Project 46: Influence of Microstructure on the Oxidation Behaviors of Refractory Complex Concentrated Alloys (RCCAs)

Semi-annual Fall Meeting

April 2022

- Student: Noah Welch (ISU)
- Faculty: Dr. Peter C. Collins (ISU)
- Industrial Mentors: Dr. Todd Butler (AFRL)

Project 46: Influence of Microstructure on the Oxidation Behaviors of Refractory Complex Concentrated Alloys (RCCAs)

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- Student: Noah Welch (ISU)
- Advisor(s): Peter Collins (ISU), Maria Quintana (ISU)

Project Duration

PhD: Fall 2020 to Spring 2024

- Problem: The oxidation mechanisms in RCCAs and the influence of microstructure on oxide formation are poorly understood.
- Objective: Investigate microstructural influence on the oxidation properties of RCCAs, specifically TaTiCr system.
- Benefit: RCCAs show great promise for future use in advanced, high-temperature structural applications.

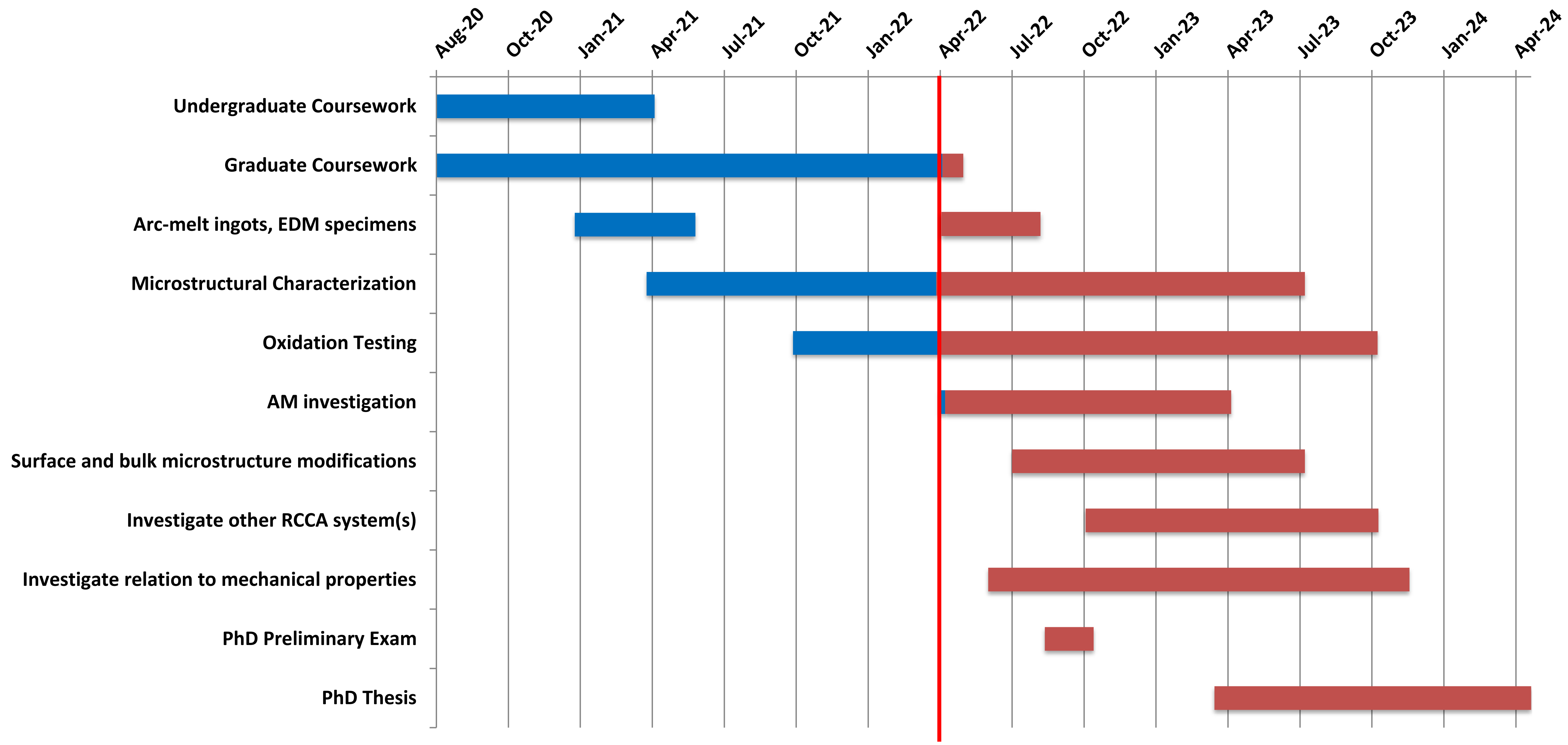
Recent Progress

- Completed TGA Oxidation tests of Ta-Ti-Cr alloys in HIP condition
- EDS, SEM, and XRD analysis of oxide structures and investigation of oxidation mechanisms in each alloy
- Promising alloy identified, investigating nearby composition ranges using AM for future oxidation testing
- Draft manuscript on oxidation behavior being sent to CANFSA IAB

Metrics

Description	% Complete	Status
1. Literature review	80%	●
2. Cast specimens at desired compositions for oxidation tests, characterize microstructure.	50%	●
3. Test oxidation performance with TGA and investigate oxidation mechanisms in various processing conditions	50%	●
4. Measure mechanical properties	0%	●
5. Investigate expansibility to other RCCA systems	0%	●

Progress


Aug-20
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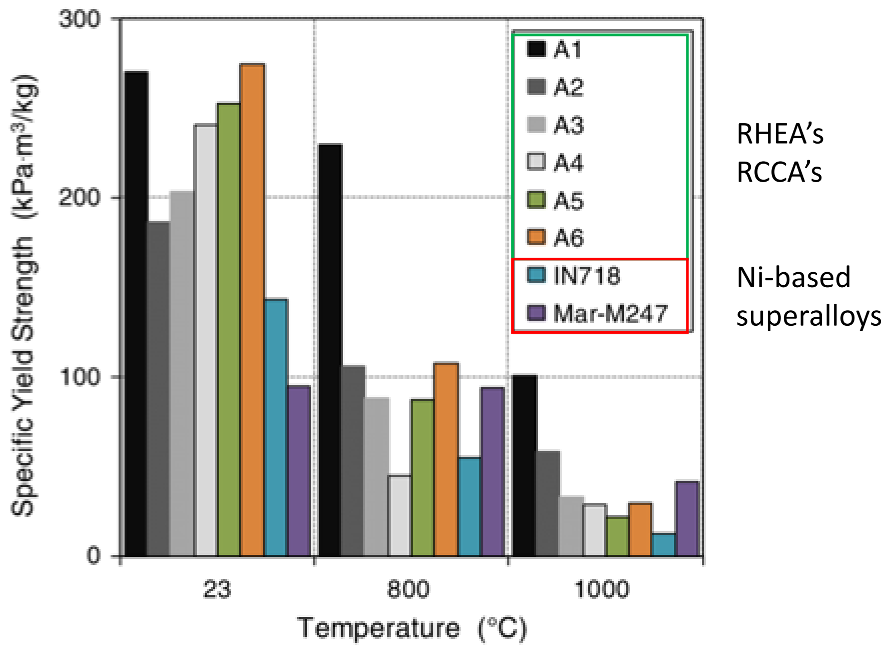
Jul-23
Oct-23
Jan-24
Apr-24
Undergraduate Coursework
Graduate Coursework
Arc-melt ingots, EDM specimens
Microstructural Characterization
Oxidation Testing
AM investigation
Surface and bulk microstructure modifications
Investigate other RCCA system(s)
Investigate relation to mechanical properties
PhD Preliminary Exam
PhD Thesis

Industrial Relevance



Comparison of refractory high entropy alloys (RHEA) and RCCA specific yield strength to two Ni-based superalloys

Implications:

- Displace Ni-based superalloys as prominent advanced structural alloys
  - Improved oxidation performance and mechanical properties
- Framework for future alloy development

Applications:

- High temperature, structural components and advanced propulsion components

Benefits:

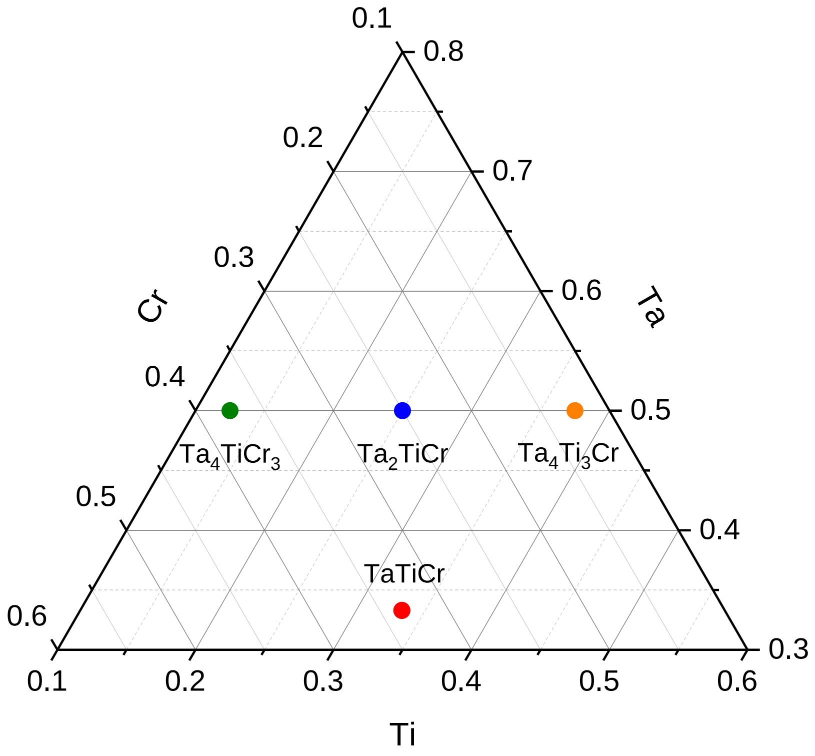
- Higher operating temperatures
- Better oxidation performance
- Improved high-temperature processes

Senkov, et al., *JOM, 2014*

Outline

- Ta-Ti-Cr system
- HIP Microstructure
- Oxidation Tests
- Post-oxidation Microstructure
- Conclusions
- Future Work

Ta-Ti-Cr System



- Characterize four alloys in system
  - TaTiCr ($Ta_{33.3}Ti_{33.3}Cr_{33.3}$)
  - Ta_4Ti_3Cr ($Ta_{50}Ti_{37.5}Cr_{12.5}$)
  - Ta_2TiCr ($Ta_{50}Ti_{25}Cr_{25}$)
  - Ta_4TiCr_3 ($Ta_{50}Ti_{12.5}Cr_{37.5}$)
- Predicted to form (Ta,Ti)-rich bcc solid solution and Cr_2-(Ta,Ti) Laves precipitates
- Initial investigation to determine promising candidates with good oxidation properties

Microstructure

Microstructure - HIP

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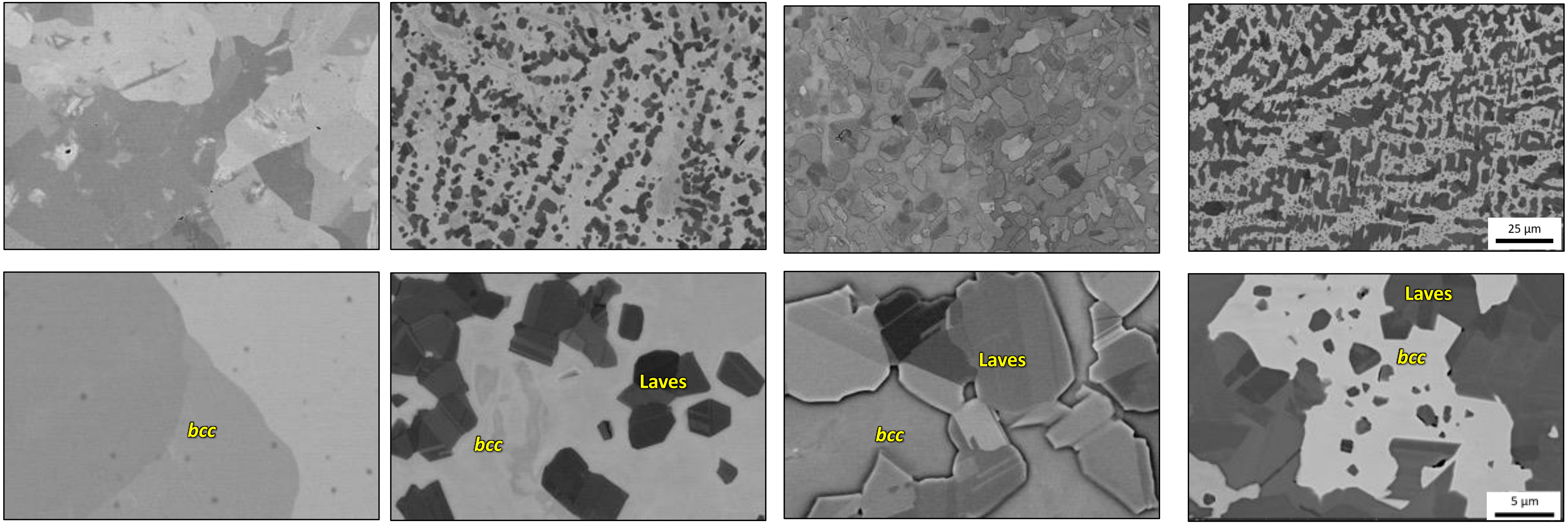
Ta_4Ti_3Cr | Ta_2TiCr | $TaTiCr$ | Ta_4TiCr_3

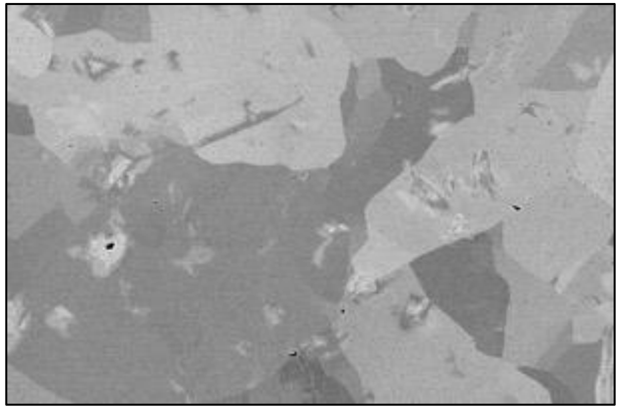


All specimens HIPed for 3 hrs, 30 ksi (207 MPa), 1400 °C

Microstructure - HIP

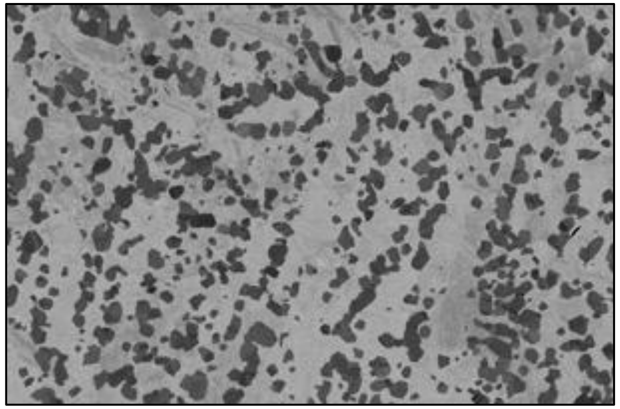
Increasing Laves fraction, increasing alloy Cr content →

Ta_4Ti_3Cr $f_{Laves} = 0$



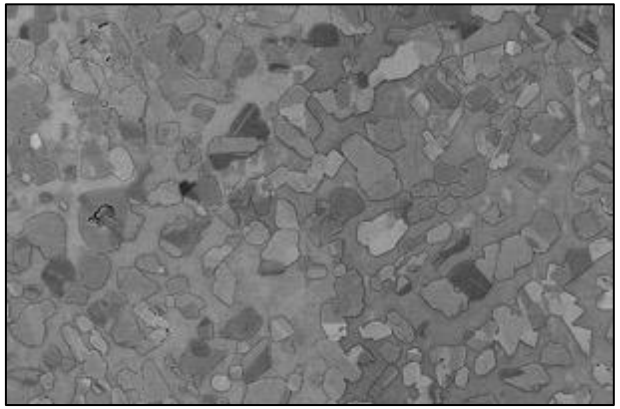
Hardness: 36.9 HRC, Density: 11.79 g/cm^3

Ta_2TiCr $f_{Laves} = 0.34$



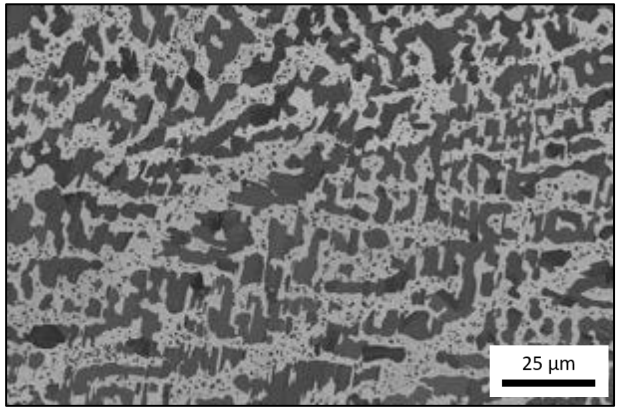
Hardness: 53.2 HRC, Density: 11.95 g/cm^3

$TaTiCr$ $f_{Laves} = 0.49$

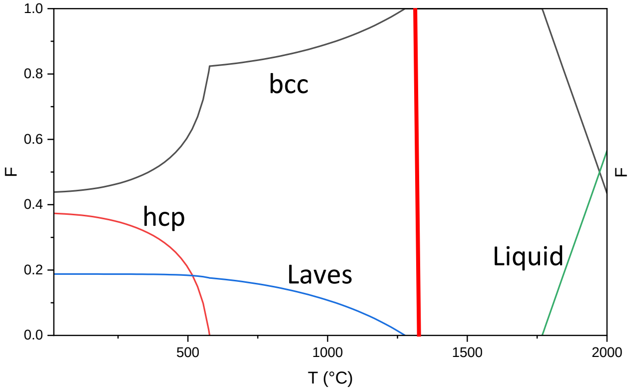


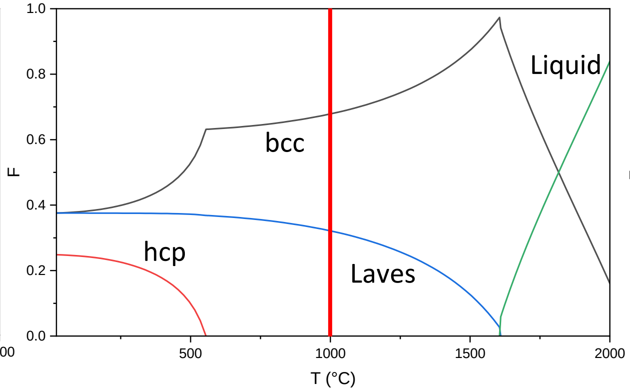
Hardness: 53.5 HRC, Density: 8.40 g/cm^3

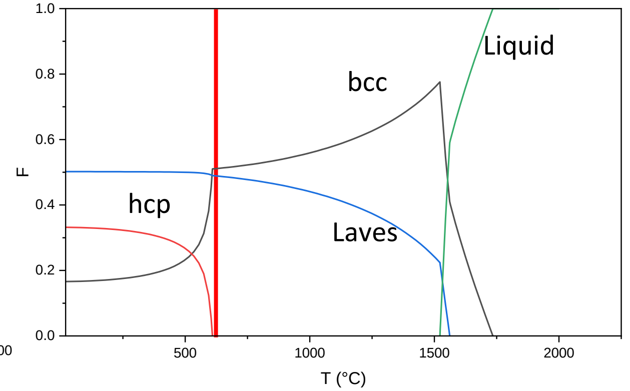
Ta_4TiCr_3 $f_{Laves} = 0.52$

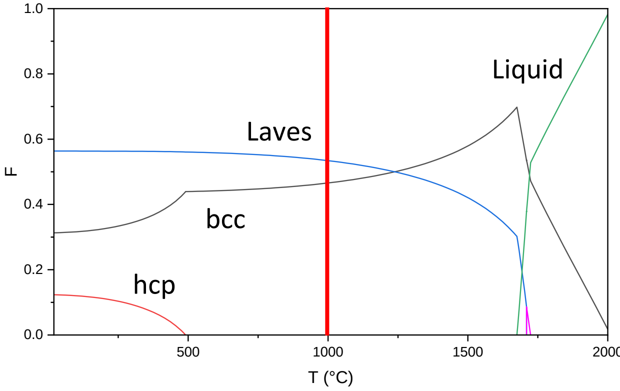


Hardness: 60.2 HRC, Density: 12.69 g/cm^3



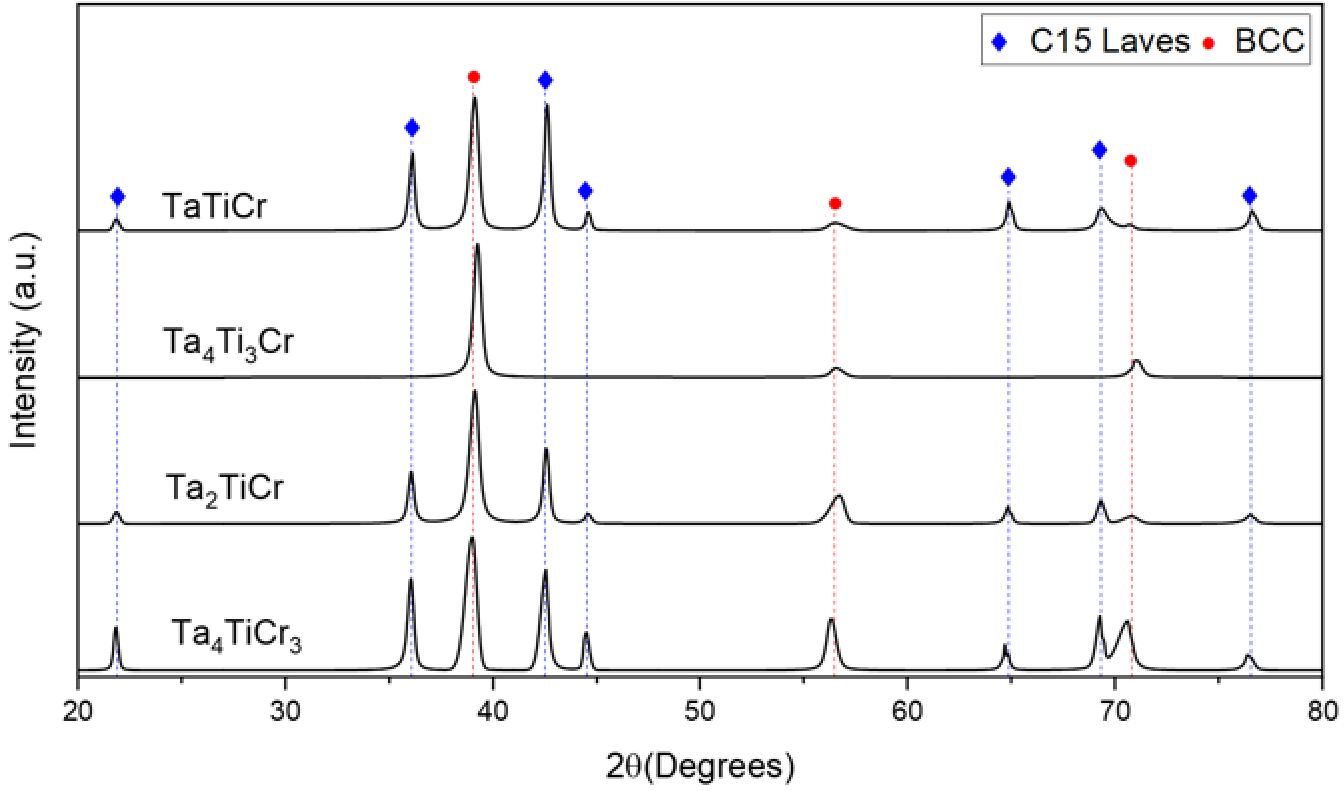






Sluggish kinetics are responsible for quasi-quenched state after cooling from 1400 °C. (Cooling rate 15 °C /min)

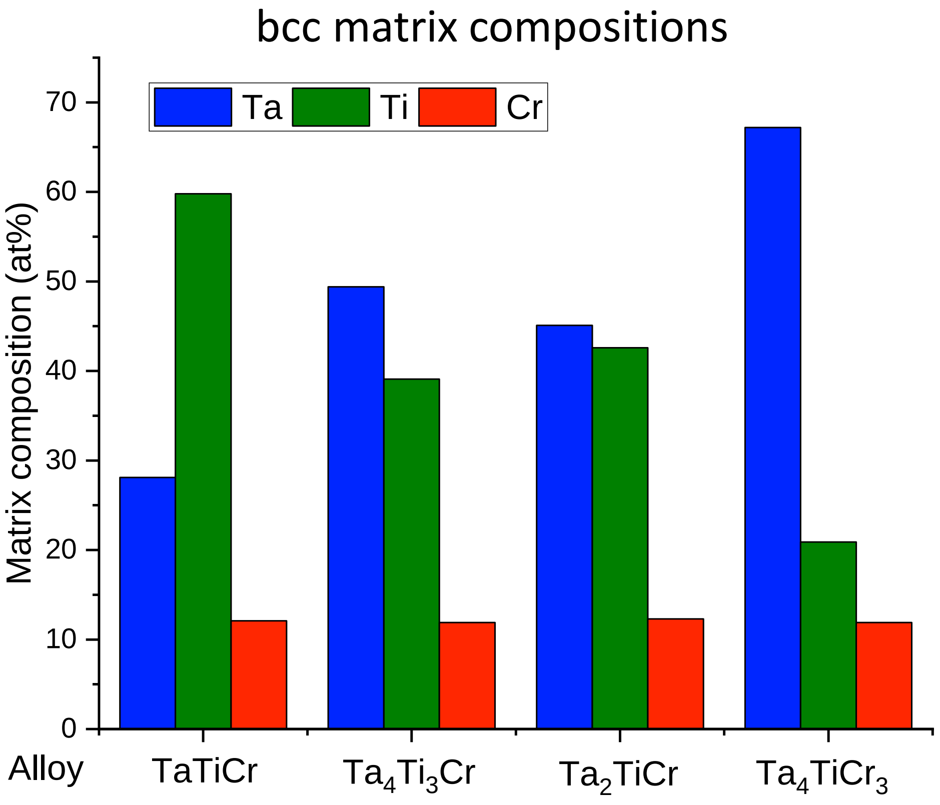
XRD Phase Verification

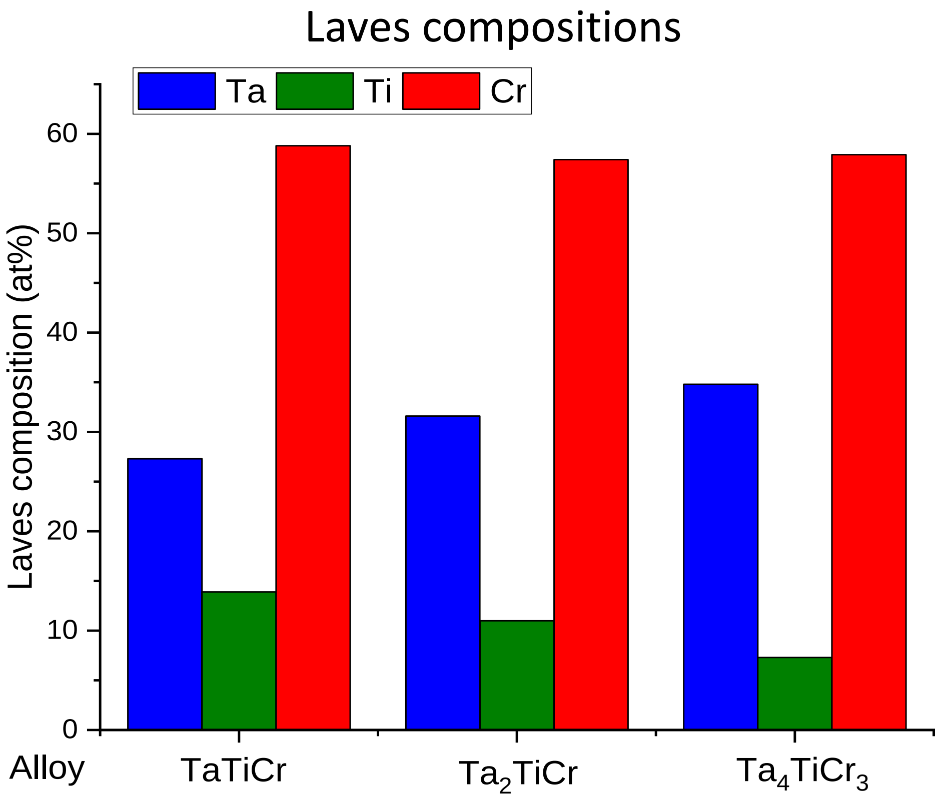


	TaTiCr	Ta_4Ti_3Cr	Ta_2TiCr	Ta_4TiCr_3
C15 Laves	7.024	-	7.036	7.047
bcc	3.243	3.247	3.254	3.264

Lattice parameters of phases (Å)

Phase Compositions





Alloy composition has a large influence on matrix composition and smaller effect on Laves composition

- Cr content in bcc matrix and Laves remains nearly constant across the four alloys
- Ta/Ti vary widely in matrix w.r.t. alloy composition (30-40%), not as much in Laves (5-6%)

*Hence, why TaTiCr matrix is so much darker in BSE images than other alloys (less Z-contrast between bcc and Laves)

Oxidation Tests

TGA Oxidation Tests – 1200°C

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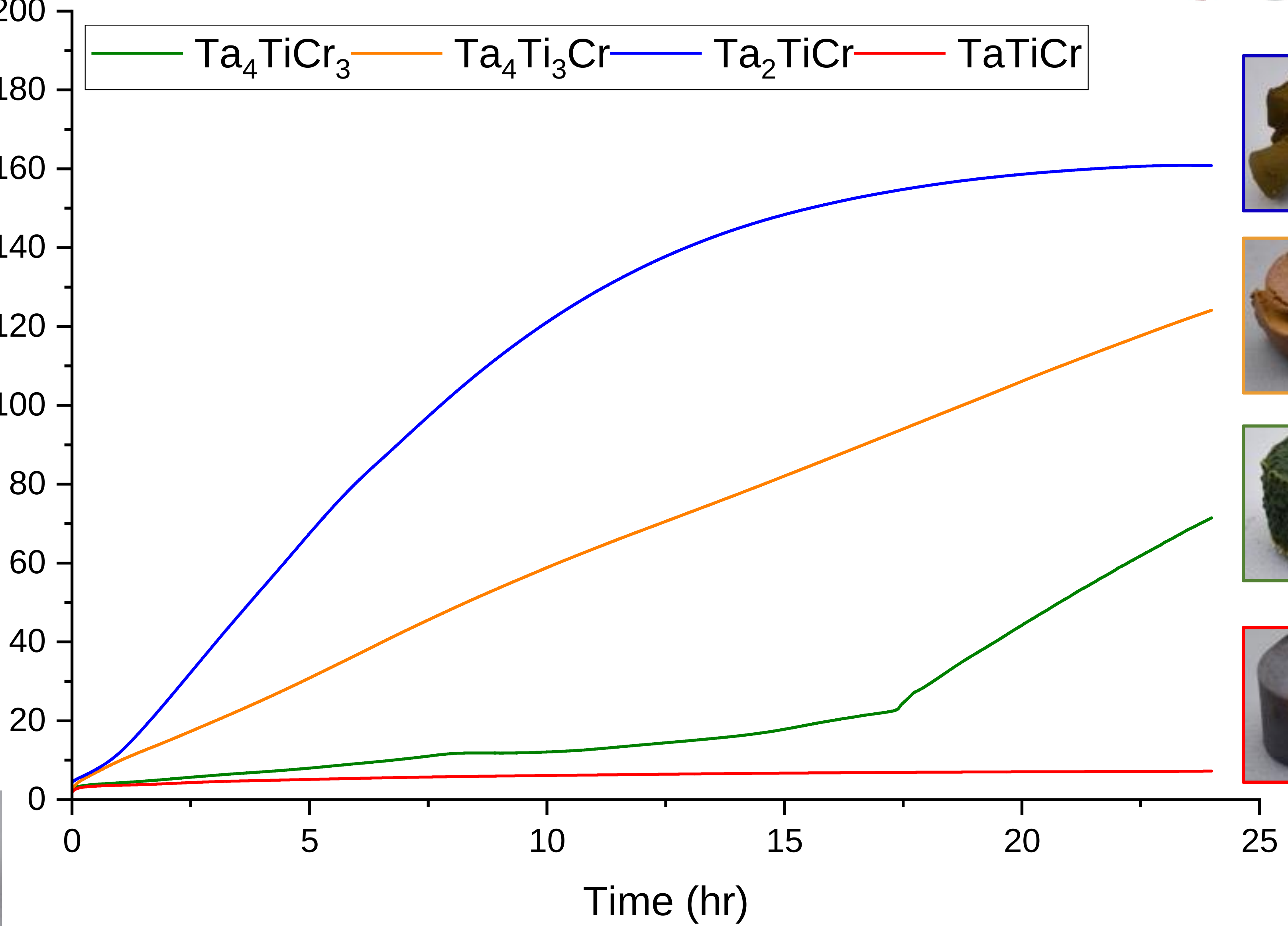


Ta_2TiCr

160.9 g/cm^2

Ta_4Ti_3Cr

124.1 g/cm^2

Ta_4TiCr_3

71.5 g/cm^2

TaTiCr

7.2 g/cm^2

Oxidation Kinetics

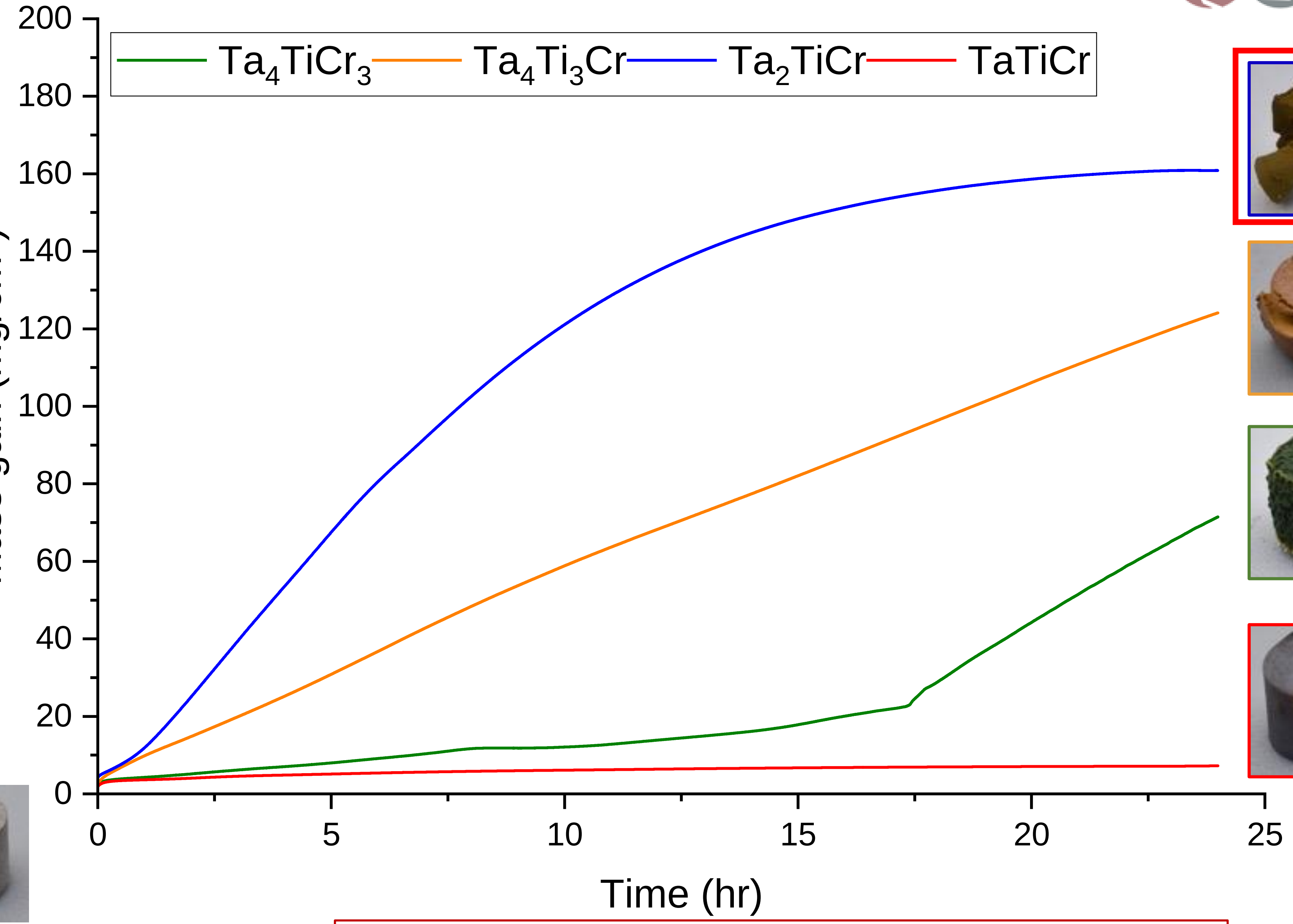
$$\Delta m = kt^n$$

- Δm = mass gain
- k = reaction rate constant
- n = time exponent
  - n >1, breakaway oxidation
  - n = 1, linear, interface-controlled
  - n = 0.5, parabolic, diffusion-controlled
  - n < 0.5, diffusion-controlled + volatilization effects

Alloy	Mass gain after 24 hrs (mg/cm^2)	k (mg/cm^2-h^n)	n	Duration
TaTiCr	7.2	3.58	0.23	0-24 hrs
Ta_4TiCr_3	71.5	3.55	0.51	0-6 hrs
		0.84	1.17	6-16 hrs
		0.01	3.19	16-24 hrs
Ta_4Ti_3Cr	124.1	7.88	0.85	0-24 hrs
Ta_2TiCr	160.9	12.06	1.03	0-24 hrs

Post-oxidation Microstructure

TGA Oxidation Tests – 1200°C



Ta$_2$TiCr

160.9 g/cm^2

Ta$_4$Ti$_3$Cr

124.1 g/cm^2

Ta$_4$TiCr$_3$

71.5 g/cm^2

TaTiCr

7.2 g/cm^2

Post-oxidation microstructure - Ta_2TiCr (1200°C, 13 hrs)

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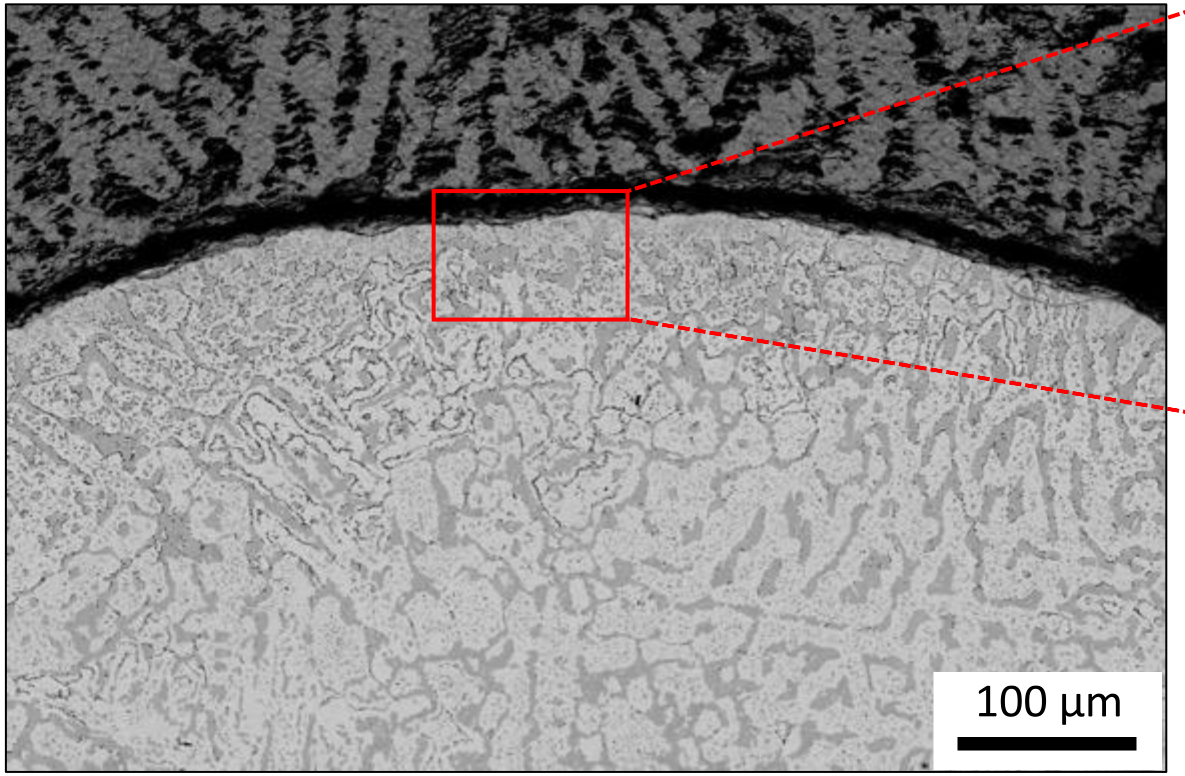
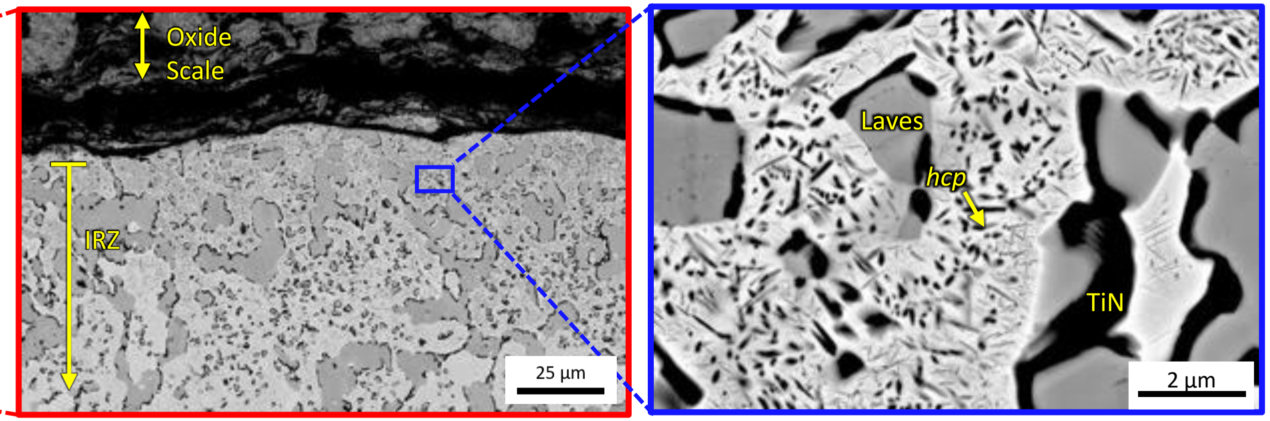
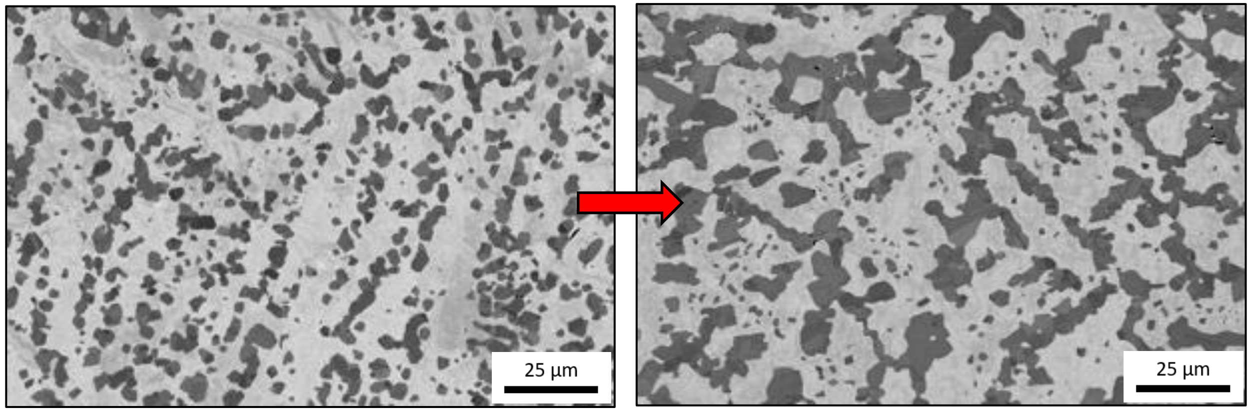




External scale: 1.15 mm
Internal reacted zone (IRZ): 150 µm

Bulk before oxidation

After 13 hrs at 1200°C



- Thick, separated oxide scale after 13 hrs
- Fine TiN and hcp precipitates along phase boundaries and in matrix.

Oxide Products – Ta_2TiCr (1200°C, 13 hrs)

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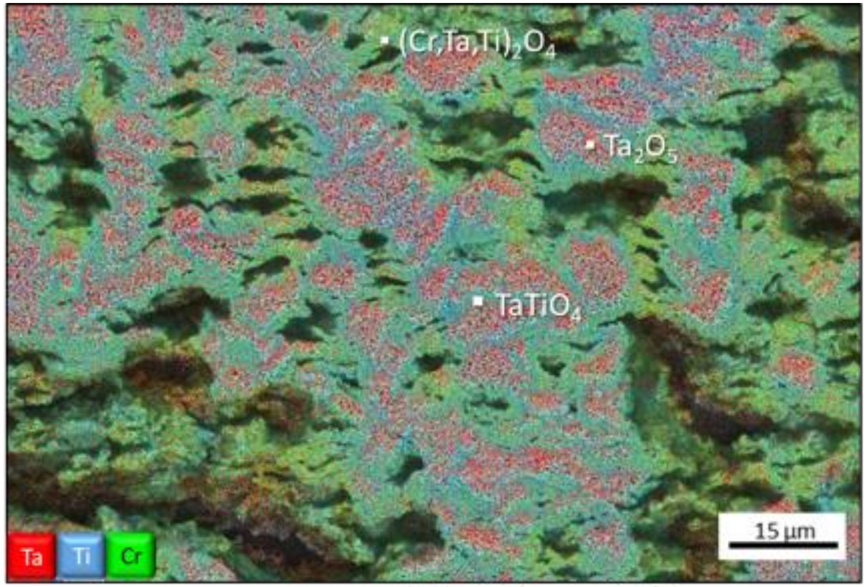
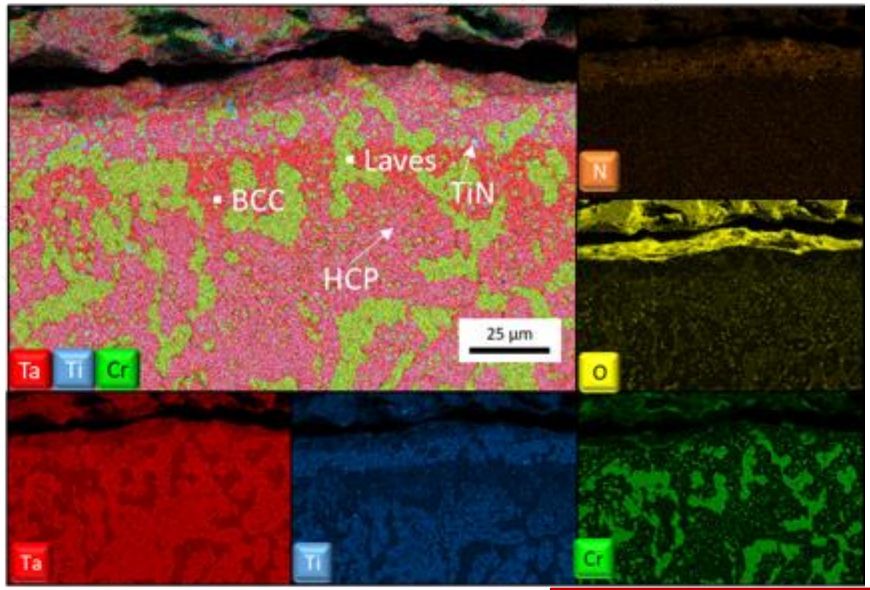
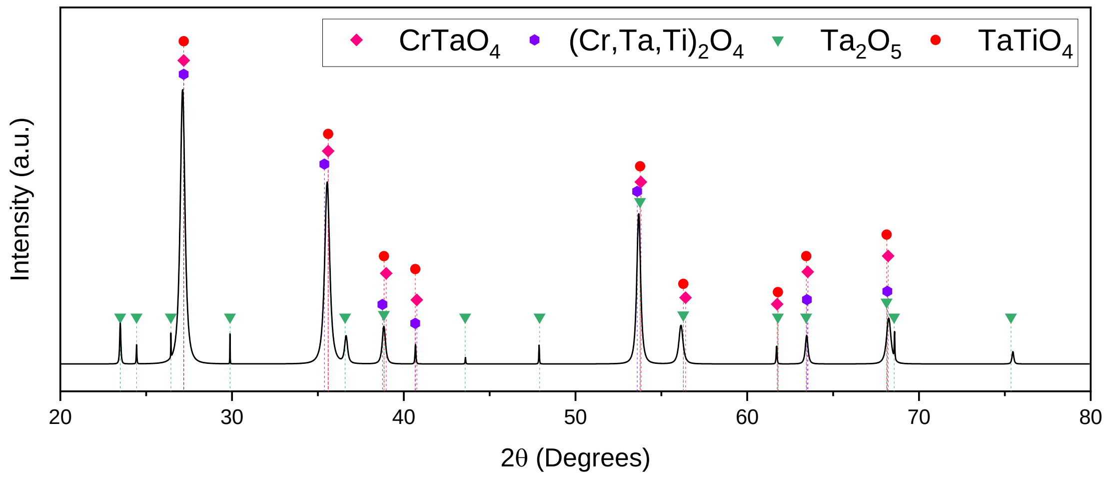
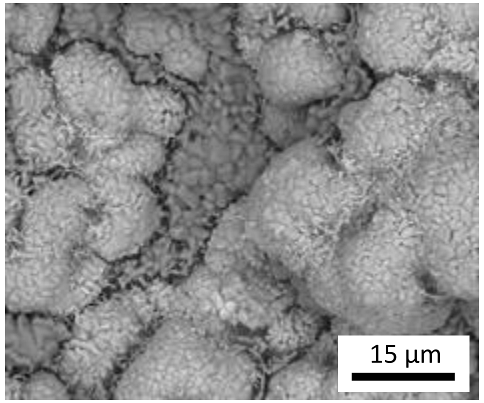




Powder XRD from oxide scale

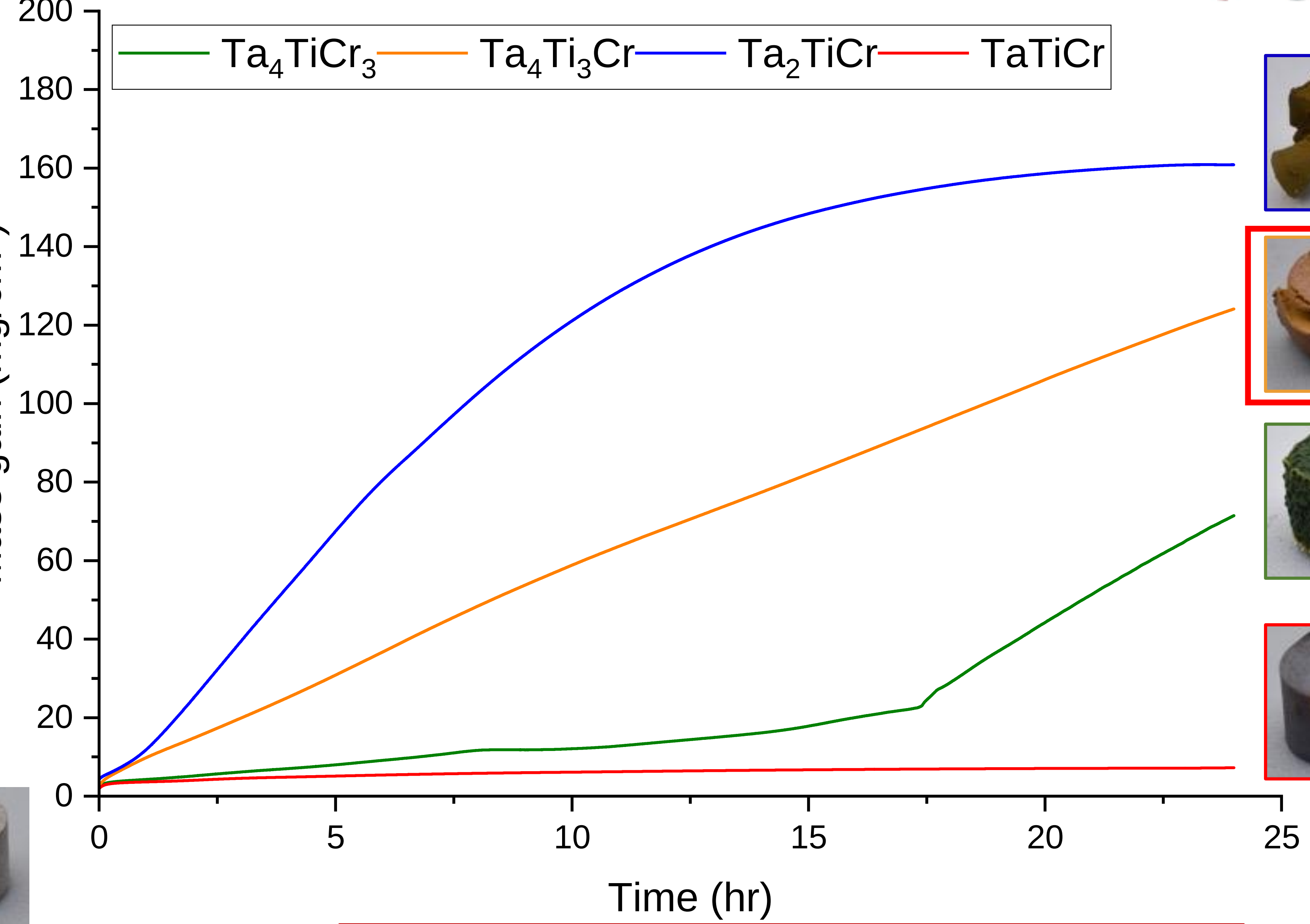


Scale surface



- Outer scale has repeating morphology due to local solute depletion phenomena from selective oxidation
- Consists primarily of "mixed" rutile oxides with pockets of Ta_2O_5
- Ta_2O_5 is harmful, offers no oxidation resistance

TGA Oxidation Tests – 1200°C



Ta_2TiCr

160.9 g/cm^2

Ta_4Ti_3Cr

124.1 g/cm^2

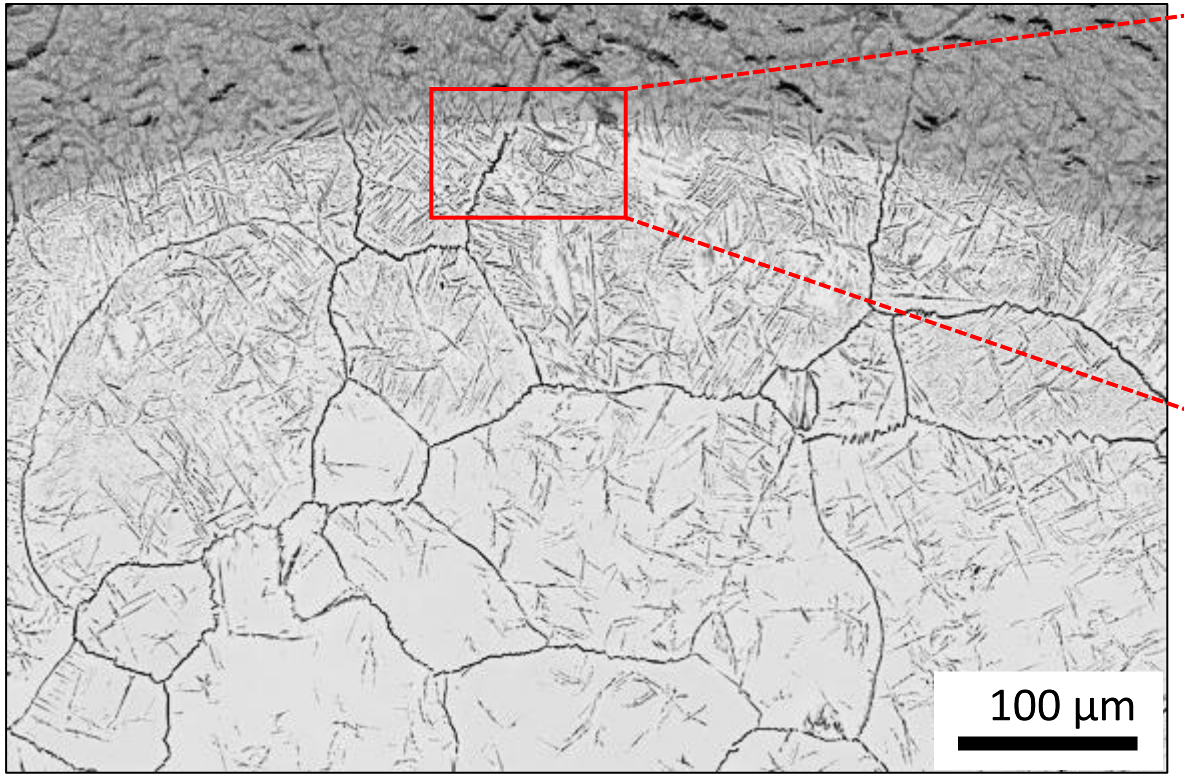
Ta_4TiCr_3

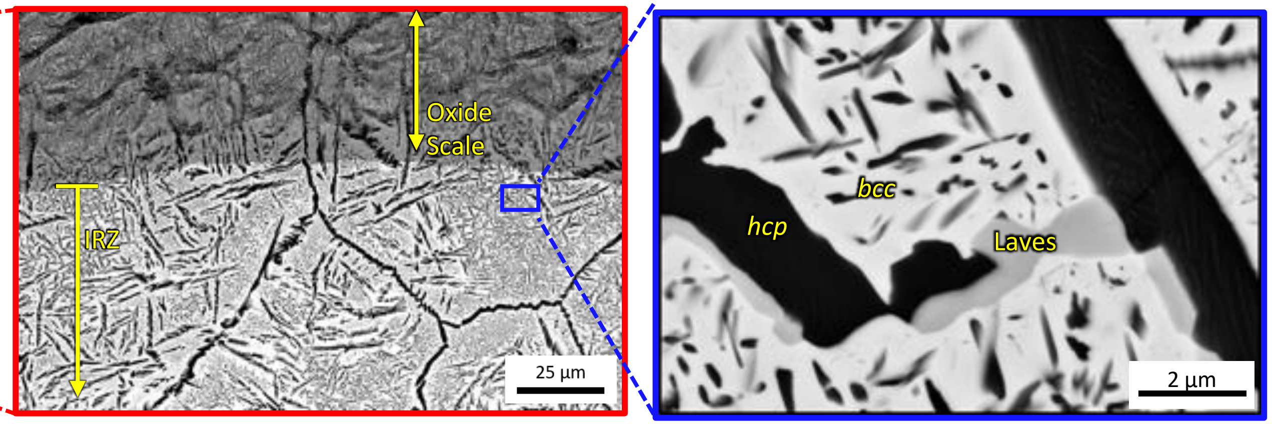
71.5 g/cm^2

TaTiCr

7.2 g/cm^2

Post-oxidation microstructure – Ta_4Ti_3Cr (1200°C, 24 hrs)

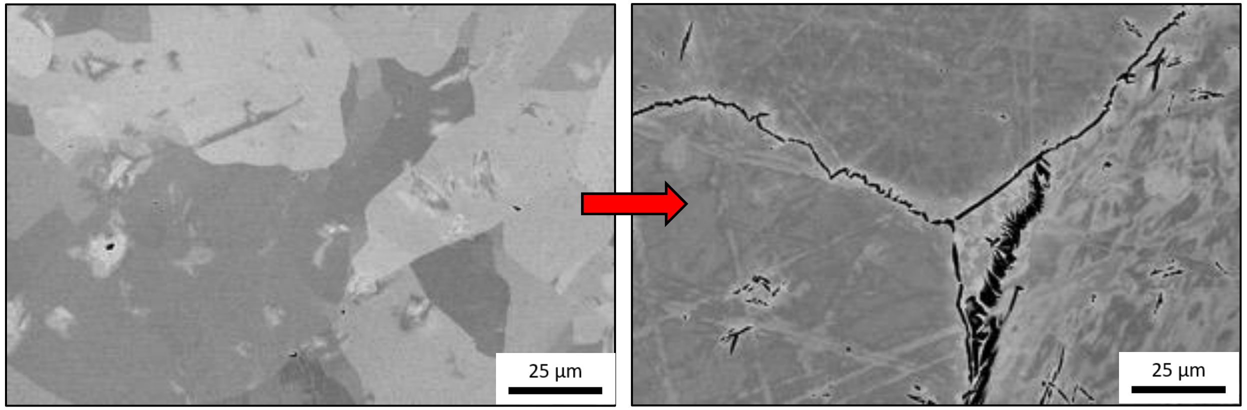




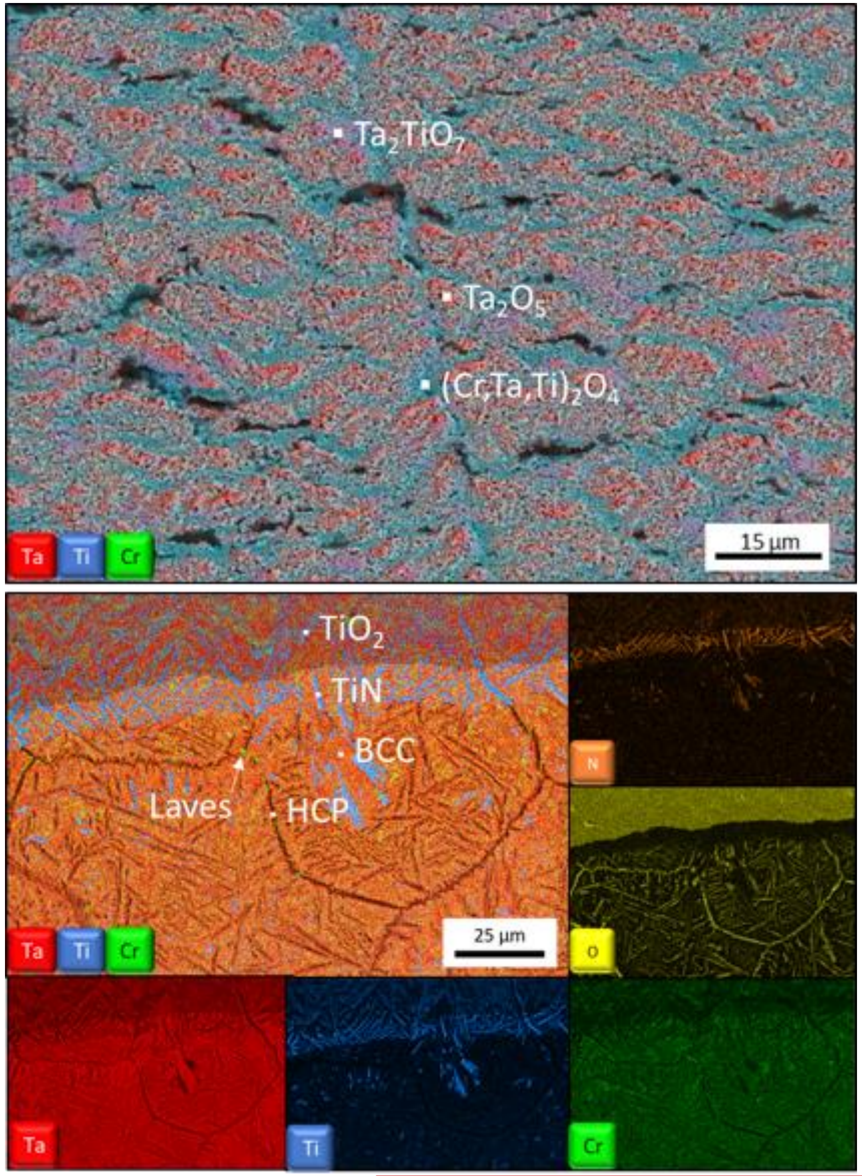
External scale: 1.29 mm
Internal reacted zone (IRZ): Through-thickness

- Thick oxide scale
- Through-thickness hcp precipitation along grain boundaries
- Fine Laves and hcp precipitates near oxide-IRZ interface

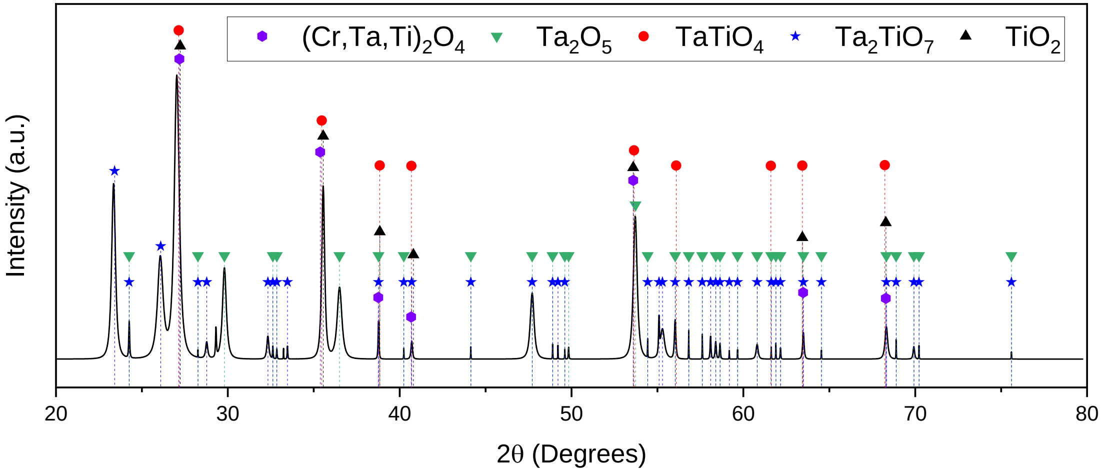
Bulk before oxidation | After 24 hrs at 1200°C



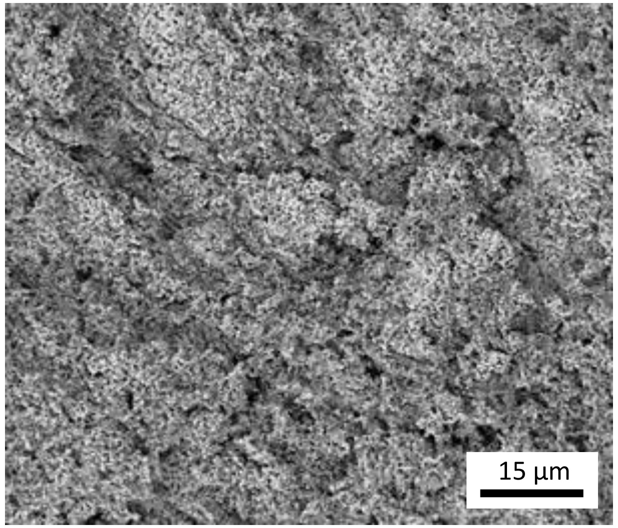
Oxide Products – Ta_4Ti_3Cr (1200°C, 24 hrs)



Powder XRD from oxide scale

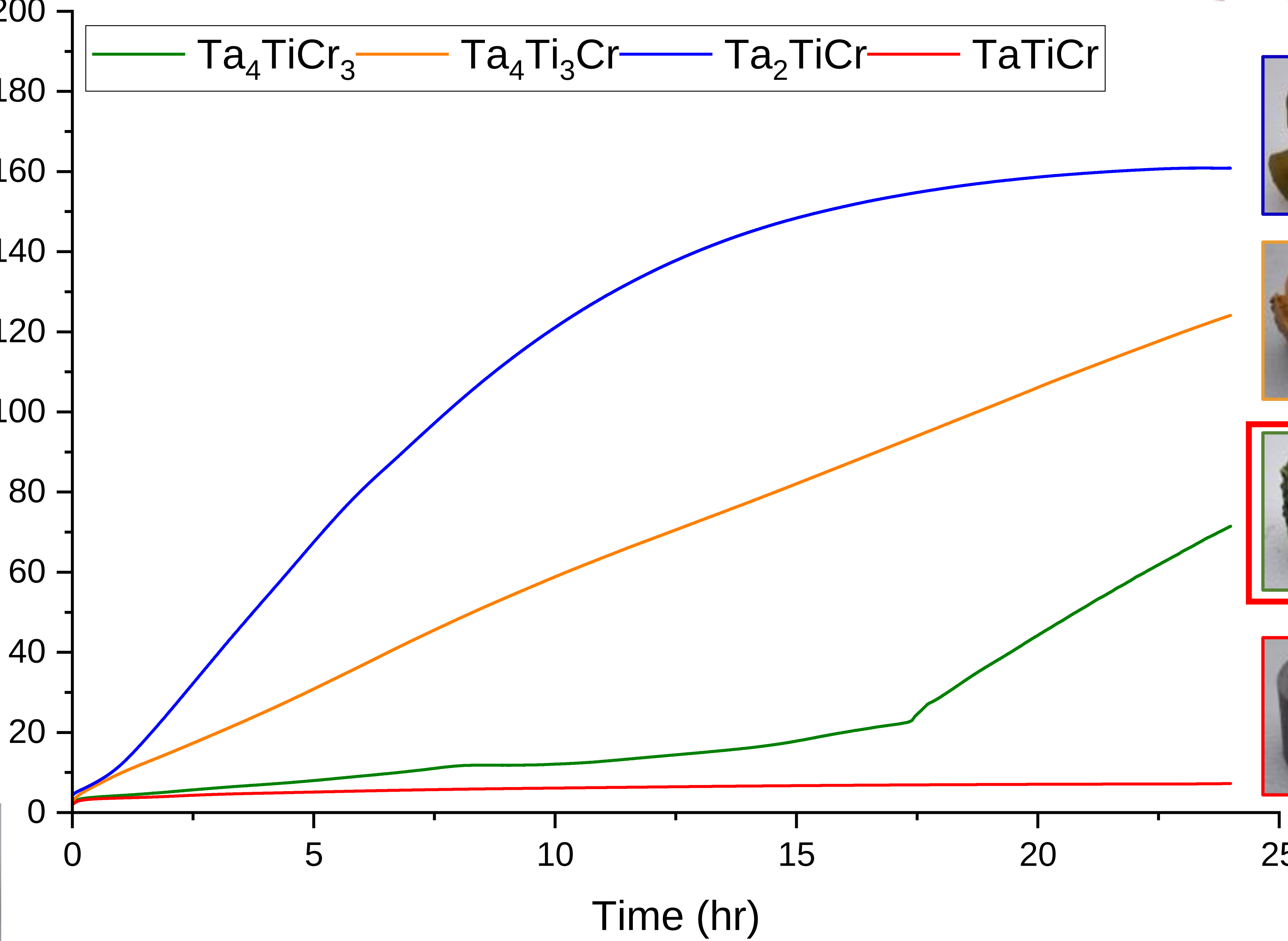


Scale surface



- Outer scale mostly Ta_2O_5 with branched $(Cr,Ta,Ti)_2O_4$ structures
- Matrix Ti depleted after oxidation, selectively oxidized

TGA Oxidation Tests – 1200°C



Ta_2TiCr

160.9 g/cm^2

Ta_4Ti_3Cr

124.1 g/cm^2

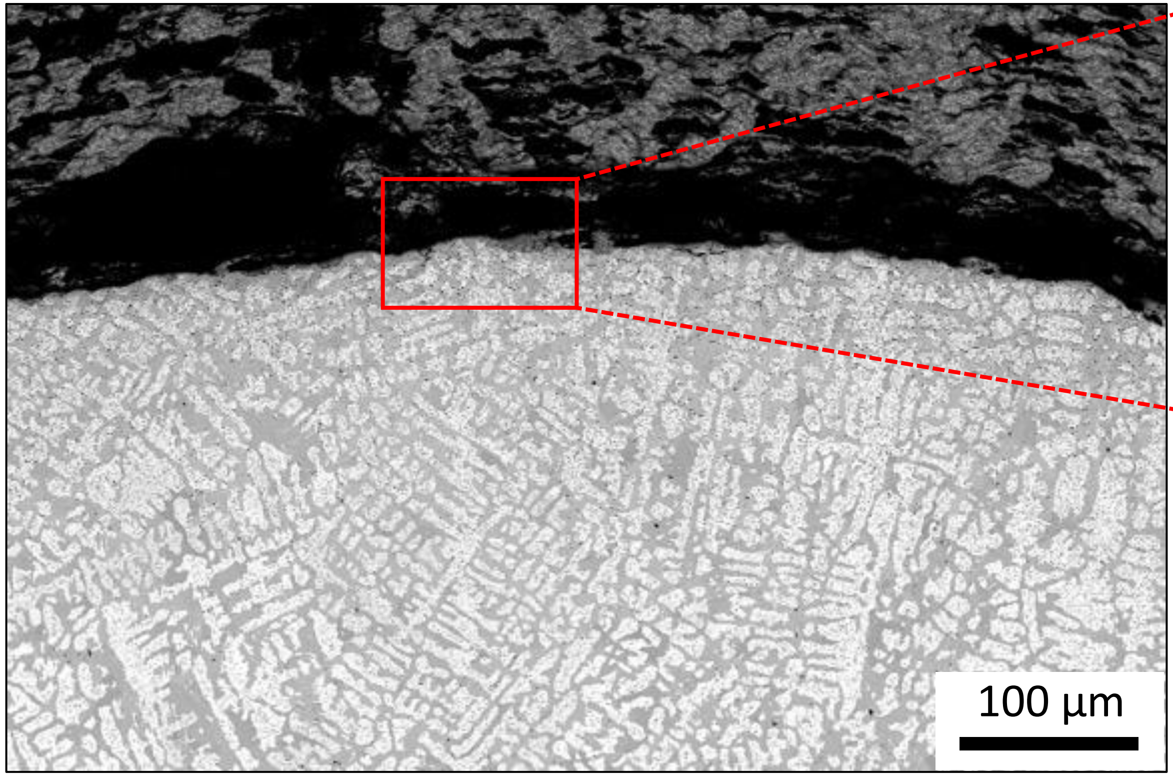
Ta_4TiCr_3

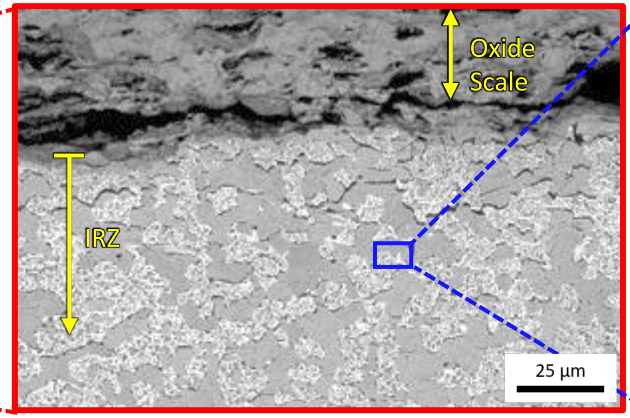
71.5 g/cm^2

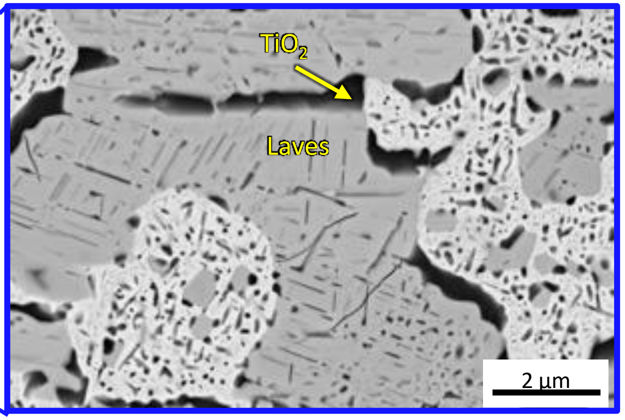
TaTiCr

7.2 g/cm^2

Post-oxidation microstructure – Ta_4TiCr_3 (1200°C, 24 hrs)



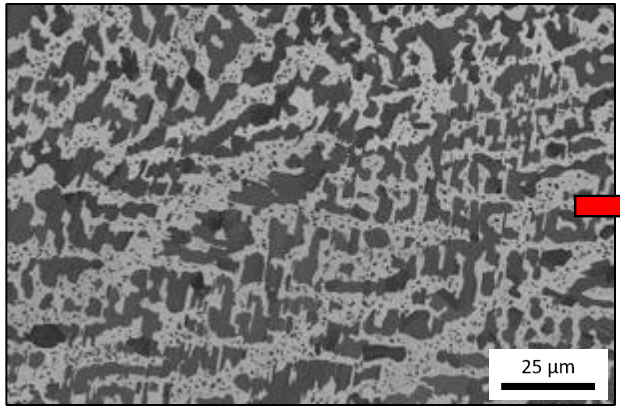




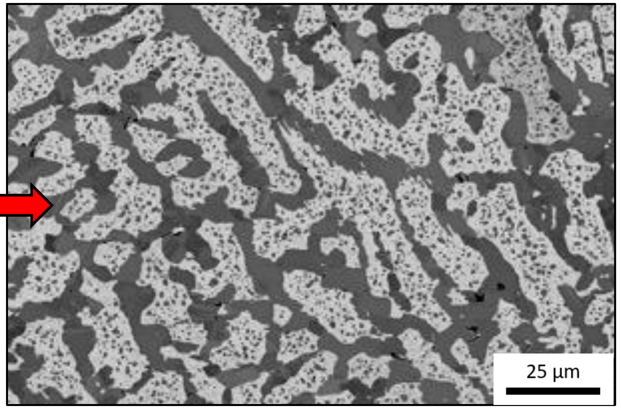
External scale: 600 µm
Internal reacted zone (IRZ): 100 µm

- Thick, separated scale
- Fine matrix precipitates and TiO_2 precipitations along phase boundaries near oxide-IRZ interface

Bulk before oxidation

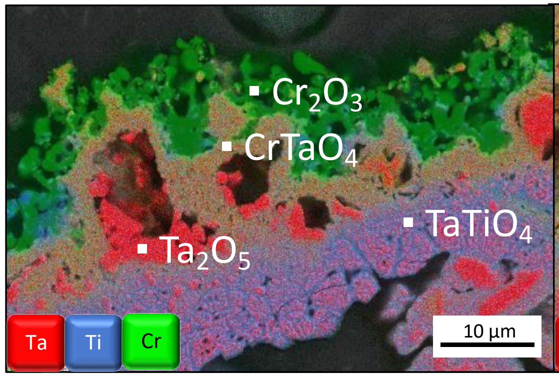


After 24 hrs at 1200°C

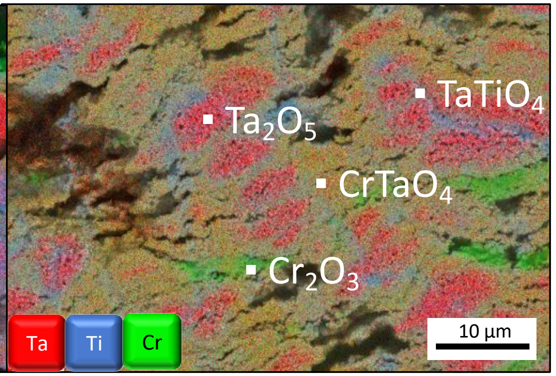


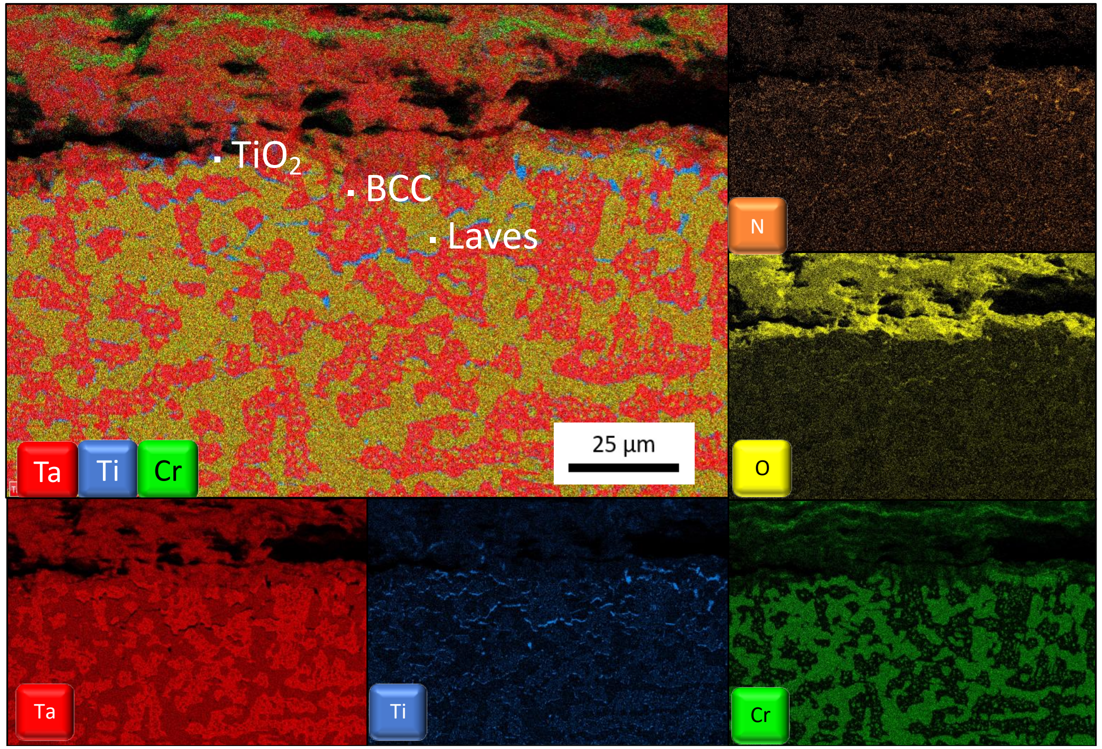
Oxide Products – Ta_4TiCr_3 (1200°C, 24 hrs)

Oxide surface

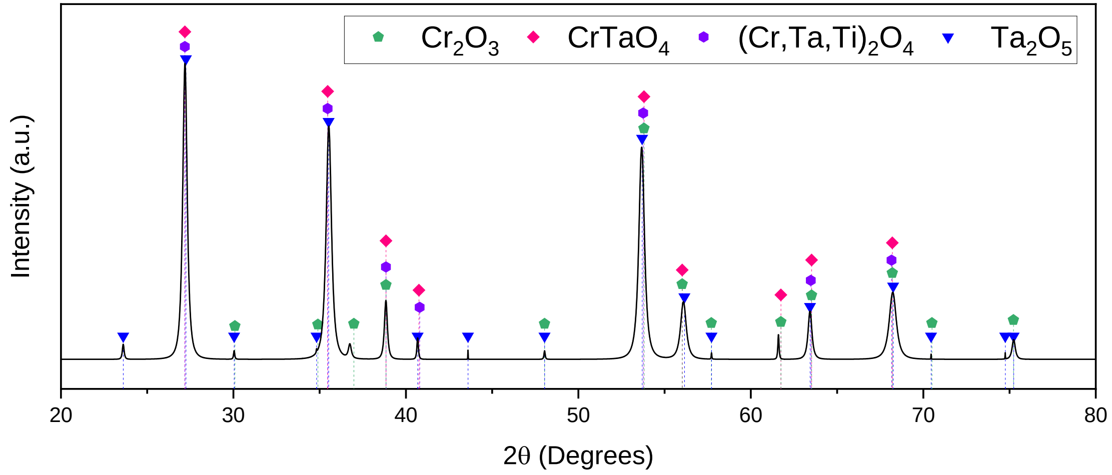


Oxide “bulk”

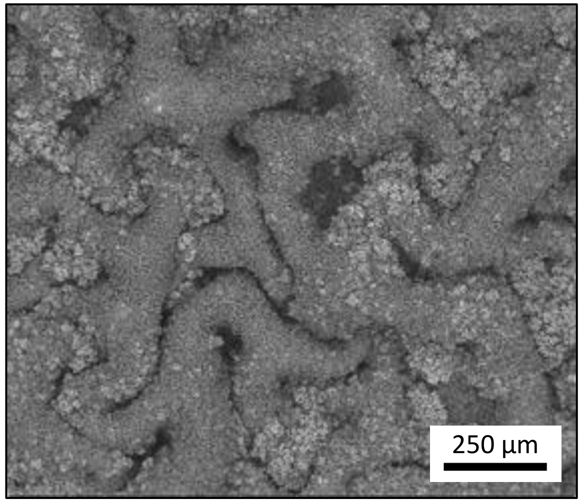




Powder XRD from oxide scale

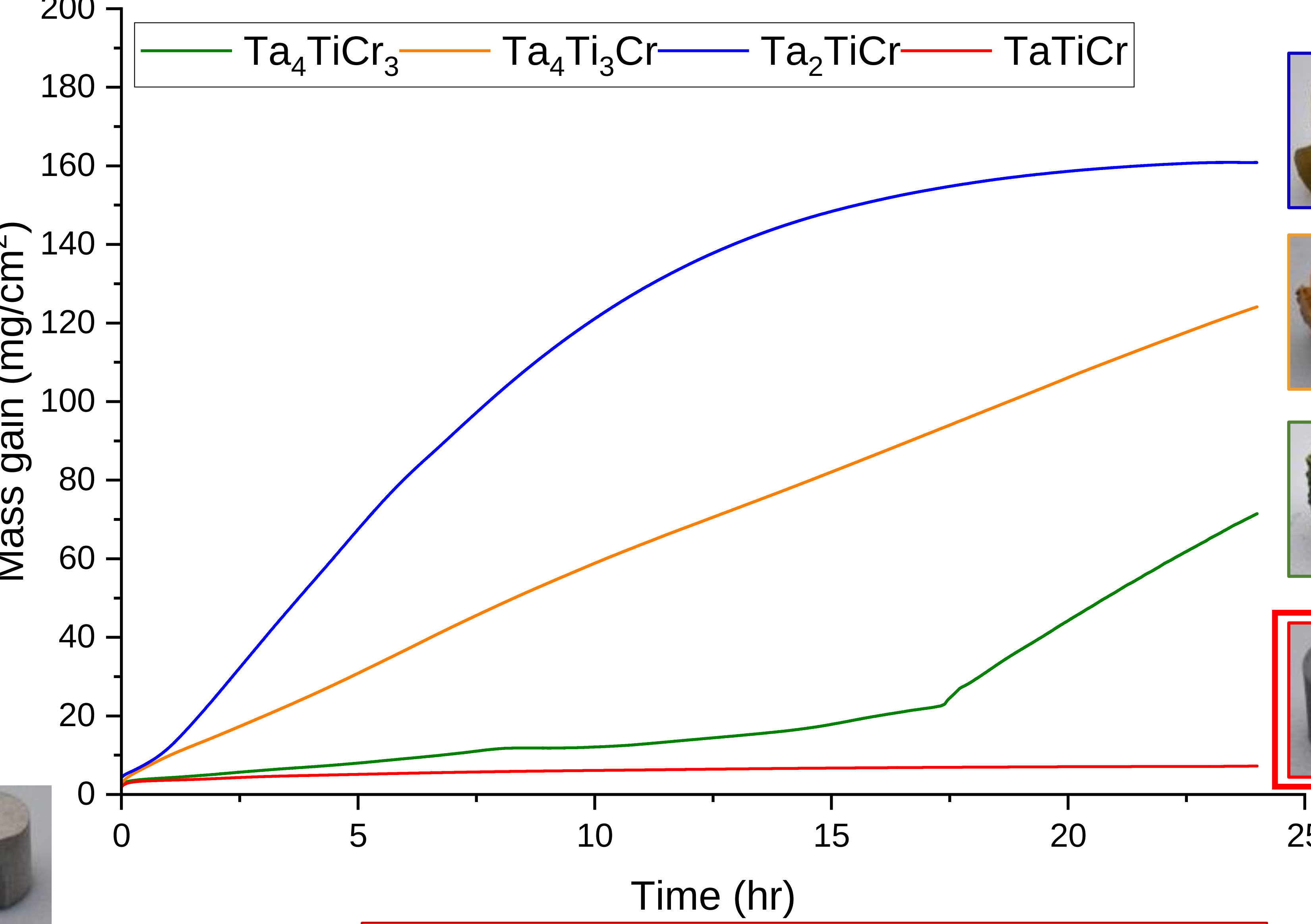


Scale surface



- 1st kinetic regime: Outer Cr_2O_3 layer provided good protection
- 2nd kinetic regime: Scale “rumpling” initiated due to volatilization, growth stress
- 3rd kinetic regime: breakaway oxidation and periodic structures

TGA Oxidation Tests – 1200°C



Ta_2TiCr

160.9 g/cm^2

Ta_4Ti_3Cr

124.1 g/cm^2

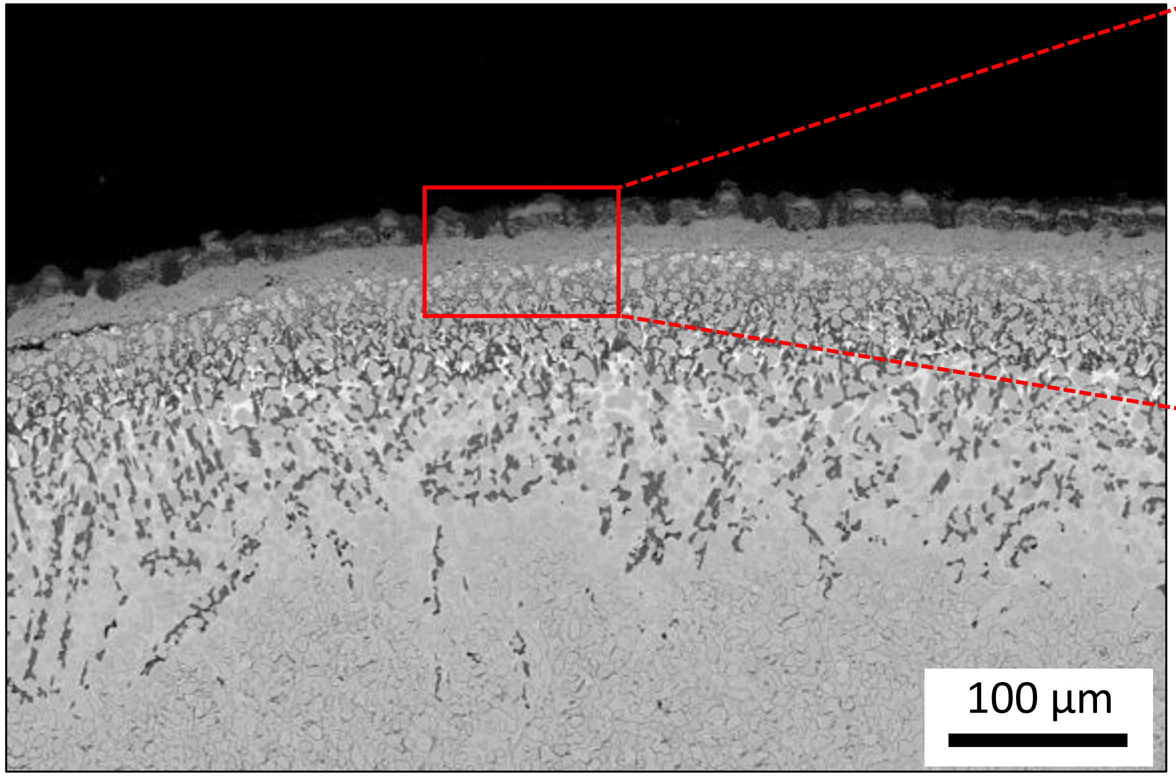
Ta_4TiCr_3

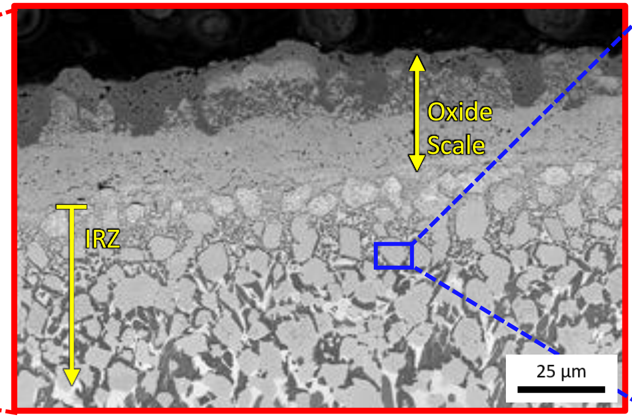
71.5 g/cm^2

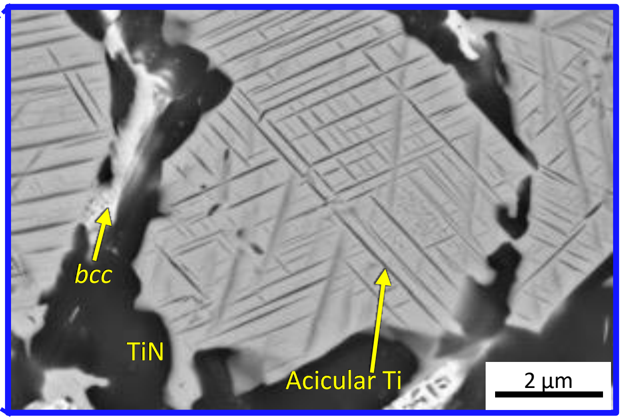
TaTiCr

7.2 g/cm^2

Post-oxidation microstructure – TaTiCr (1200°C, 24 hrs)



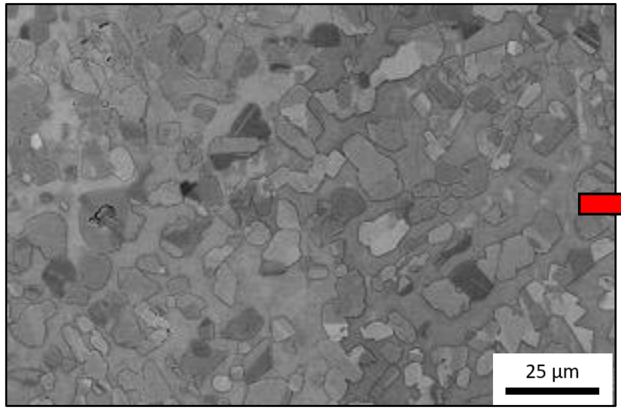




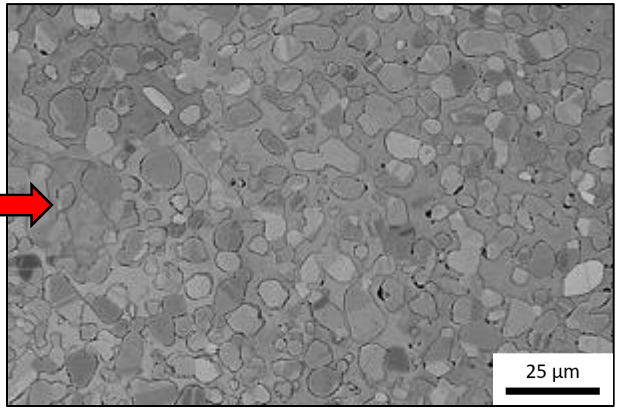
External scale: 30 µm
Internal reacted zone (IRZ): 170 µm

- Adherent, layered oxide scale
- Coarse, lenticular TiN precipitates in matrix from high Ti matrix concentration
- Fine, acicular Ti-rich precipitates in Laves particles near oxide-IRZ interface

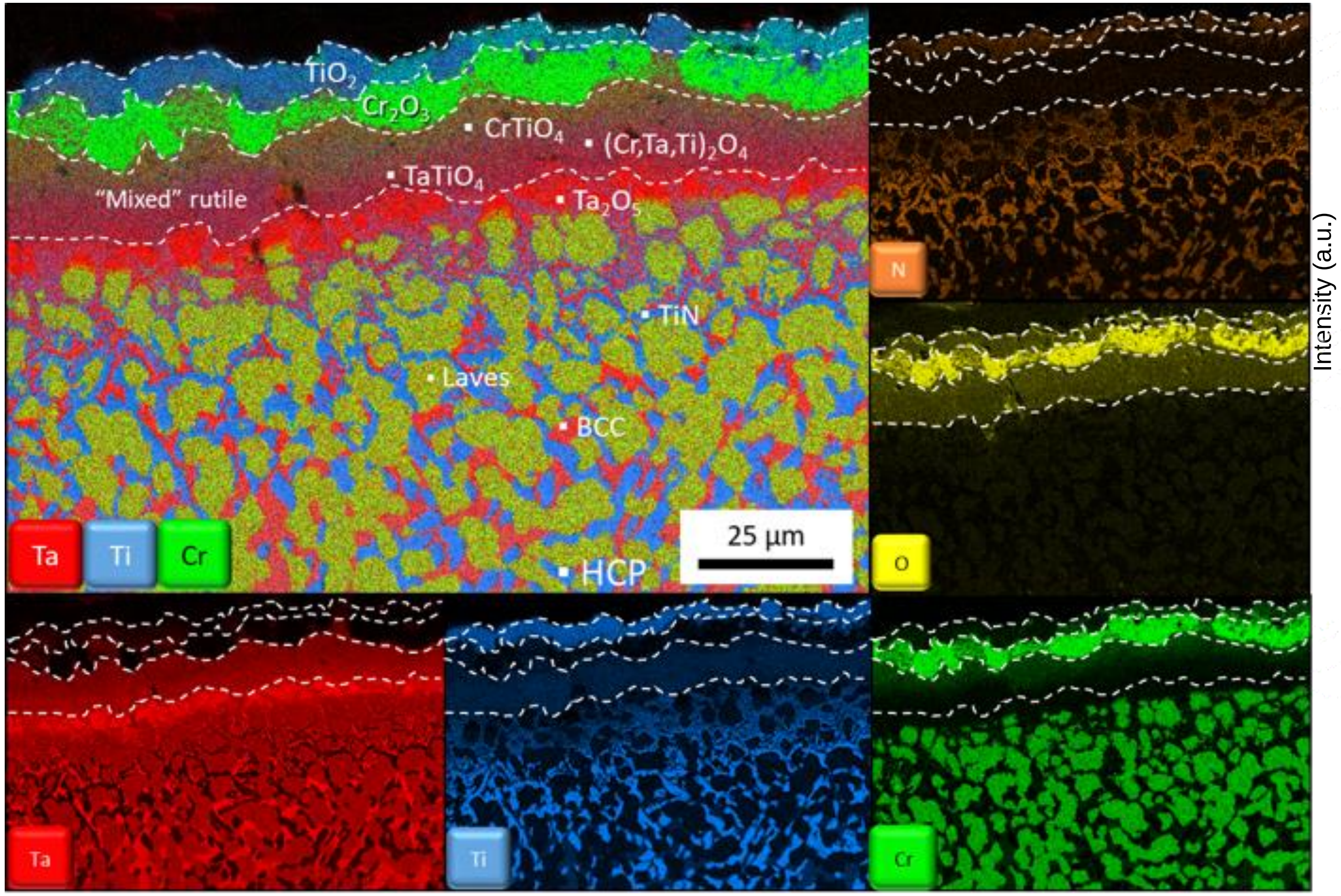
Bulk before oxidation



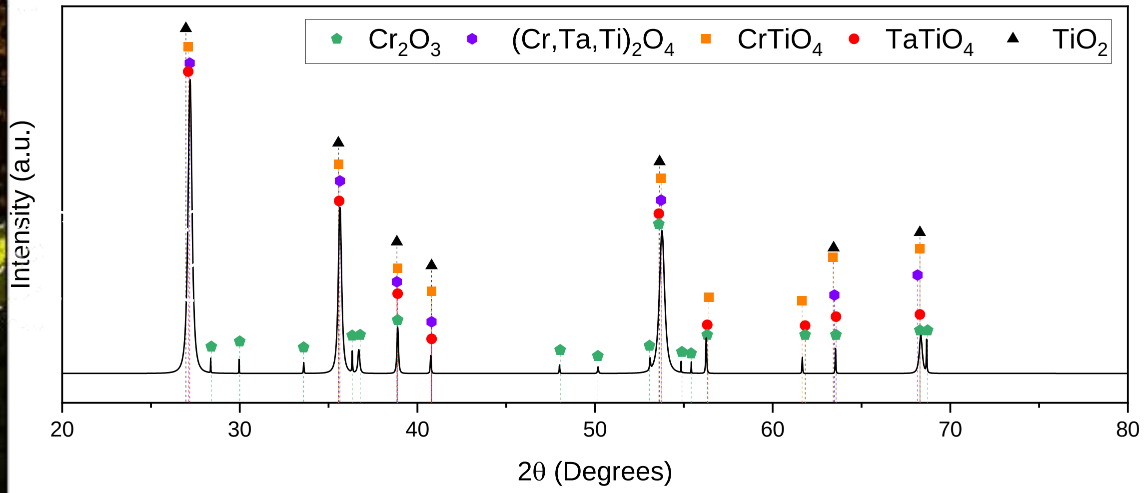
After 24 hrs at 1200°C



Oxide Products – TaTiCr (1200°C, 24 hrs)



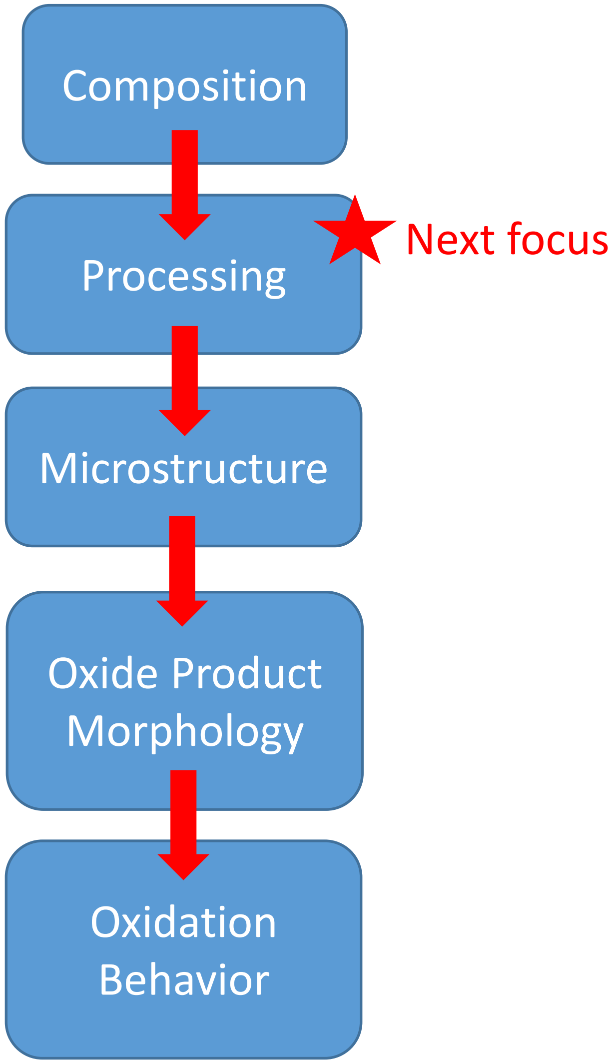
Powder XRD from oxide scale



- Outer scale contains TiO_2, Cr_2O_3, and "mixed" rutile structured $CrTiO_4$, $(Cr,Ta,Ti)_2O_4$, and $TaTiO_4$
- Coarse TiN morphology in IRZ may support continuous, protective scale growth

Conclusions

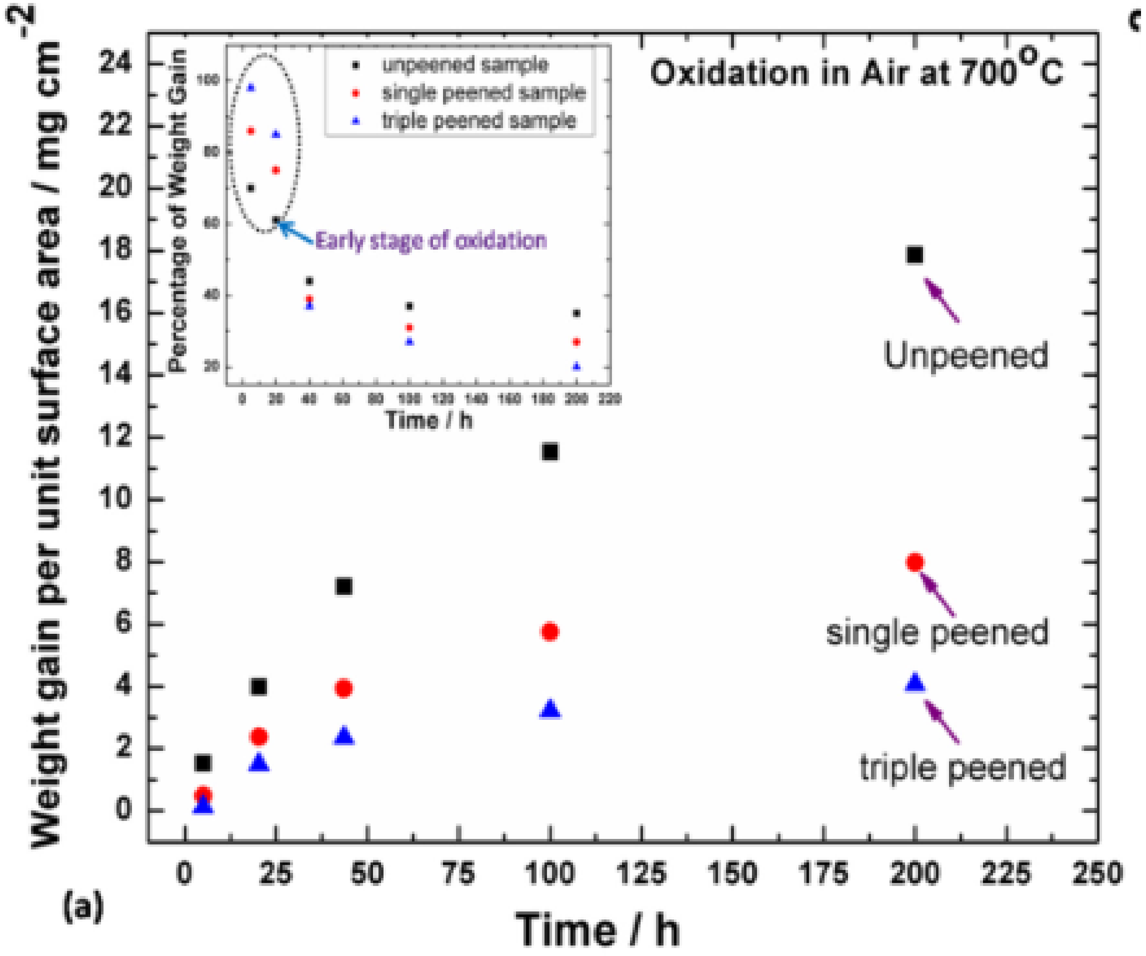
- All alloys formed similar oxide structures, however oxide morphology varied drastically
- Good performance requires continuous oxide morphology and no deleterious oxide formation
- Laves act as ”Cr reservoirs” for Cr_2O_3 formation, coarse internal TiN morphology may reduce O ingress and support continuous oxide morphology
- Design for:
  - Laves phase to provide Cr
  - High Ti content in matrix to form advantageous TiN morphology
  - Low Ta content to dissuade Ta_2O_5 formation



Future work

AM and LSP surface modification

- Explore Ta-lean/Ti-rich compositions using Optomec Laser Engineered Net Shaping (LENS) system and measure oxidation performance in as-printed/HIPed conditions
- Investigate effect of Laser Shock Peening (LSP) on TaTiCr as an oxidation inhibitor and a recrystallization starter to modify surface microstructure



Mass gain of grade P91 steel in unpeened, single peened, and triple peened conditions

Rai, et al., *Applied Surface Science, 2019*

Future Work

- Planned publication: *High-Temperature Oxidation Behavior of TaTiCr, Ta_4Ti_3Cr, Ta_2TiCr, and Ta_4TiCr_3 Concentrated Refractory Alloys*
- Compression Tests on HIP specimens
- Composition range exploration with AM
- Laser Shock Peening Experiments

Thank you!

Noah Welch
njwelch@iastate.edu

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Noah Welch
njwelch@iastate.edu

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[2] A. Rai, Enhancement of oxidation resistance of modified P91 grade ferritic-martensitic steel by surface modification using laser shock peening, Applied Surface Science, vol. 495, 143611, 2019.