Mo, Nb-based refractory alloy for ultra-high temperature applications

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초내열 신합금 개발의 필요성

원자력 발전의 안전 문제 제고

신에너지원 셰일 가스의 등장

가스 복합 화력 발전 원리

- 가스 복합 화력 발전 수요 증가

→ 전세계적 가스 발전소 신설 증대

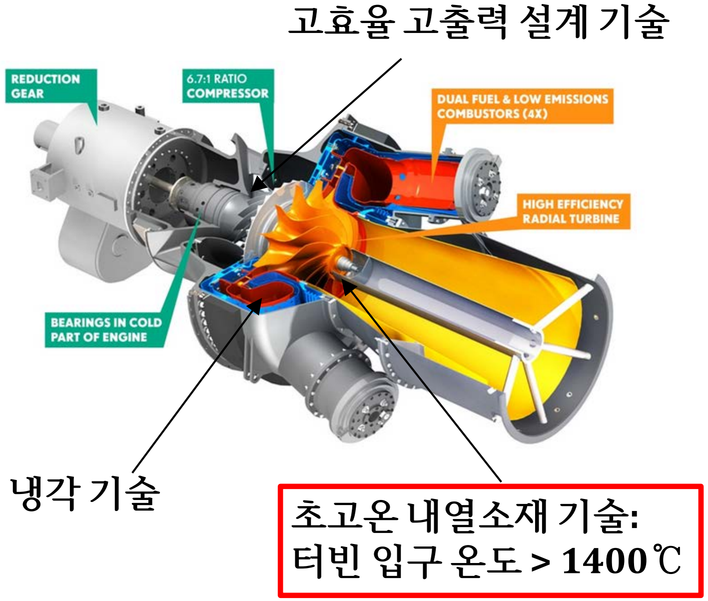
→ 고효율의 화력 발전 기술 필요성 증가

(복합 화력 발전 효율 60% 이상)

초내열 신합금 개발의 필요성

주요 가스 터빈 기술

Target: 가스 터빈 효율 > 40%



주요 가스 터빈 기술

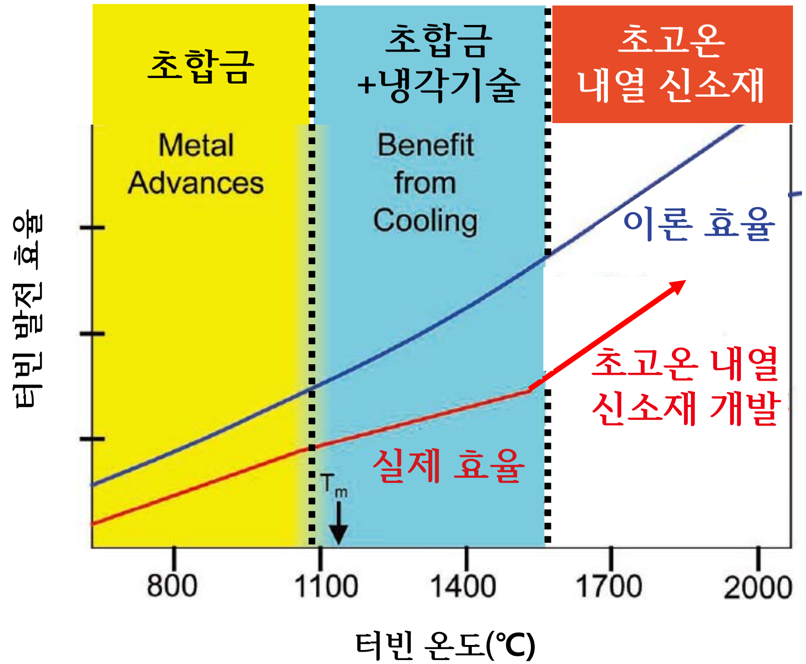


표 2 복합화력발전용 가스터빈 사양

Class	최초출시	터빈입구 온도	효율		출력(1:1)	
			단순	복합	단순	복합
D급	1980년대	1100℃	35%급	50%급	110MW	160MW
F급	1990년대	1300℃	37%급	55%급	180MW	280MW
G급	2000년대	1400℃	38%급	58%급	280MW	390MW
H급	2010년대	1500℃	39%급	60%급	320MW	460MW

- **Ni계 초합금의 가용 온도(1100℃)의 한계**

  → 냉각 기술로 극복, **but** 엔진 효율 감소

- 초고온 내열 신소재 개발

  → 냉각 기술 완화 및 가스 터빈 온도 상승

  → 가스 터빈 발전 효율 상승

Candidates: Mo, Nb-based refractory alloy

Candidate Elements for High temperature

	W	Re	Ta	Mo	Nb
Melting point	3407	3180	3014	**2617**	**2467**
Density	19.3	21.0	16.6	**10.2**	**8.6**
Tensile strength (GPa, 20°C)	0.7-3.5	0.7-2.0	0.2-0.5	0.7-1.4	0.4-0.7
Tensile strength (GPa, 1000°C)	0.3-0.5	0.4-0.7	0.1	0.1-0.2	0.04-0.1

Ni : 8.9 g/cm^3

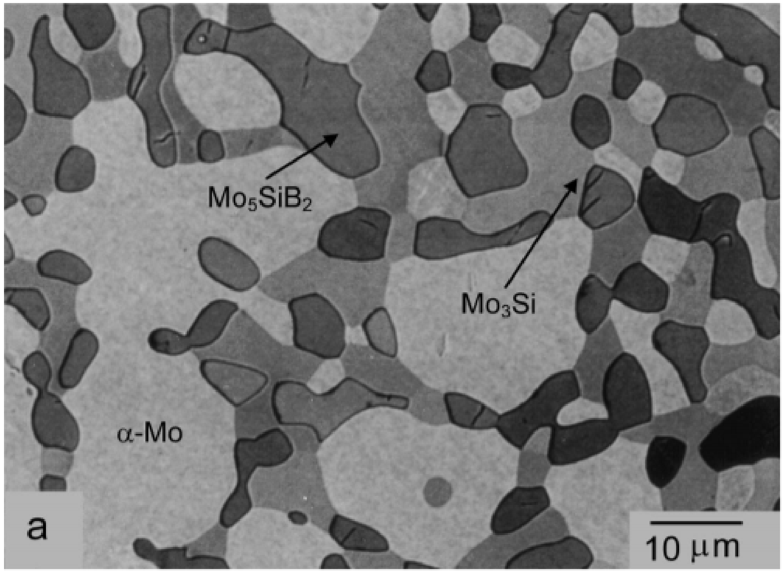
- **Nb, Mo: High melting point(~2500 ℃),**
  lower density than other refractory elements(Ta, W, Re..)

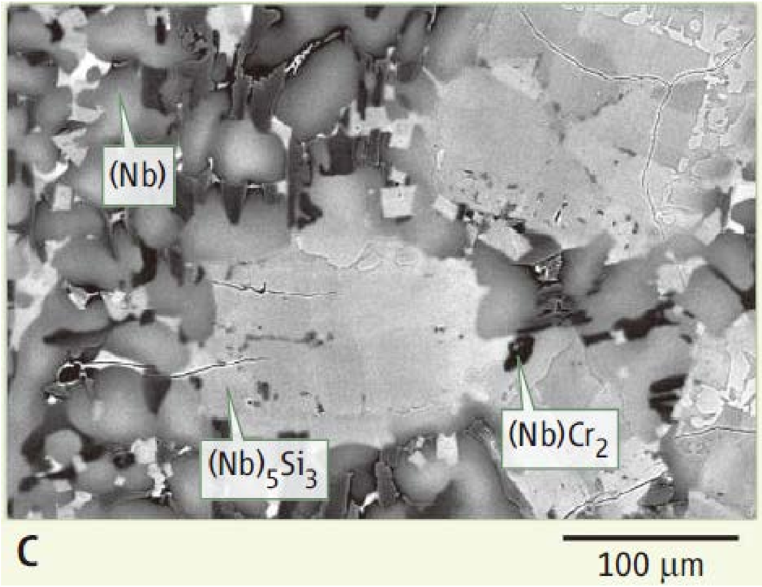
  → Good candidates for gas turbine application

- **Poor oxidation resistance → alloying with Si → Metal-Silicide composites**

Candidates: Mo, Nb-based refractory alloy

Mo – Si – B | **Nb – Si(– Ti – Hf – Cr – Al)**





- **Mo: Alloying with Si, B**

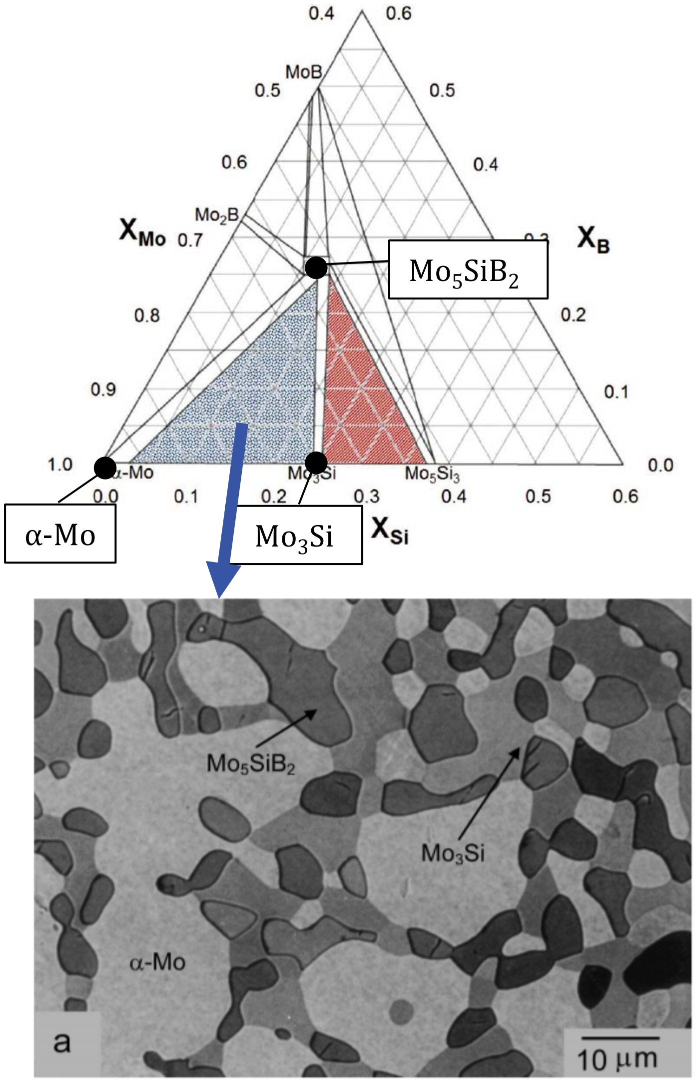
  → Mo + Mo_3Si(A15) + Mo_5SiB_2 (T2) 3phase composites

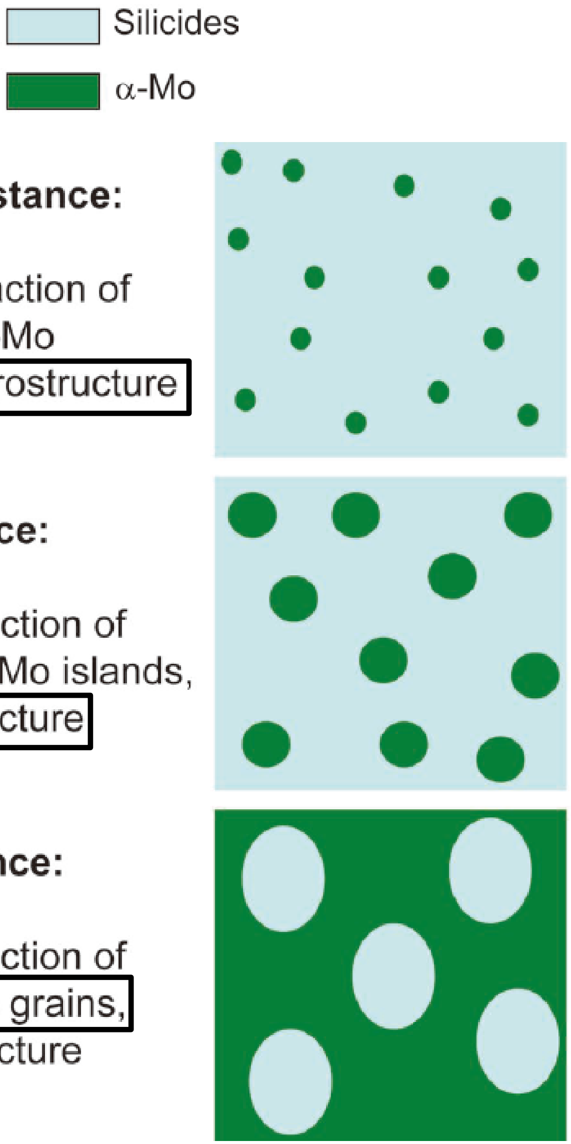
- **Nb: Based on Nb-Si (Si: 12 ~ 20 at.%), alloying with Ti, Hf, Cr…**

  → Nb + TM_5Si_3($D8_8$ or β) + NbCr2 (Laves)

- **BCC solid solution: Ductility** ⟷ • **Silicide: Oxidation resistance, Creep resistance**

Mo – Si – B phase diagram





Oxidation Resistance:

Small volume fraction of discontinuous α-Mo islands, fine microstructure

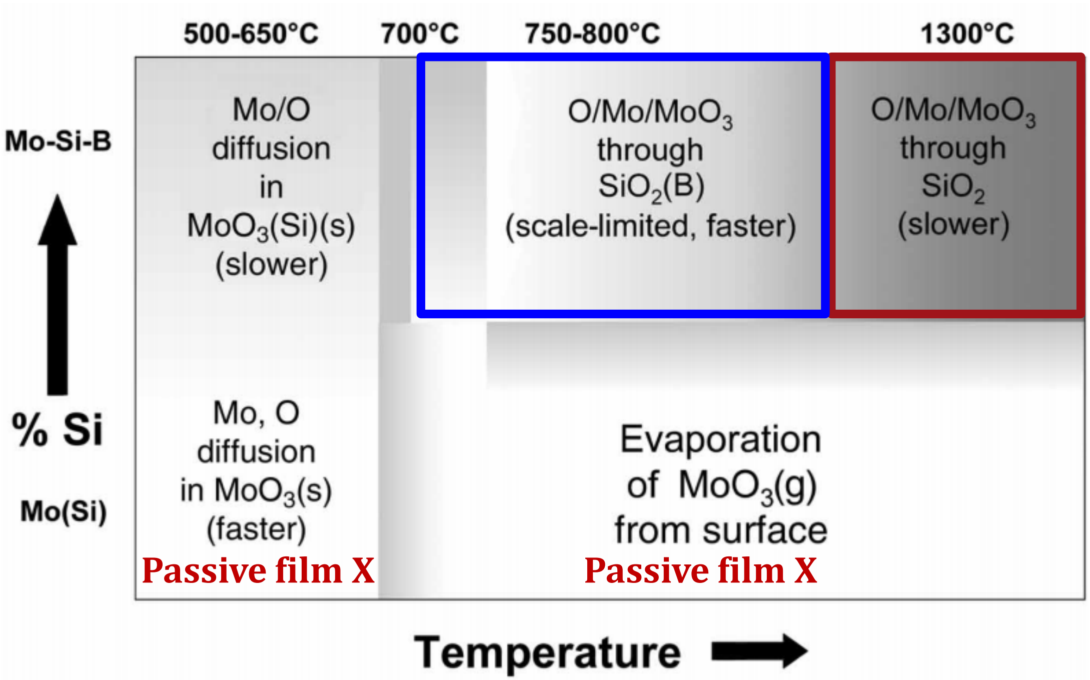
Creep Resistance:

Small volume fraction of discontinuous α-Mo islands, coarse microstructure

Damage Tolerance:

Large volume fraction of continuous α-Mo grains, coarse microstructure

Passive film for oxidation resistance



MRS bulletin 28.09 (2003): 639-645.

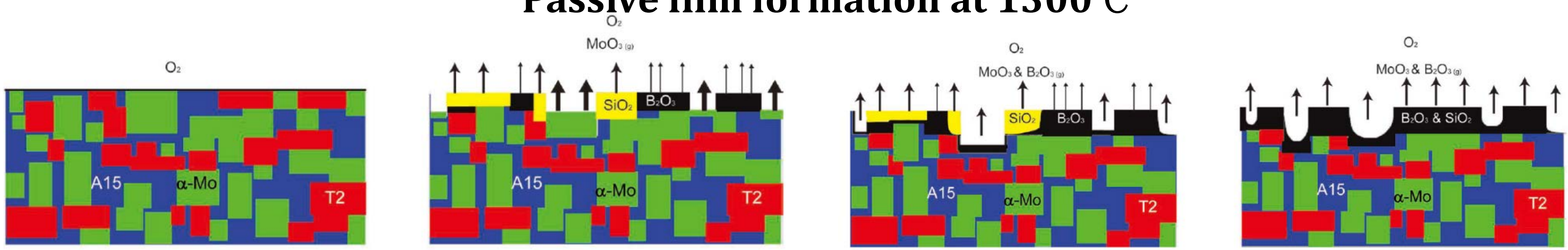
Oxdiation rate

700~1000℃ > 1300℃↑

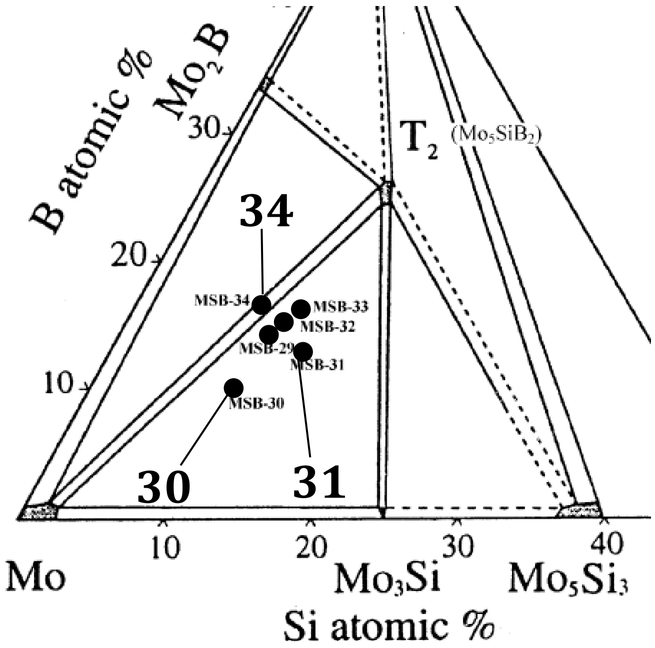
MoO_3 vs passive film(silica)

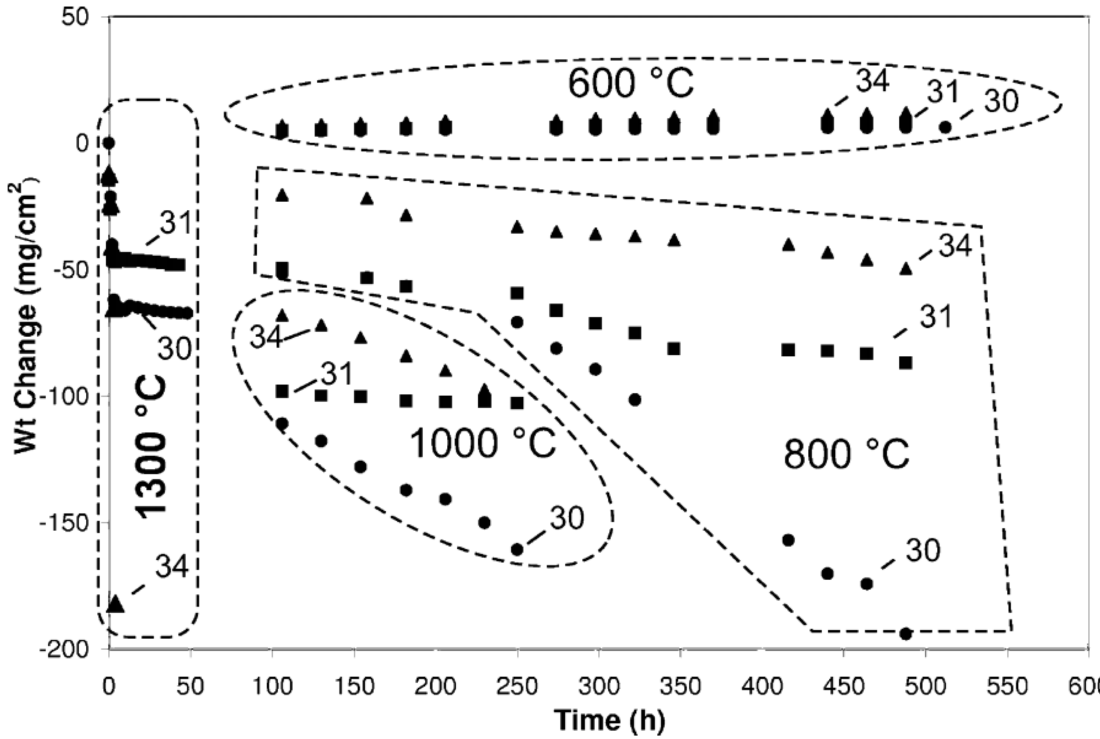
At low T, energy to form passive film is not enough

Passive film formation at 1300℃



Passive film for oxidation resistance



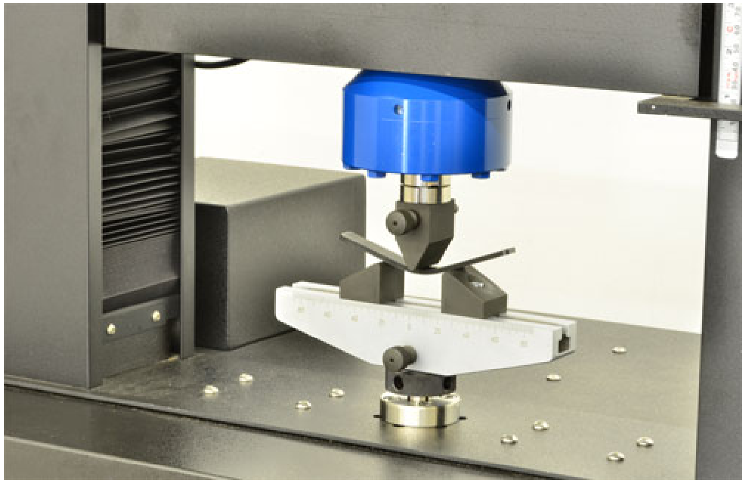


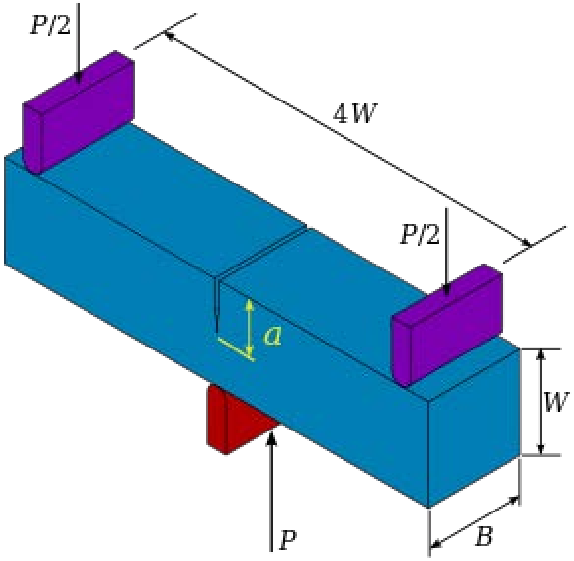
Materials Science and Engineering: A 344.1 (2003): 328-339.

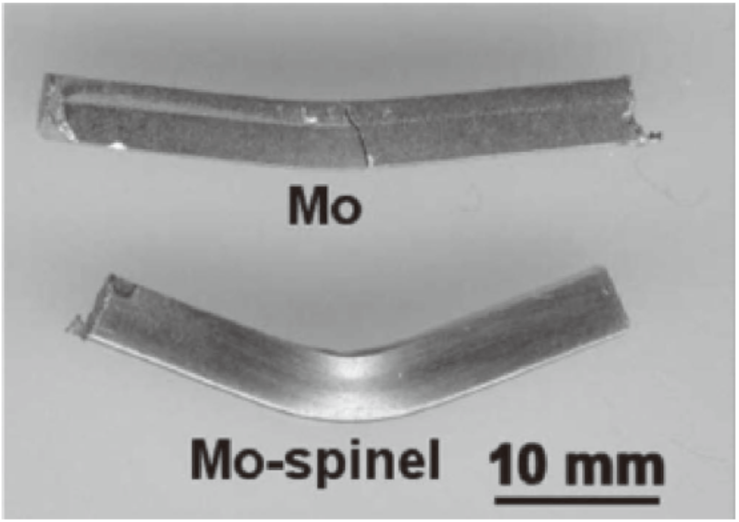
- **Poor oxidation resistance of #30: Large Mo volume fraction**
- **Best performance #31: T2 dendrite + eutectic**
- **Silicides + Si, B % of intermetallic compounds + microstructure**

Fracture toughness of Mo-Si-B alloy

3-point bending test







$$K_I = \frac{4P}{B}\sqrt{\frac{\pi}{W}}\left[1.6\left(\frac{a}{W}\right)^{1/2} - 2.6\left(\frac{a}{W}\right)^{3/2} + 12.3\left(\frac{a}{W}\right)^{5/2} - 21.2\left(\frac{a}{W}\right)^{7/2} + 21.8\left(\frac{a}{W}\right)^{9/2}\right]$$

- **3-point bending test is used to measure fracture toughness at room temperature**

Fracture toughness of Mo-Si-B alloy

Material	Processing Technique	α-Mo vol.%	α-Mo Morphology	Test Geometry	Fracture Toughness, K_Q, [MPa√m]
Mo-4.2Si-1.1B	Cast and Annealed (1600 °C/24 h)	42	Discontinuous	3PB, Chevron-notched	9.0
Mo-4.2Si-1.1B-1.1Zr	Cast and Annealed (1600 °C/24 h)	42	Discontinuous	3PB, Chevron-notched	12.4
Mo-4.2Si-1.1B-1.7Zr	Cast and Annealed (1600 °C/24 h)	42	Discontinuous	3PB, Chevron-notched	13.5
Mo-4.2Si-1.1B-3.5Zr	Cast and Annealed (1600 °C/24 h)	42	Discontinuous	3PB, Chevron-notched	12.6
Mo-4.2Si-1.1B-0.9Ti	Cast and Annealed (1600 °C/24 h)	42	Discontinuous	3PB, Chevron-notched	10.0
Mo-4.2Si-1.1B	Arc-cast	38	Discontinuous	DC(T) 25 °C	7.2
Mo-4.2Si-1.1B	Arc-cast	38	Discontinuous	DC(T) 25 °C	7.8#
Mo-6.1Si-1.2B	HIPped Powder	21	Discontinuous	DC(T) 25 °C	4.1
Mo-6.1Si-1.2B	HIPped Powder	21	Discontinuous	DC(T) 1300 °C	8.1
Mo-6.1Si-1.2B	HIPped Powder (Mo & Mo-20Si-10B (at.%))	21	Discontinuous	DC(T) 25 °C	5.7
Mo-6.1Si-1.2B	HIPped Powder (Mo & Mo-20Si-10B (at.%))	21	Discontinuous	DC(T) 1300 °C	7.5
Mo-6.1Si-1.2B	HIPped Powder (Mo & Mo-20Si-10B (at.%))	21	Discontinuous	DC(T) 1300 °C	7.7#

- **Poor ductility at room temperature attribute to poor toughness**
- **Fracture toughness is effected by morphology of alloy**
  → Large α-Mo fraction, continuous α-Mo is favorable to toughness
- **Target: K > 20 MPam$^{0.5}$**

Intrinsic toughening

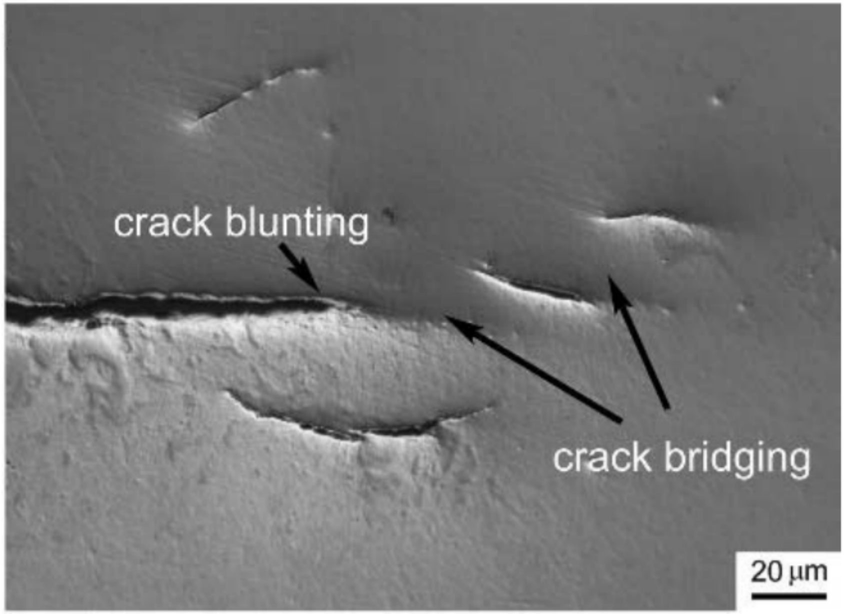
Extrinsic toughening

Crack blunting: sharp crack → blunt crack

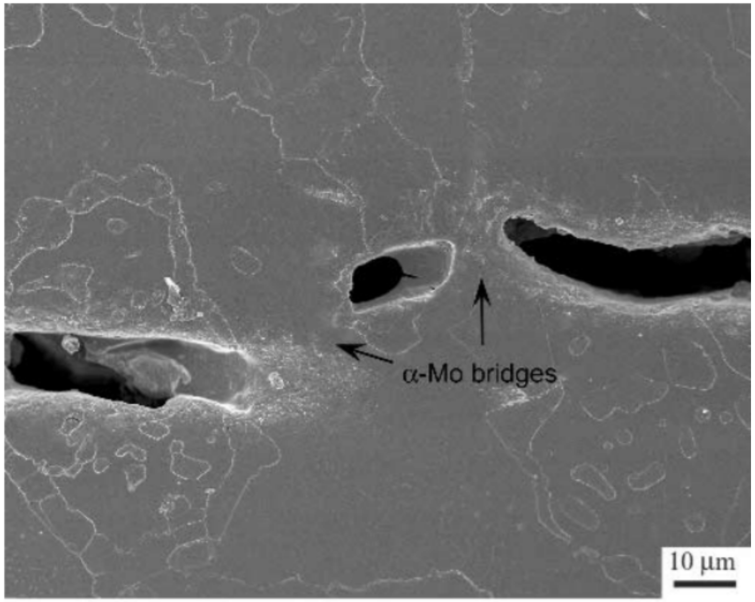
Crack bridging: impede crack propagation

α-Mo ↑↑

Crack blunting



Crack bridging



Kruzic, J. J. et al., *M. M. T. A* 36.9 (2005): 2393-2402.

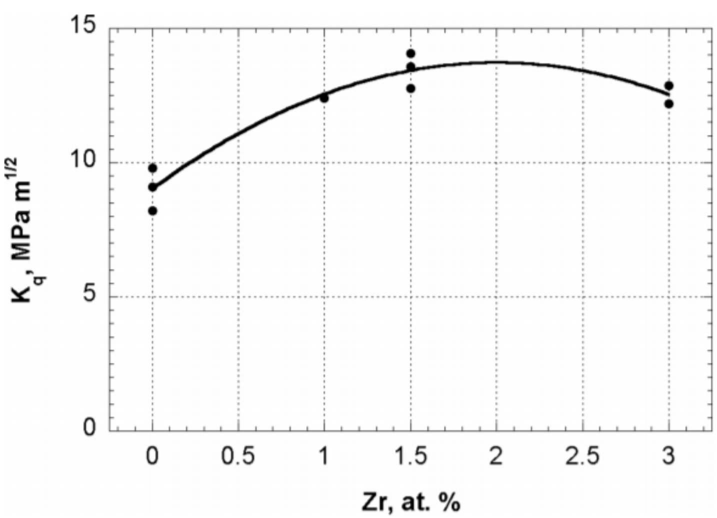
Fracture toughness of Mo-Si-B alloy

Intrinsic toughening

Mo-12Si-8.5B-Zr (at.%)

Table III. Fracture Toughness K_q of Mo-Si-B Alloys Microalloyed with Zr

Nominal Composition At. Pct	Area of Triangle Broken during Test, mm^2	Absorbed Energy, mJ	G, J/m^2	K_q, MPa$\sqrt{m}$	K_q, MPa$\sqrt{m}$, Average ± Standard Deviation
Mo-12Si-8.5B	2.94	0.68	231	9.1	9.0 ± 0.8
Mo-12Si-8.5B	2.88	0.775	267	9.8	
Mo-12Si-8.5B	3.19	0.603	189	8.2	
Mo-12Si-8.5B-1Zr	2.82	1.09	432	12.4	
Mo-12Si-8.5B-1.5Zr	3.05	1.575	516	13.6	13.5 ± 0.7
Mo-12Si-8.5B-1.5Zr	2.89	1.32	457	12.8	
Mo-12Si-8.5B-1.5Zr	3.48	1.93	555	14.1	
Mo-12Si-8.5B-3Zr	2.54	1.284	466	12.9	12.6 ± 0.5
Mo-12Si-8.5B-3Zr	2.76	1.149	416	12.2	



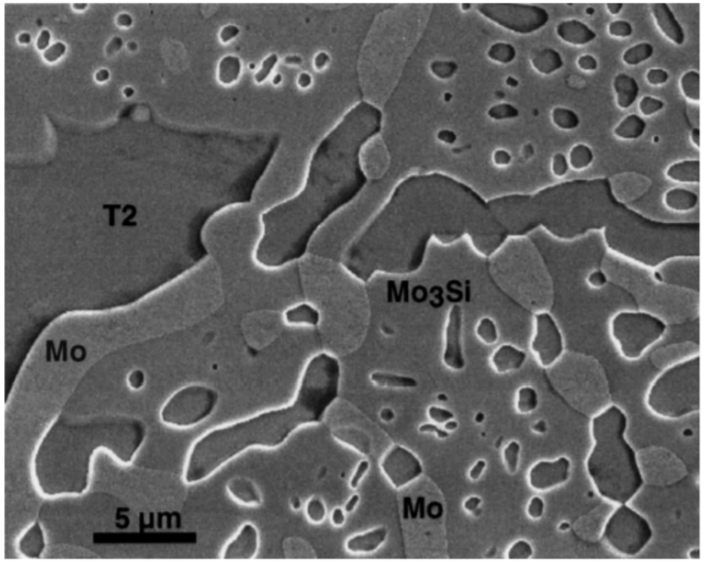
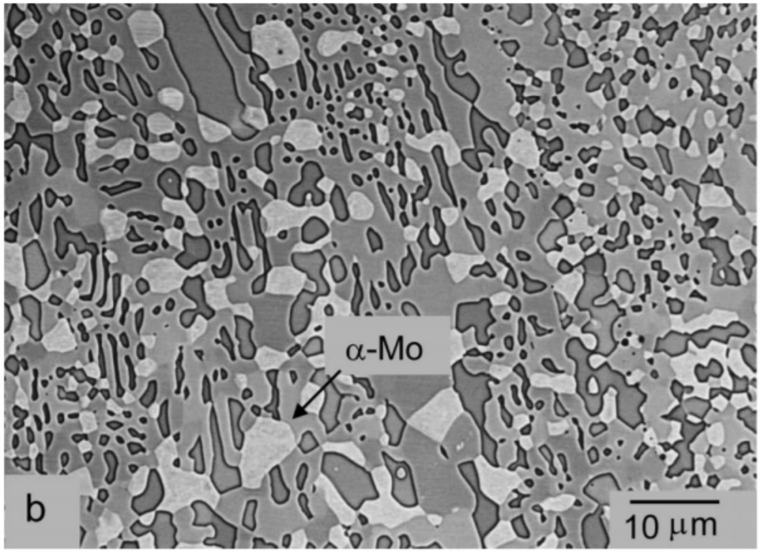
Schneibel, J. H., et al. M. M. T. *A* 36.3 (2005): 525-531.

- **Ductility α-Mo is affected by interstitial atoms, especially, C/O ratio**
- **Addition of Ti and Zr**
  → getter C and O → control ductility of α-Mo

Fracture toughness of Mo-Si-B alloy

Extrinsic toughening

Mo-4.2Si-1.1B (wt.%)

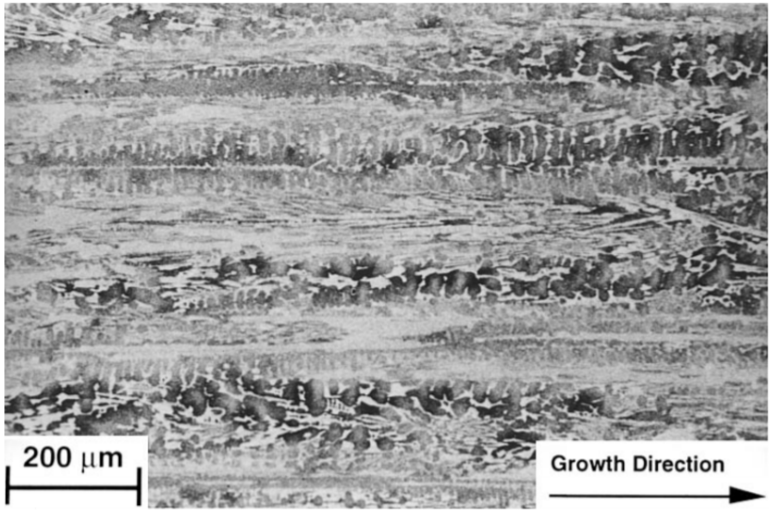
Arc-melted	**HIPed with powder**
	
Choe et al., M. M. T. A 34.2 (2003): 225-239.	Schneibel, et al. Intermetallics 9.1 (2001): 25-31.
K_{IC} = 7.2 MPam$^{0.5}$	K_{IC} = 14.8 MPam$^{0.5}$

- **Mo-4.2Si-1.1B (wt.%): α-Mo volume fraction: 38%**
- **Continuous α-Mo increase fracture toughness extrinsically**

MASC(Metal And Silicide Composite)

Nb-25Ti-8Hf-2Cr-2Al-16Si (at%)

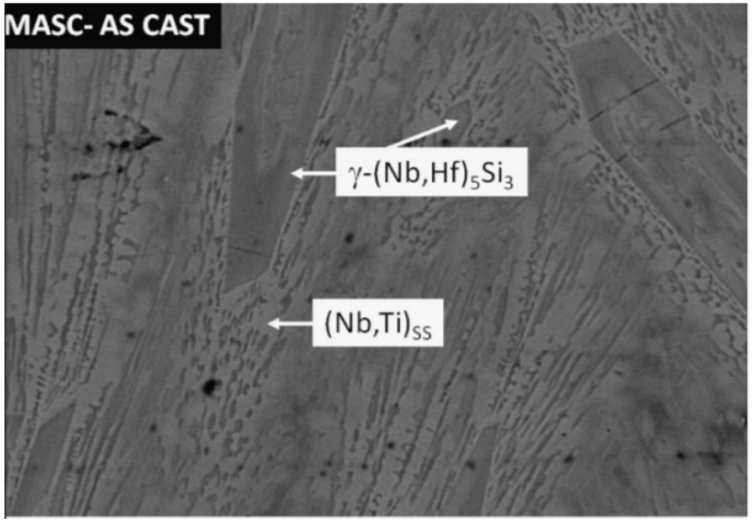
Directionally solidified



Bewlay, B. P., M. R. Jackson, and H. A. Lipsitt. MSE A 27.12 (1996): 3801-3808.

BCC + $(Ti,Hf,Nb)_3Si$ + $(Ti,Hf,Nb)_5Si_3$ $D8_8$

As-cast



Mathieu, S., et al. Corrosion science 60 (2012): 181-192.

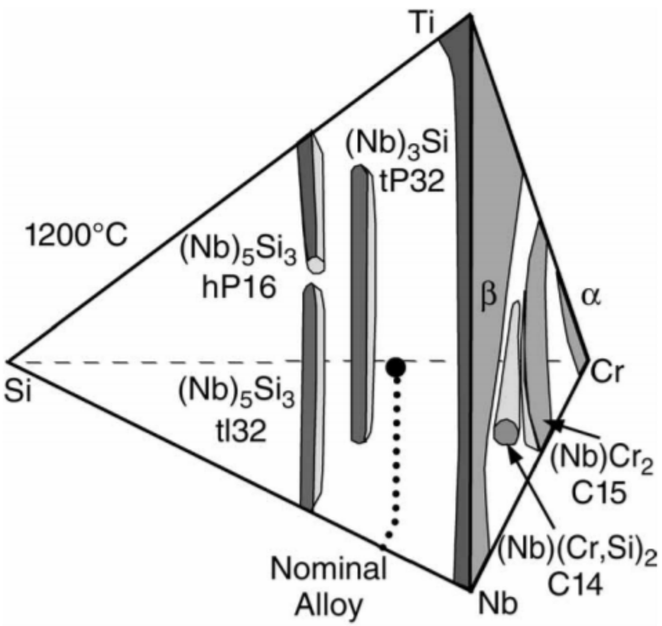
BCC + $(Ti,Hf,Nb)_5Si_3$ $D8_8$

- **Based on Nb-16Si (at%) Ti, Hf, Cr, Al were added to improve oxidation resistance**
- **High fracture toughness(K_{IC} = 19 ~ 22MPam$^{0.5}$)**
- **Patented by General Electronics(US Patent 5942055, 1999)**

Nb-Si alloy: MASC

Table I: Target Chemistries of the Selected Experimental Alloys (at.%).

Alloy	Nb	Ti	Cr	Fe	Hf	Si	Al	Ge	Sn
1	46.8	22.5	6	3	2	12.5	2	5	1.2
2	44.8	19.5	13	...	2	17.5	2	...	1.2
3	46.8	21.5	9	...	2	17.5	2	...	1.2
4	46.8	22.5	6	3	2	12.5	2	5	1.2

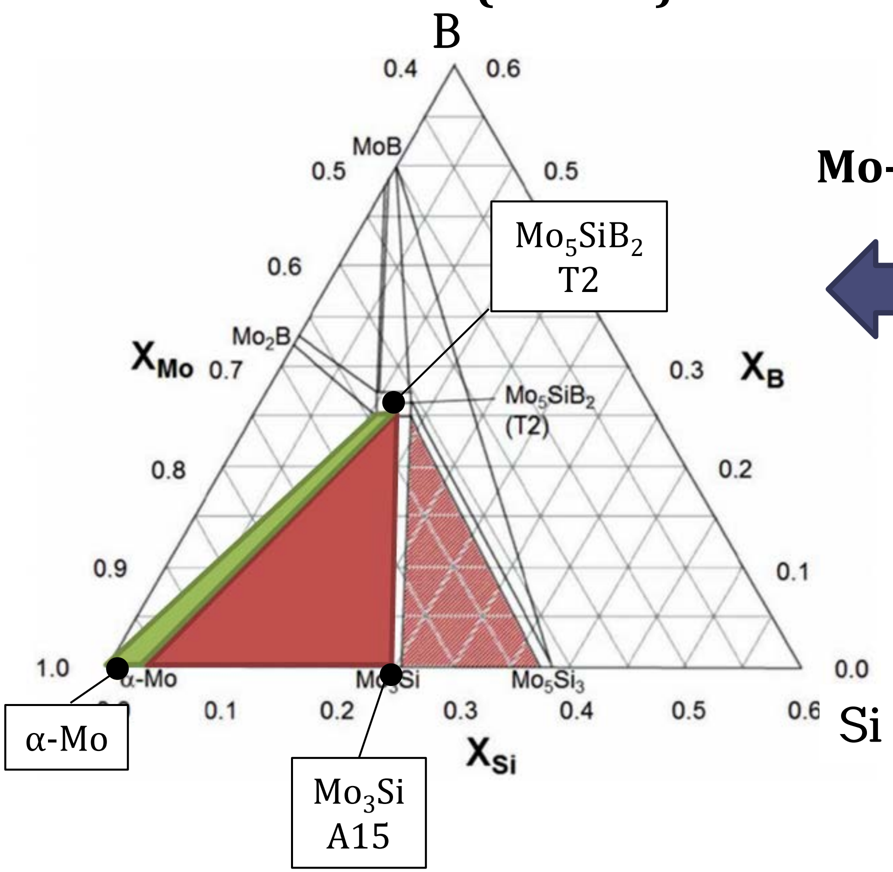


- **Nb:(Ti + Hf) ~ 2: creep resistance**
- **Fe, Cr: Laves $Nb(CrFe)_2$: oxidation resistance**
- **Sn: oxidation resistance at low temperature**
- **Al: oxidation resistance(Al_2O_3)**
- **Ge: additional oxidation resistance**

Bewlay, B. P., et al. MRS bulletin 28.09 (2003): 646-653.

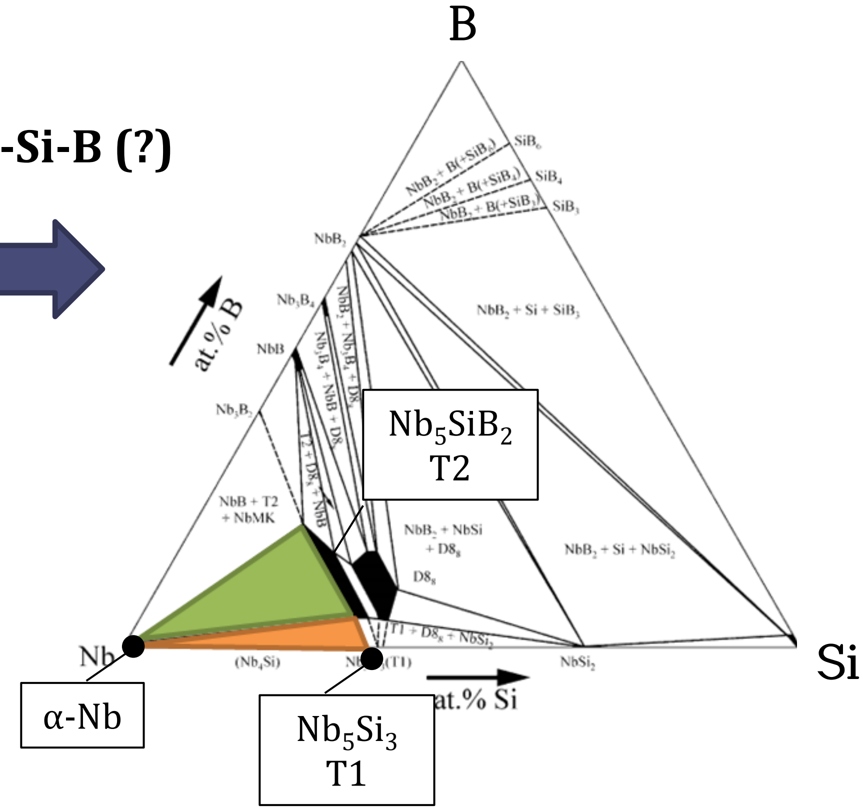
Mo–Nb–Si–B alloy

Mo-Si-B (1600℃)



Mo-Nb-Si-B (?)

Nb-Si-B (1600℃)



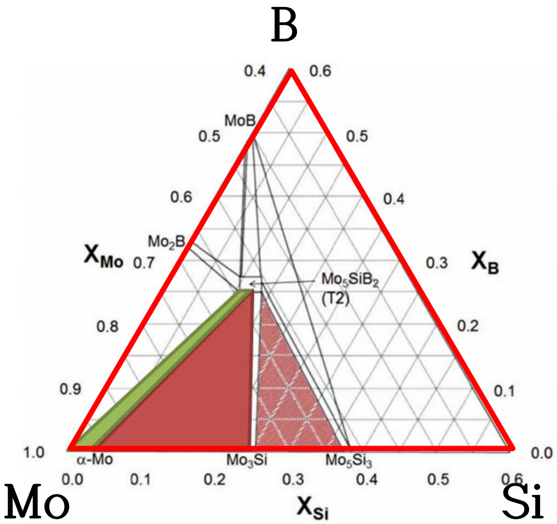
α(BCC) + A15 + T2

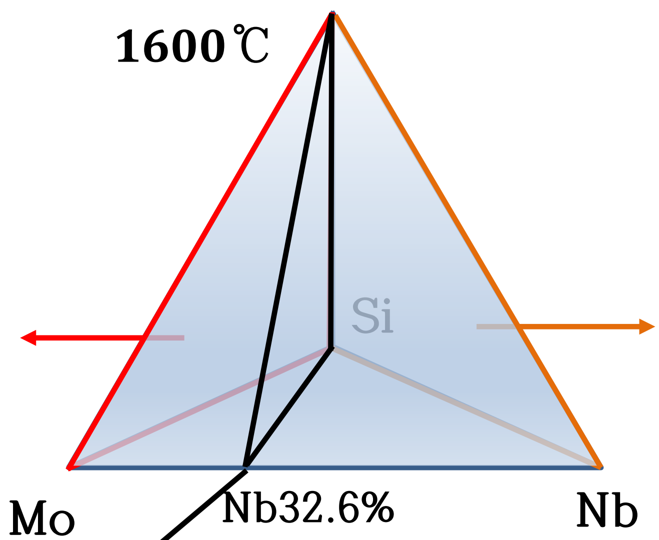
α(BCC) + T2

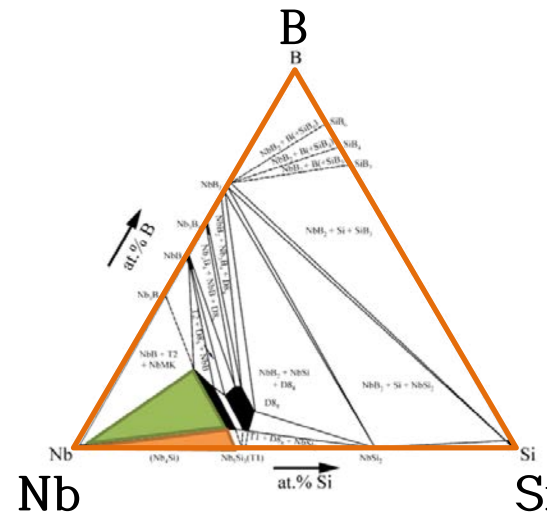
α(BCC) + T1 + T2

- **Mo-Si-B: α(Mo) + A15(Mo_3Si) + T2(Mo_5SiB_2)**
- **Nb-Si-B: α(Nb) + T1(Nb_5Si_3) + T2(Nb_5SiB_2)**

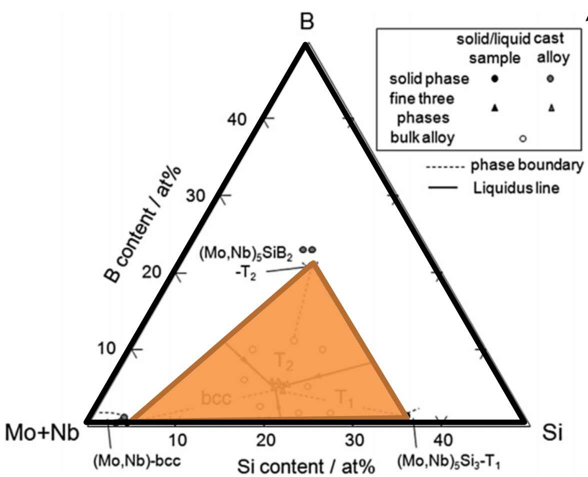
Mo-Nb-Si-B alloy







Mo-32.6Nb-Si-B



Intermetallics 72 (2016): 1-8.

N. Takata et al. (2016):

Mo-32.6Nb-Si-B phase diagram

α-Mo + A15 + T2 3 phase region ↓↓

α-Mo + T1 + T2 3 phase region ↑↑

⬇

(Mo,Nb)-Si-B: much room for further development

Thank you
for kind attention!