PROJECT
ZIA-PHASES

The emergence of ZIA phases

M.A. Tunes, H.V. Tin, R.I. Neto, J.A. Valdez,
S. Fensin, J.K. Baldwin, O. El-Atwani and S.A. Maloy
Los Alamos National Laboratory

Historical background

Jean Discart
L'Atelier de Poterie
Tangier, Morocco

Reactive Hot Pressing (RHP) and MAX Phases

392 NATURE April 24, 1965 VOL. 206

CERAMICS

'Reactive Hot Pressing': a New Ceramic Process

REACTIVE hot pressing is a new process by which powdered materials can be densified and materi... of considerable strength can be produced. The term 're... hot pressing' is new and has been coined to disti... this process from other known ceramic processes... as sintering, hot pressing or pressure fabrication. ... (3,000–15,000 lb./in.²) on the 'reactive' solid a consid... interparticle bonding can be achieved in different ce... materials. Thus, this new process combines the... reactivity of a solid during a phase change with pr... to obtain a very strong and dense material. I... present investigation, hydrated silicates, hydroxid... hydrated oxides and carbonates were used. The... products after decomposition were oxides and silica... all cases.

A. C. D. CHAKLADER

Department of Metallurgy,
University of British Columbia,
Vancouver 8, Canada.

***Monatshefte Für Chemie*, *98*(2), 329–337, 1967**

Die Kristallstruktur von Ti_3SiC_2 — ein neuer Komplexcarbid-Typ

Von

W. Jeitschko und H. Nowotny

Aus dem Institut für physikalische Chemie der Universität Wien

Mit 5 Abbildungen

(Eingegangen am 7. Dezember 1966)

der $TiSi_2$-reichen Seite angesetzt. Die Ausgangskomponenten waren Pulver von Titanhydrid (Metal Hydrides Inc., Mass., Grade E), Silicium (Péchiney, 99,9%) und Reaktorgraphit. Die Pulvermischungen wurden in abgeschlos-... $a = 3{,}06_8$, $c = 17{,}66_9$ Å und $c/a = 5{,}75_9$. Die Titan-Atome besetzen die Punktlagen 2a) ... Atome die Punktlage 2b) un... lage 4f) ($z_C = 0{,}567_5$) in der ... Struktur gehört zu den K... Bauelementen [T_6C].

The crystal structure o... means of single crystal pho... the hexagonal cell were fou... and $c/a = 5.75_9$. The titaniu... and 4f) ($z_{Ti} = 0.135$), the ... atoms 4f) ($z_C = 0.567_5$) of th... crystal structure type belon... having octahedral groups [T...

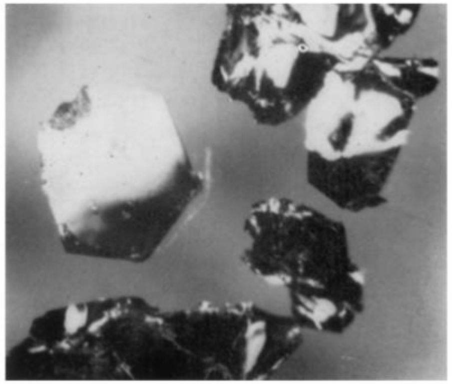


Abb. 1. Unverformter Kristall (hexagonale Symmetrie) und verformte Kristalle von Ti_3SiC_2. 50-fach

J. Am. Ceram. Soc., 79 (7), 1955-56, 1996.

journal — J. Am. Ceram. Soc., 79 [7] 1955-56 (1996)

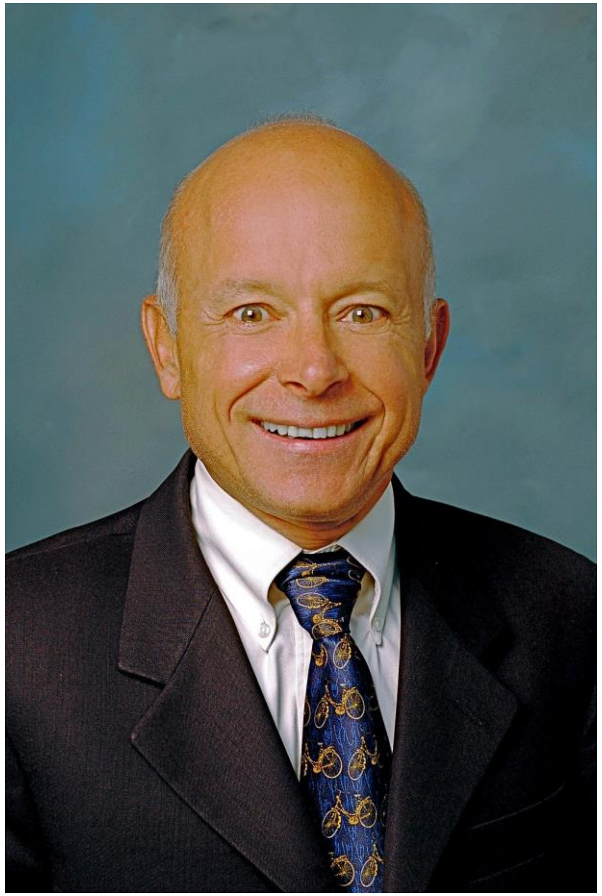
Synthesis and Characterization of a Remarkable Ceramic: Ti_3SiC_2

Michel W. Barsoum* and Tamer El-Raghy*

Department of Materials Engineering, Drexel University, Philadelphia, Pennsylvania 19104

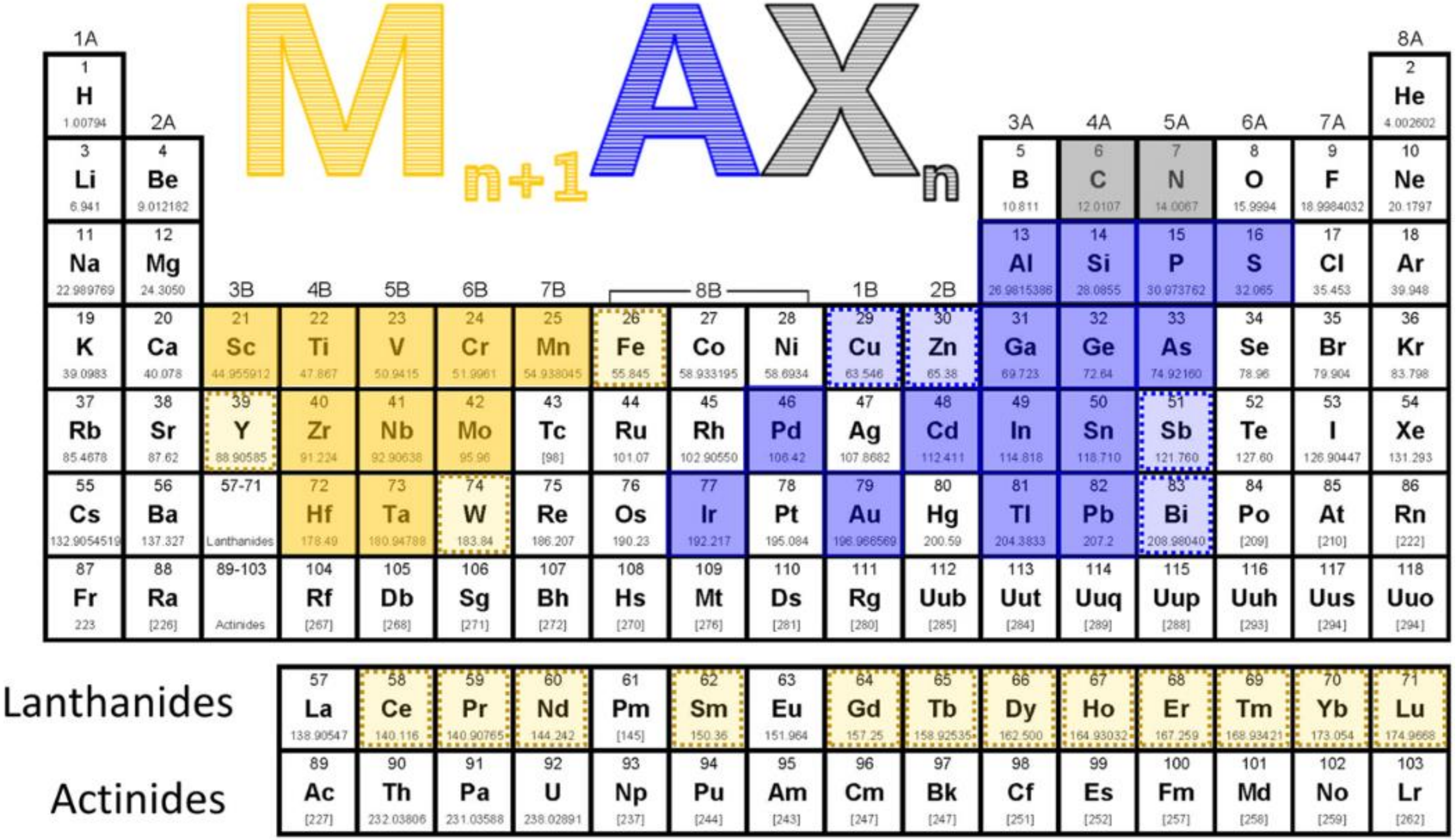
Polycrystalline bulk samples of Ti_3SiC_2 were fabricated by reactively hot-pressing Ti, graphite, and SiC powders at 40 MPa and 1600°C for 4 h. This compound has remarkable properties. Its compressive strength, measured at room temperature, was 600 MPa, and dropped to 260 MPa at 1300°C in air. Although the room-temperature failure was brittle, the high-temperature load–displacement curve shows significant plastic behavior. The oxidation is parabolic and at 1000° and 1400°C the parabolic rate constants were, respectively, 2×10^{-8} and 2×10^{-5} $kg^2 \cdot m^{-4} \cdot s^{-1}$. The activation energy for oxidation is thus ≈300 kJ/mol. The room-temperature electrical conductivity is 4.5×10^6 $\Omega^{-1} \cdot m^{-1}$, roughly twice that of pure Ti. The thermal expansion coefficient in the temperature range 25° to 1000°C, the room-temperature thermal conductivity, and the heat capacity are respectively, 10×10^{-6} °C^{-1}, 43 W/(m·K), and 588 J/(kg·K). With a hardness of 4 GPa and a Young's modulus of 320 GPa, it is relatively soft, but reasonably stiff. Furthermore, Ti_3SiC_2 does not appear to be susceptible to thermal shock; quenching from 1400°C into water does not affect the postquench bend strength. As significantly, this compound is as readily machinable as graphite. Scanning electron microscopy of polished and fractured surfaces leaves little doubt as to its layered nature.

Professor Barsoum's MAX Phases Empire in 2021



Source: Wikipedia.org

Drexel UNIVERSITY



Goossens, N., Tunca, B., Lapauw, T., Lambrinou, K., & Vleugels, J. (2021)
MAX phases, structure, processing, and properties. *Encyclopedia of Materials: Technical Ceramics and Glasses*, 2–3, 182–199

We are interested in materials for application in extreme environments: high-temperature and irradiation. And MAX Phases…

Acta Materialia 169 (2019) 237–247

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

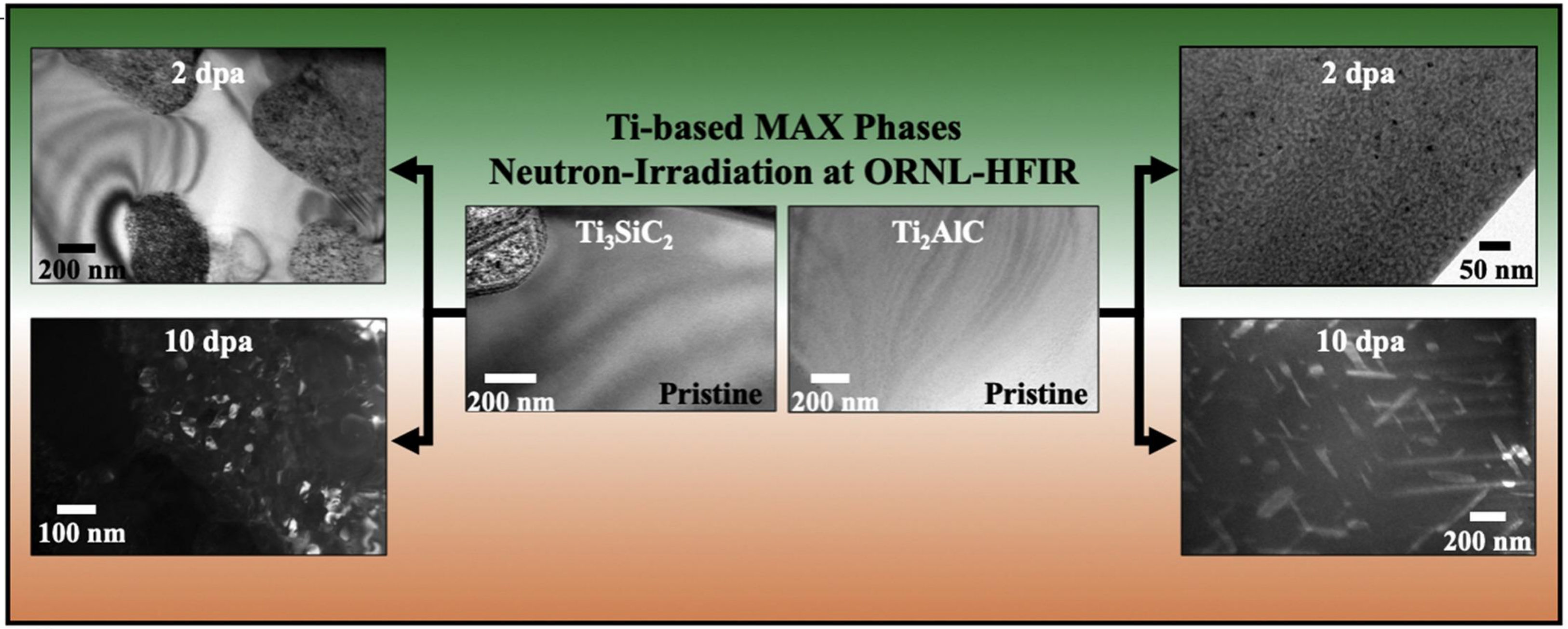
ELSEVIER

Full length article

A Transmission Electron Microscopy study of the neutron-irradiation response of Ti-based MAX phases at high temperatures

Matheus A. Tunes [a,*], Robert W. Harrison [b], Stephen E. Donnelly [a], Philip D. Edmondson [c]

[a] School of Computing and Engineering, University of Huddersfield, Queensgate, HD1 3DH, Huddersfield, United Kingdom
[b] School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Sackville Street, M1 3NJ, Manchester, United Kingdom
[c] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, United States



Project's Outline

- **Work-to-date and main objectives.**
- **The ZIA phases project.**
  - **Synthesis and characterization: SEM, EDX, and TEM**
- **Potential of ZIA phases in extreme environments.**

Work-to-date

Can we extend the MAX phase concept beyond carbides and nitrides? Yes, intermetallic silicides!

THE CRYSTAL STRUCTURES OF Mn_3Ni_2Si, V_3Ni_2Si, Nb_3Ni_2Si AND RELATED Cr AND Ta COMPOUNDS

E. I. Gladyshevskii, Yu. B. Kuz'ma, and P. I. Kripyakevich

I. Franko L'vovsk State University

Translated from Zhurnal Strukturnoi Khimii, Vol. 4, No. 3,
pp. 372-379, May-June, 1963
Original article submitted February 6, 1962

The existence was established of ternary R_3Ni_2Si compounds (R = Mn, V, Nb), of the η-phase structure type (space group Fd3m – O_h^7, Z = 16) with completely ordered distributions of all component atoms. Compounds of the η-phase type, with similar but undetermined compositions, are found in the Cr-Ni-Si and Ta-Ni-Si systems.

together Mn (electrolytic), Ni (99.9%) and Si (99.5%) in a porcelain crucible, using a high-frequency furnace (hydrogen atmosphere). As the alloying was not accompanied by combustion, a chemical analysis was not carried out.

Three specimens were used in the x-ray analysis: 1) a cast specimen (no heat treatment); 2) a specimen annealed at 1000° for 24 hr; 3) a specimen annealed at 800° for 120 hr. Annealing was carried out in evacuated quartz am-

The η-phase in the Nb-Ni-Si system was also obtained in an almost pure state (see Fig. 2).

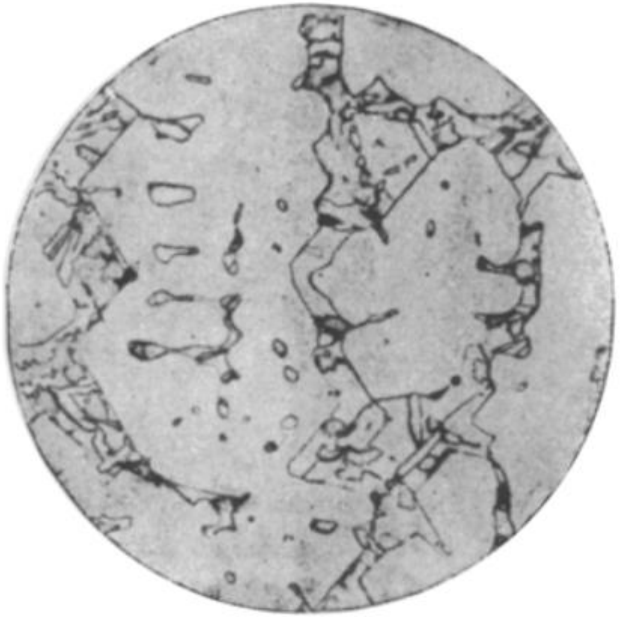
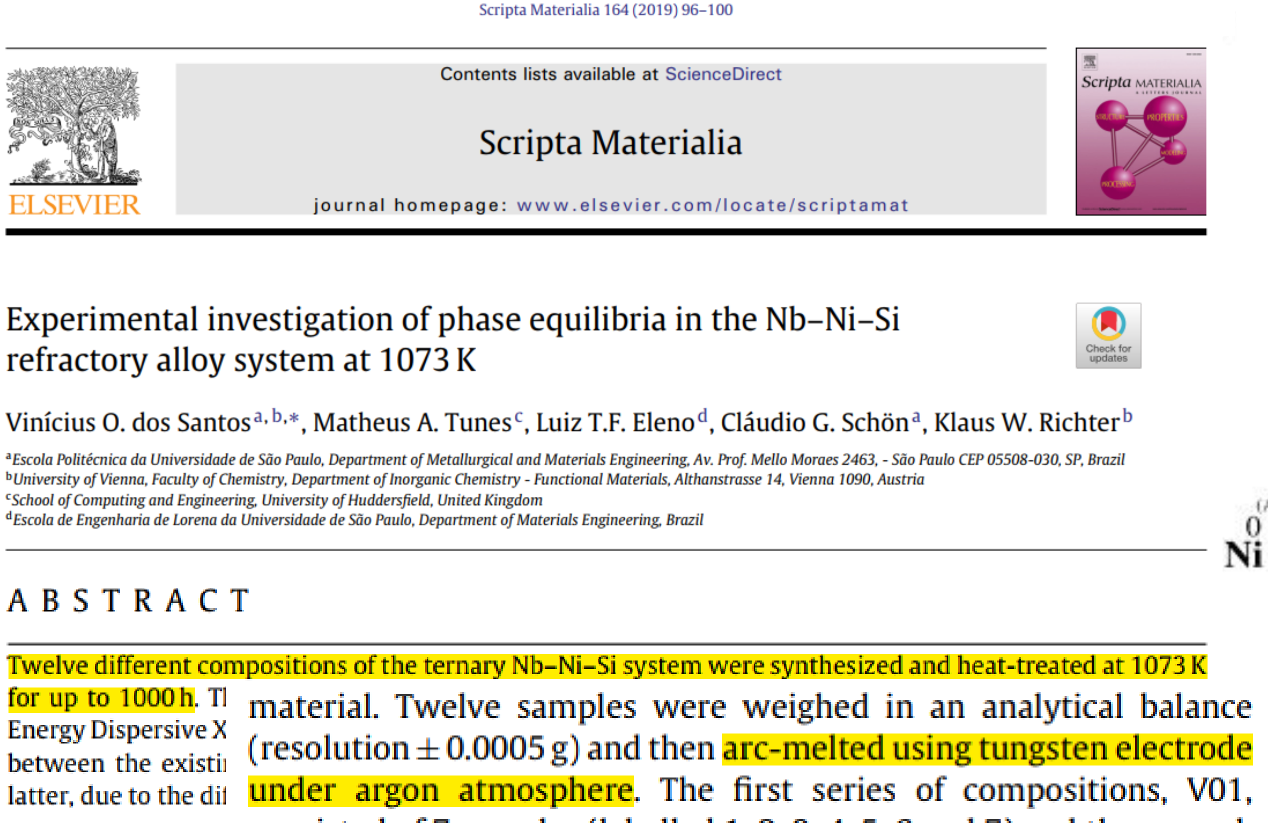


Fig. 2. Microstructure of the alloy Nb_3Ni_2Si (composition of materials used). Magnification 200.

Re-assessing the Nb-Si-Ni system: 2019.
Can we stabilize the Nb_3SiNi_2 phase?


Scripta Materialia 164 (2019) 96–100

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Experimental investigation of phase equilibria in the Nb–Ni–Si refractory alloy system at 1073 K

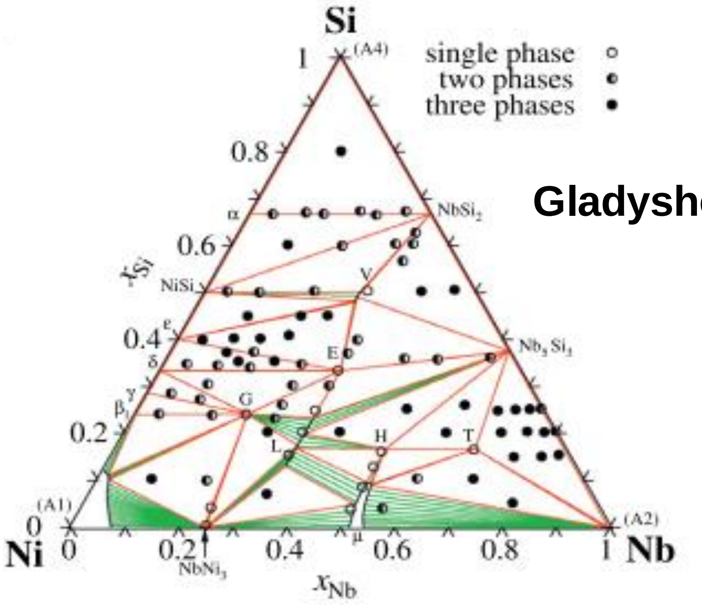
Vinícius O. dos Santos[a,b,*], Matheus A. Tunes[c], Luiz T.F. Eleno[d], Cláudio G. Schön[a], Klaus W. Richter[b]

[a]Escola Politécnica da Universidade de São Paulo, Department of Metallurgical and Materials Engineering, Av. Prof. Mello Moraes 2463, - São Paulo CEP 05508-030, SP, Brazil
[b]University of Vienna, Faculty of Chemistry, Department of Inorganic Chemistry - Functional Materials, Althanstrasse 14, Vienna 1090, Austria
[c]School of Computing and Engineering, University of Huddersfield, United Kingdom
[d]Escola de Engenharia de Lorena da Universidade de São Paulo, Department of Materials Engineering, Brazil

A B S T R A C T

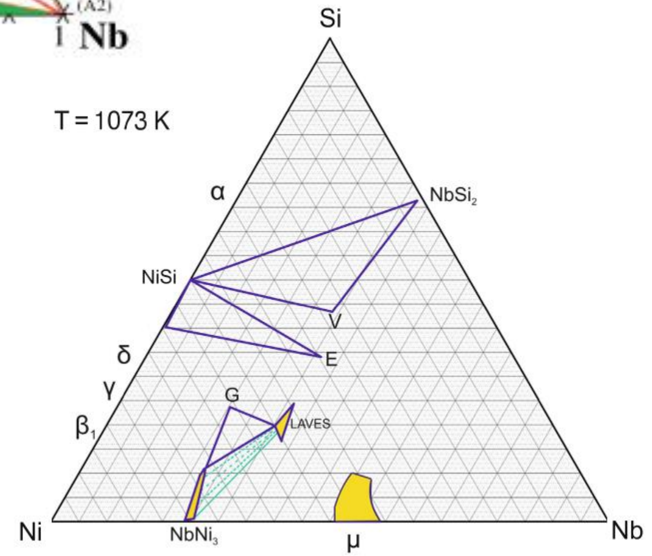
Twelve different compositions of the ternary Nb–Ni–Si system were synthesized and heat-treated at 1073 K for up to 1000 h. Tl
Energy Dispersive X
between the existi
latter, due to the dif

material. Twelve samples were weighed in an analytical balance (resolution ± 0.0005 g) and then arc-melted using tungsten electrode under argon atmosphere. The first series of compositions, V01,



Gladyshevskii et al. 1962

Corrected phase diagram at 1073 K: No H-phase.



800°C/120 hours: Gladyshevskii et al. 1962
800°C/1000 hours: us, 2019.

Re-assessing the Nb-Si-Ni system: 2020.
We are looking for the H-phase again!

Journal of Alloys and Compounds 842 (2020) 155373

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

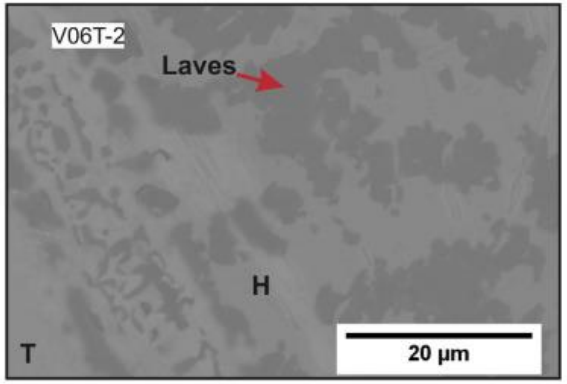
Experimental investigation of phase equilibria in the Nb–Ni–Si refractory alloy system at 1323 K

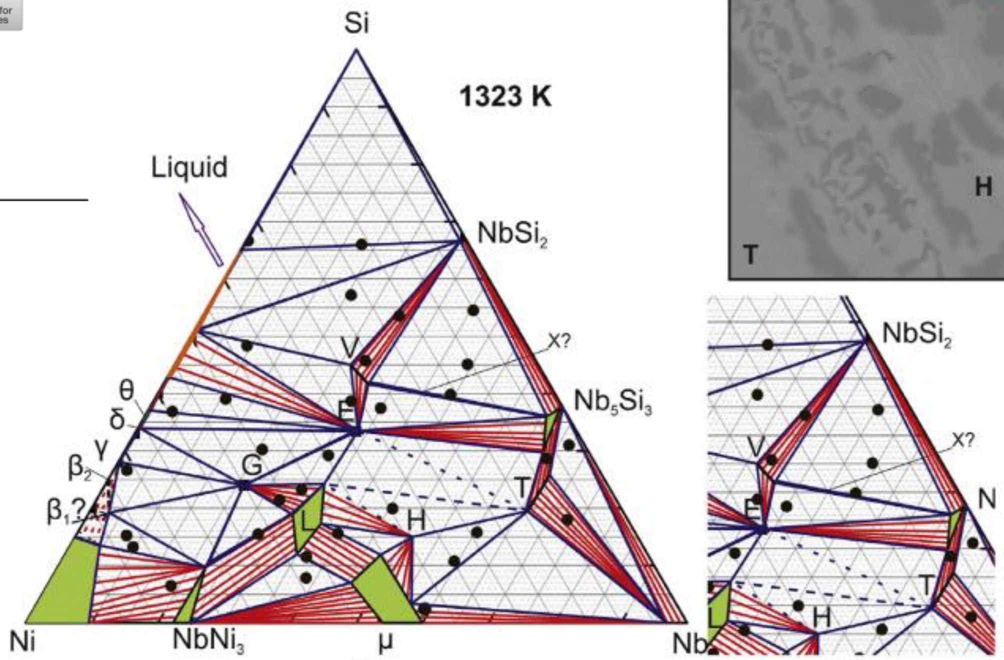
Vinícius O. dos Santos [a, b], Luiz T.F. Eleno [c], Cláudio G. Schön [a, *], Klaus W. Richter [b]

[a] Escola Politécnica da Universidade de São Paulo, Department of Metallurgical and Materials Engineering, Av. Prof. Mello Moraes, 2463, CEP 05508-030, São Paulo, SP, Brazil
[b] University of Vienna, Faculty of Chemistry, Department of Inorganic Chemistry - Functional Materials, Althanstrasse 14, 1090, Vienna, Austria
[c] Escola de Engenharia de Lorena da Universidade de São Paulo, Department of Materials Engineering, Brazil

The samples were first arc-melted under Ar using Zr as getter material and then encapsulated in quartz tubes under low pressure of argon and homogenized at 1323 K. The samples were annealed for 336 h in all series. After the prescribed times the capsules were

Sample	Sample Composition (at%)			Phase	Phase Composition (at%)			Space Group	Lattice Parameters (Å)		
	Nb	Ni	Si		Nb	Ni	Si		a	B	c
V06T-2	45.56	34.57	19.88	Laves	34.06	44.48	21.44	P63/mmc	4.82		7.79
				T	64.44	13.7	21.87	P4/mcc	6.18		5.03
				H	49.69	34.96	15.35	Fd-3mS	11.17		

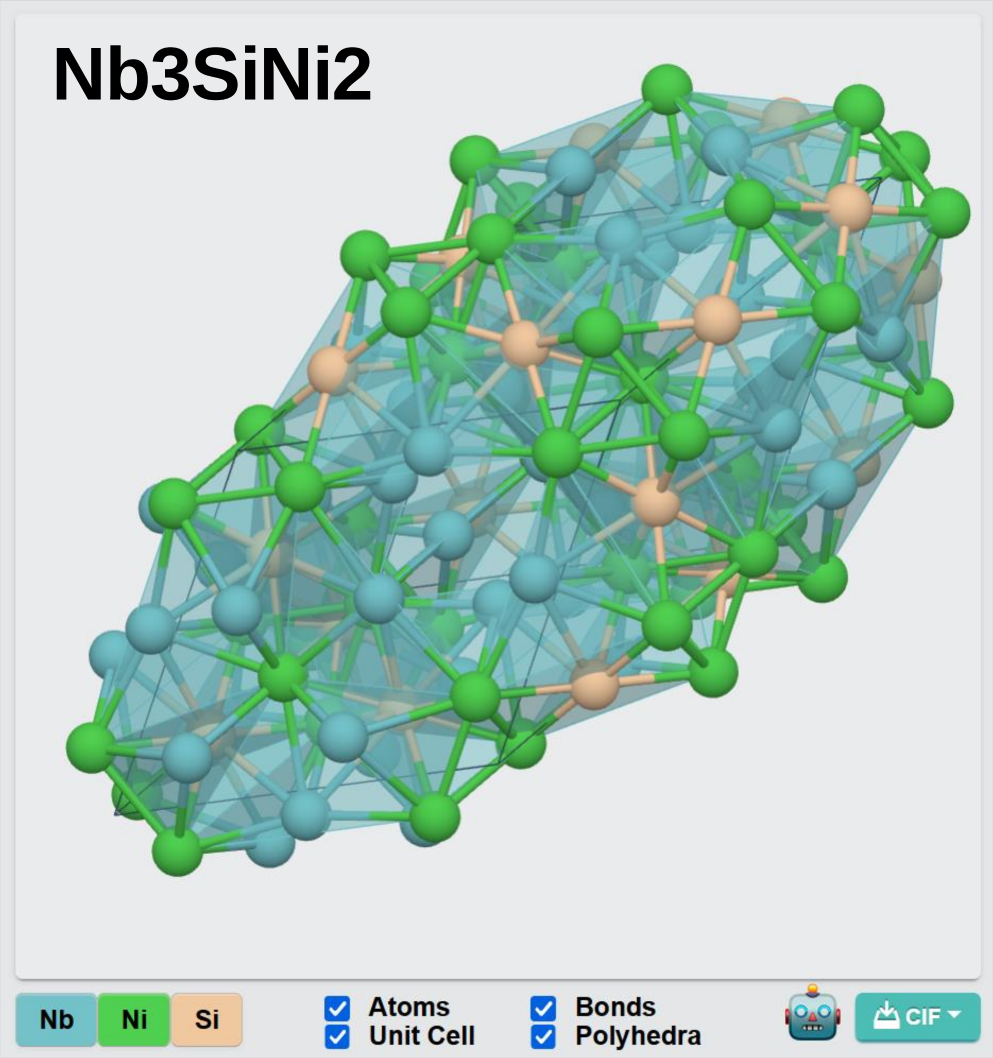




(a) (b)

800°C/120 h: Gladyshevskii et al. 1962
800°C/1000 h: us, 2019.
1050°C/336 h: us, 2020.

H-phase appears, but never in its pure form



The ZIA phases project

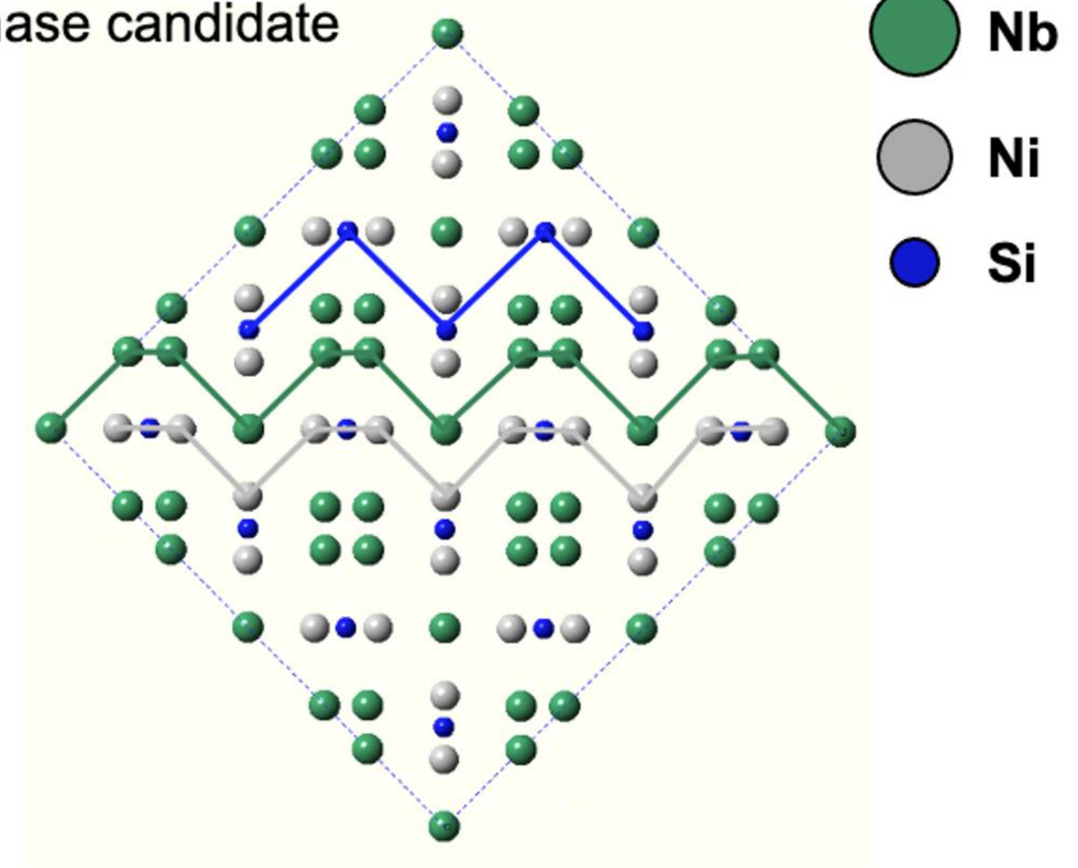
The ZIA phases project

Zig-zag Intermetallic Advanced phases

PROJECT ZIA-PHASES

- It is a challenge to synthesize and stabilize the H-phase.
- We brought this problem to LANL.
- We want to understand if:
  - R_3SiNi_2 compounds with R = Nb, Mo, Ta, Hf, W … represent a novel class of materials.
  - If this novel class can be applied in extreme environments.

Nb_3SiNi_2 – H phase
ZIA phase candidate



Using arc melting, we produced a sample with the Nb_3SiNi_2 stoichiometry

First objective:
Find the H-phase (Nb_3SiNi_2)

H-phase has been found in the as-cast sample

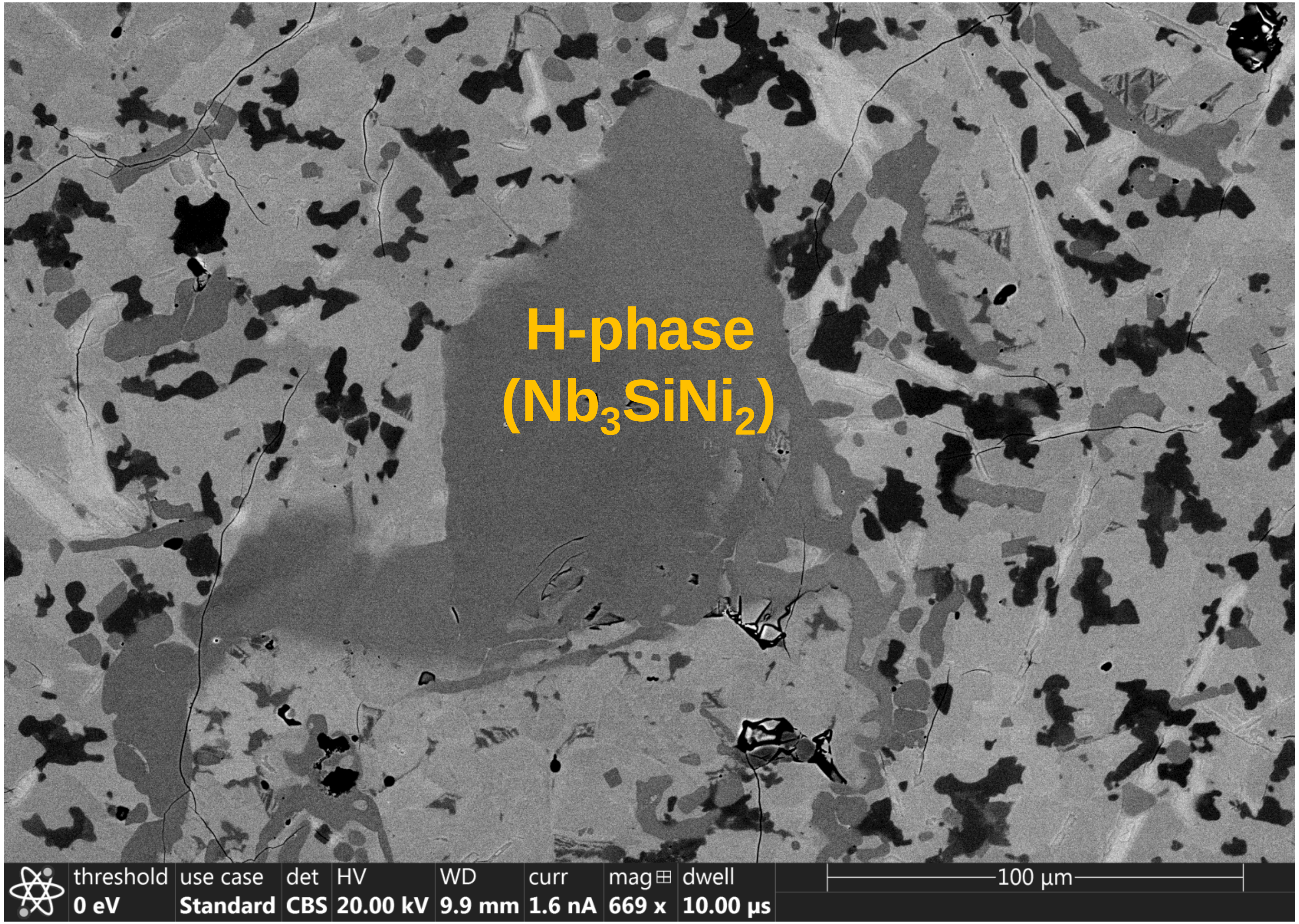
Expected Compositions

	Nb3 Si Ni2		*H Phase*	
	Stoichiometry	at.%	Ratios	
Nb	3	50%	3	Nb/Si
Si	1	17%	1.5	Nb/Ni
Ni	2	33%		

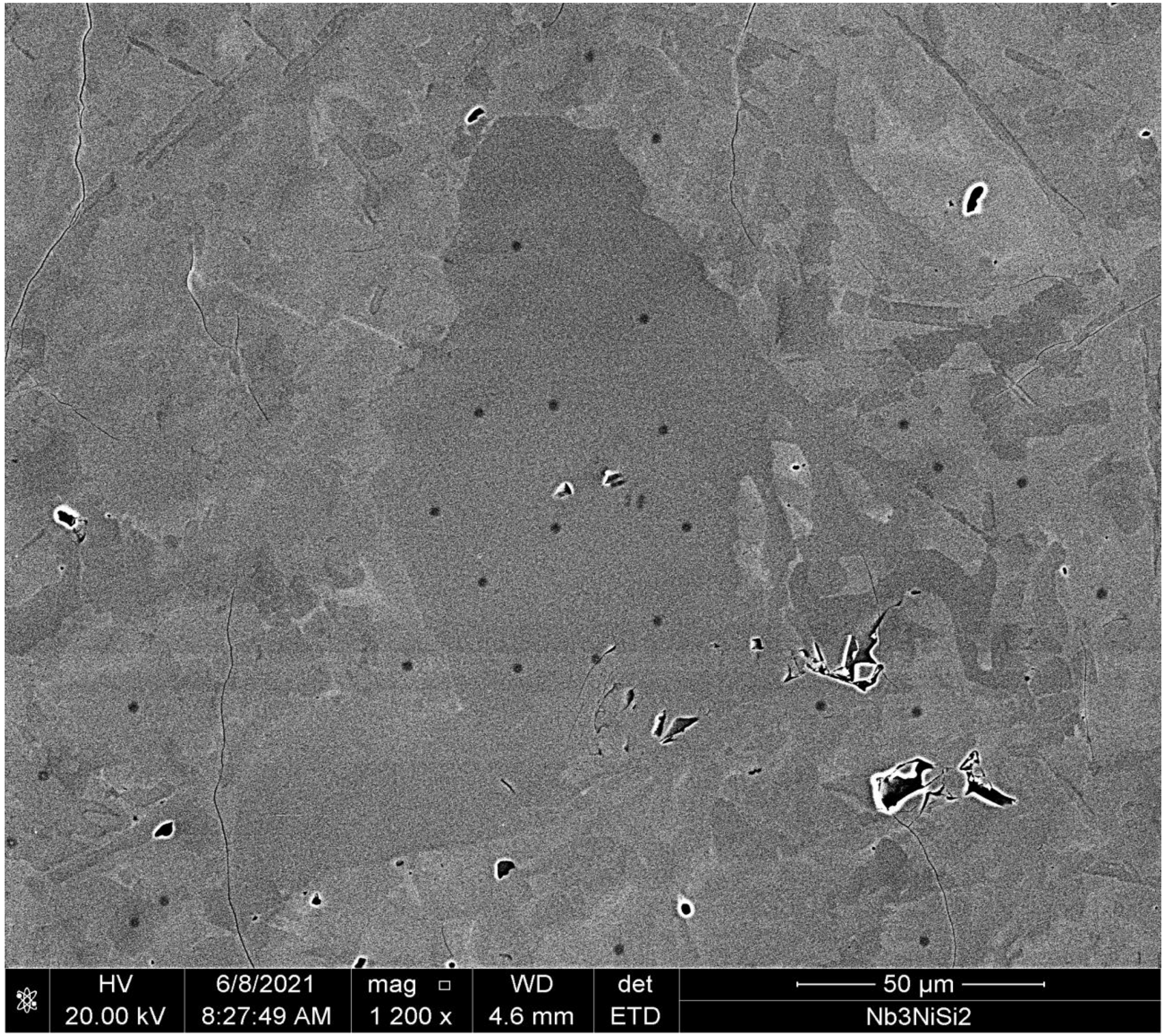
Measured Compositions

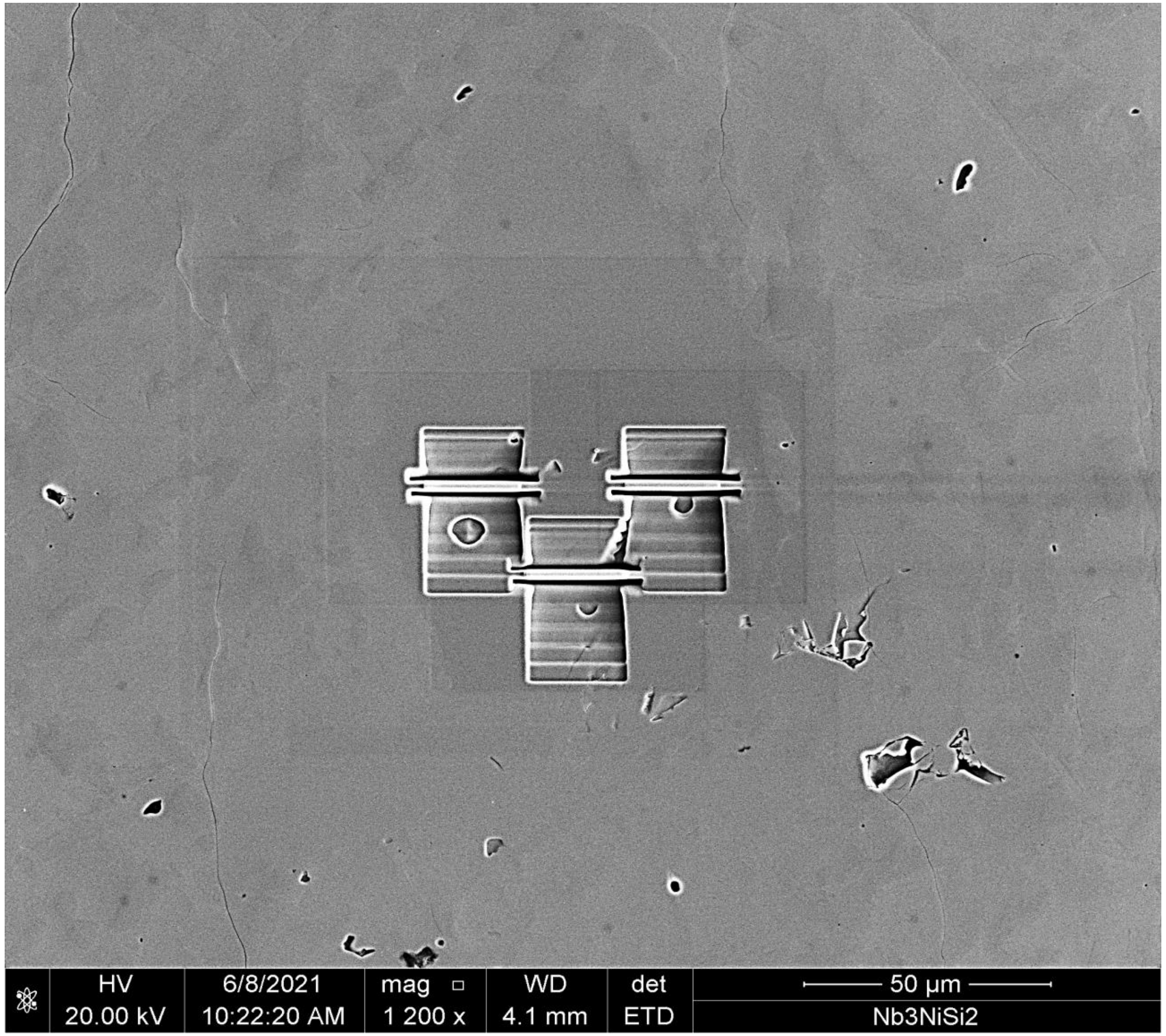
Element	Weight %	MDL	Atomic %	Net Int.	Error %
Si K	8.26	0.04	20.08	4348.72	6.56
Ni K	29.16	0.13	33.92	5116.37	2.68
Nb L	62.59	0.09	46.00	15333.20	5.19

- **Si is overestimated by EDX.**
- **Equilibrium not attained.**
- **Compositions may also be slightly off.**

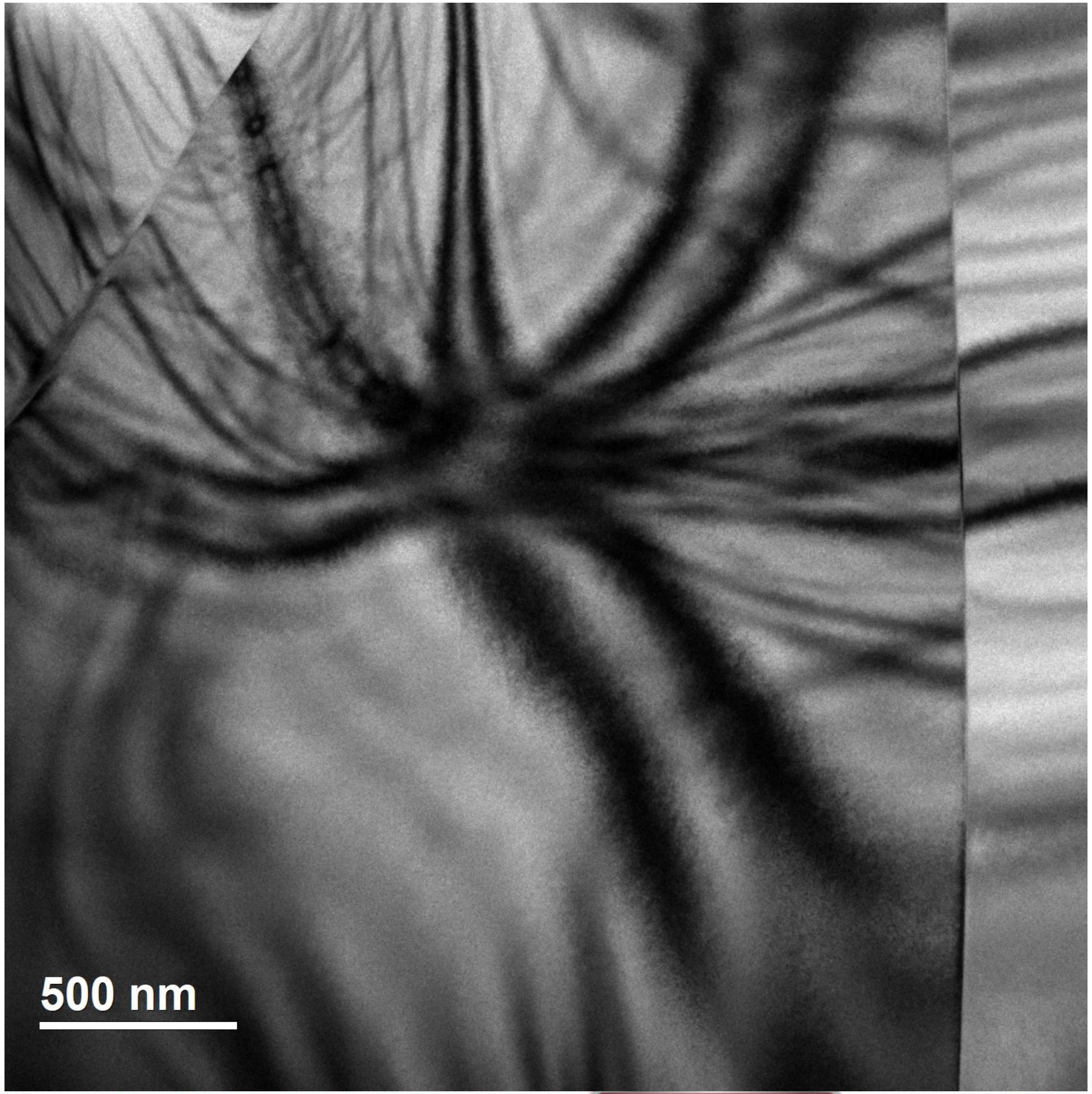


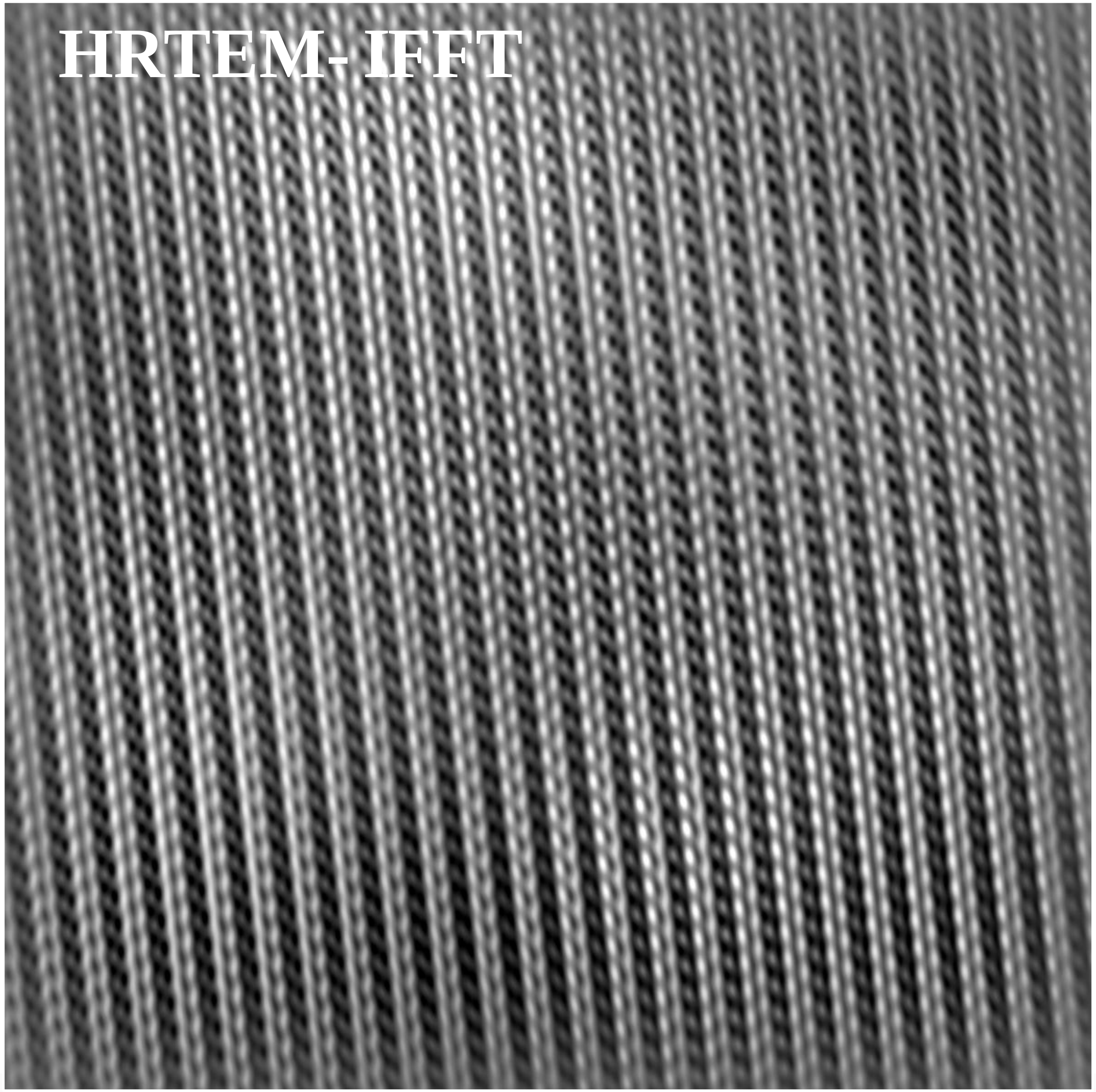
We decided to do TEM on the H-phase field (as-cast)





A distinct nanolayered structure has been observed!





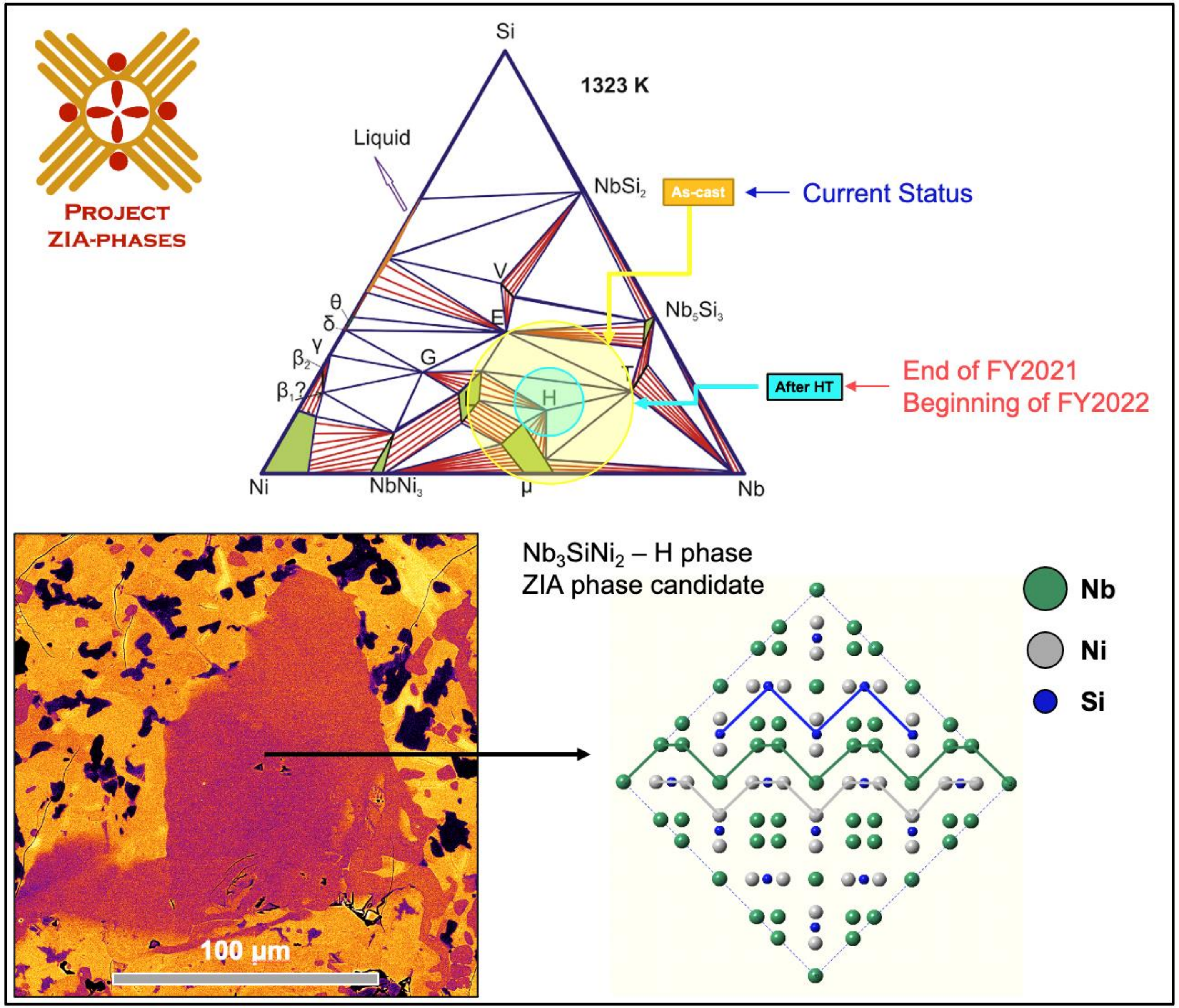
Summary of the sample as-cast

1. The Nb—Si—Ni system with 312 stoichiometry is not under equilibrium.

2. H-phase field has been observed at RT (for the first time) using arc melting.

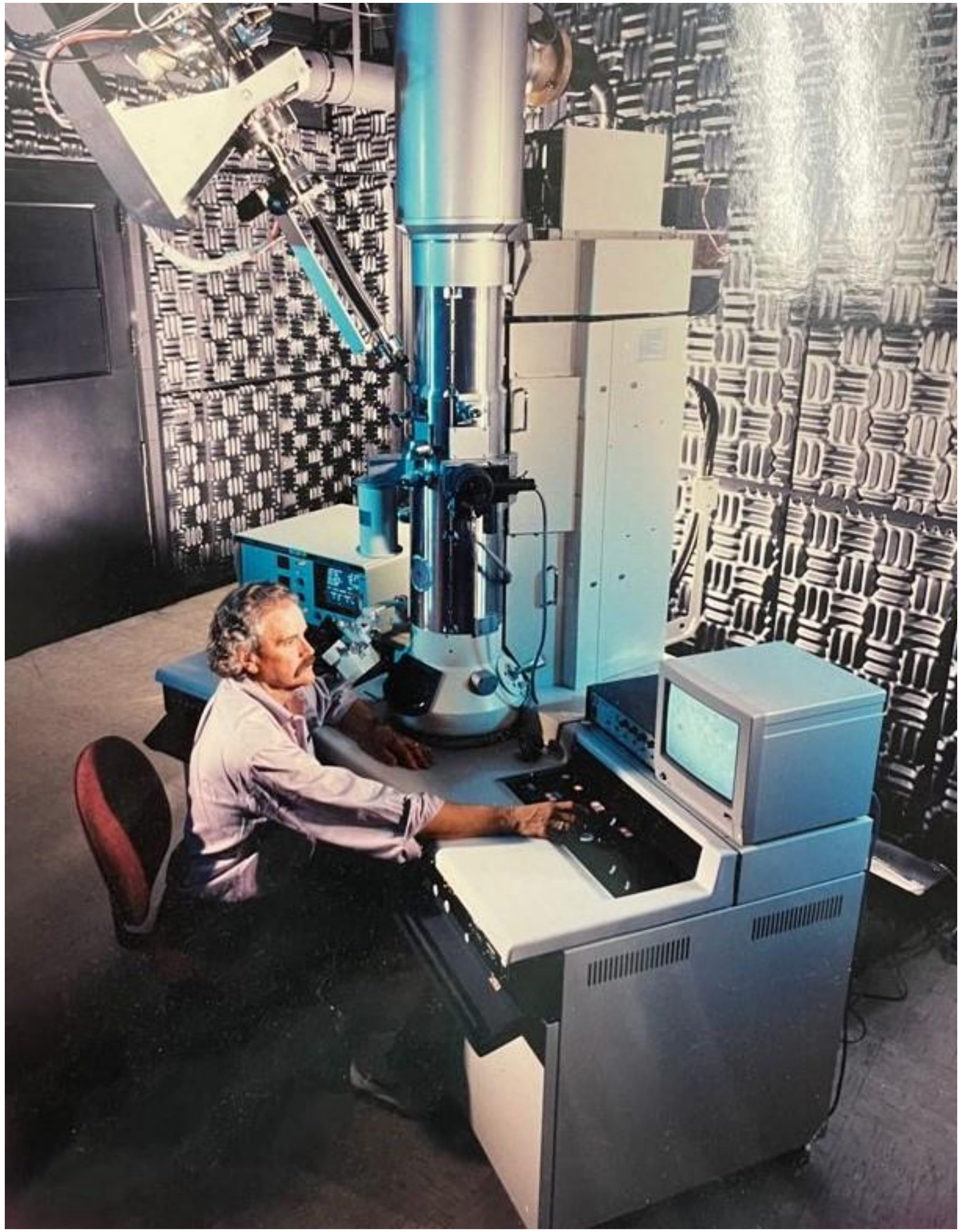
3. H-phase is indeed a nanolayered superstructure.

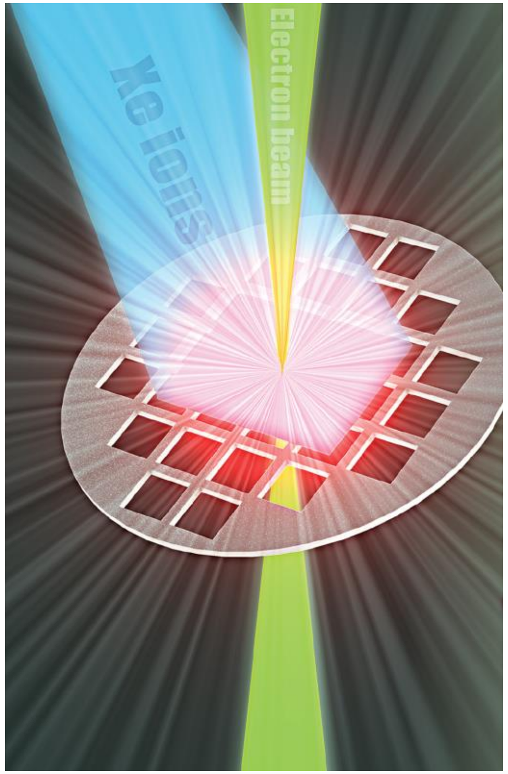
4. Next steps:
- New HT routes.
- Will the system converge to the H-phase pure?
- Investigating different synthesis methodologies?



Potential application of ZIA phases

In situ TEM ion irradiation at the Argonne National Laboratory (IVEM Facility)



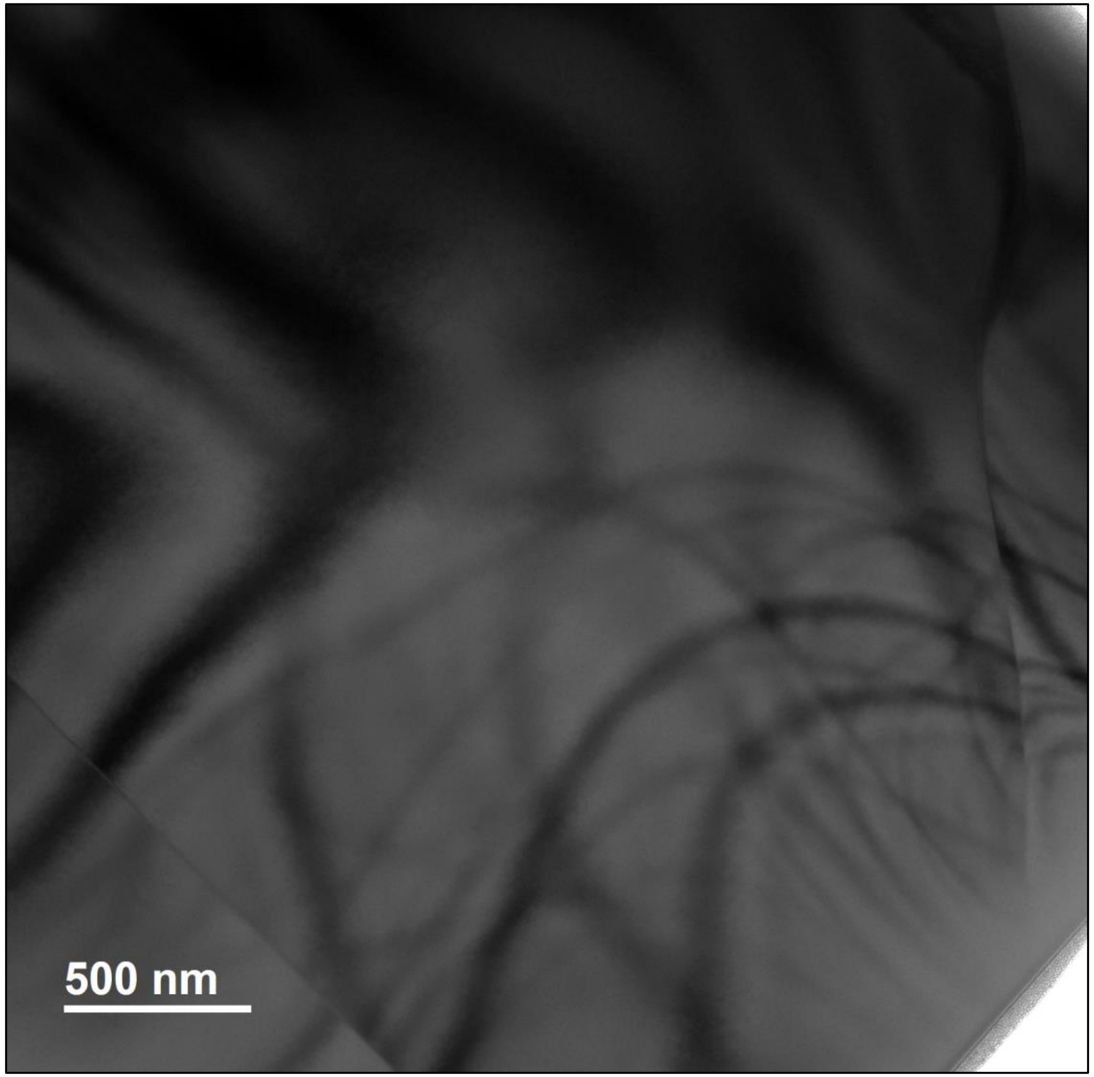


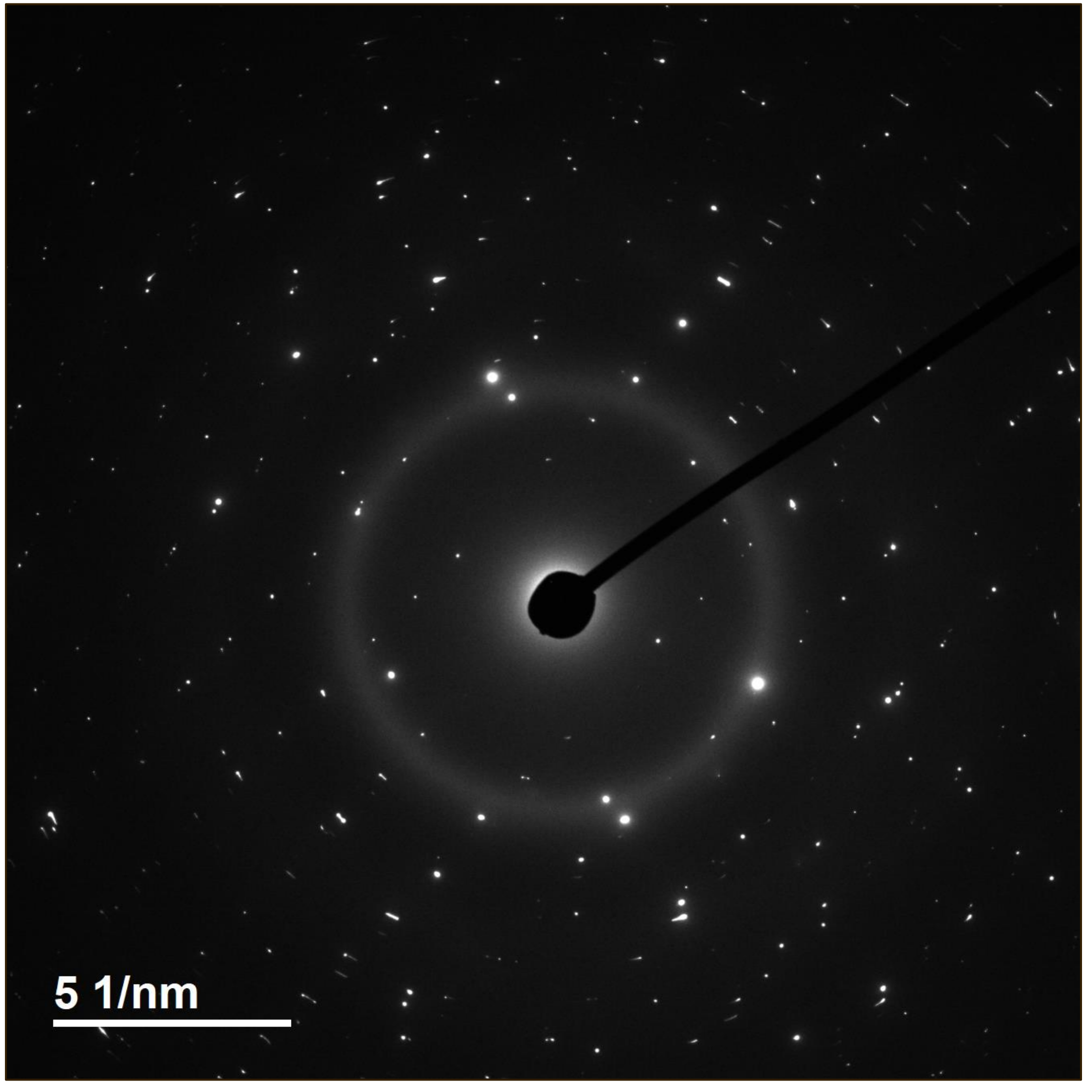
Nuclear Science User Facilities

Argonne NATIONAL LABORATORY

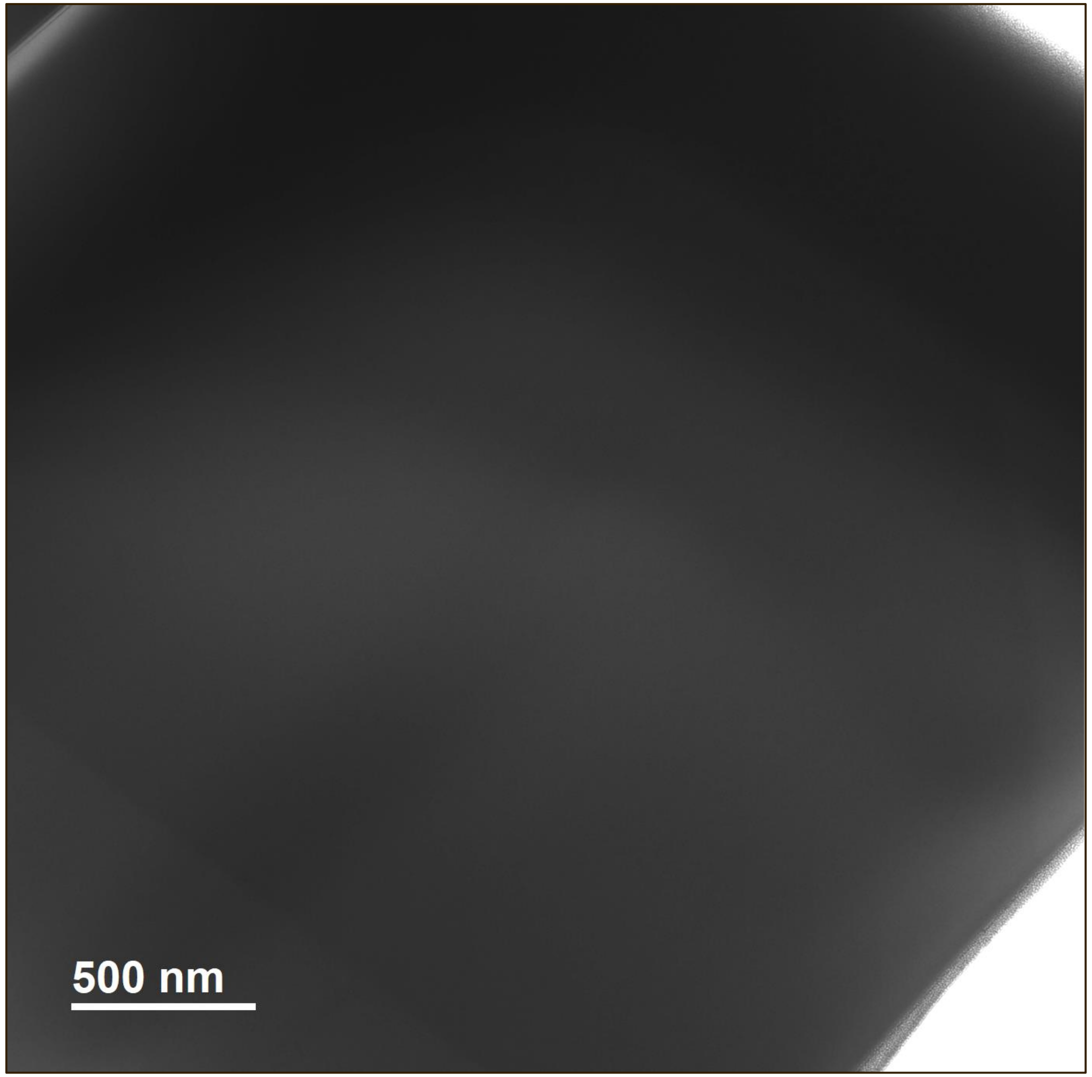
Work in partnership with Dr. H.V. Tin (LANL)

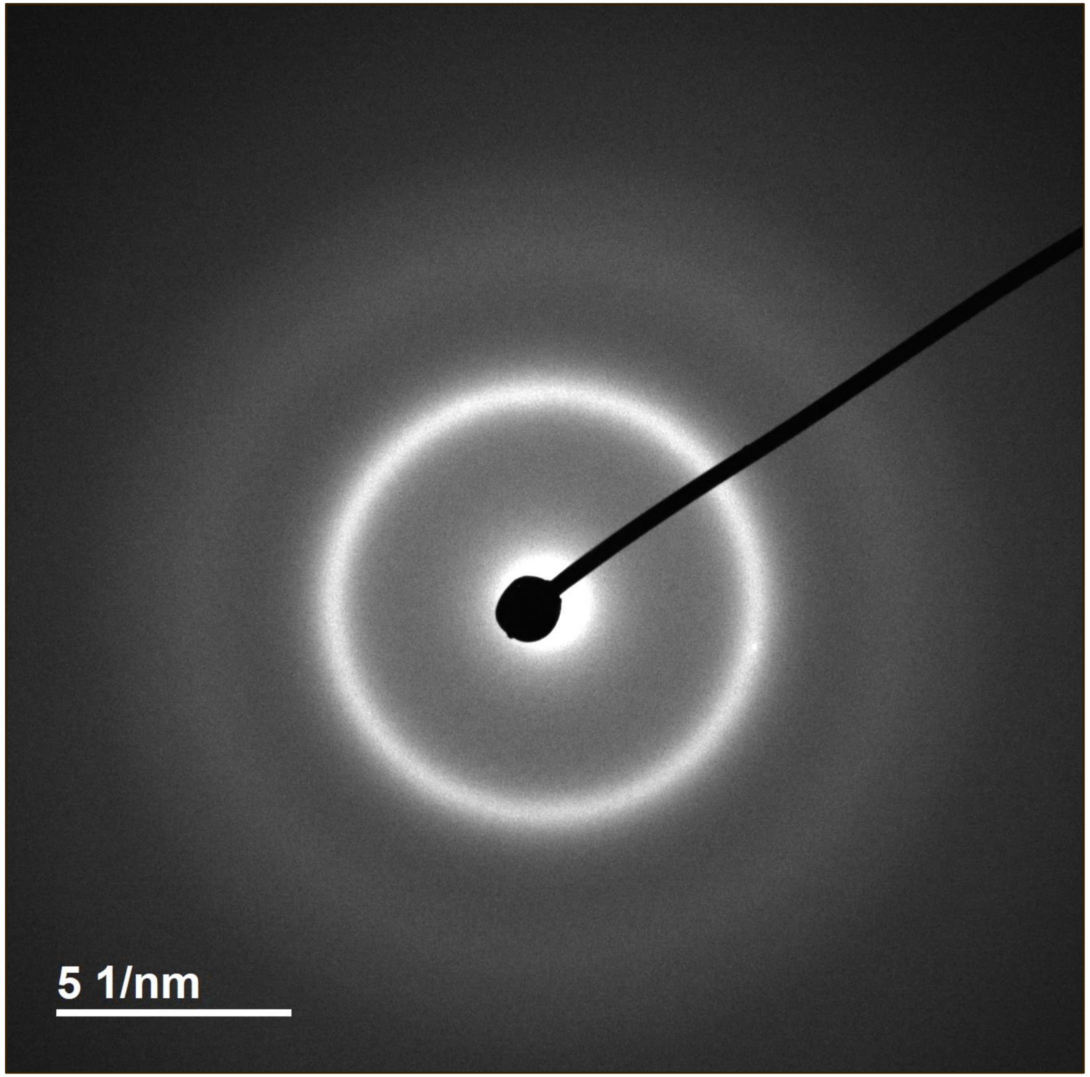
ANL-IVEM Irradiations at 573 K: ~0.1 dpa



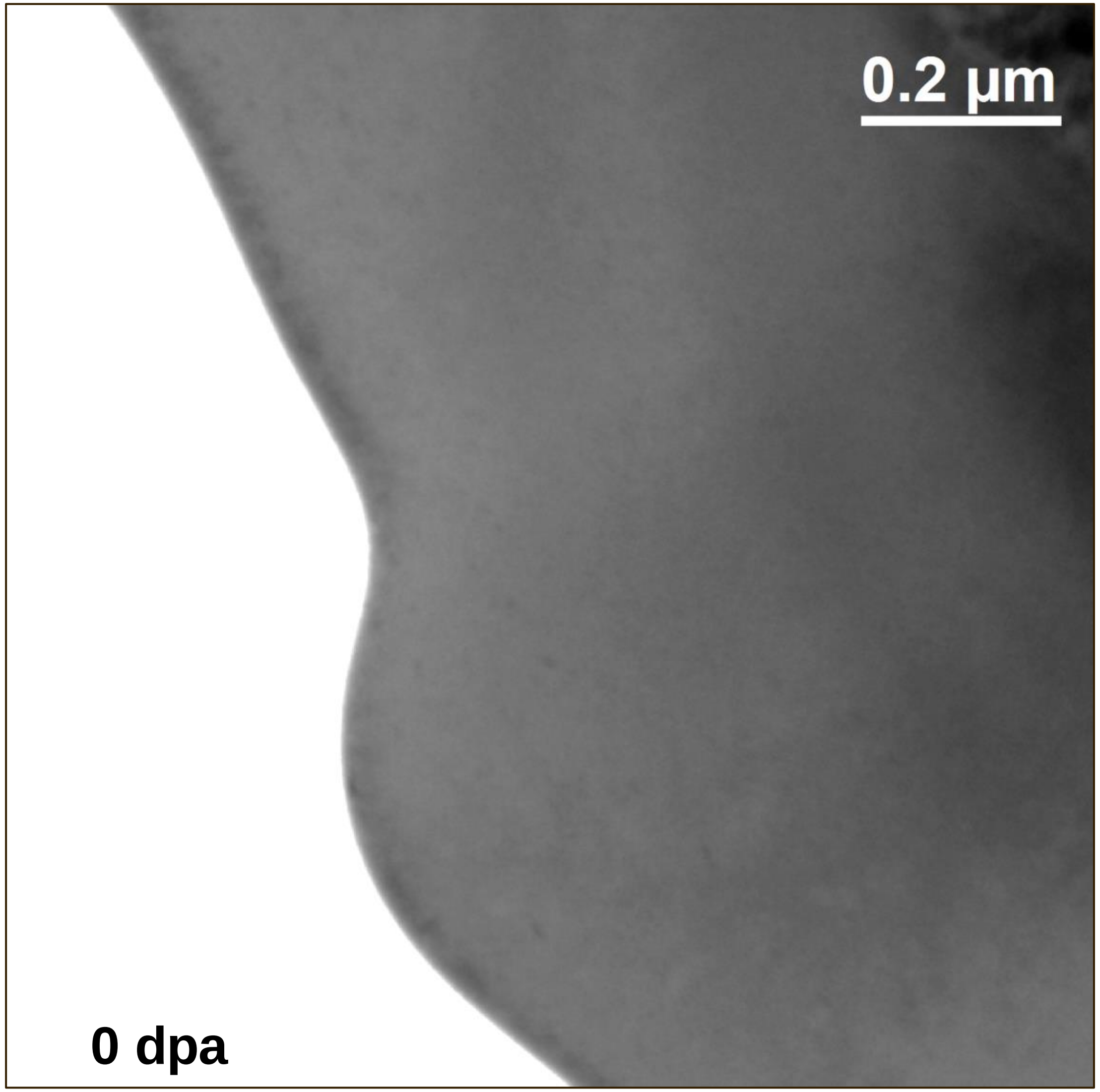


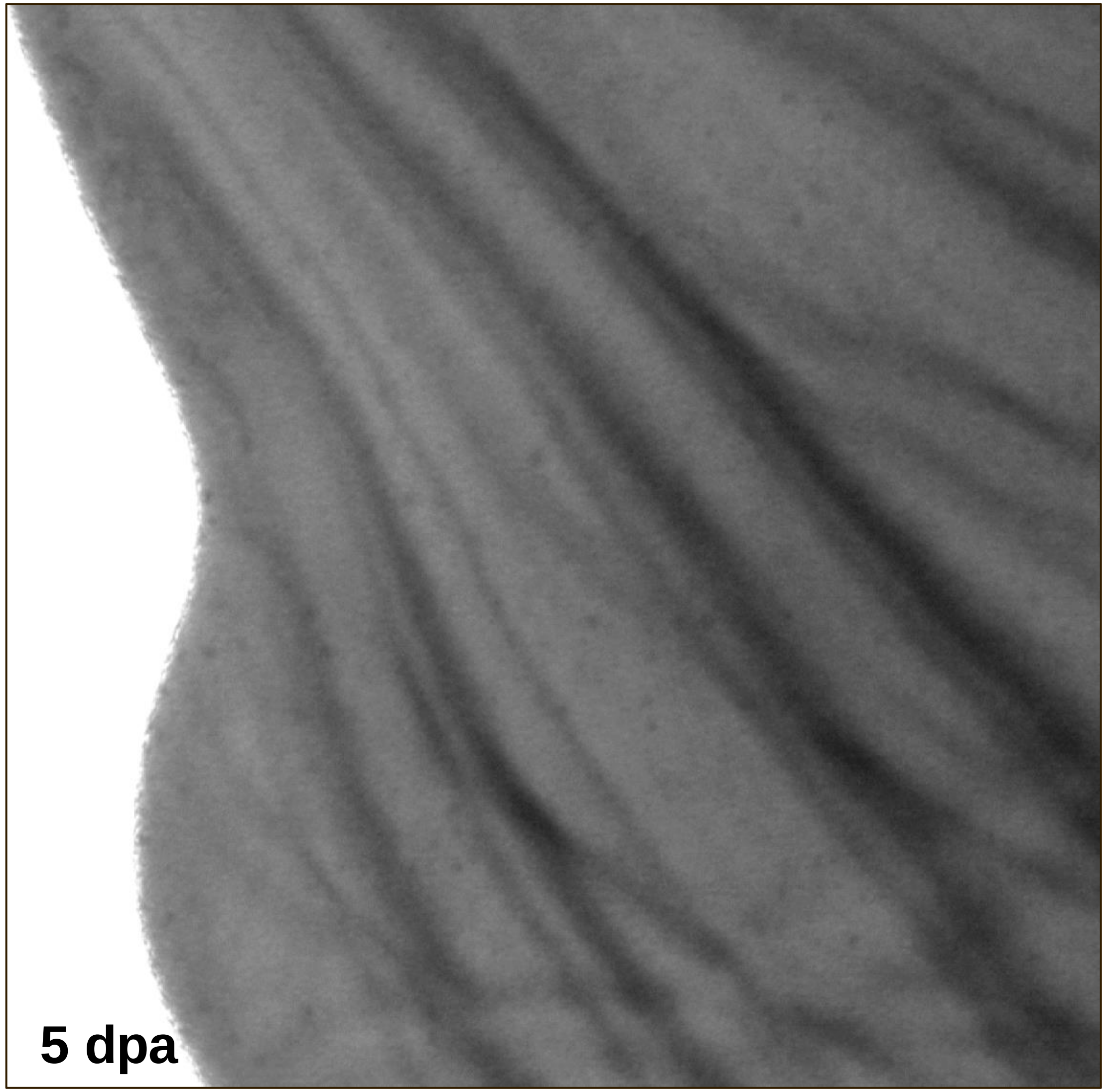
ANL-IVEM Irradiations at 573 K: ~1.0 dpa





ANL-IVEM Irradiations at 1073 K





Summary of the Project

- **A novel class of ternary silicides is emerging, thus extending the MAX phase concept beyond carbides and nitrides.**
- **Challenge is to produce a pure ZIA phase: as so it is for MAX phases.**
- **Refractory nanolayered intermetallic-ceramic compounds. Mechanical properties? Physical-chemical properties? And so on…**
- **Promising application in high-temperature irradiation environments. (although we tested only as-cast sample seemly off equilibrium/stabilization).**

Materials at Extremes

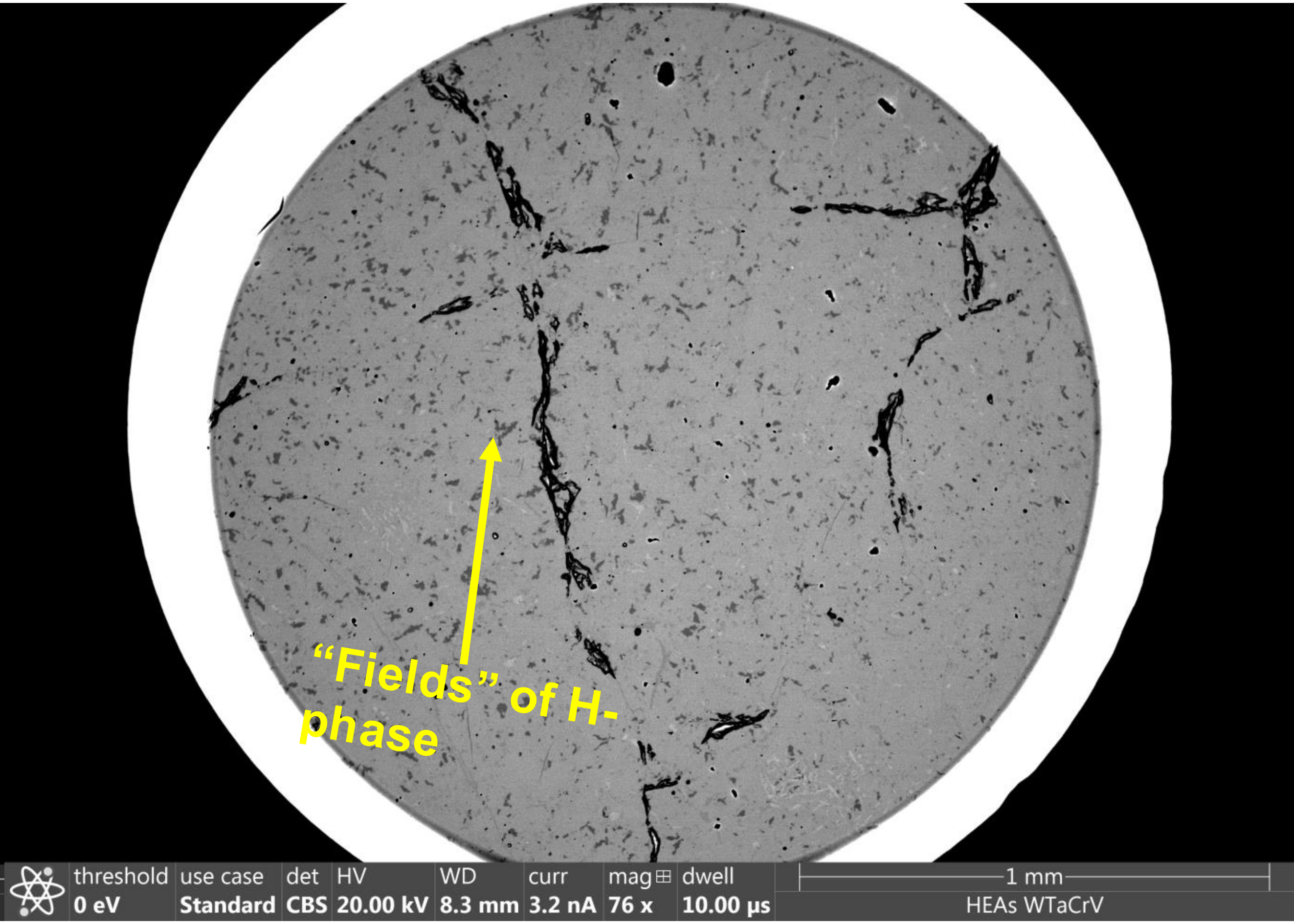
Thank you!

PROJECT
ZIA-PHASES

| tunes@lanl.gov |

| materialsatextremes.wordpress.com |

HT results



800°C for 120 hours: Gladyshevskii et al. 1962
800°C for 1000 hours: us, 2019.
1050°C for 336 hours: us, 2020.
1148°C for 336 hours: LANL, 2022.

XRD as-cast and HT