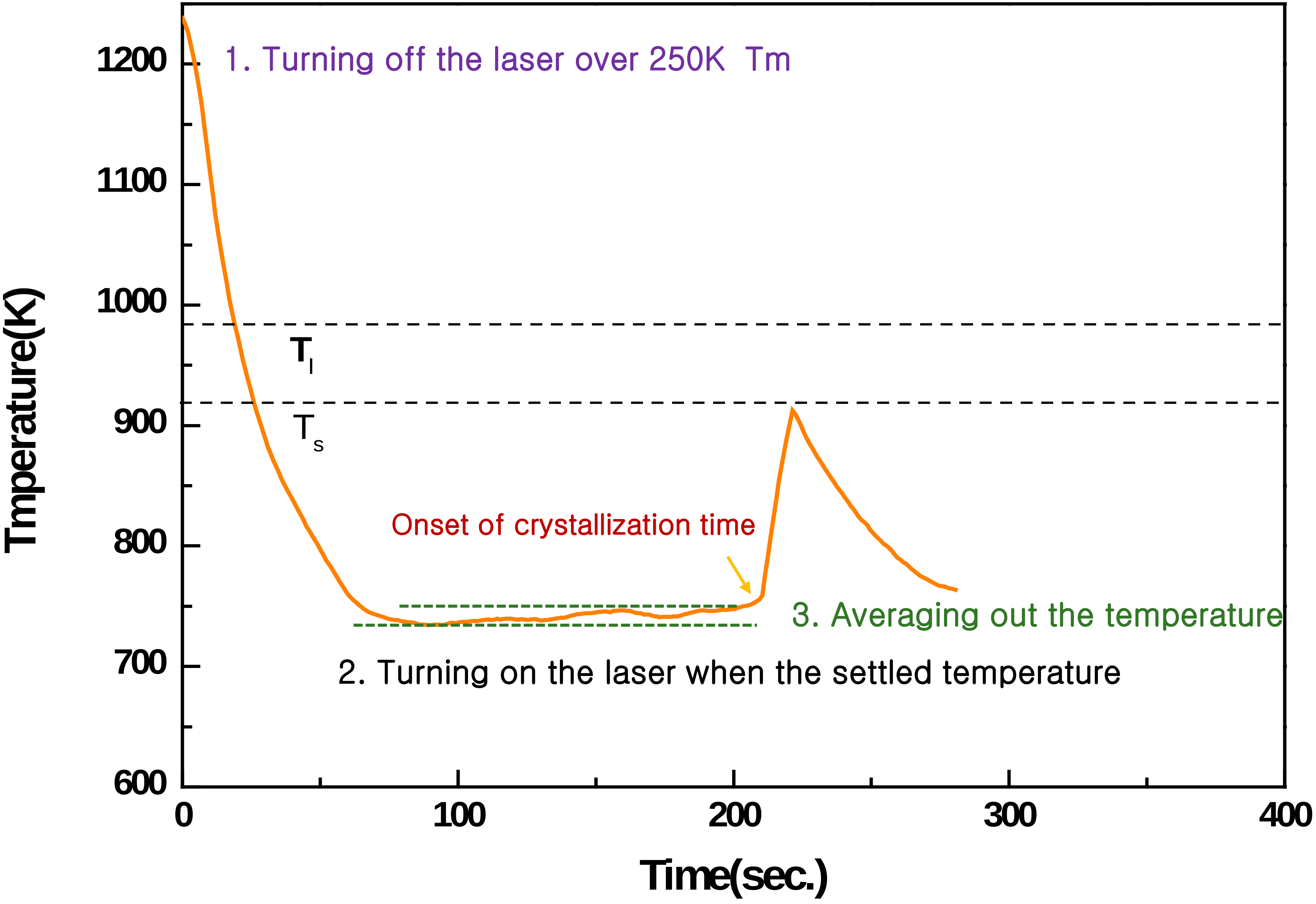


Cooling curve and density temperature profiles of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

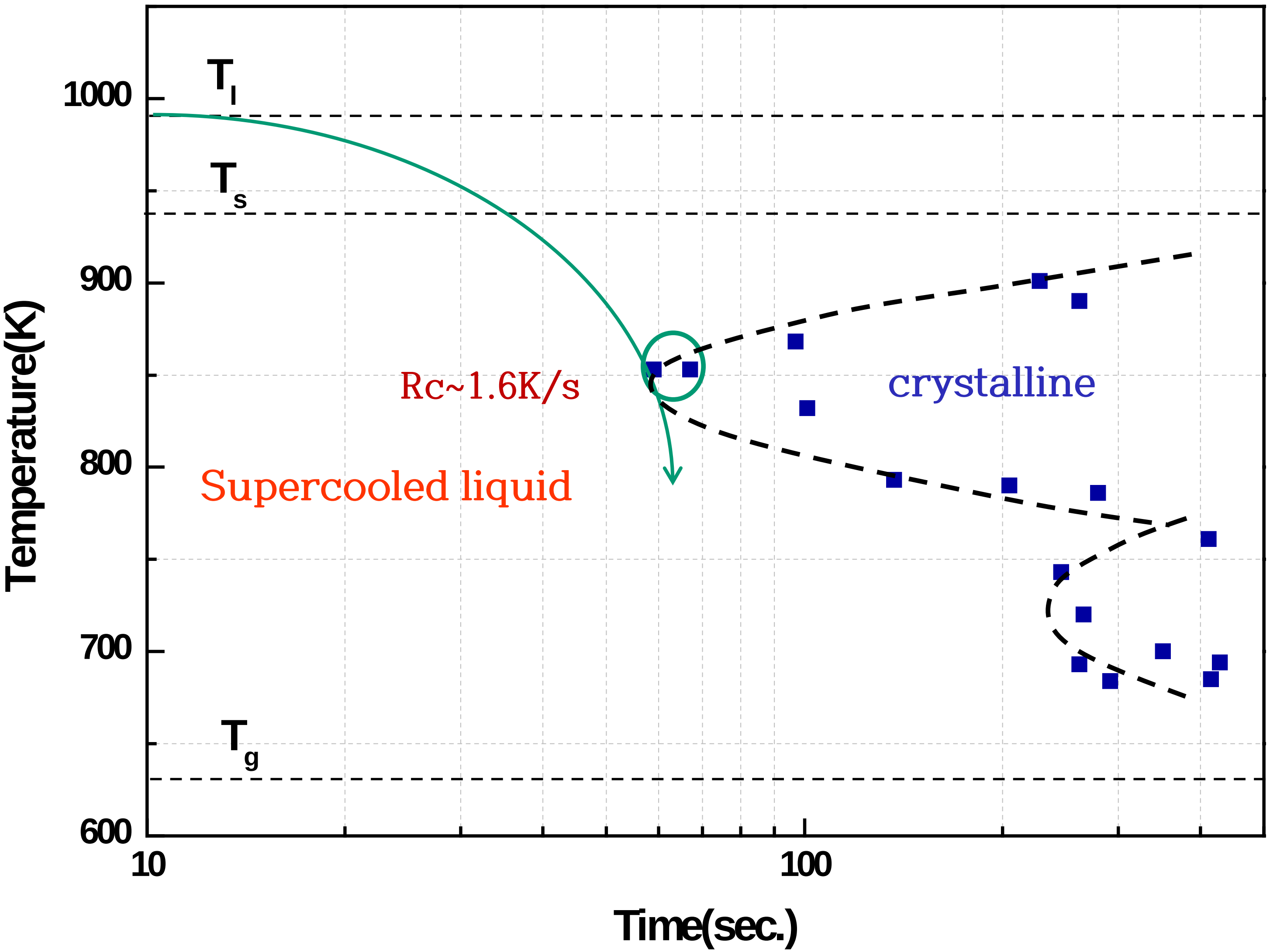
- Volume : CCD camera / Temperature measurement : pyrometer



Measurement of TTT diagram _ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$



Measurement of TTT diagram _ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$



Specific heat capacity

$$\boxed{mC_p\left(\frac{dT}{dt}\right)=4\pi r^2\sigma\varepsilon\left(T^4-T_s^4\right)}$$

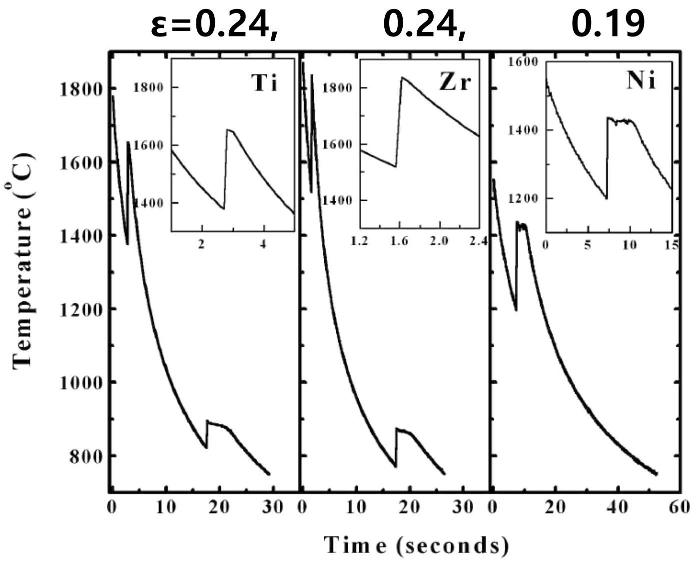
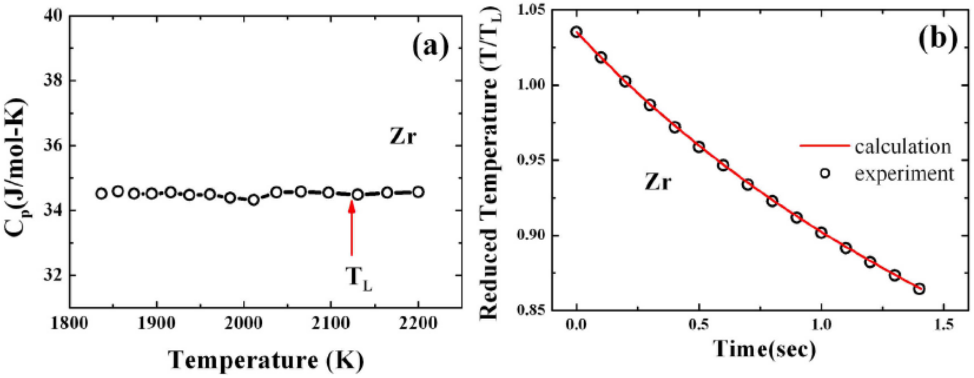


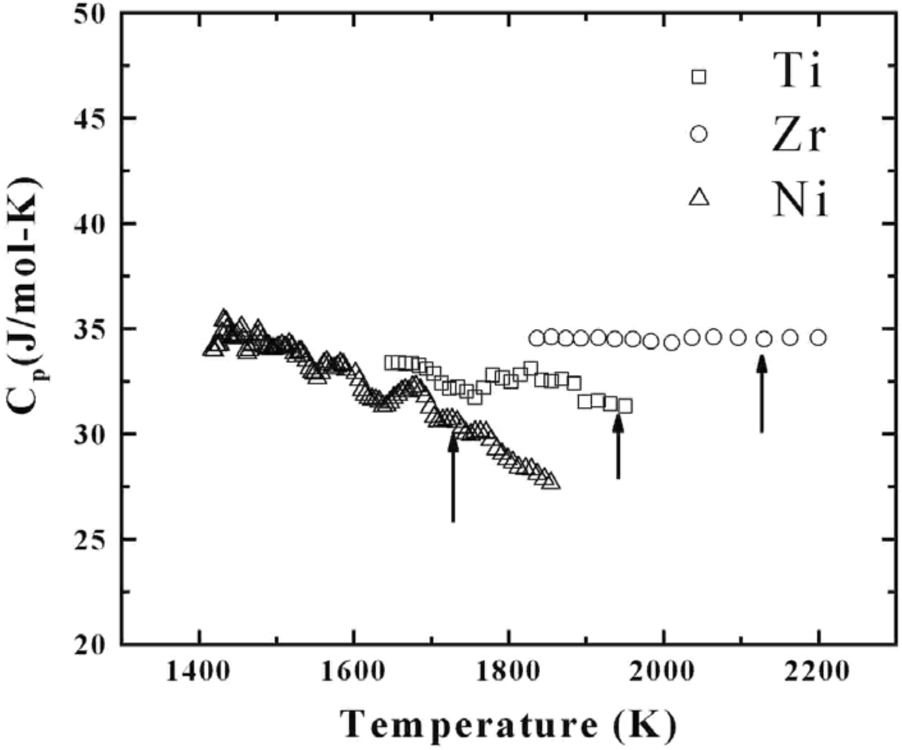
Figure 6.1. Free cooling curves of Ti, Zr and Ni, measured in the ESL. Inset figures show recalescences at high temperature.



$$t=\frac{mC_p}{4\sigma\varepsilon AT_r^3}\left(\ln\left(\frac{(T+T_r)(T_i-T_r)}{(T-T_r)(T_i+T_r)}\right)+2\tan^{-1}\left(\frac{T}{T_r}\right)-2\tan^{-1}\left(\frac{T_i}{T_r}\right)\right)$$

@kriss.re.kr

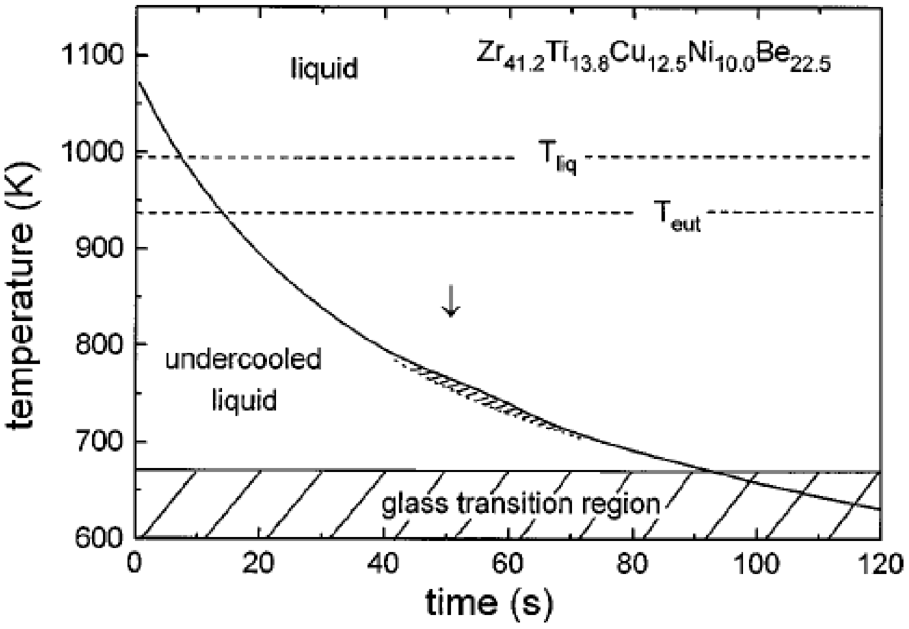
Specific heat of pure elements

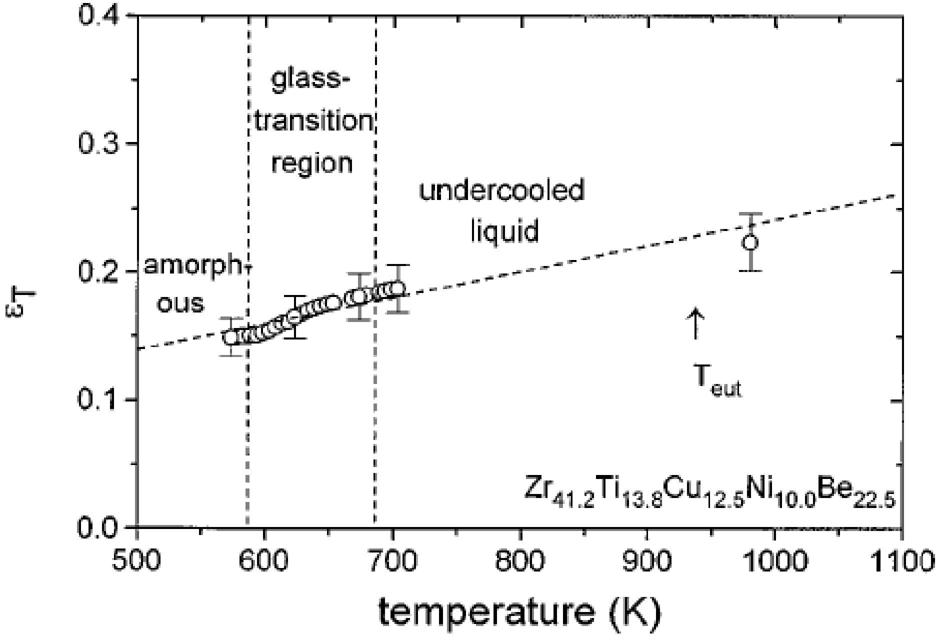


Emissivity

$$mC_p\left(\frac{dT}{dt}\right)+Power=4\pi\sigma\varepsilon\left(T^4-T_o^4\right)$$

$$Steady \quad condition, \quad \left(\frac{dT}{dt}\right)=0$$



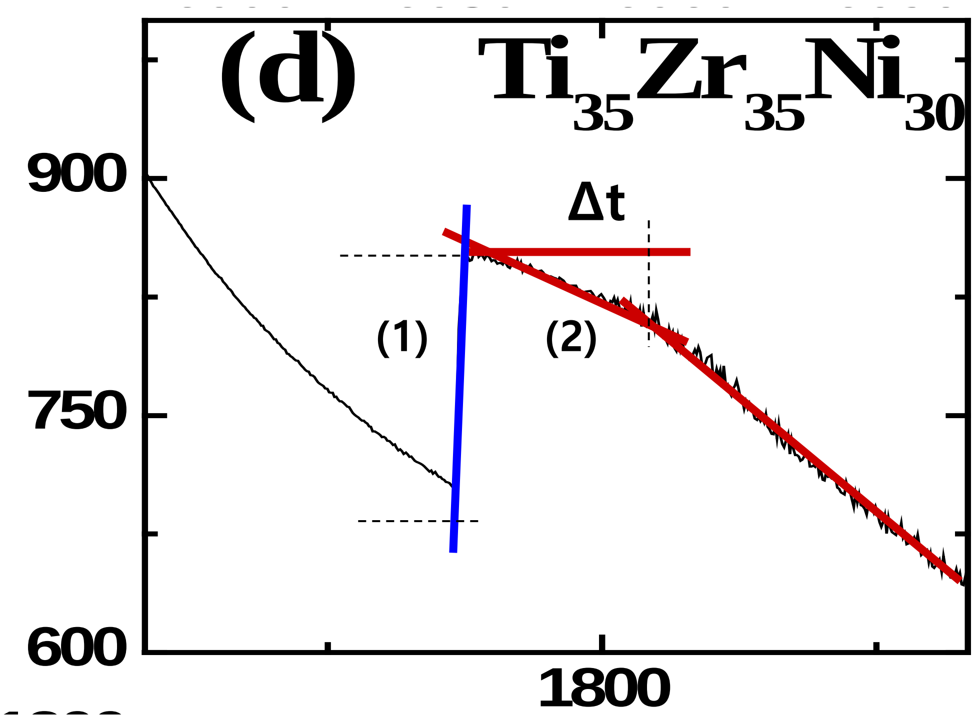


Kim, et.al., APL v68 (1995)

Fusion Enthalpy

$$\Delta H_f = (1) + (2) = C_p \Delta T_r + (4\pi\sigma\varepsilon(T_P{}^4 - T_o^4)\Delta t - 4\pi\sigma\varepsilon(T_P{}^4 - T_{end}^4)\Delta t)$$

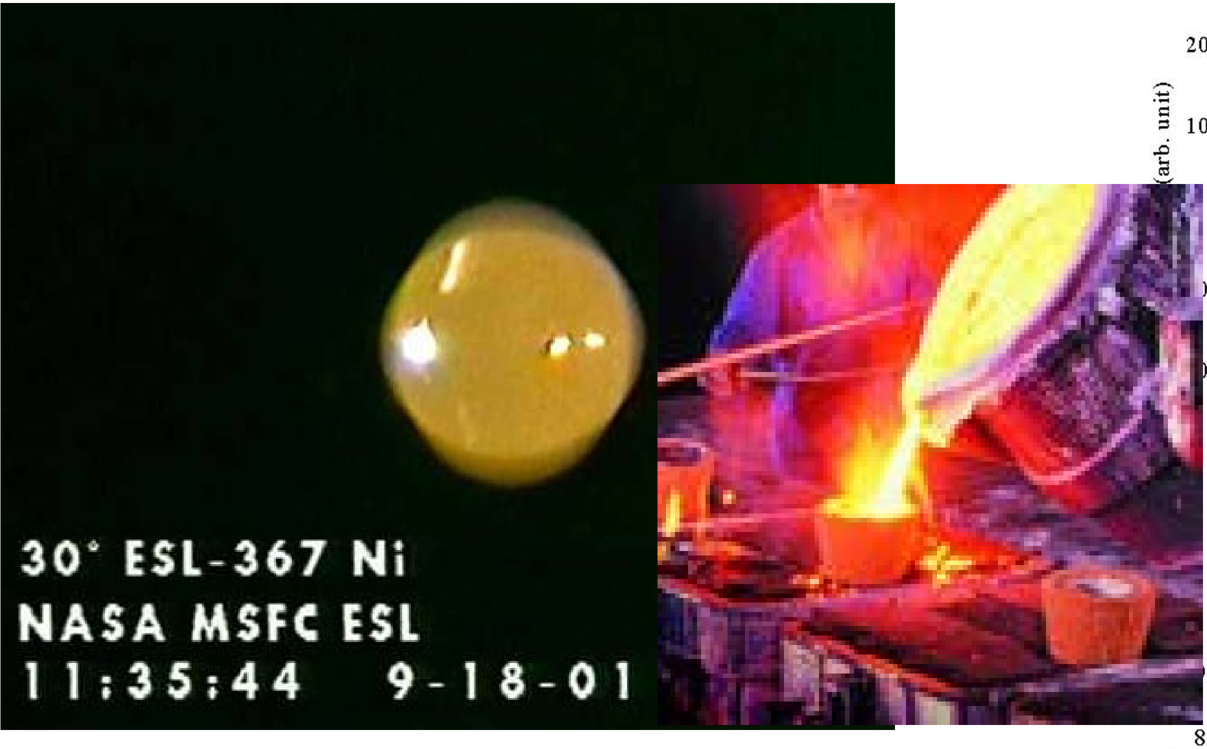
Crystallization



이근우: gwlee@kriss.re.kr

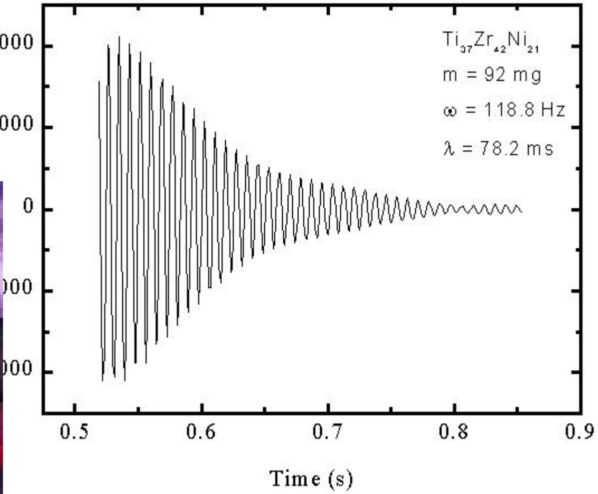
Viscosity & Surface Tension: Oscillation

Snapshot of surface oscillations in a Ni droplet



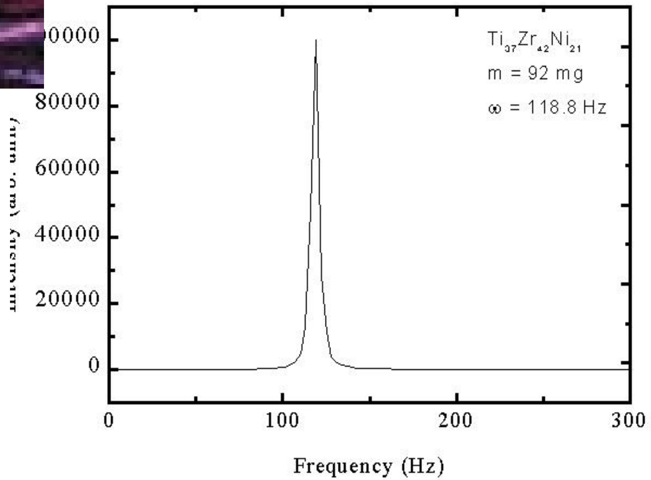
Damped oscillations

Exponential decay of amplitude



Power Spectrum

Single frequency

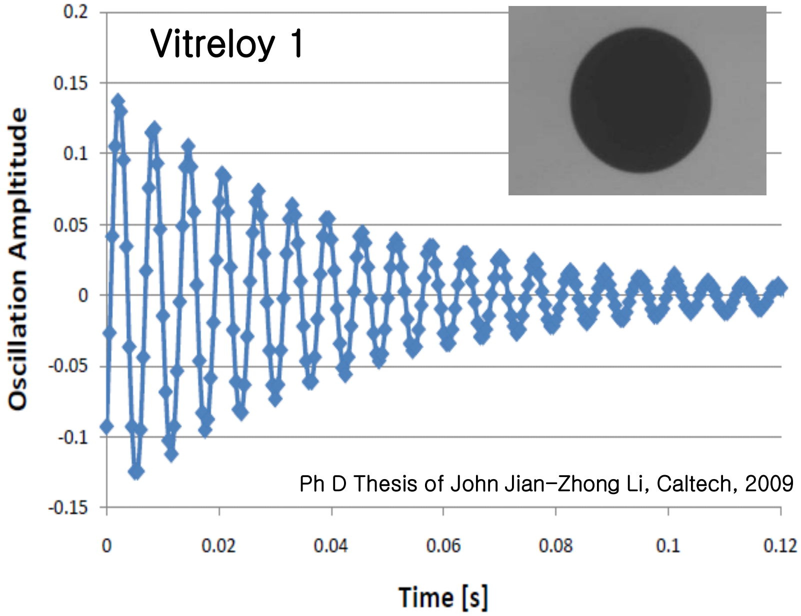


Caution: No distortion from spherical symmetry allowed multiple modes will be excited

Measurement of thermophysical properties

- Volume : CCD camera / Temperature measurement : pyrometer

- Surface tension & Viscosity : oscillating the sample by with a pulse of AC voltage



Ph D Thesis of John Jian−Zhong Li, Caltech, 2009

$$\omega_2^2 = \frac{8\gamma}{\rho r_0^3}$$

Surface tension

Oscillation frequency

Radius
when melt adopts
a spherical shape

Density

$$\frac{1}{\tau_2} = \frac{5\eta}{\rho r_0^2}$$

Viscosity

Decay time
constant

- Specific heat & total hemispherical emissivity : $\frac{m}{M} C_P \frac{dT}{dt} = -\sigma_{SB} \varepsilon_T A(T^4 - T_S^4)$

- Time- temperature-transformation curve : isothermal treatment

Oscillating drop 방식으로 고온에서 metal의 점도/ 표면 장력 측정 가능

Oscillating drop

- Induce surface oscillations in a levitating liquid droplet of radius ‘R_o’, mass ‘m’
- Measure the frequency of oscillation (ω)
- Measure the damping constant (λ)

- Damped resonant oscillations:

$$R = R_0 (1 + \delta \cos(\omega t) e^{-\lambda t})$$

Rayleigh (1879)

- Resonant frequency determined by surface tension:

$$\omega_l = \sqrt{\frac{l(l-1)(l+2)\gamma}{\rho R_o^3}}$$

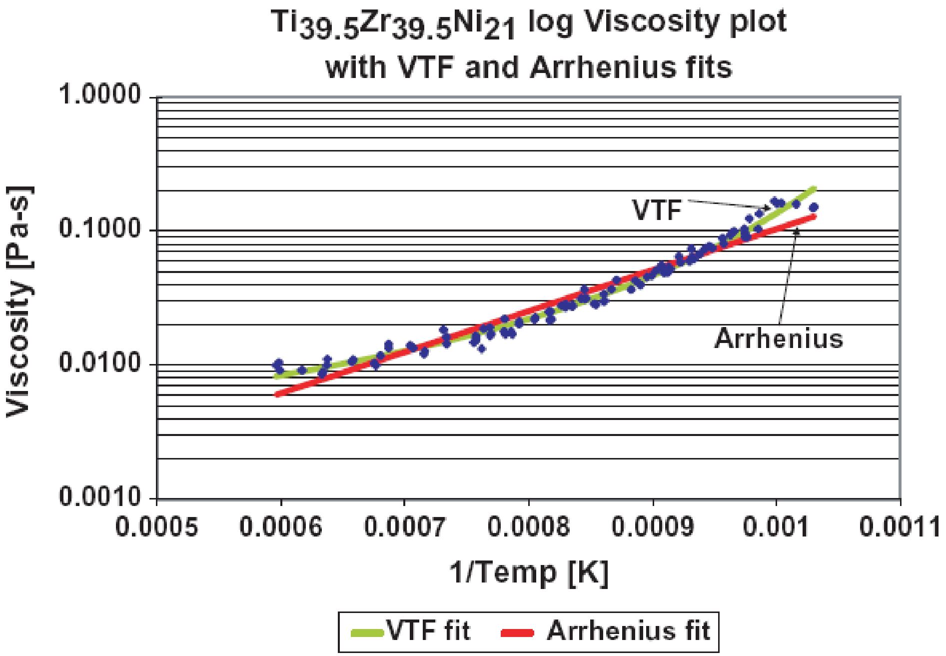
- Damping determined by viscosity:

$$\lambda_l = \frac{(l-1)(2l+1)\eta}{\rho R_o^2}$$

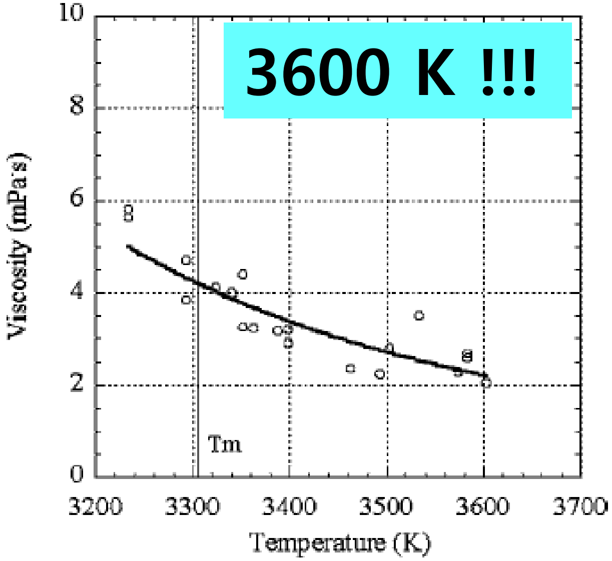
Lamb (1881)

High Temp. Viscosity

JOURNAL OF APPLIED PHYSICS 100, 103523 2006



Hyers, et.al., Philosophical Magazine Vol. 86, 2006(341-347)



3600 K !!!

FIG. 5. Viscosity of equilibrium and nonequilibrium liquid Os as a function of te

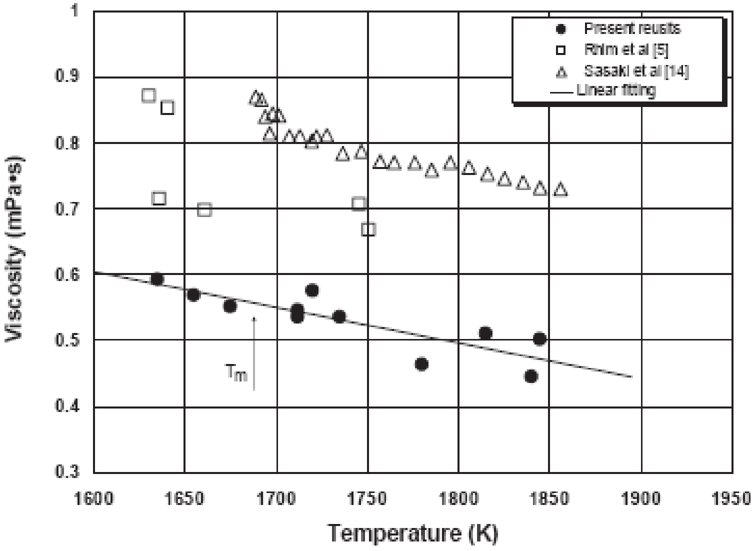
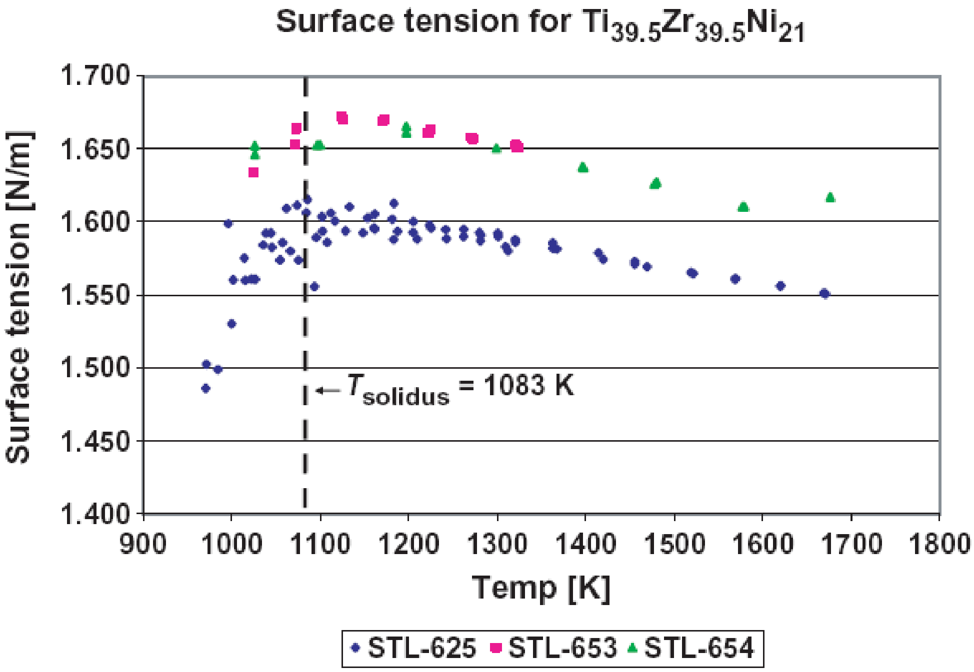


Fig. 8. Viscosity of molten silicon as a function of temperature.

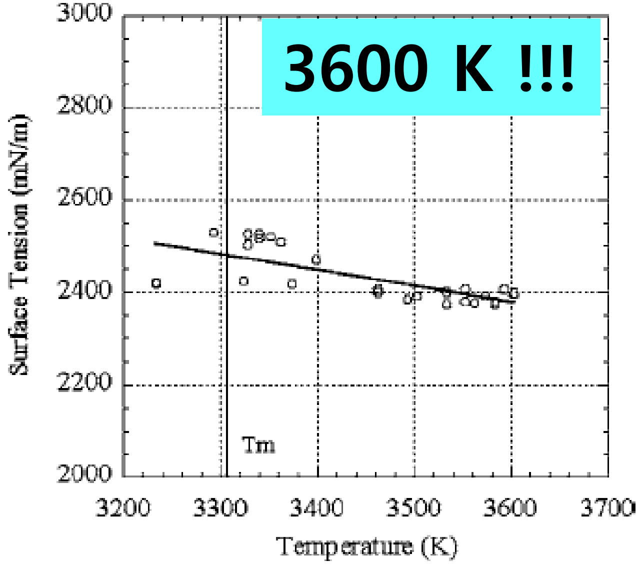
이근우: gwlee@kri

High Temp. Surface Tension

Hyers, et.al., Philosophical Magazine Vol. 86, 2006(341–347)



JOURNAL OF APPLIED PHYSICS 100, 103523 2006



3600 K !!!

FIG. 4. Surface tension of equilibrium and nonequilibrium liquid Os as a function of temperature.

Density

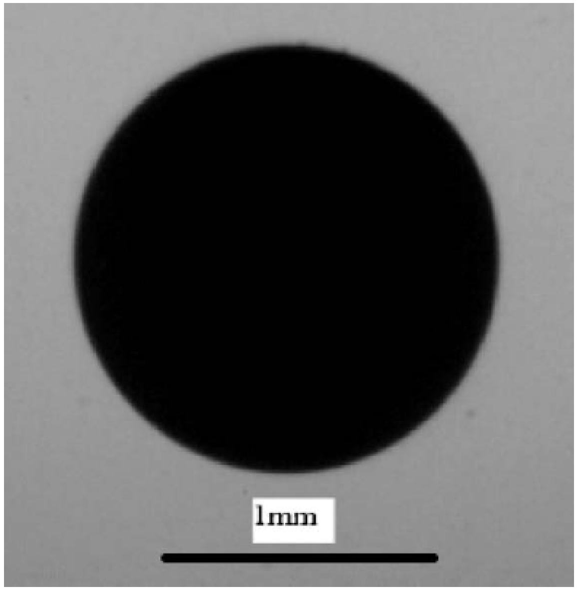
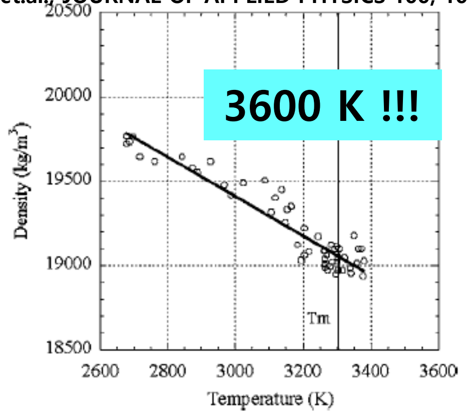


Fig. 2. A typical side view of a levitated molten silicon from which the density and the specific volume could be extracted.

Paradis, et.al., JOURNAL OF APPLIED PHYSICS 100, 103523 2006



3600 K !!!

FIG. 3. Density of equilibrium and nonequilibrium liquid Os as a function of temperature.

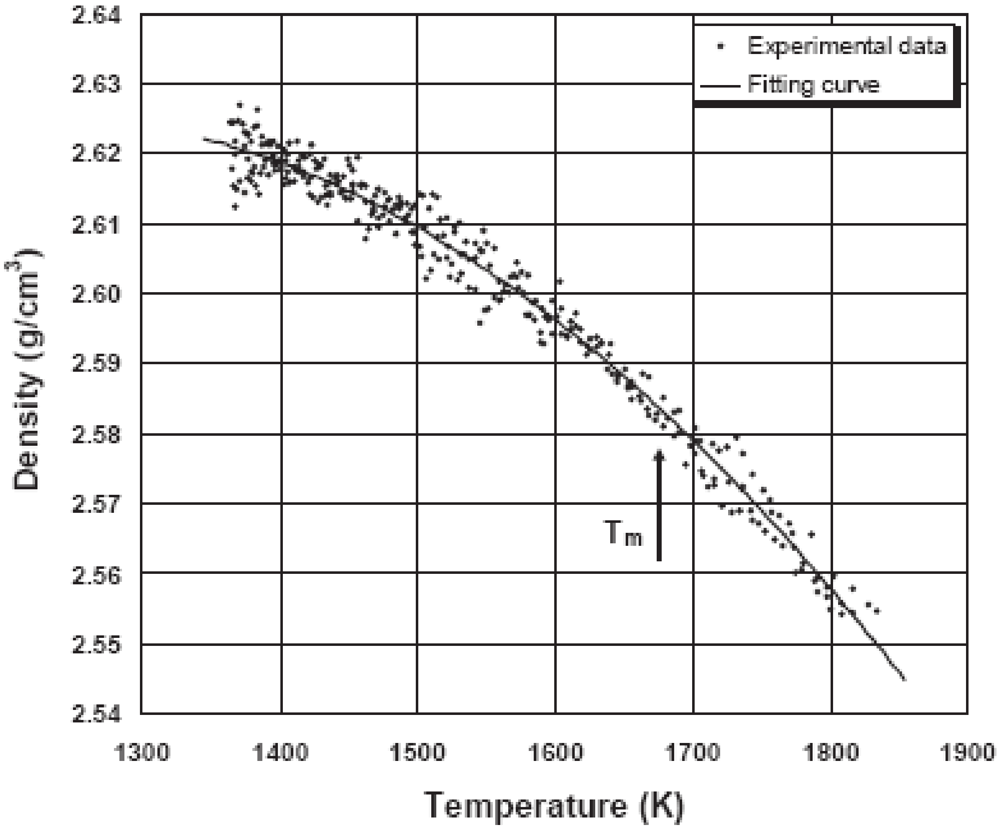
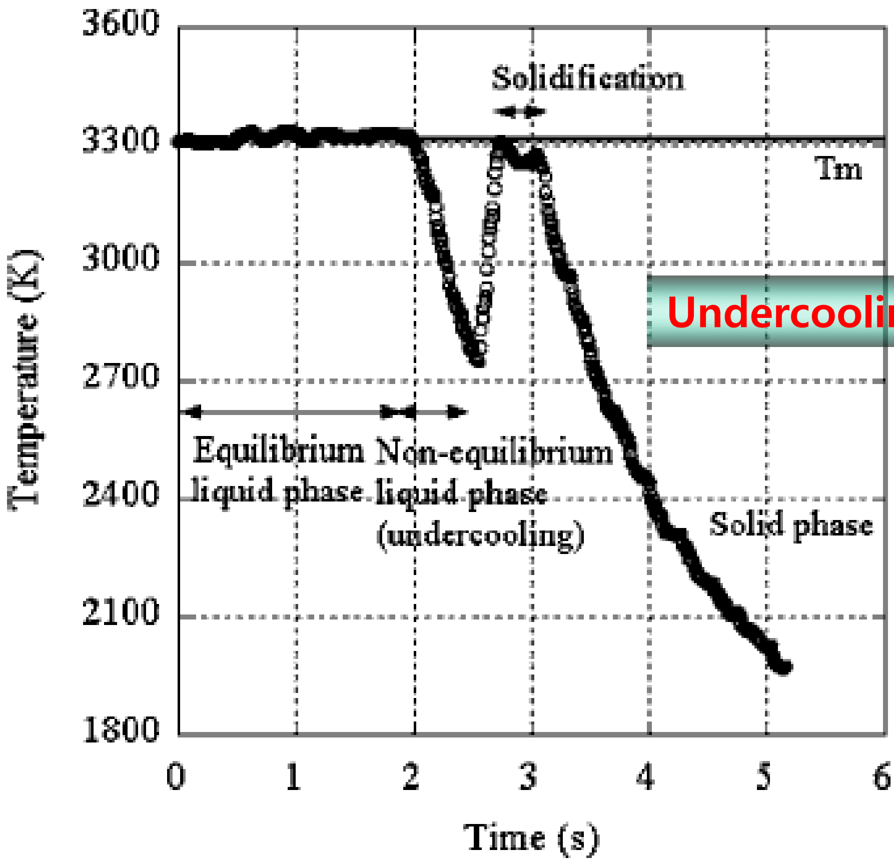


Fig. 4. Temperature dependent density of molten silicon.

Crystallization: Undercooling of Os

Paradis, et.al., JOURNAL OF APPLIED PHYSICS 100, 103523 2006

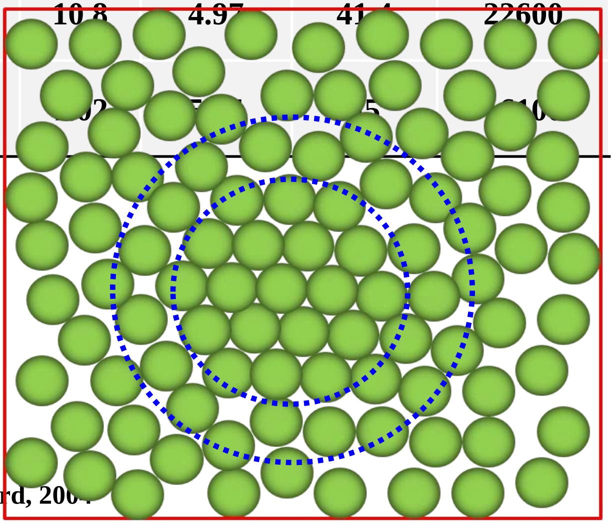


Undercooling:~575 K

FIG. 2. Temperature history for an Os sample (diameter: ~1.76 mm; mass: 64.18 mg) showing heating slightly above the melting temperature (~3340 K), a radiative cooling rate of 1015 K/s, an undercooling of ~575 K, recalescence, and solidification.

Interfacial free energy of some elements

	ΔT_r ΔT_{hyp} (K)	σ [1] (J/m²)	σ (J/m²)	α= σ/ΔH_f	r* (nm)	ρ (g/cm³)	η_m [2] (10^{-3} Pa/s)	C_p (J/mol·K)	ΔH_f [3] (J/mol)
Ti	309 341	0.168	0.141 0.152	0.42 0.454	1.46 1.43	4.11	5.2	42.67	14550
Zr	332 345	0.158	0.154±0.009 0.159±0.010	0.410 0.423	1.54 1.52	6.08	4.67	42.5	19300
Hf	339 339	0.229	0.193±0.012	0.404	1.47	12.24	7.07	60.3	24070
Nb	443 563	0.262	0.258±0.016 0.303±0.024	0.394 0.462	1.33 1.23	7.63	4.94	52.0	29300
Rh	413 546	0.279	0.261±0.018 0.313±0.029	0.439 0.527	1.08 1.19	10.8	4.97	41.4	22600
Fe	195 357	0.269	0.158 0.228	0.33 0.478	1.45 1.15	[illegible]	[illegible]	[illegible]	[illegible]



- Turnbull : α = 0.45 for most metals

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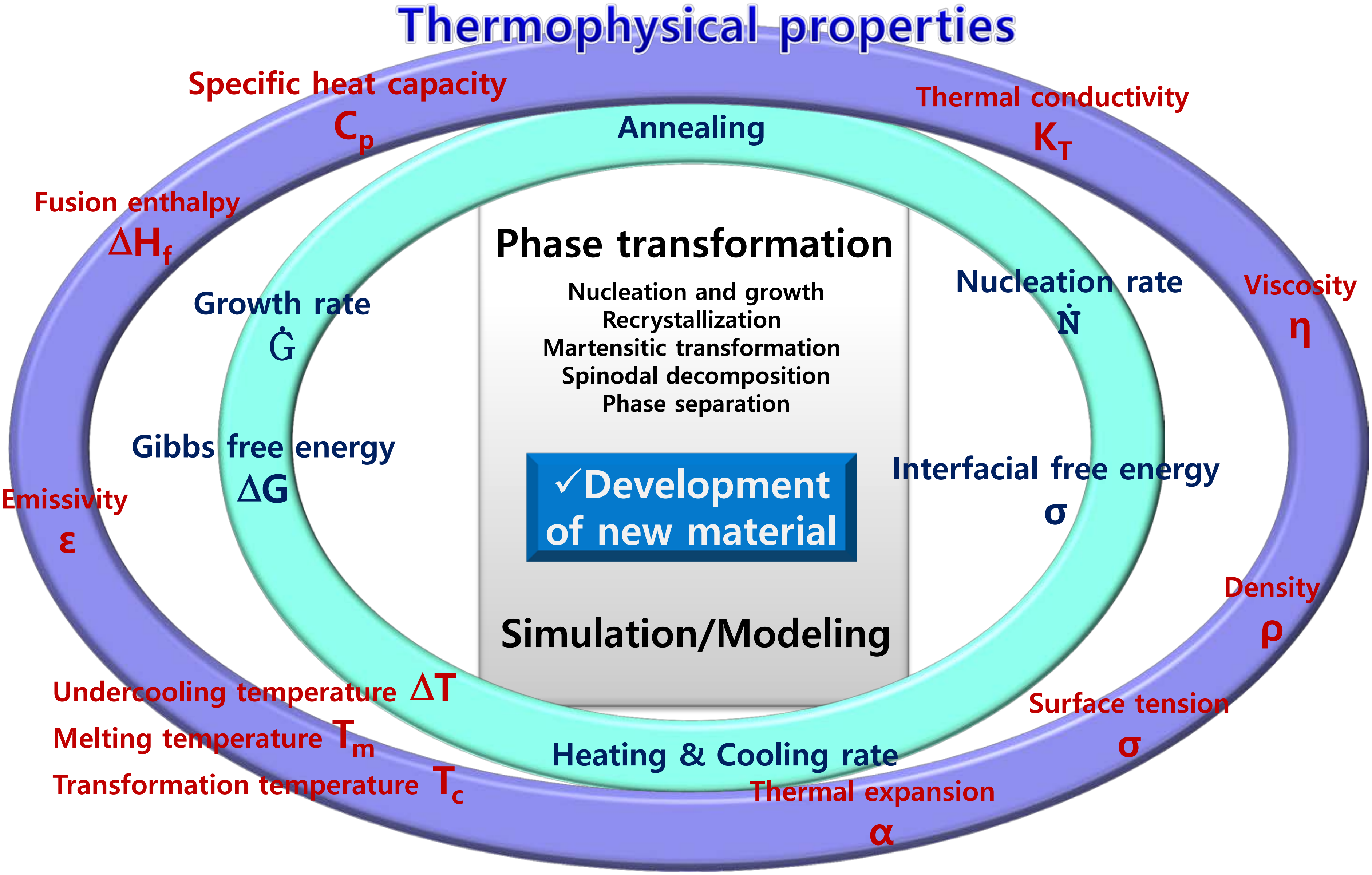
[1] B. Vinet, L. Magnusson, H. Fredriksson, P. J. Desré, *J. Colloid Interf. Sci.* 255 (2002) 363

[2] T. Ishikawa, P.-F. Paradis, J. T. Okada, Y. Watanabe, *Meas. Sci. Technol.* 23 (2012) 025305

[3] W. F. Gale, T. C. Totemeier, in “Smithells Metals Reference Book”, 8th ed. Butterworth-Heinemann, Oxford, 200

Development of extreme condition endurance materials



Thermophysical properties

Specific heat capacity C_p

Annealing

Thermal conductivity K_T

Fusion enthalpy ΔH_f

Growth rate $\dot{G}$

Phase transformation

Nucleation and growth
Recrystallization
Martensitic transformation
Spinodal decomposition
Phase separation

Nucleation rate $\dot{N}$

Viscosity η

Gibbs free energy ΔG

✓Development of new material

Interfacial free energy σ

Emissivity ε

Density ρ

Simulation/Modeling

Undercooling temperature ΔT
Melting temperature T_m
Transformation temperature T_c

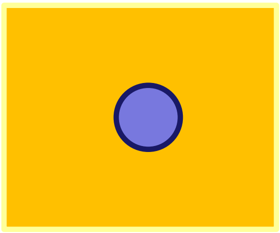
Surface tension σ

Heating & Cooling rate

Thermal expansion α

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

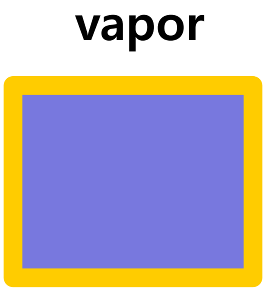
- Interfacial energy ⇨ ΔT_N

No superheating required!

- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

Melting: Liquid ← Solid



Incentive Homework 2:
superheating이 일어나는 경우 정리 **PPT 3 page** 이내

Nucleation

*** *Homogeneous Nucleation of crystal in supercooled liquid***

→ Well-defined by Turnbull and his coworker theoretically / experimentally.

*** *Heterogeneous Nucleation***

→ detailed theory ~ less satisfactory

Nucleation ~ a function of the temperature in liquids that are not in motion

but In practice, liquids are often exposed to dynamic conditions.

< Two main type of dynamically stimulated nucleation >

1) completely metastable supercooled liquid containing no crystal
   → Nucleation by friction, ultrasonic vibration, pressure pulse , etc.

2) A phenomenon that the # of crystals is greatly increased by dynamic methods in solidifying liquid → It is difficult to conclude that it is not due to the fragmentation of pre-existing crystals.

*** *Dynamically Stimulated Nucleation***

→ very poor understood

Chapter 4. microscopic Heat Flow Considerations

4.1 Qualitative Observation

Solidification: Liquid → Solid

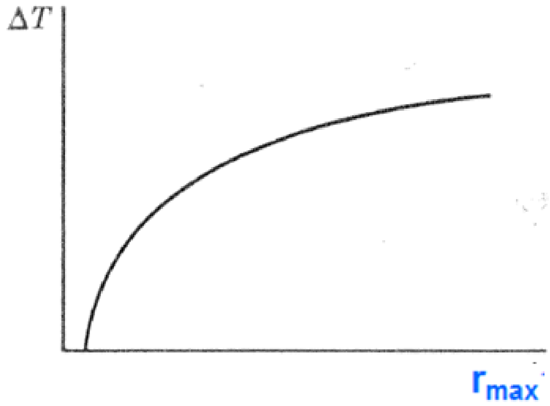
Presence of "Metastable supercooled liquid"

1) Atomic consideration

→ If it is curved, "escape angle" changes with curvature.

$\therefore T_{E,\ \text{small crystal}} < T_{E,\ \text{large crystal}}$

Thus, at any temperature below T_E, there is a radius of curvature at which the rates of melting and of freezing are equal. = critical radius r*



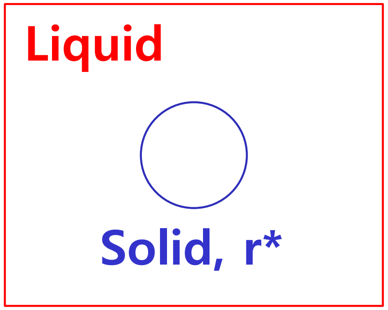
2) Thermodynamic treatment of equilibrium access a curved interface

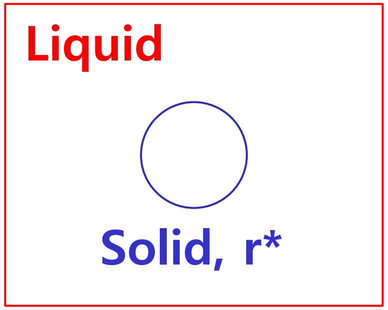
Extra pressure ΔP due to curvature

For incompressible solid,

$$\boxed{\frac{L\Delta T}{T_E} = \frac{2\gamma_{SL}}{r^*}, \quad \text{or} \quad r^* = \frac{2\sigma T_E}{L\Delta T}}$$

ΔH, ΔS : independent of temperature





Liquid

Solid, r*

$T_E + \Delta T$ (-) 면, $R_M < R_F \rightarrow r \uparrow$

$\rightarrow T_E \rightarrow T_E'' \uparrow \rightarrow \Delta T$ (-) $\uparrow \rightarrow R_M \ll R_F$

For small departures from equilibrium, the rate is approximately proportional to the departure (ΔT); however, the actual rate depends upon the crystallographic orientation of the interface.

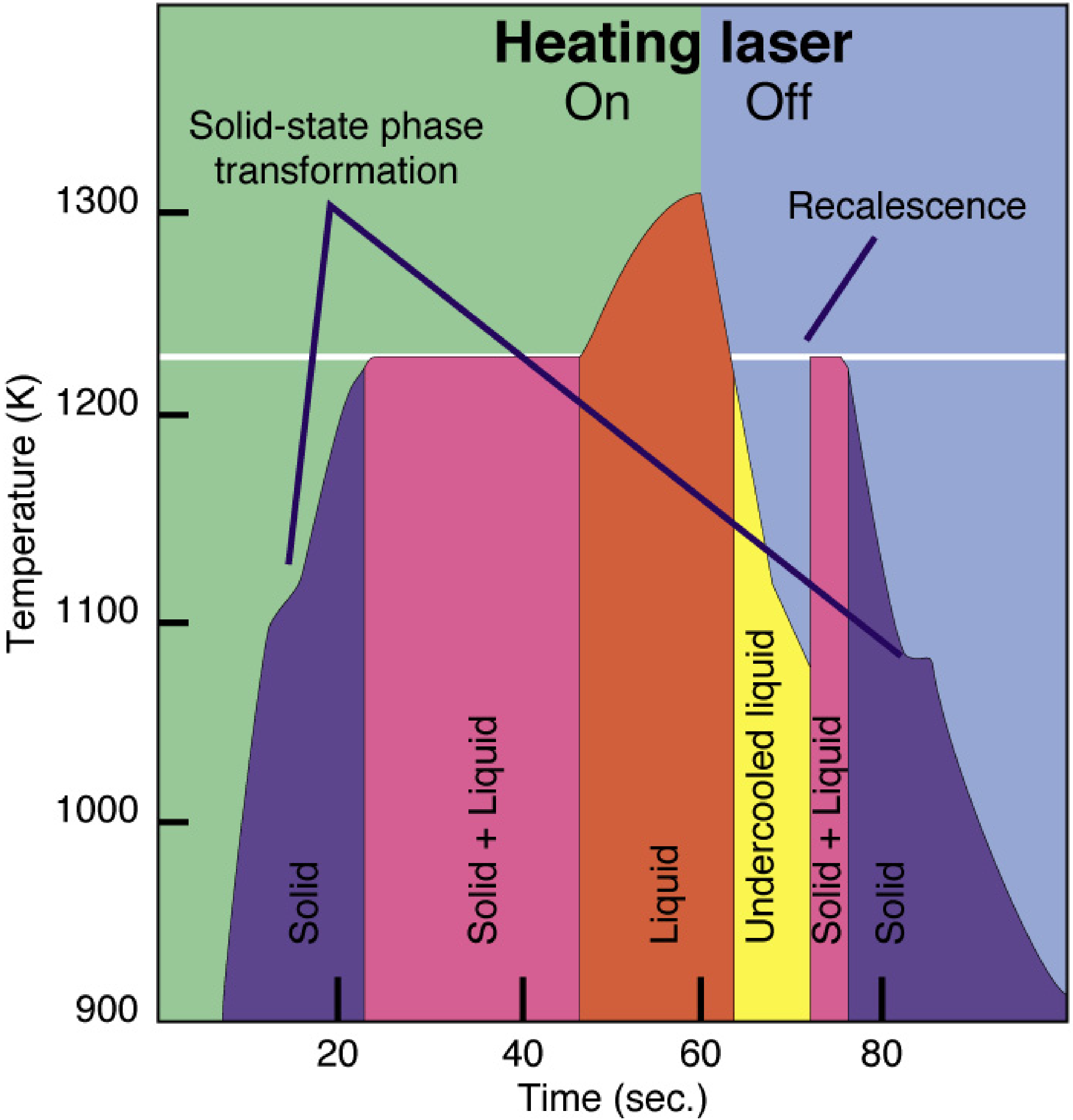
It should be emphasized that the foregoing remarks relate to the actual temperature of the interface itself; this may be different from the temperature of the liquid or solid at even a short distance from the interface because of the “**latent heat of fusion**” that is generated at the interface during solidification or is absorbed there during melting.

Who can explain the clear difference between two movies?

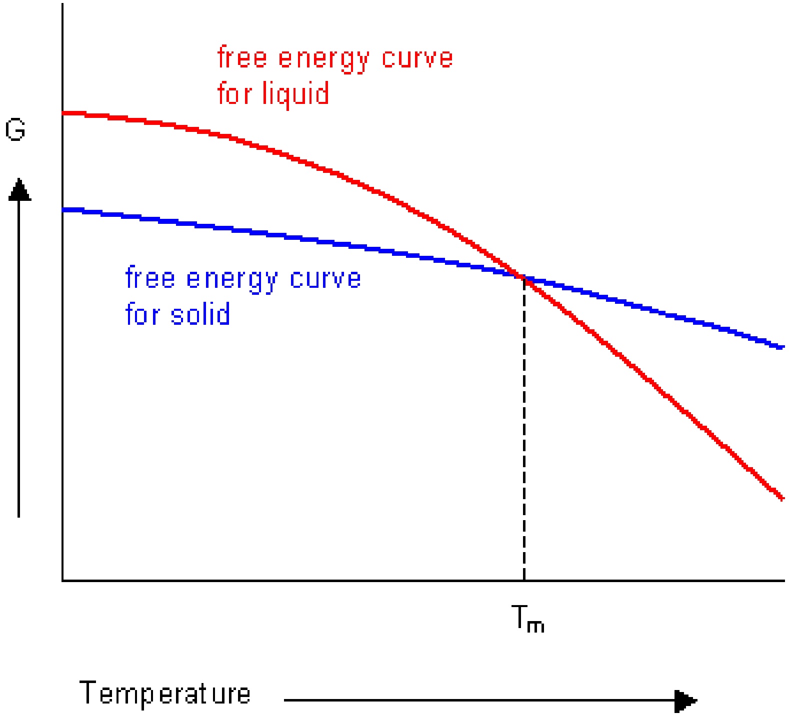
ZrCuAl alloy with non-purified Zr

ZrCuAl alloy with purified Zr

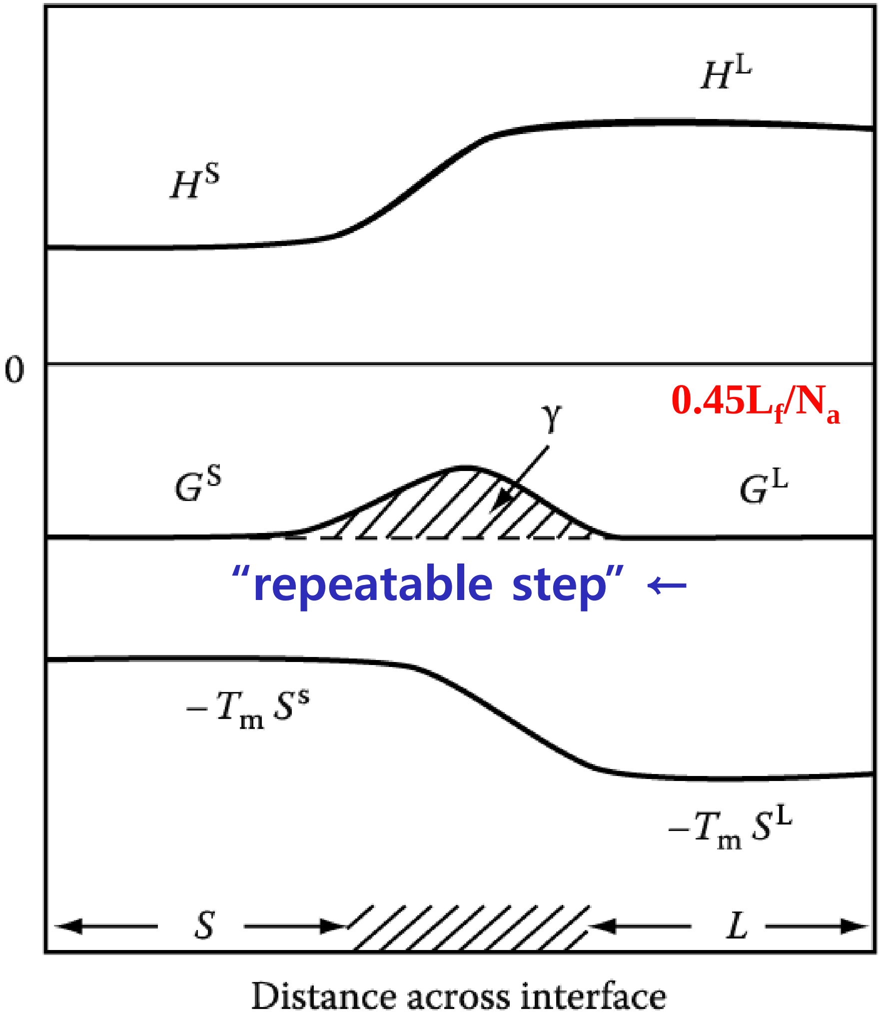
Melting and Freezing Using ESL



* Broken bond model → calculation of the E of solid/ liquid interface



at equilibrium melting temp.



$0.45L_f/N_a$

"repeatable step" ←

Showing the origin of the solid/ liquid interfacial energy, γ

$\gamma_{SL} \approx 0.45\ \gamma_b$ (= $0.15\gamma_{SV}$)
for the most metals

$\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$

$T_{interface} < T_E$ → solidification ↑ → latent heat ↑ → ΔT ↓

The “removal of latent heat” therefore controls the rate at which solidification can continue, and the interface temperature adjusts itself so that it corresponds to the rate of solidification determined by the externally imposed thermal conditions.

The local rate of growth at any point on the surface therefore depends on the thermal conditions and on the orientation of the surface, since this influences the relationship between temperature and rate of growth.

The interplay of the anisotropy of growth rate with the effects of the geometry of the surface on local heat flow is responsible for the very complicated morphology that may occur during solidification.