Beyond Ni-base Superalloys: Refractory Metal Silicides for Ultrahigh Temperature Structural Applications

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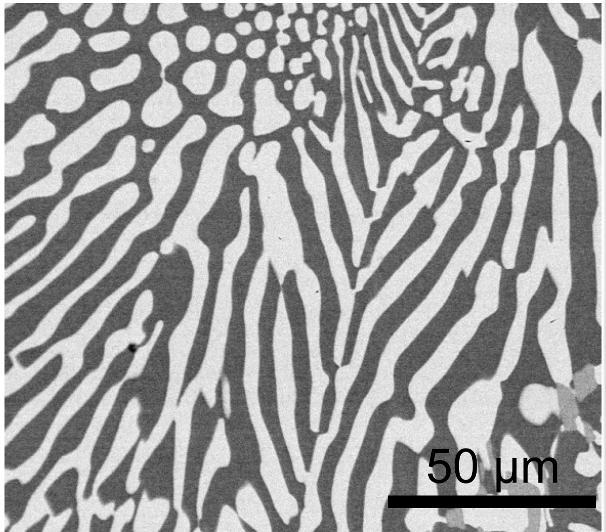

http://ec.europa.eu/research/transport/projects/items/ultmat_en.htm

Outline

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- Motivation for novel RM based high temperature alloys
  - Main Advantage: High Melting Points beyond 2000°C
  - Main (Scientific) Issues: Creep, Oxidation, Density
  - Further Issues: Fatigue, Fracture Toughness, Crack Propagation, Manufacturing, …tbc
- Case study 1: Mo-Si-B(-Ti) alloys
- Case study 2: Nb-Si(-Cr-V) eutectics
- Conclusions
- Acknowledgements

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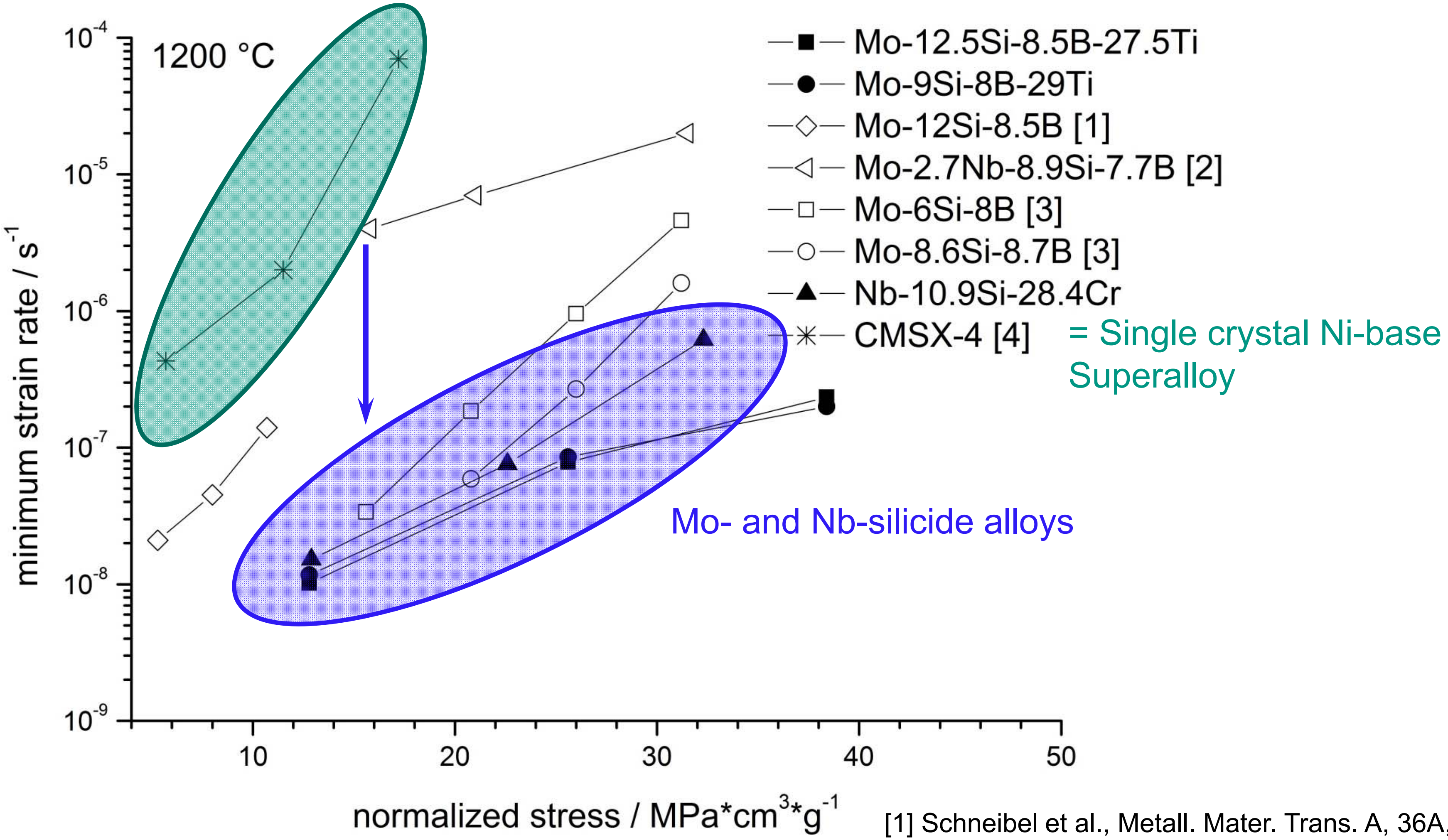
Refractory metal silicides: creep resistance potential



[1] Schneibel et al., Metall. Mater. Trans. A, 36A, 2005
[2] Jèhanno et al., Mater. Sci. Eng. A, 463, 2007
[3] Jain and Kumar, Acta Mater., 58, 2010
[4] Heilmaier et al., JOM 61 (7), 2009

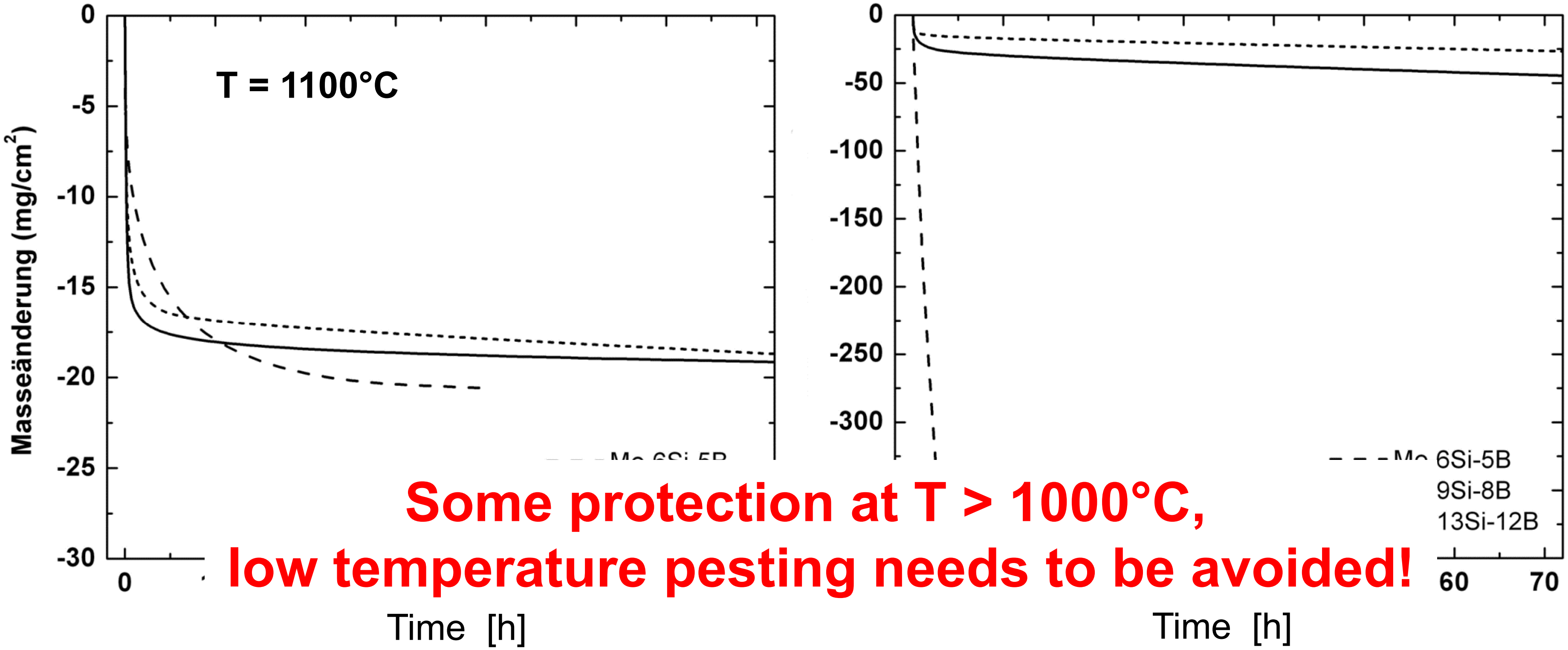
Outline

- Motivation on high temperature alloys
  - Main (Scientific) Issues: Creep, Oxidation, Density

→ **Outstanding creep resistance**

→ **What about oxidation resistance and density?**

The ternary system Mo-Si-B: oxidation in air



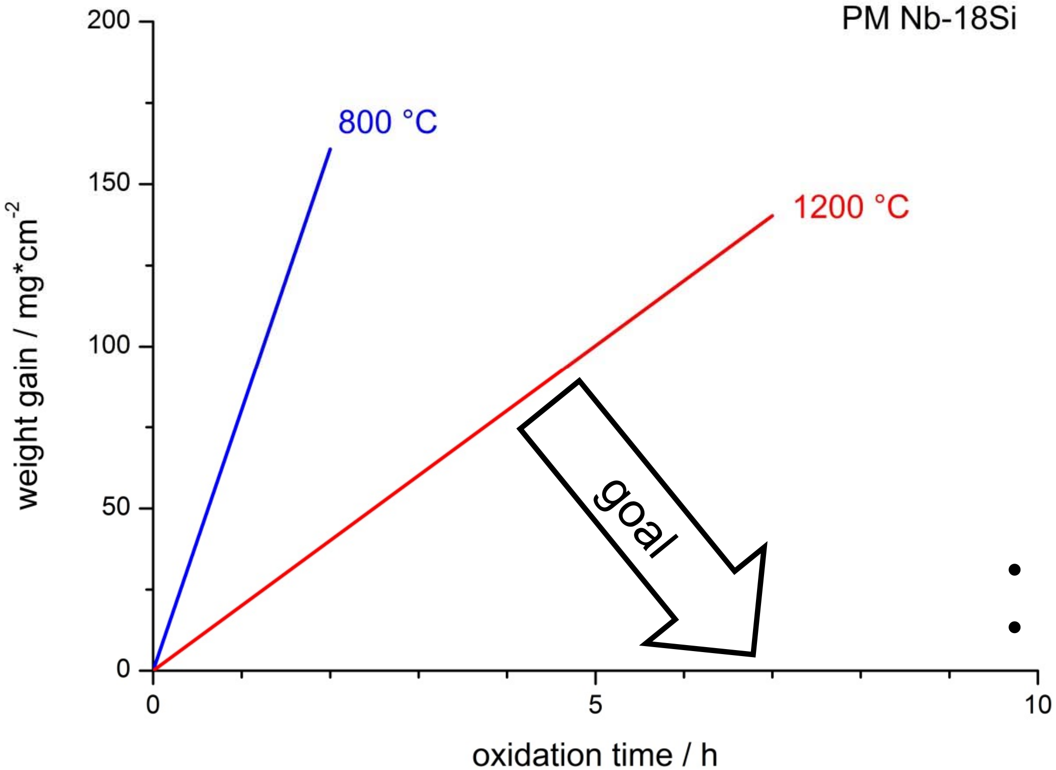
→ Initial weight loss due to MoO_3 sublimation („pesting“), then

→ Protection due to formation of Borosilicate glass layer

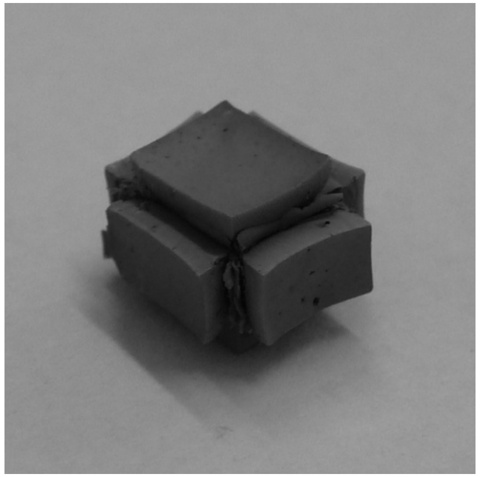
→ dependent on (i) amount of intermetallics and (ii) microstructural fineness

The Binary Nb-Si System

→ **Isothermal high temperature oxidation:** **linear weight gain, no protection**



PM Nb-18Si, 800 °C, 2h



- Rapidly growing
- non protective

Nb_2O_5

Addition of alloying elements necessary - two alloying concepts:

(a) Chromium addition

(b) Vanadium addition

Case study 1: The Mo-Si-B(-Ti) Alloy System

Background: Mo-Si-B ternary phase diagram

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Mo_{ss} + Mo_3Si + T_2

Oxidation / Creep resistance high

Fracture toughness adequate

Optimal Mo_{ss} + T_1 + T_2

Oxidation / Creep resistance very high

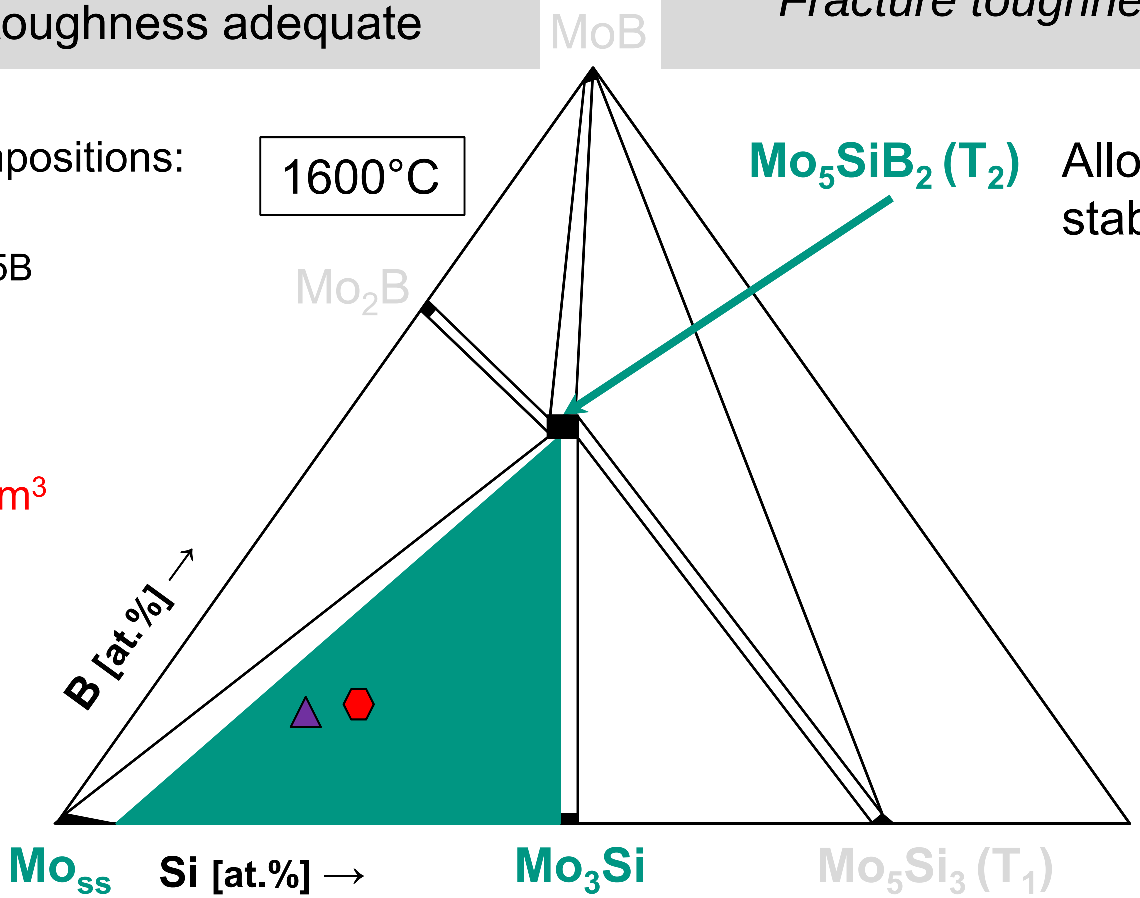
Fracture toughness adequate

Typical alloy compositions:

- Mo-12.5Si-8.5B
- Mo-9Si-8B

$T_m \geq 2000°C$

Density ≈ 9.5 g/cm³



Isothermal section, schematically after Nunes&Perepezko 1997

Alloying elements for stabilising T_1:

W, Ta (ρ↑)

Nb (Ox. ↓)

Ti (ρ ↓)

Why Titanium Alloying in Mo-Si-B Alloys?

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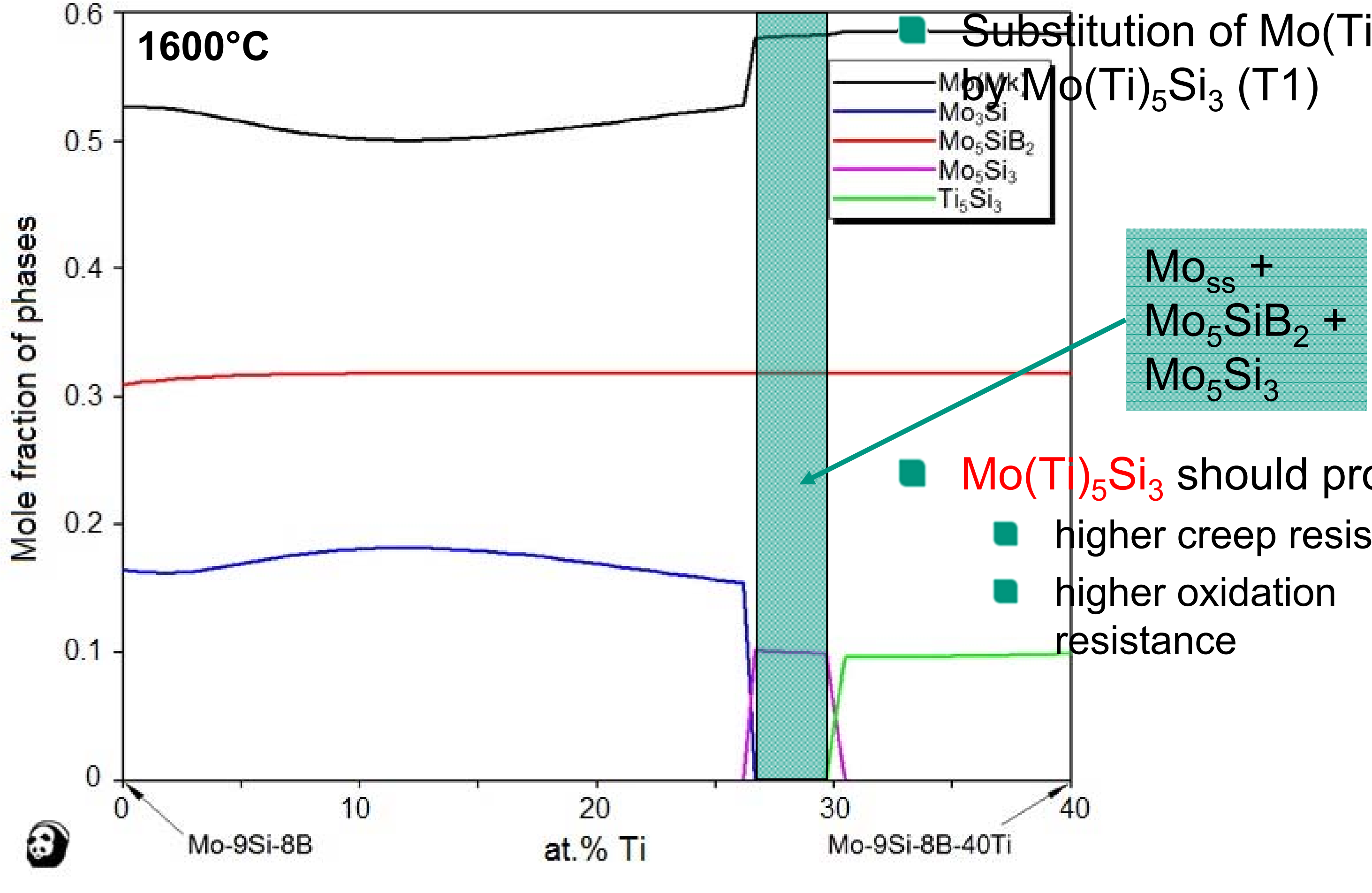

- Substitution of $Mo(Ti)_3Si$ by $Mo(Ti)_5Si_3$ (T1)

- $Mo(Ti)_5Si_3$ should provide:
  - higher creep resistance
  - higher oxidation resistance

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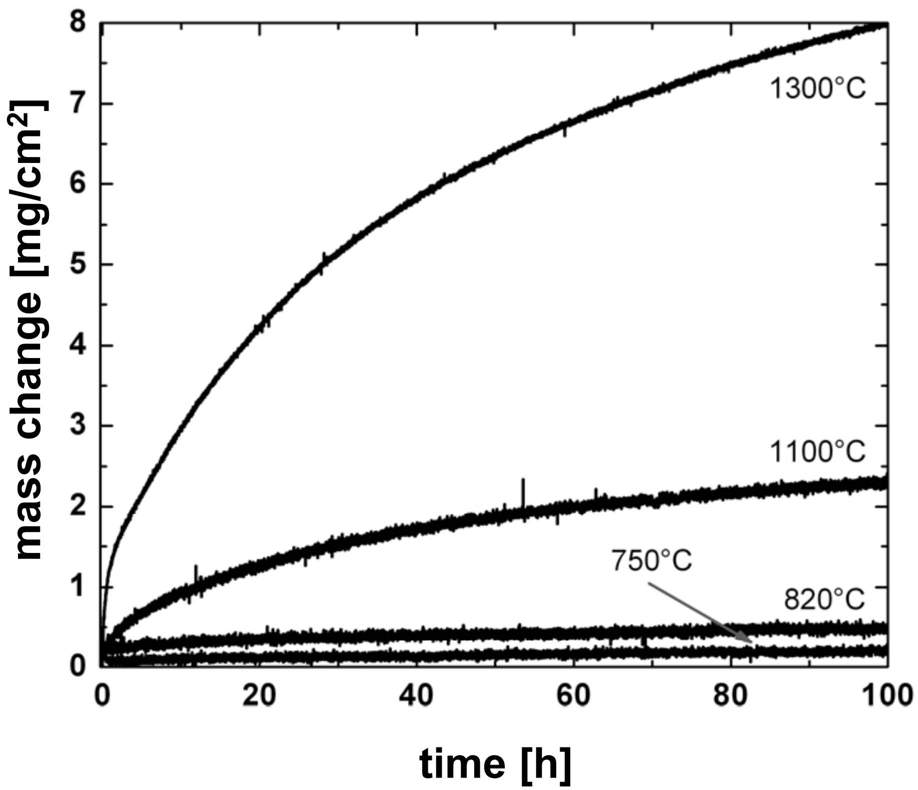
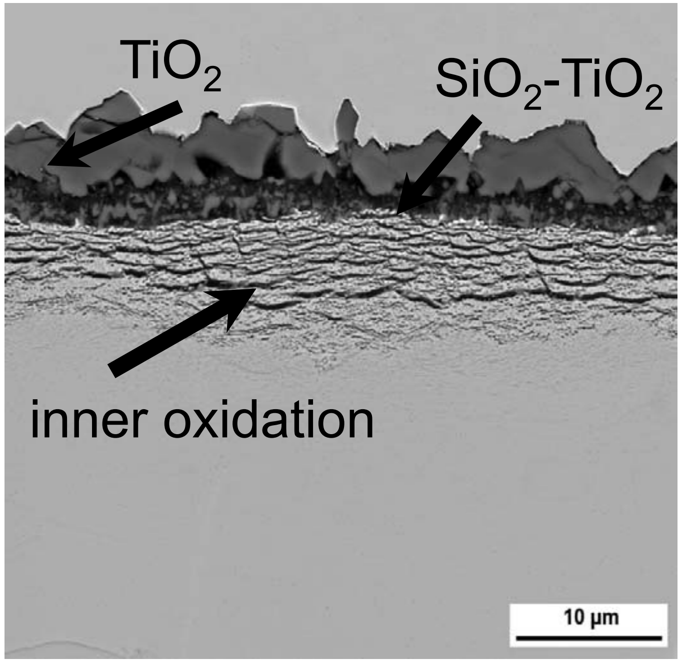
Oxidation resistance of monolithic $Mo(Ti)_5Si_3$ (= Mo-37Si-40Ti)

- Arc-melted and heat treated 1600°C/100h, oxidation in air





SEM (BSE) micrograph

Burk et al., Scripta Mater., **66**, 2012.

→ weight gain (indicating full protection) even in the pesting regime due to

→ formation of a duplex oxide layer with **SiO_2 matrix**

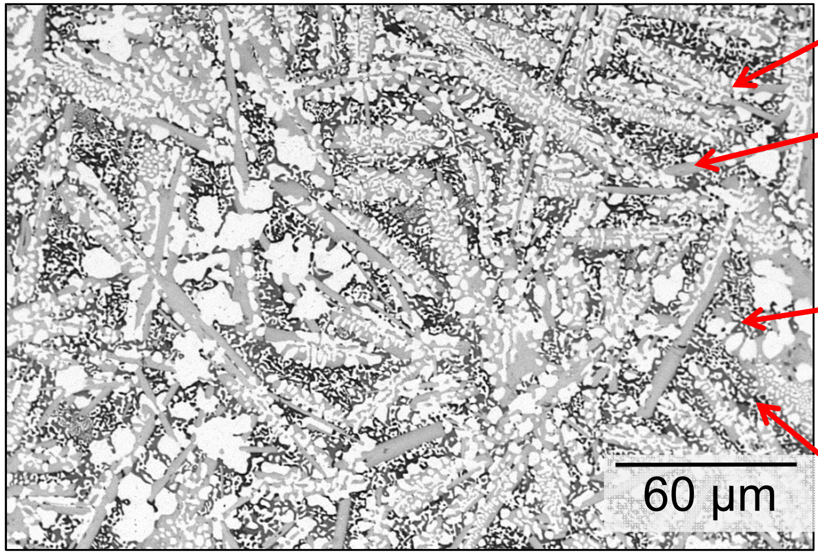
Multiphase Mo-Si-B-Ti Alloys

- Alloys were arc-melted and homogenized at 1500°C/20h
- Reduction in density to values < 8 g/cm^3

- Microstructure of Alloys

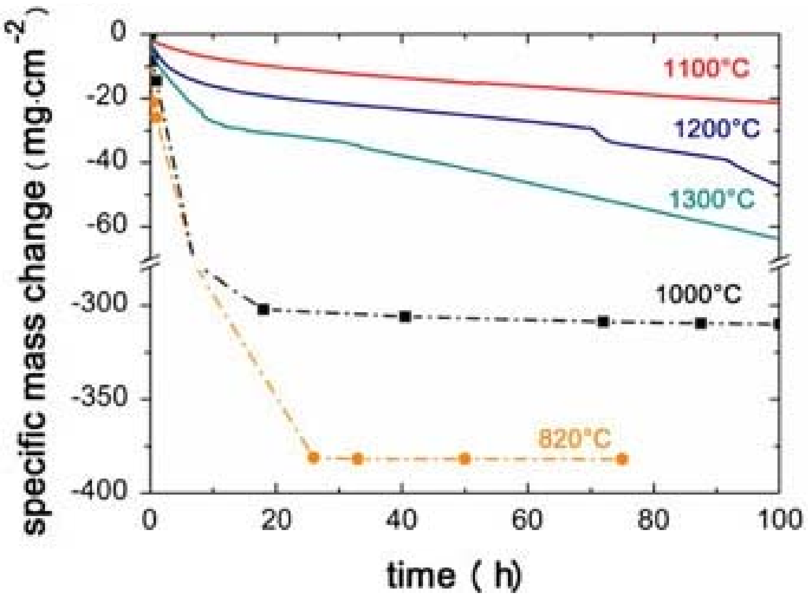
Mo-12.5Si-8.5B-27.5Ti [at.%]

ρ = **7.7 g/cm^3**



Oxidation in Air

Still low temperature pesting, no continuous SiO_2 scale formed!



Si+B pack cementation on Mo-Si-B-Ti alloy (see e.g. Perepezko, Annu. Rev. Mater. Res. 2015)

- Substrate material Mo-12,5Si-8,5B-27,5Ti homogenized at 1600 °C for 100 h
- Pack-cementation:
  - 70 wt.% Al_2O_3 + 25 wt.% Si+B + 5 wt.% NaF
  - Co-deposition of Si and B at 1000°C for 40 h
  - Conditioning at 1400°C for 10 h

Test parameters:

Temperature in °C	Oxidation Mode	Time sample A in h	Time sample B in h	Time sample C in h
800	Thermal cycling	500	1000	1000
1100	Isothermal	100	100	
	Thermal cycling	250	500	500
1200	Isothermal	100	100	
	Thermal cycling	250	500	500

Layer Arrangement after Conditioning

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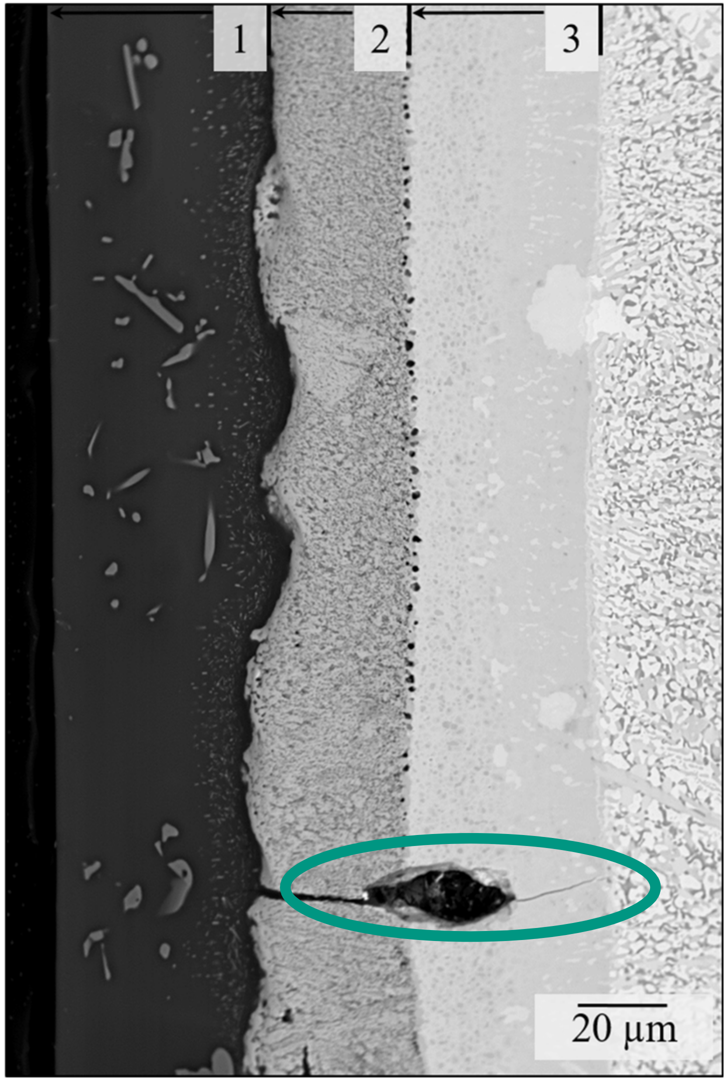
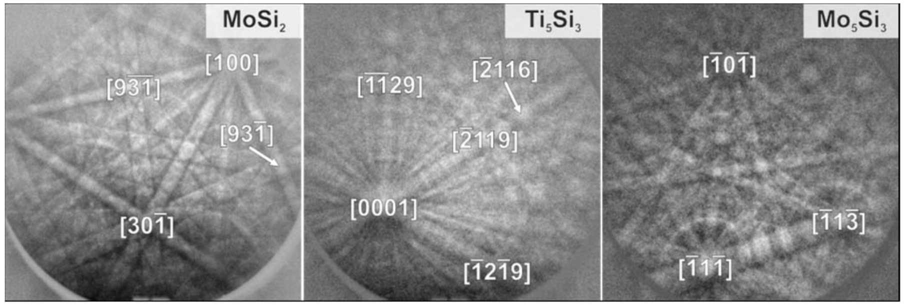
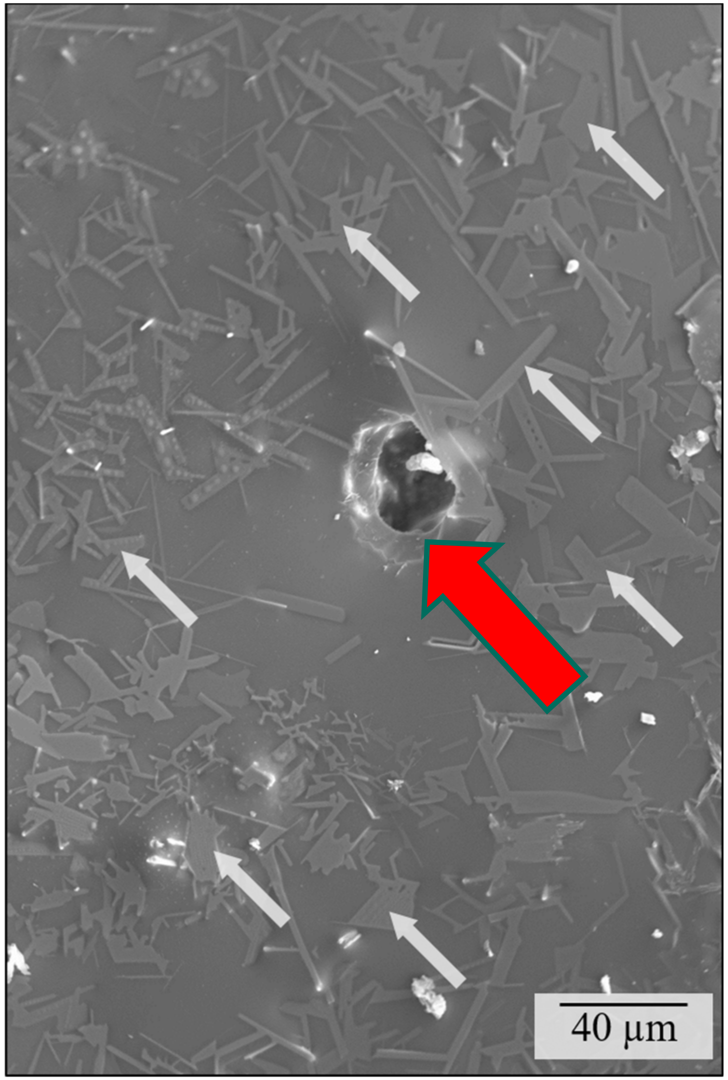




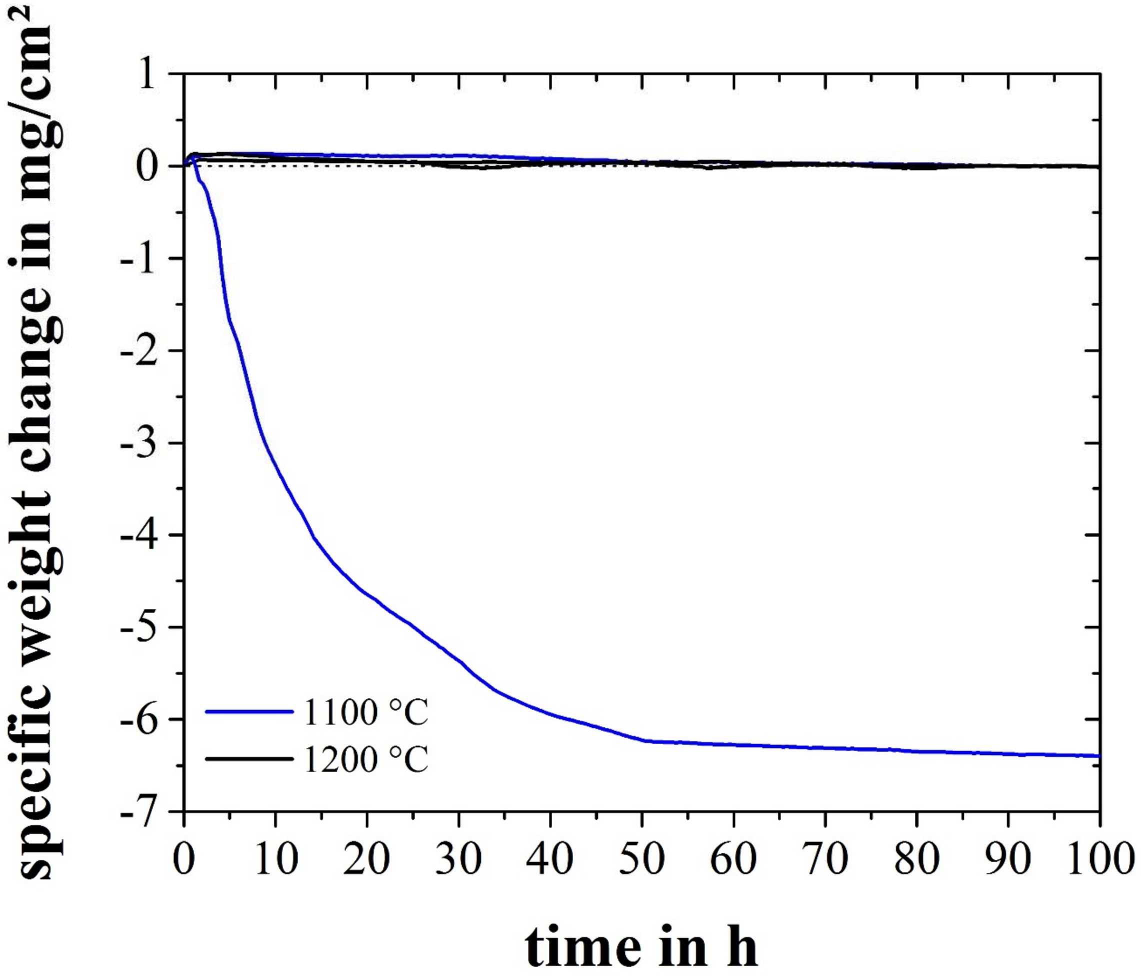
- Layer consists of:
  1) Borosilicate with Al_2O_3 and TiO_2 particles
  2) $MoSi_2$ with probably MoB particles
  3) Ti_5Si_3 layer with $MoSi_2$ and Mo_5Si_3 particles
- Cracks and pores filled by Borosilicate

Layer Surface after Conditioning



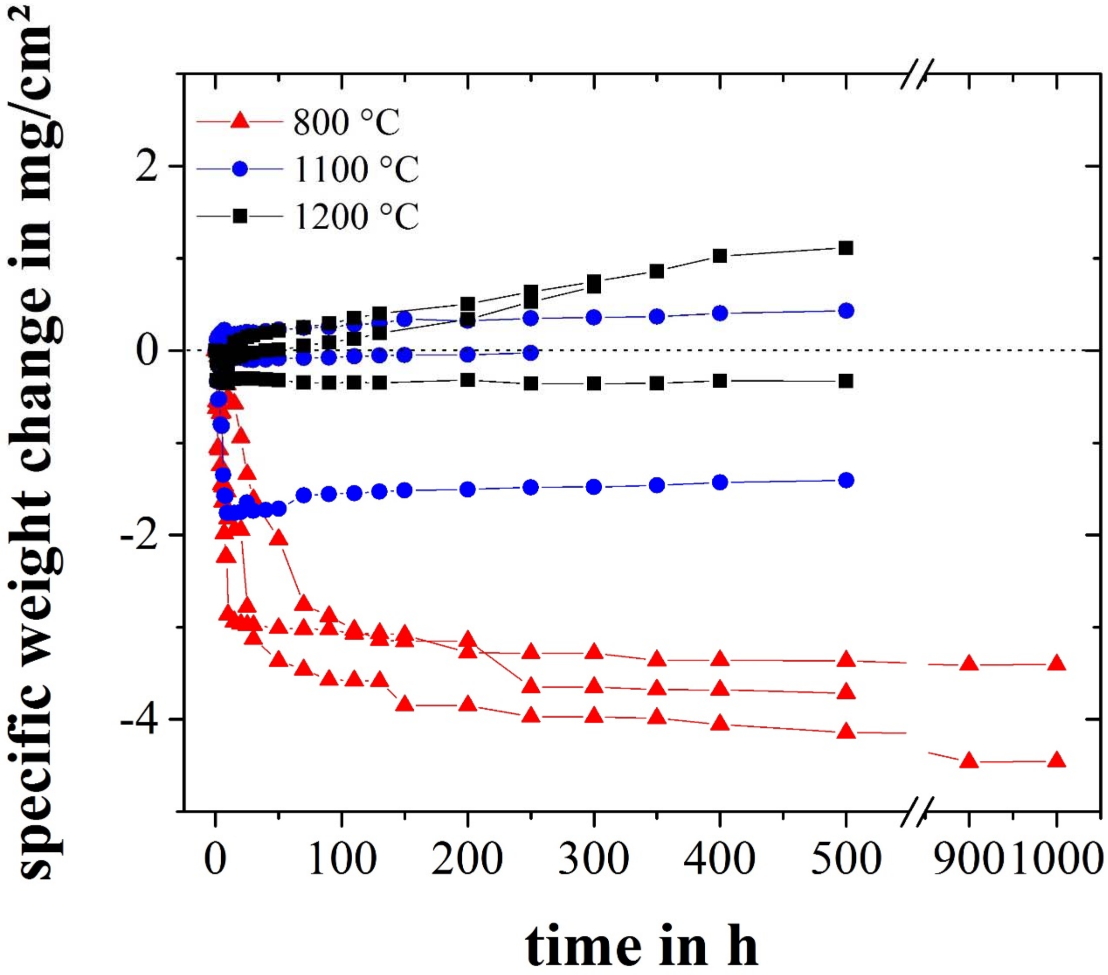
- TiO_2 particles in plate-like shape on borosilicate layer (marked by white arrows)
- Some cavities found as surface defects (red arrow)

Isothermal Oxidation (TGA)



- 1100 °C initial weight loss due to (random) appearance of surface defects but passivation after 50 h
- 1200 °C no weight change

Cyclic Oxidation



- 800 °C initial small weight loss due to small surface defects but passivation after 100 h
- 1100 and 1200 °C weight gain
- Very little weight change up to 1000 h

Comparison with uncoated Mo-12.5Si-8.5B-27.5Ti

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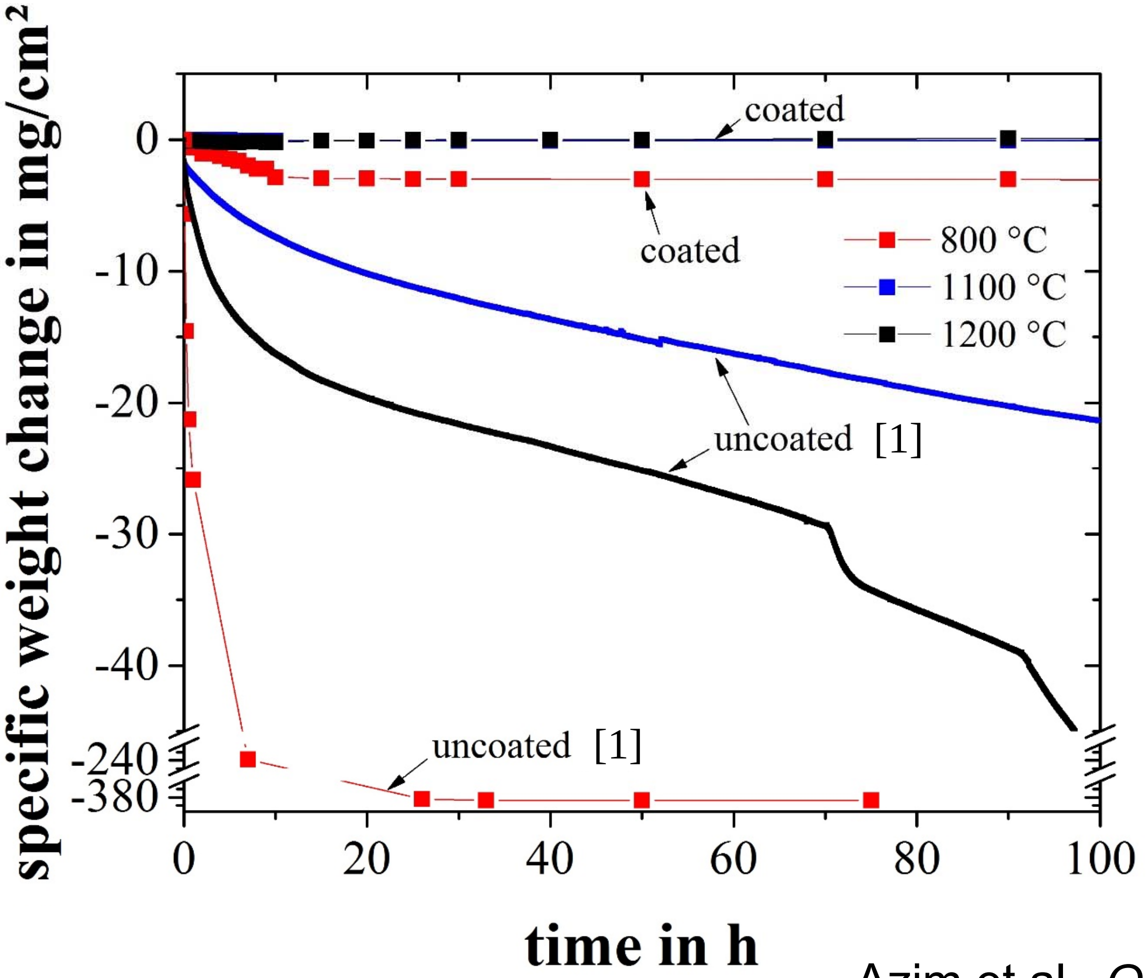

- Weight change at 1100 and 1200°C negligible compared to uncoated alloy
- Uncoated alloy at 800 °C consumed after 20 h

Azim et al., *Oxidation of Metals* (2013)

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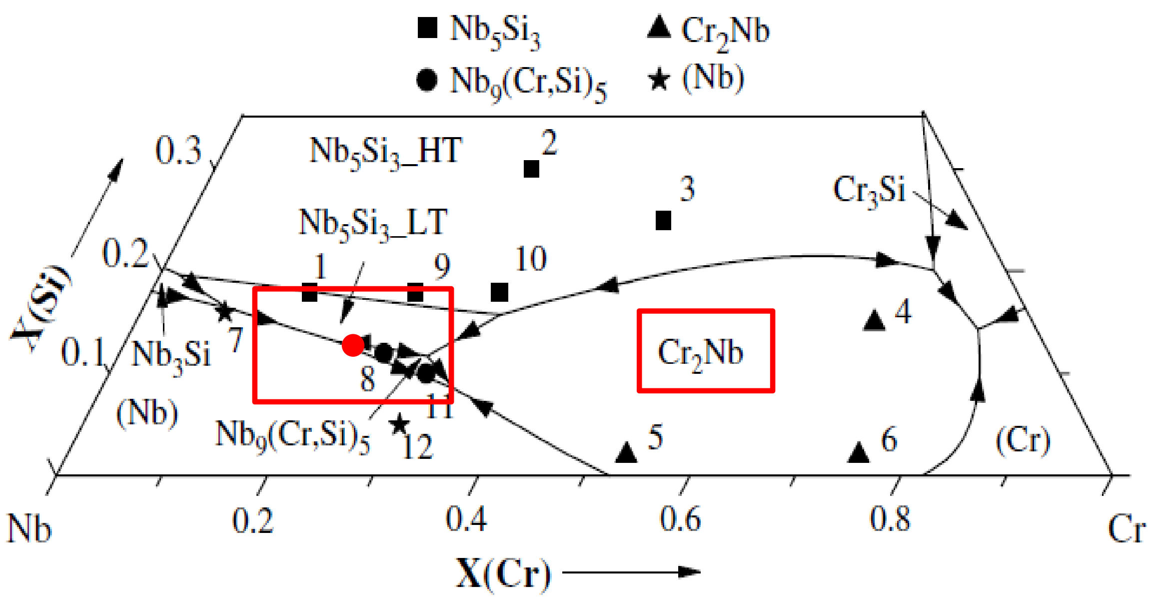
Case Study 2: Nb-Si-Cr(-V) eutectics

Ternary Eutectic in Nb-Si-Cr



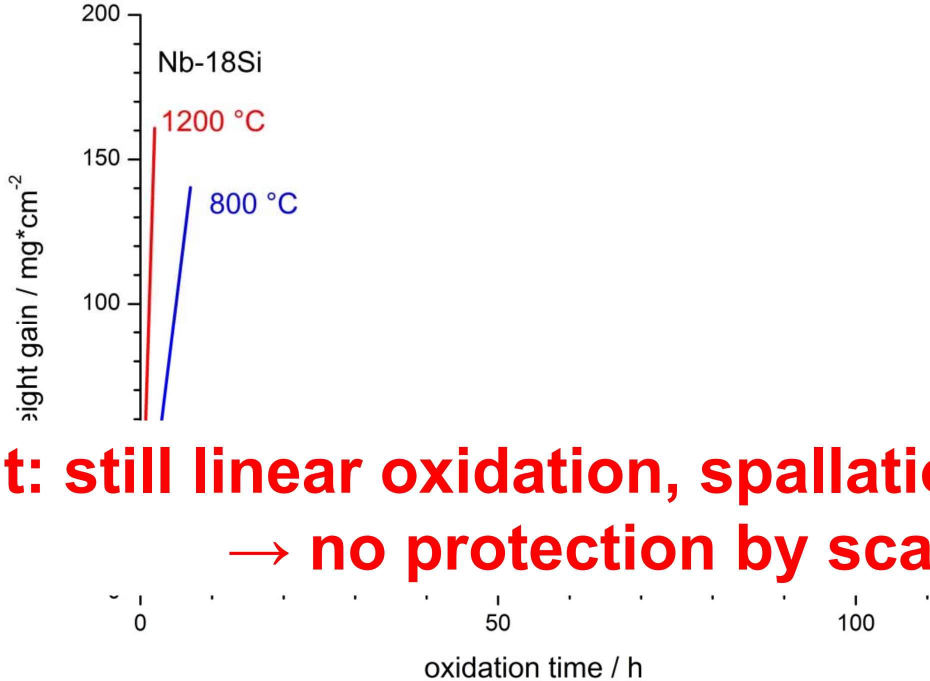
Partial liquidus projection of the system Nb-Si-Cr [Bewlay et al, [2009]

→ Nb-Si-Cr system shows ternary eutectic consisting of $(Nb)_{ss}$, Nb_9SiCr_4 & Cr_2Nb: desirable for directional solidification (DS)

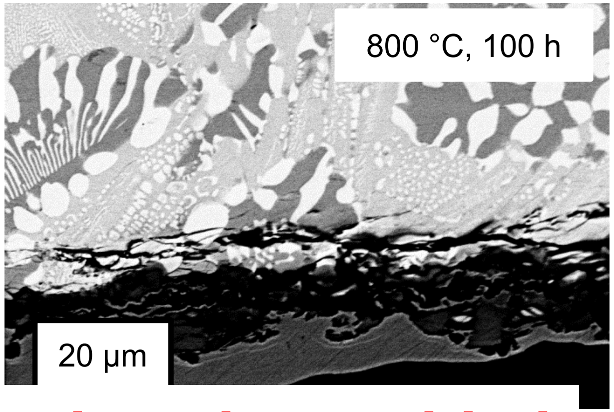
→ Cr_2Nb enables the formation of the better protective oxide $NbCrO_4$

Density 7.7 g/cm^3!

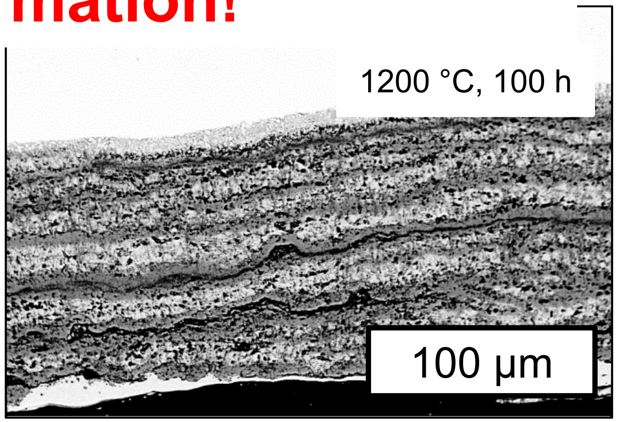
Isothermal oxidation of ternary eutectics



Nb-8.66Si-33.15Cr



But: still linear oxidation, spallation needs to be avoided
→ no protection by scale formation!



alloy composition	k_l / $mg*cm^{-2}*h^{-1}$		phase fraction Cr_2Nb / %
	800 °C	1200 °C	
Nb-18Si	80.4	20.0	-
Nb-8.66Si-33.15Cr	0.018	0.18	32.7 ± 7.6
Nb-10.9Si-28.4Cr	0.054	0.21	17.7 ± 4.9

Influence of Vanadium on oxidation resistance of Nb-Si-Cr eutectics

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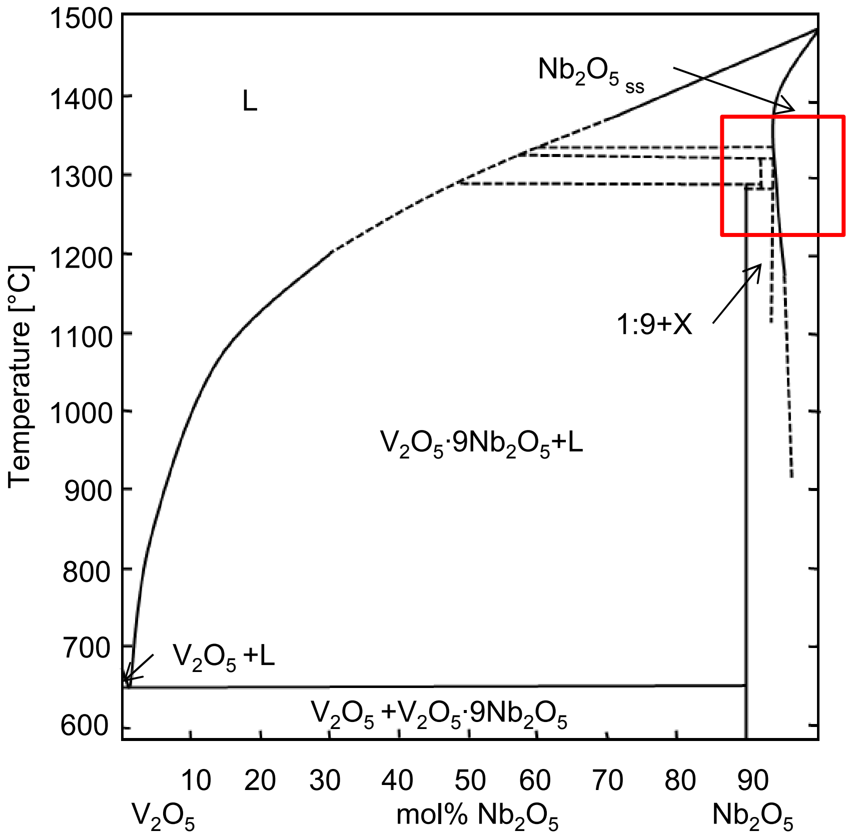
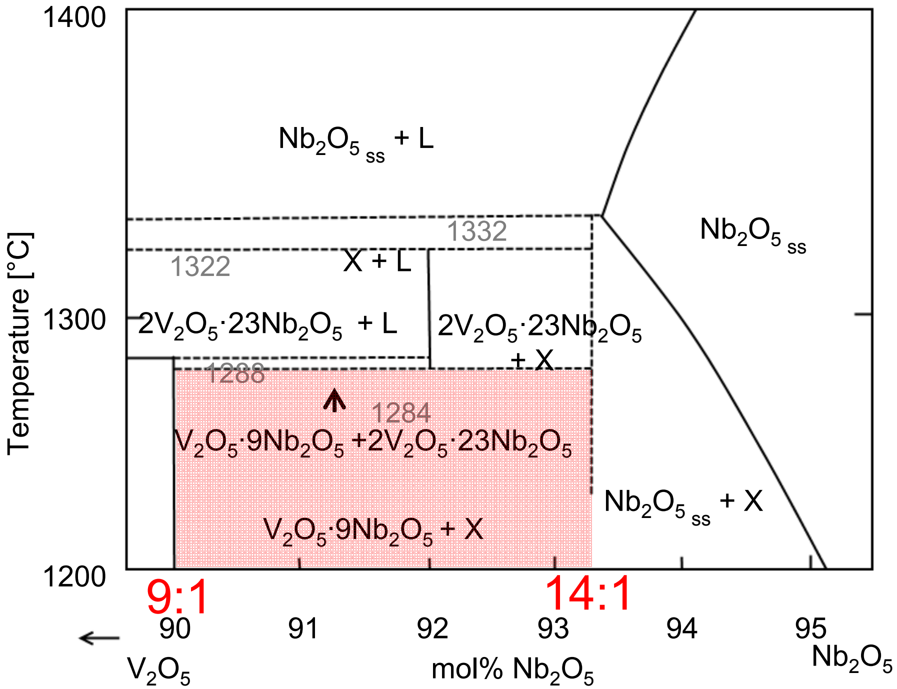


J.L. Waring, R.S.Roth, Phase equilibria in the system Vanadium Oxide-Niobium Oxide, J. of Research of the National Bureau of Standards – A. Physics and Chemistry Vol. 69A, No.2 (1963), p. 119 - 129



Binary Nb-V system:
→ formation of the dense, adherent oxide $V_2O_5 \cdot 9Nb_2O_5$ in the designated compositional range

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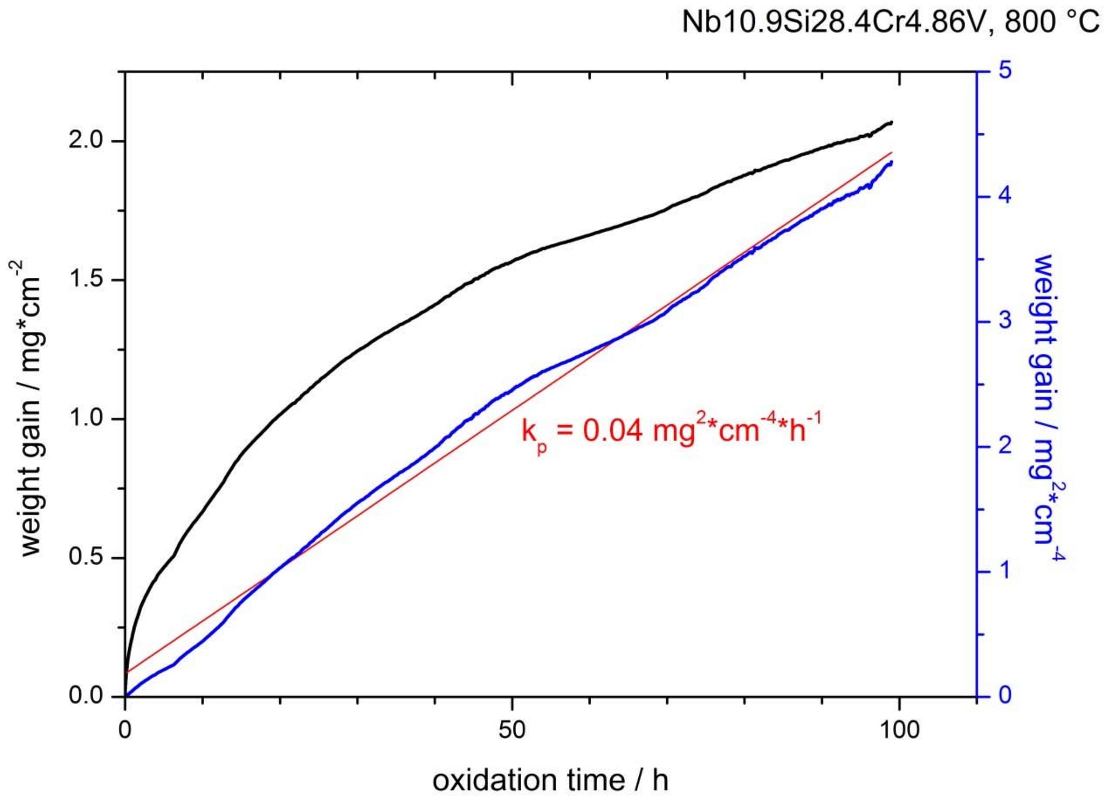
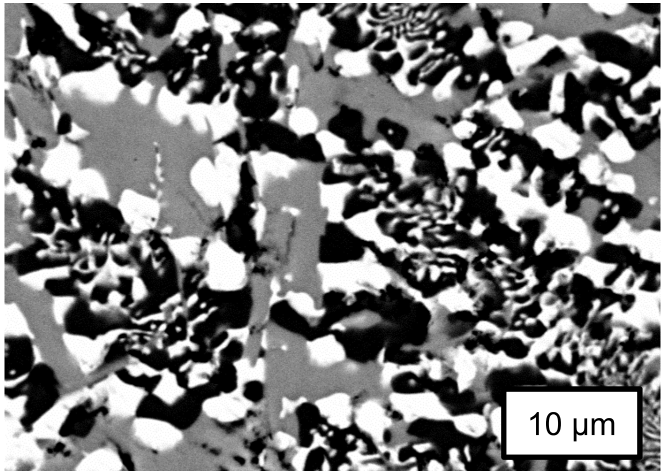
Combined effect of V and Cr on oxidation resistance

→ Nb10.9Si28.4Cr4.86V (Nb:V ratio = 11.5:1)





phase	areal fraction / %
(Nb)	18.8 ± 1.9 (14.6)
Cr_2Nb	20.8 ± 1.6 (17.7)
Nb_9SiCr_4	60.4 ± 3.2 (67.7)

V evenly distributed in all three phases (EDS)

→ weight gain following a parabolic rate law!

→ scale formation needs to be clarified, but no spallation!

Conclusions

1. Creep Resistance in both alloy systems is found superior to Ni-base superalloys even without utilizing processes such as DS or SX
2. Weight/density can be favorably low in both alloy systems, i.e. < 8 g/cm^3 without sacrificing other properties
3. Oxidation resistance:

- Nb-silicides:
  - Alloying with Cr decreases oxidation rate constant, but does not supress spallation and oxide cracking
  - V supresses spallation
  - A combination of Cr and V leads to parabolic oxidation rate constant at 800°C, indicates sufficient protection
- Mo-silicides:
  - Pesting at intermediate T cannot be avoided due to slow kinetics of borosilicate glass formation
  - Pack cementation leads to virtually full protection with very low weight changes and exhibits self-healing capcity

Acknowledgements

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Thank you very much for your attention!