Effect of V on the carbon distribution in carbide-free bainite during isothermal transformations

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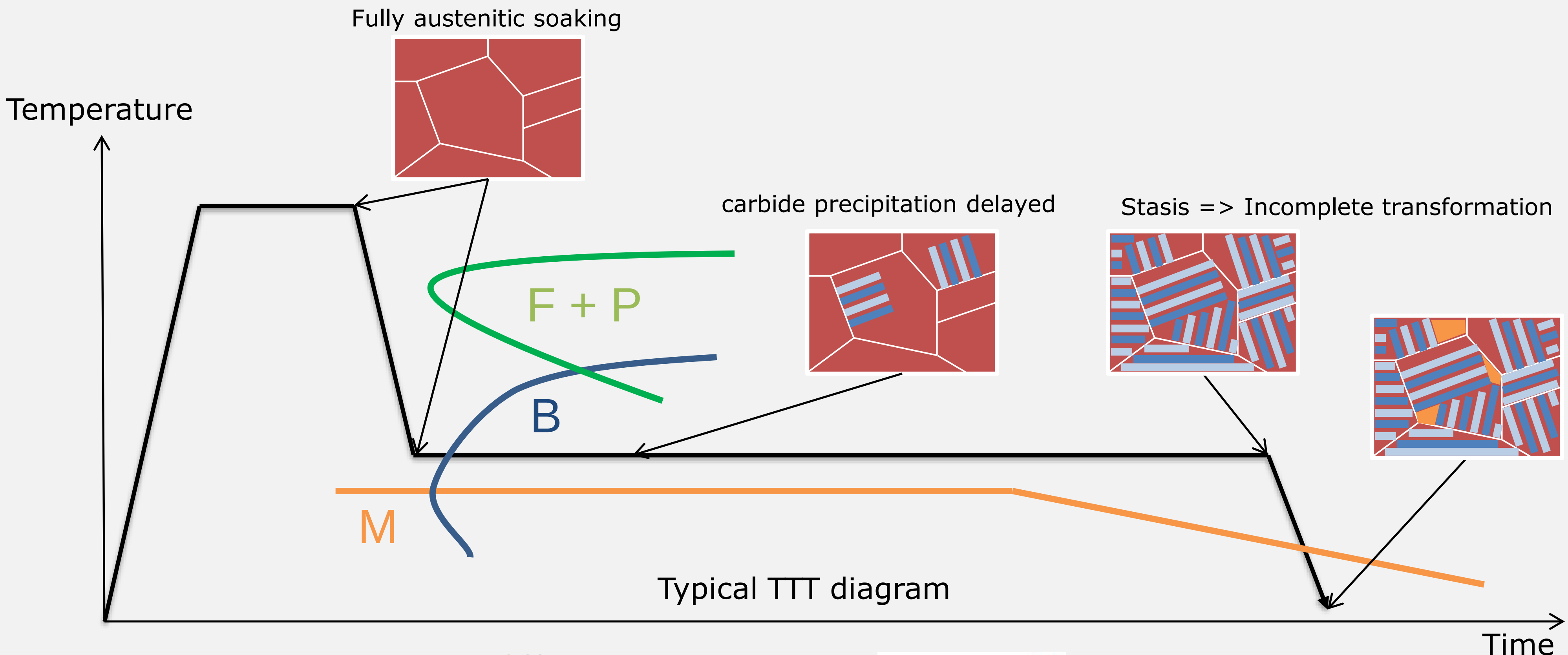
HSLA 2022, Nanjing China - 10th November 2022

Introduction - Carbide Free Bainitic Steels

- Multiphase microstructure
  - A ferritic matrix (B) with a lath morphology
  - Retained austenite (A) (interlath and granular) → stabilized at RT by carbon partitioning during the bainitic transformation (carbide precipitation delayed by Si additions)
  - Fresh martensite (M) → obtained during final cooling



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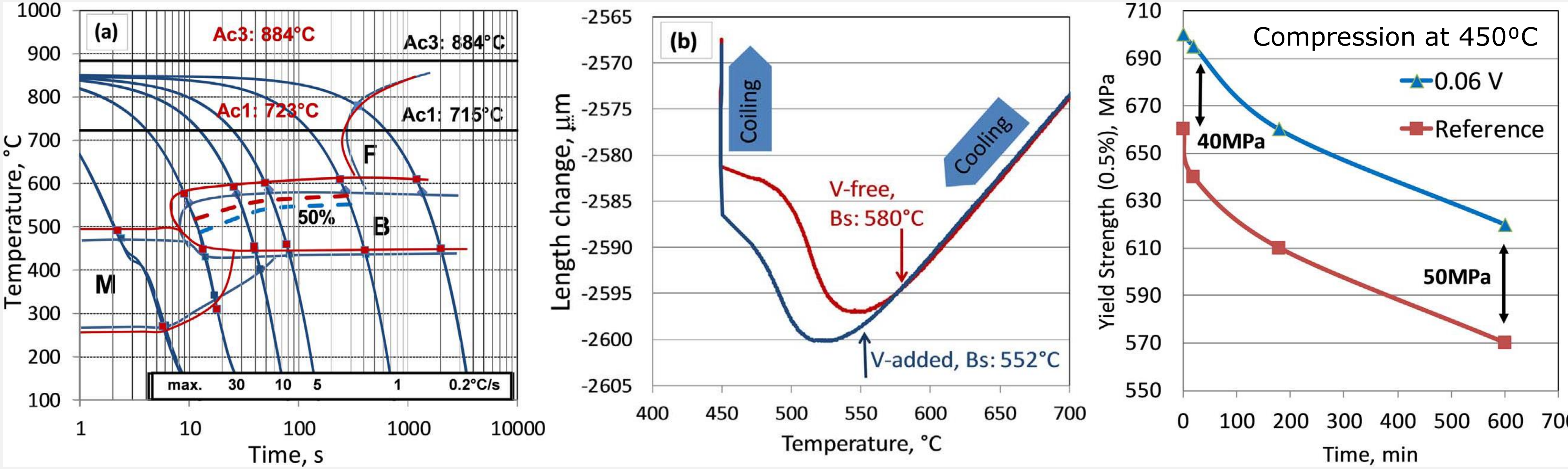
Introduction - Vanadium in Very Low Carbon Bainitic Steels



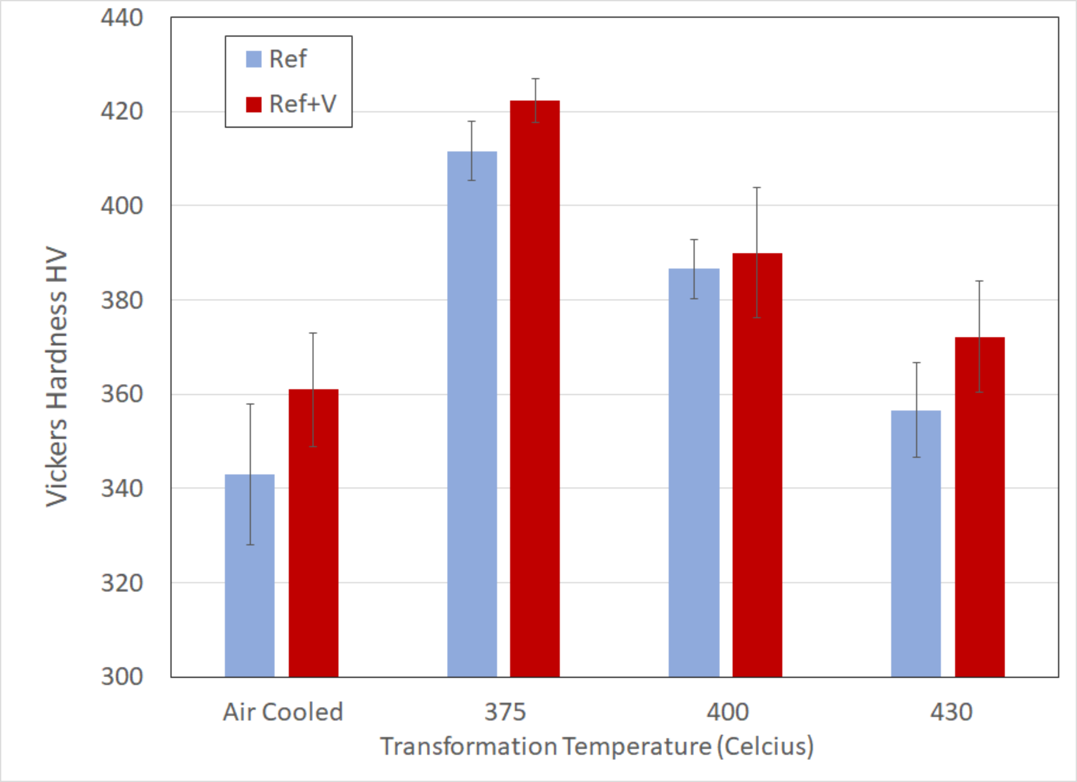
Blue lines Fe-0.06C-1.85Mn-0.16Cr-0V

Red lines Fe-0.06C-1.85Mn-0.16Cr-0.06V

Vanadium does not usually precipitate in a standard bainitic cycle, however single phase V-added low carbon bainite alloys are strengthened due to the increased hardenability and temper resistance of V in solution.

F. Fazeli, B.S. Amirkhiz, C. Scott, M. Arafin, L. Collins, Mater. Sci. Eng. A 720 (2018) 248–256.

Vanadium in Carbide Free Bainitic Steels



Vanadium will not precipitate in a standard CFB cycle either, however V-added CFB steels are usually stronger – why?

We studied the carbon distribution in bainite, austenite and martensite during and after the bainitic transformation using *in situ* High Energy Synchrotron XRD in transmission mode (mm scale) and *ex situ* using TEM-EELS (μm scale) and 3D Atom Probe (nm scale).

This is the first time these three techniques have been applied simultaneously.

Sample	C	Mn	Si	Mo	V	Al	N
Ref	0.22	2.2	1.8	0.2	-	0.01	0.0028
Ref+V	0.22	2.2	1.8	0.2	0.15	0.01	0.0027

Alloy	Ae_1 (calc)	Ac_1 (exp)	Ae_3 (calc)	Ac_3 (exp)	T_{sol} V(CN)	B_s (calc)	M_s (calc)
Ref	707°C	700°C	831°C	933°C	-	556°C	375°C
Ref+V	713°C	748°C	840°C	975°C	1067°C	556°C	375°C

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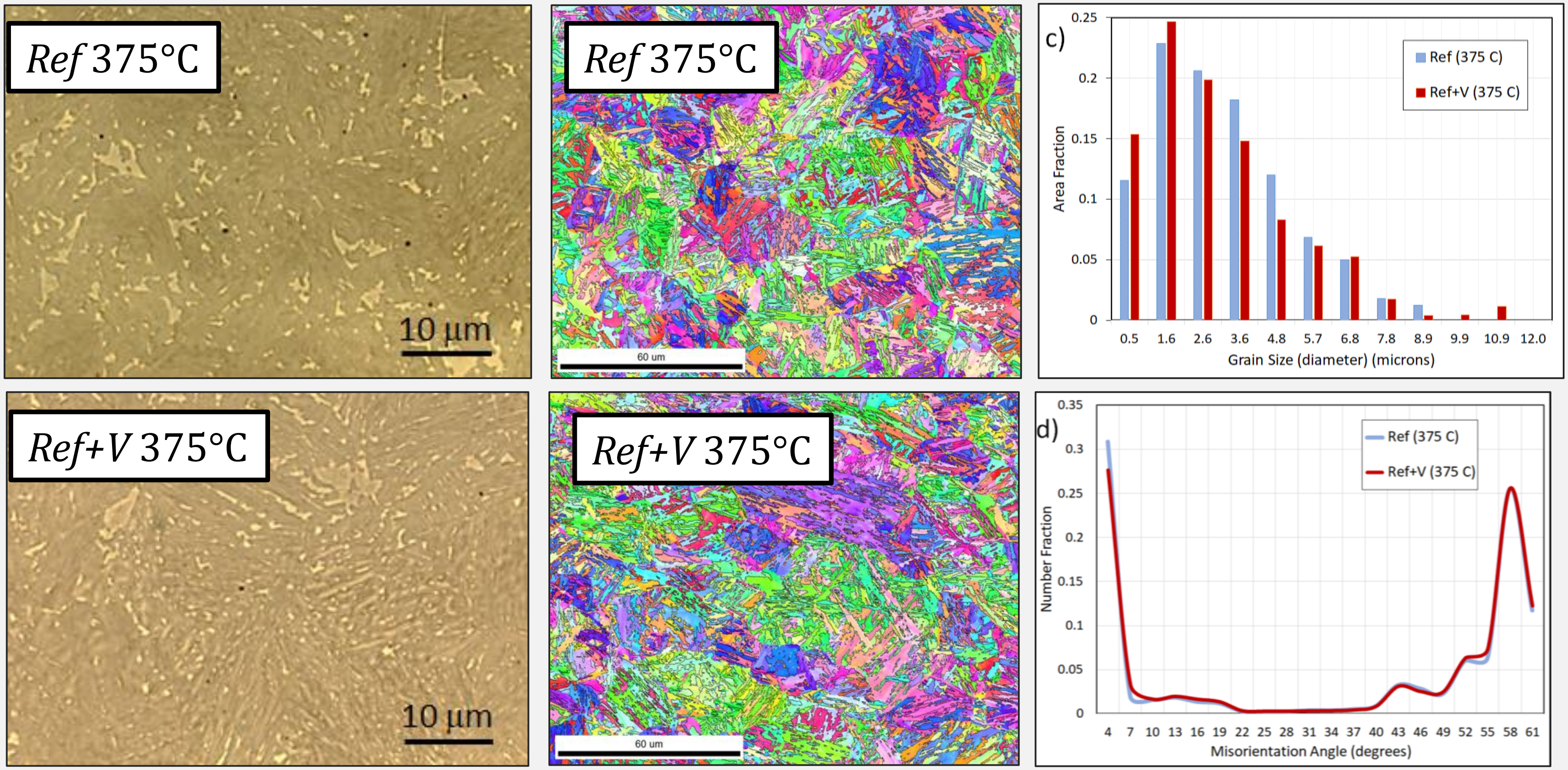
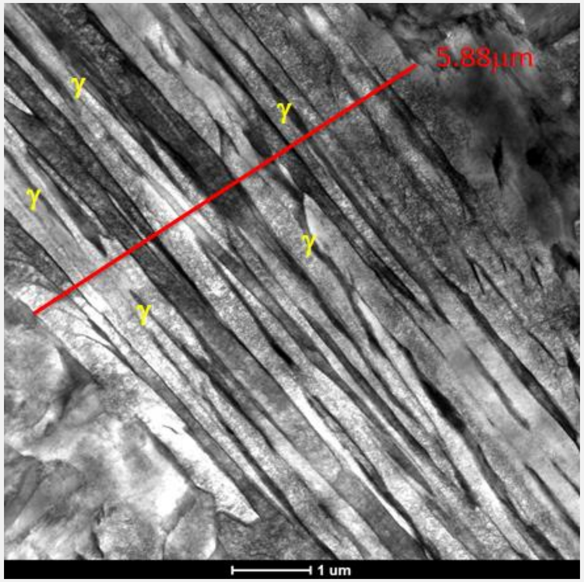
Results – SEM microstructure investigations



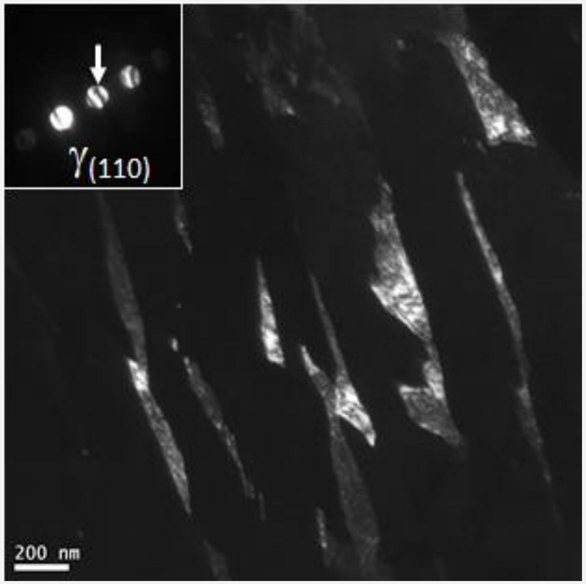
- Lower bainitic structures.
- No major differences between *Ref* and *Ref+V* transformed at 375°C and at 400°C except for a refinement of MA islands.

I. Pushkareva, B. Shalchi-Amirkhiz, S.Y.P. Allain, G. Geandier, F. Fazeli, M. Sztanko, C. Scott. (2020) Metals 10(3) 392.

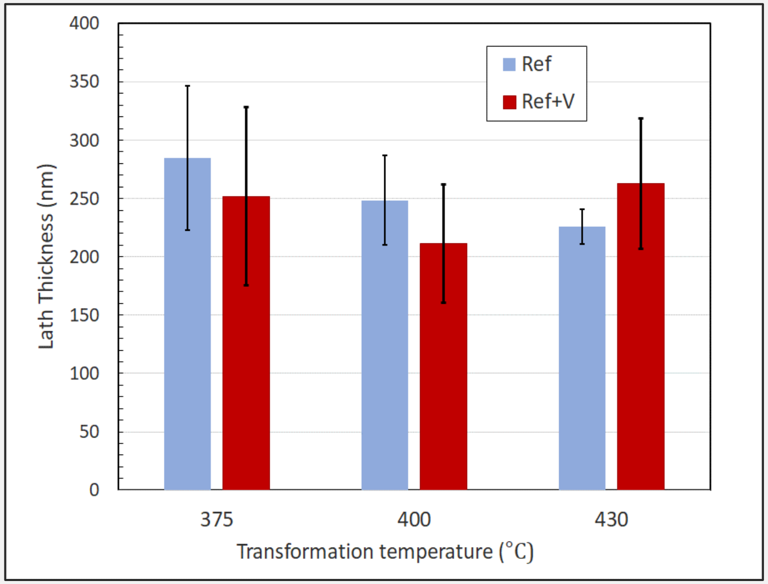
Results – TEM microstructure investigations



Bright field STEM image of the Ref alloy transformed at 430°C.

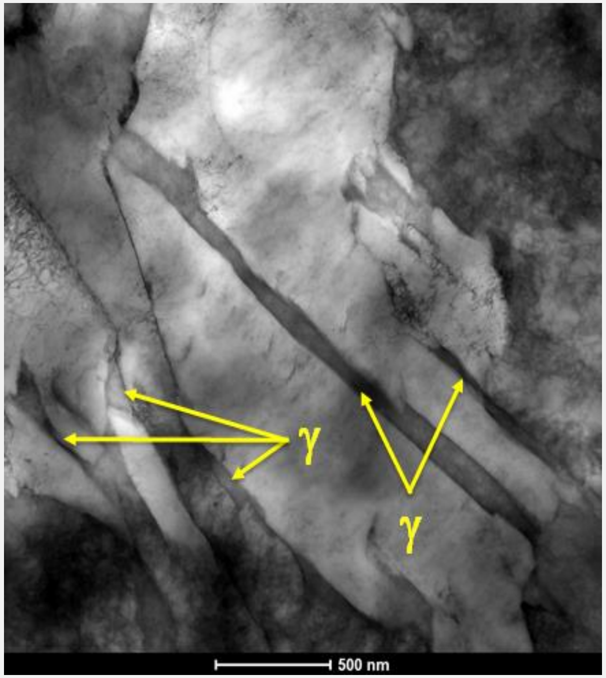


Dark field STEM image showing austenite films ($\gamma_{(110)}$ reflection) from Ref+V transformed at 430°C.

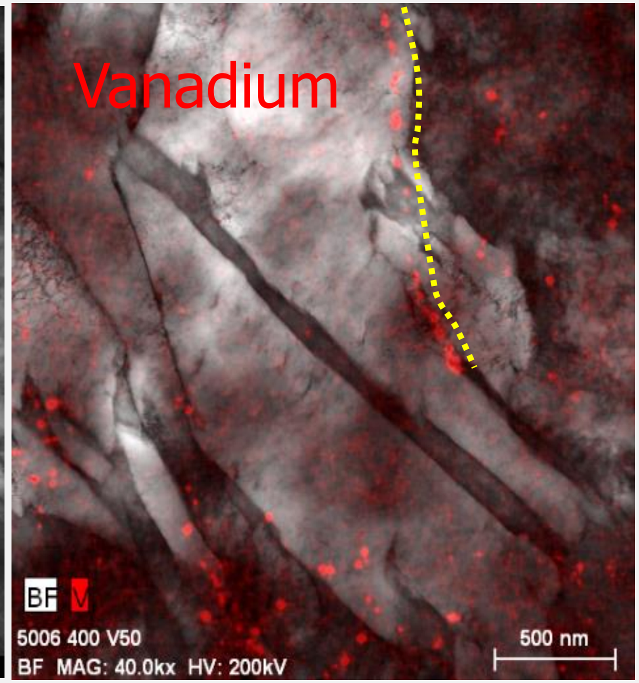


TEM shows no strong influence of Vanadium or transformation temperature on bainite lath widths

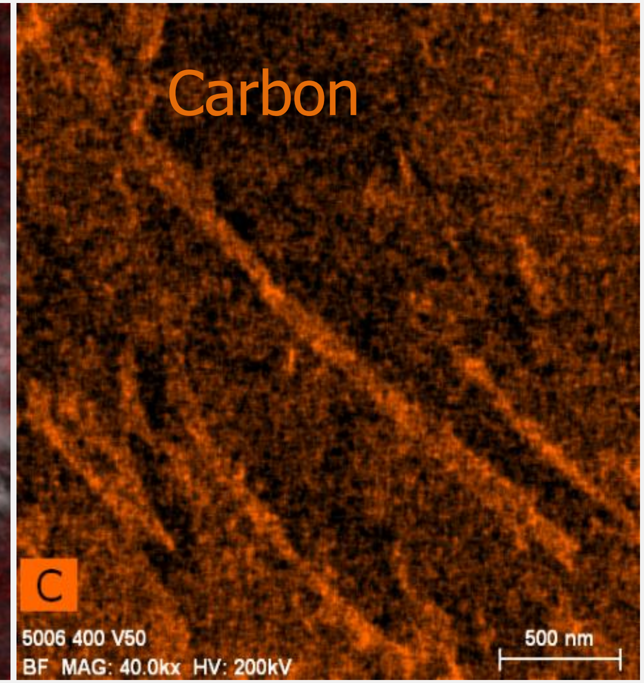
Results – TEM precipitation studies



Bright field STEM image of Ref+V transformed at 400°C.



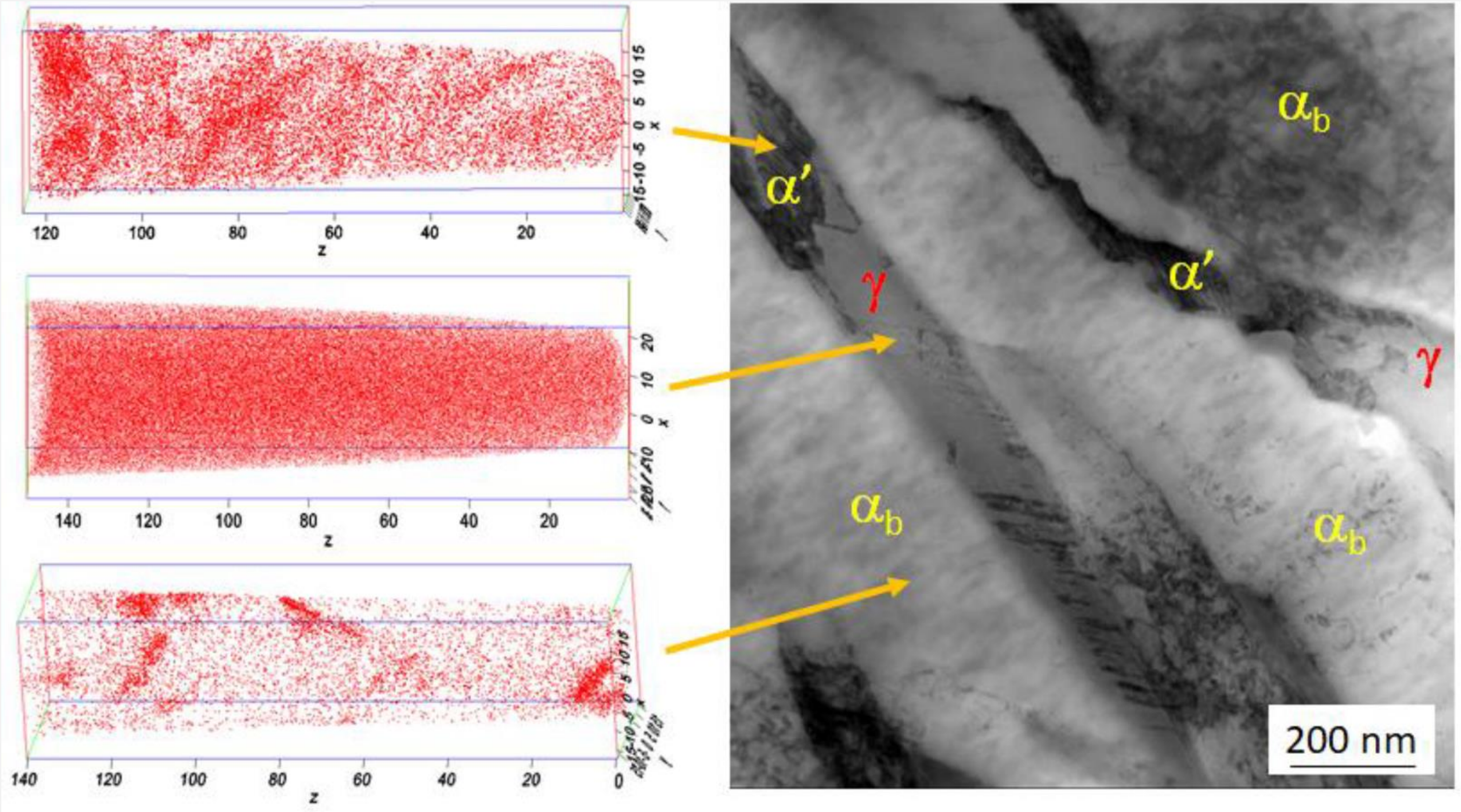
Superimposed EDX vanadium map (red) from the same area.



EDX carbon map (qualitative) from the same area.

TEM shows some coarse undissolved Vanadium containing particles from the hot band – no correlation with bainite or RA. Do not appear to be VC. Very few fine precipitates were detected.

Results – Atom Probe Studies



Ref alloy transformed at 430ºC. APT reconstructions show typical carbon distributions for martensite, austenite and bainitic ferrite. Successful runs on 42 tips.

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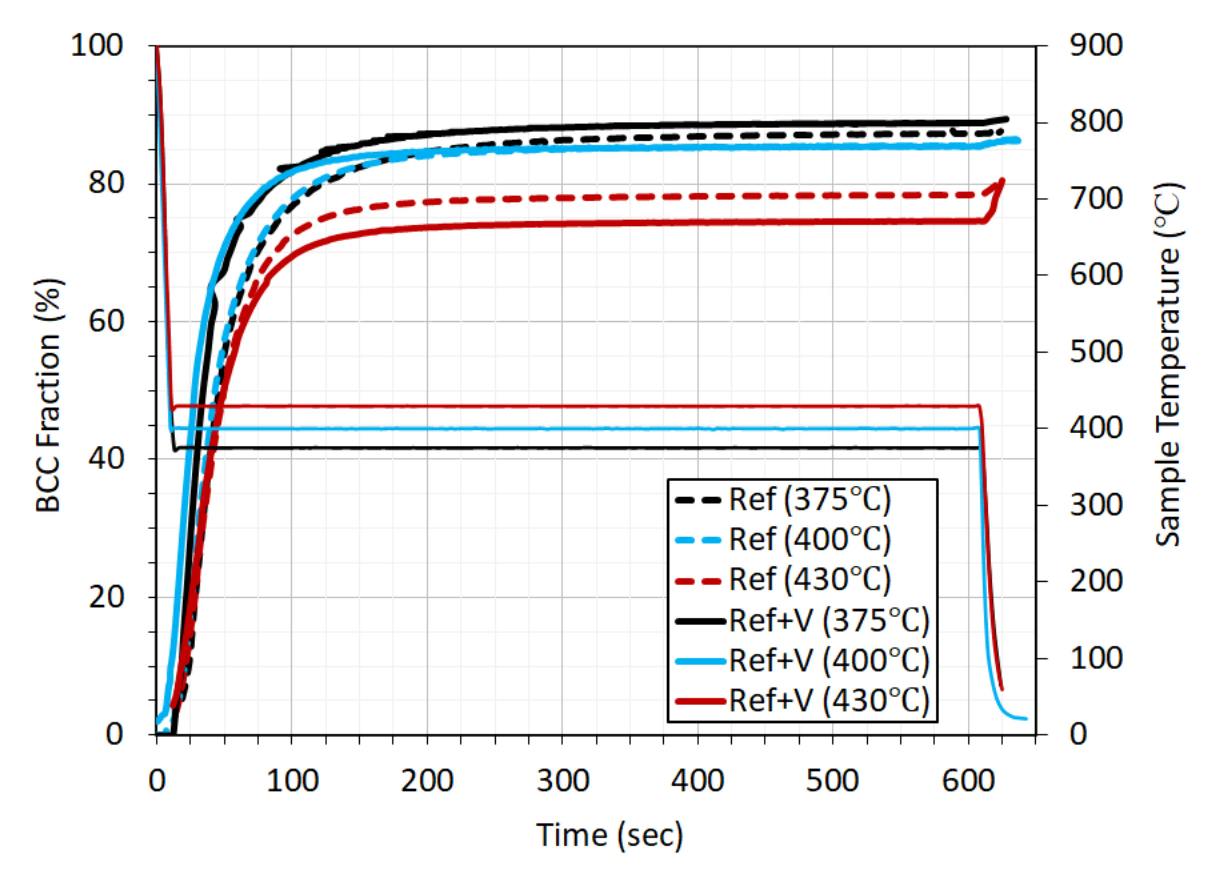
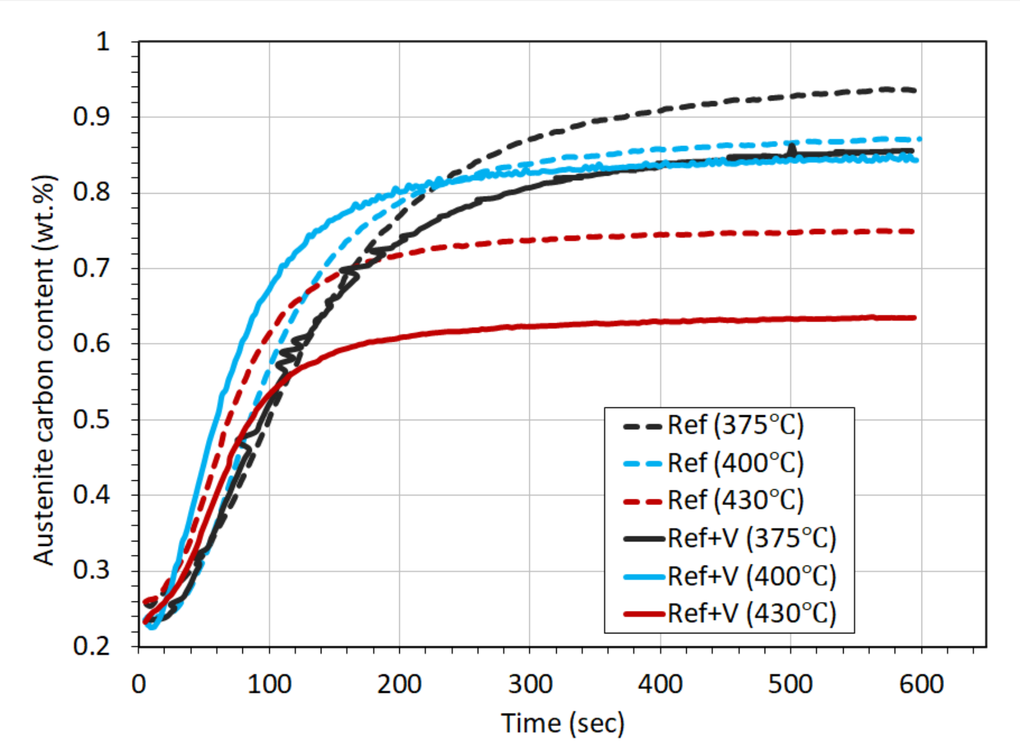
Results - HEXRD transformation kinetics and phase fractions



	T (°C)	F_b (%)	F_γ (%)	$F_{\alpha'}$ (%)
Ref	375	87.4	12.3	0.3
	400	85.6	13.5	0.9
	430	78.4	19.1	2.5
Ref+V	375	88.7	10.7	0.6
	400	85.3	13.8	0.9
	430	74.7	19.4	5.9

- RA fraction increases as transformation temperature decreases
- Sigmodal kinetics and temperature dependent stasis (no significant effect of V)
- Final martensite transformations occur at 430°C only (V slightly increases $F_{\alpha'}$)

Results - HEXRD carbon content at stasis in austenite



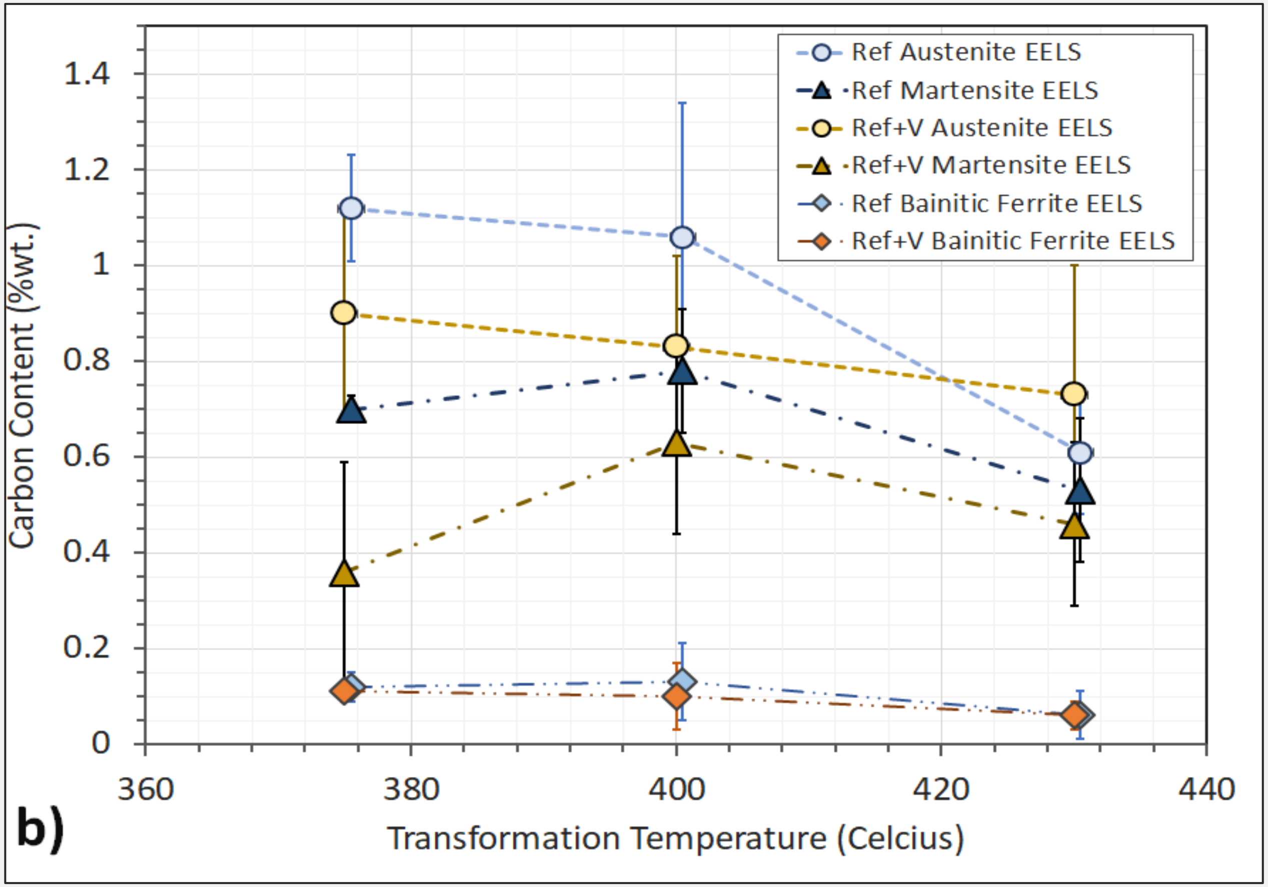
	T (°C)	F_γ HEXRD @ 600s (%)	C_γ HEXRD (wt.%)	C_b HEXRD (wt.%)
Ref	375	12.6	0.94	0.12
	400	14.4	0.87	0.11
	430	21.6	0.75	0.07
Ref+V	375	11.3	0.86	0.14
	400	14.7	0.85	0.11
	430	25.3	0.63	0.08

$$C_\gamma = C_0 + \frac{a_\gamma - a_{\gamma 0}(T)}{0.033}$$

- Carbon content in austenite determined considering the relative evolution of the lattice parameter
- Note that carbon partitioning to austenite continues long after the transformation stops. V addition appears to slow down the partitioning kinetics.
- No ferrite is formed during cooling so the carbon content in bainitic ferrite at stasis (375-430°C) can be obtained from a simple mass balance equation:

$$C_0 = C_b(1 - F_\gamma) + C_\gamma\, F_\gamma$$

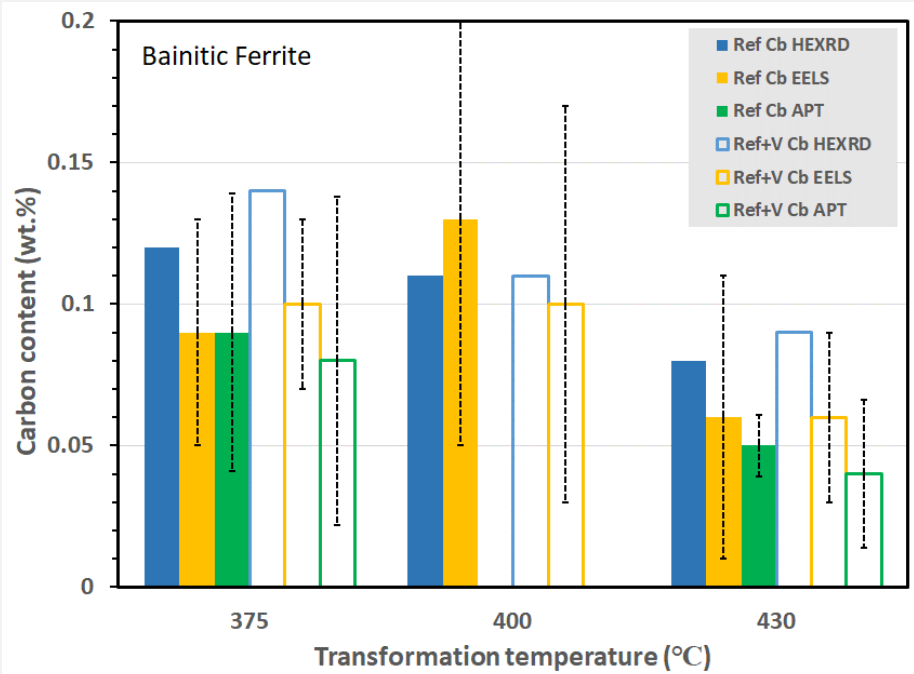
Results - TEM EELS Carbon Measurements



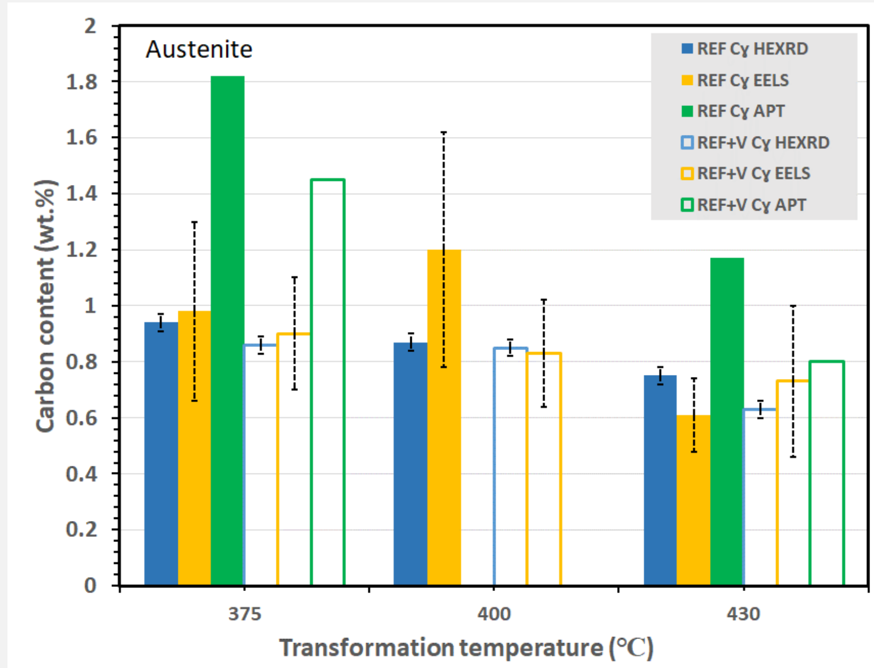
- EELS measurement precision is +/- 4% and the detection limit for solute carbon is 0.02-0.03 wt. %
- Large scattering on C_γ measurements reflects a real distribution. Mean values slightly higher than obtained by HEXRD
- Carbon in martensite is lower (less enriched austenite transformed during final cooling)

Results – HEXRD v EELS v APT

Alloy	Transformation Temperature	C_γ HEXRD (wt.%)	C_γ EELS (wt.%)	C_γ APT (wt.%)	$C_{\alpha'}$ EELS (wt.%)	C_b HEXRD (wt.%)	C_b EELS (wt.%)	C_b APT (wt.%)
Ref	375°C	0.94	0.98 (9)	1.82 (2)	0.70 (1)	0.12	0.09 (12)	0.11 (12)
Ref	400°C	0.87	1.20 (7)	-	0.78 (4)	0.11	0.13 (4)	-
Ref	430°C	0.75	0.69 (8)	1.17 (1)	0.49 (5)	0.08	0.07 (10)	0.05 (7)
Ref+V	375°C	0.86	0.90 (9)	1.45 (2)	0.36 (3)	0.14	0.10 (13)	0.08 (12)
Ref+V	400°C	0.85	0.83 (10)	-	0.63 (9)	0.11	0.10 (3)	-
Ref+V	430°C	0.63	0.73 (8)	0.80 (1)	0.46 (7)	0.09	0.06 (5)	0.04 (9)

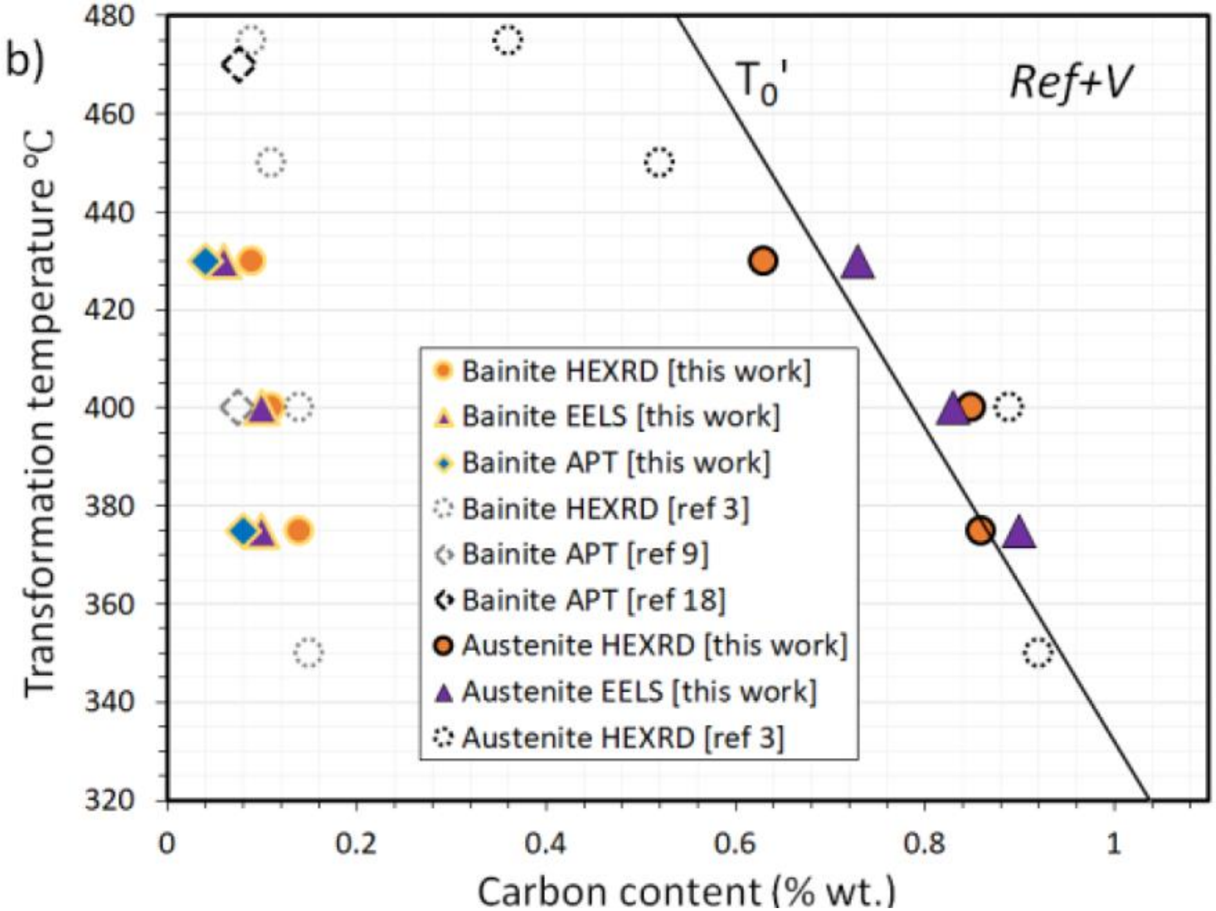


No clear influence of V on C_b



Adding V *slightly* decreases C_γ

Mean values – comparison with literature



[3] R. Rementeria, J.D. Poplawsky, M.M. Aranda, W. Guo, J.A. Jimenez, C. Garcia-Mateo, F.G. Caballero, Acta Mater. 125 (2017) 359–368.

[9] E.V. Pereloma, Mater. Sci. Technol. (United Kingdom) 32 (2016) 99–103.

[18] G. Miyamoto, K. Shinbo, T. Furuhara, Scr. Mater. 67 (2012) 999–1002.

- Consistent results, HEXRD appears give higher C_b values. This is not due to lattice tetragonality.
- High fraction of carbon trapped in bainite (even with low C_0), much higher than PE solubility in bcc → this C is lost for austenite stabilization although it contributes to bainitic ferrite strength.

Structure-properties modelling

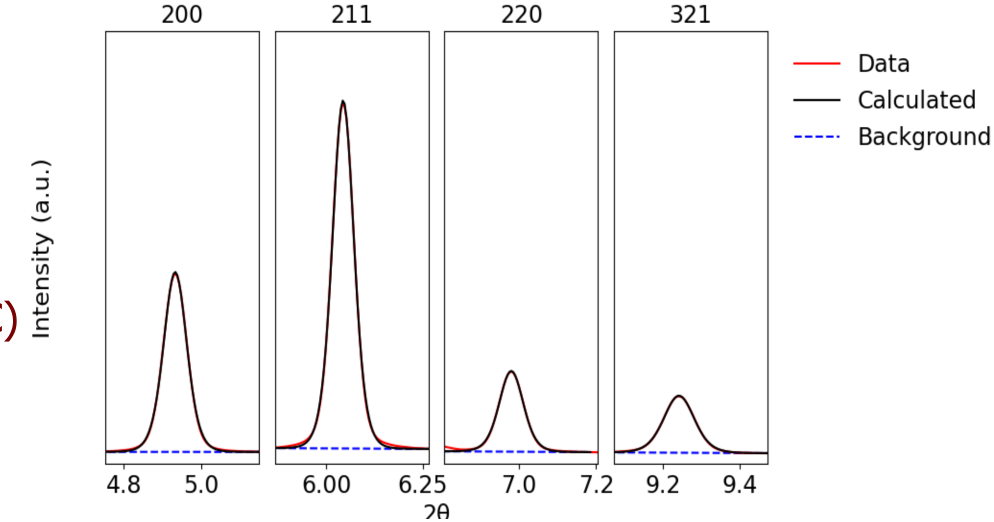
Vanadium effect on CFB microstructure:

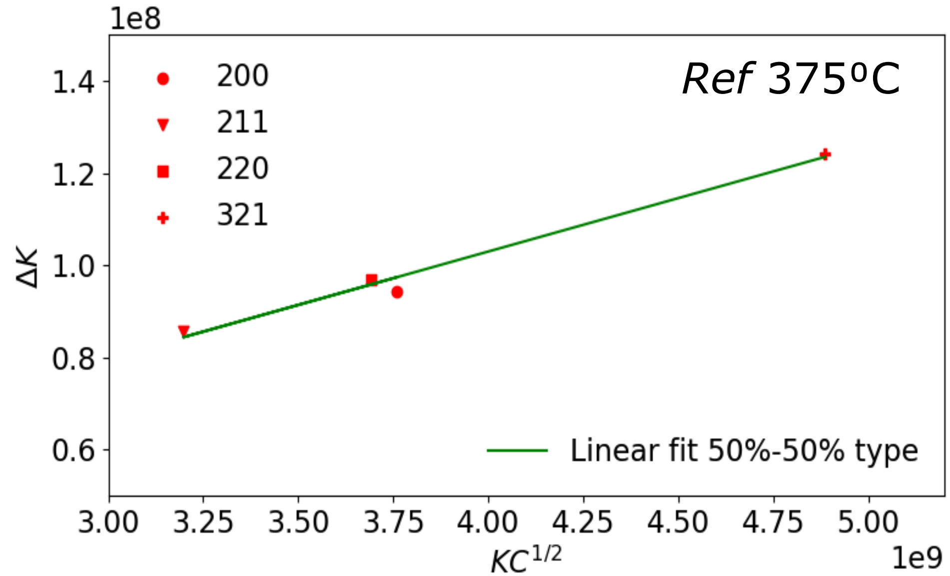
- Does not change the transformation kinetics
- Does not change the final fraction of RA
- RA carbon content is slightly lower
- Fractionally more martensite is formed (at 430ºC)
- No change in bainitic lath widths
- No measurable change in bainitic ferrite carbon content
- No significant precipitation of V

Only dislocation density left to check

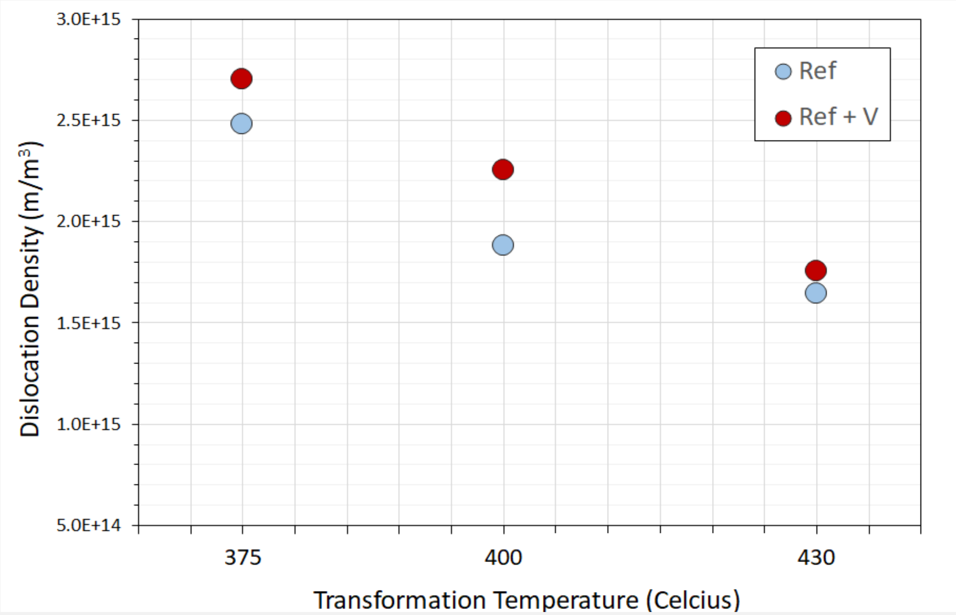
Use modified Williamson-Hall method:

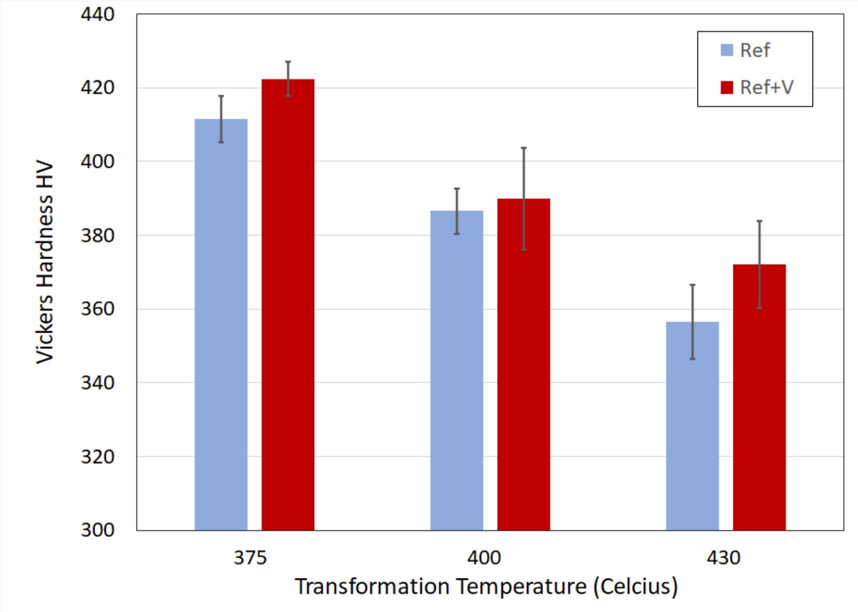
J. Macchi, G. Geandier, J.Teixeira, S. Denis, F. Bonnet, S. Y. P. Allain Materialia Volume 26, December 2022, 101577.





Structure-properties modelling





- Dislocation density measurements are strongly correlated to the measured hardness behaviour.
- Inverse correlation of hardness with RA mean carbon content.
- Vanadium additions increase the value of ρ at all transformation temperatures tested.
- Similar to the effect in very low C bainite – but the mechanism(s) is/are quite different!

At least 3 competing mechanisms: V slows down C partitioning to austenite. RA is softer, easier to deform during the transformation (reduces ρ) but less stable so more martensite forms during cooling (increases ρ, especially at high T). However, solute V (+ΔC_b?) slows down static + dynamic recovery in bainite (increases ρ).

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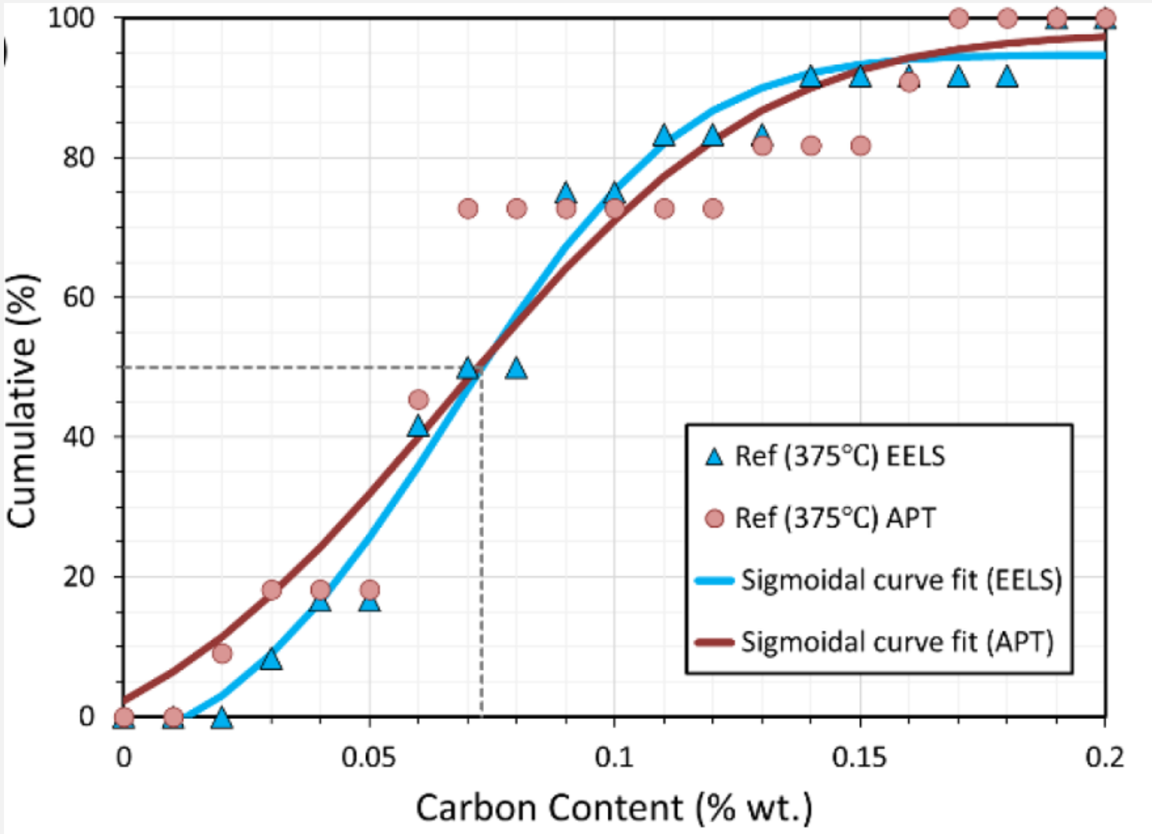
Going further – statistical analysis

Alloy	Transformation Temperature	C_γ HEXRD (wt.%)	C_γ EELS (wt.%)	C_γ APT (wt.%)	$C_{\alpha'}$ EELS (wt.%)	C_b HEXRD (wt.%)	C_b EELS (wt.%)	C_b APT (wt.%)
Ref	375°C	0.94	0.98 (9)	1.82 (2)	0.70 (1)	0.12	0.09 (12)	0.11 (12)



- The concentration of excess carbon in bainitic ferrite varies widely from region to region.
- Excess carbon trapped in bainite does not follow a normal distribution – bias is towards lower carbon contents.
- Could this be correlated with bainite lath width ?

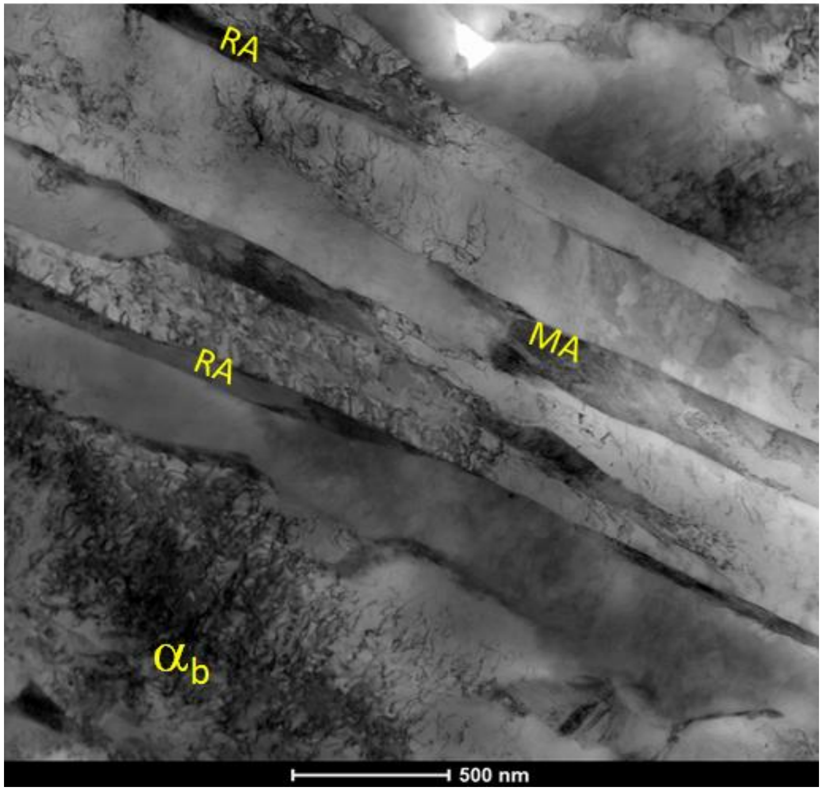
Conclusions

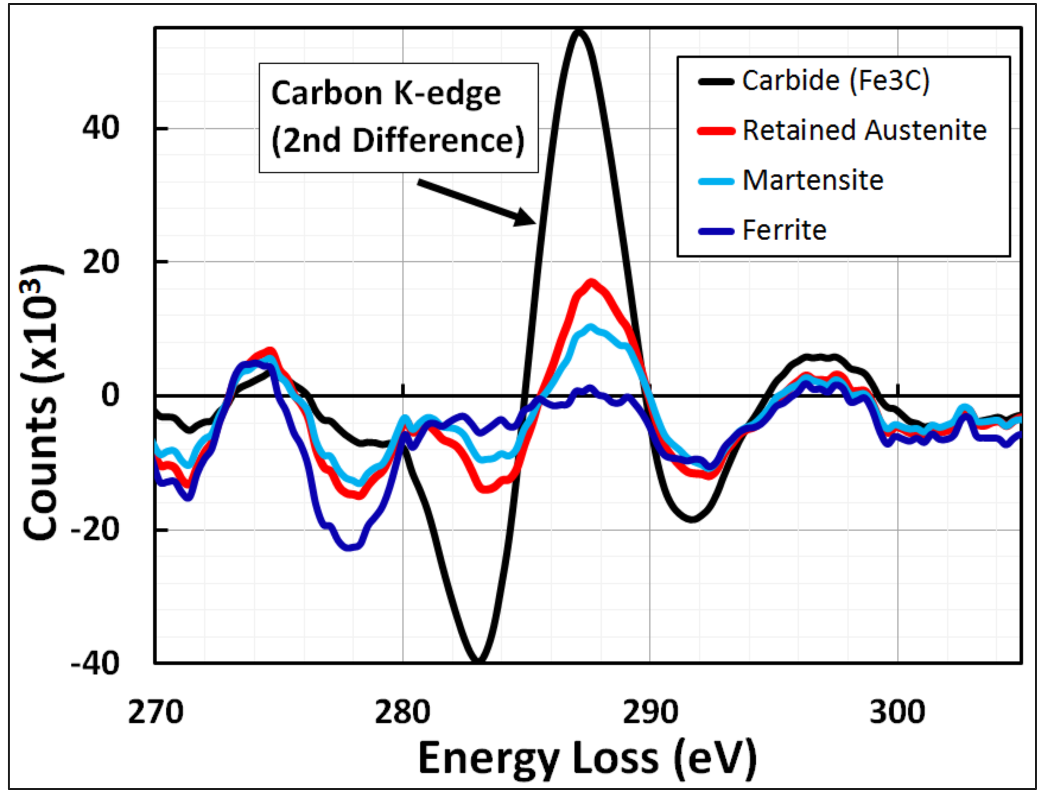
- The influence of V on the microstructure evolution of isothermally transformed CFB steels has been studied.
- Three advanced techniques at different length scales have been coupled to investigate the carbon content in the constituent phases (bainitic ferrite / austenite / martensite) of CFB steels.
- The three methods give similar results showing that a large fraction of carbon C_b remains trapped in bainitic ferrite even at high transformation temperatures. C_b is not strongly influenced by vanadium additions.
- Effect of vanadium in CFB (solid solution):
  - No significant effect on kinetics, stasis, final phase fractions bainite lath size or C_b
  - No evidence of precipitation strengthening
  - Slows the rate of carbon partitioning to austenite, slight reduction in final $C\gamma$
  - Increases dislocation density ρ in BF at all tested temperatures
  - Final mechanical properties correlate well with ρ (and inverse correlation with $C\gamma$)

Thank you for your attention!

Backup slides

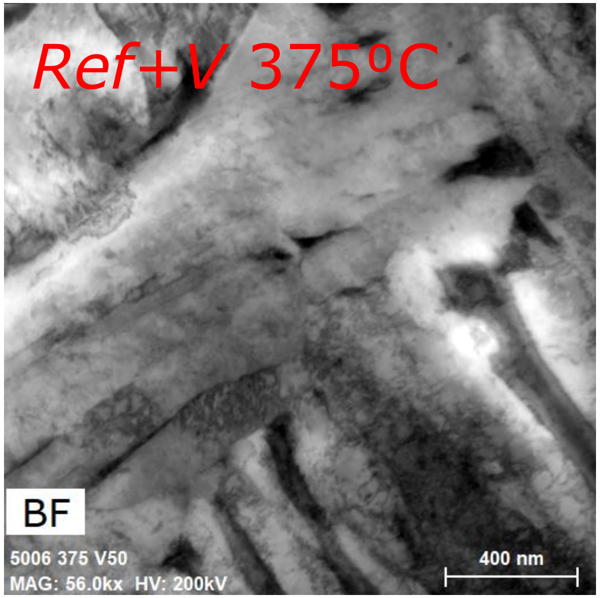
Materials and Methods – TEM EELS

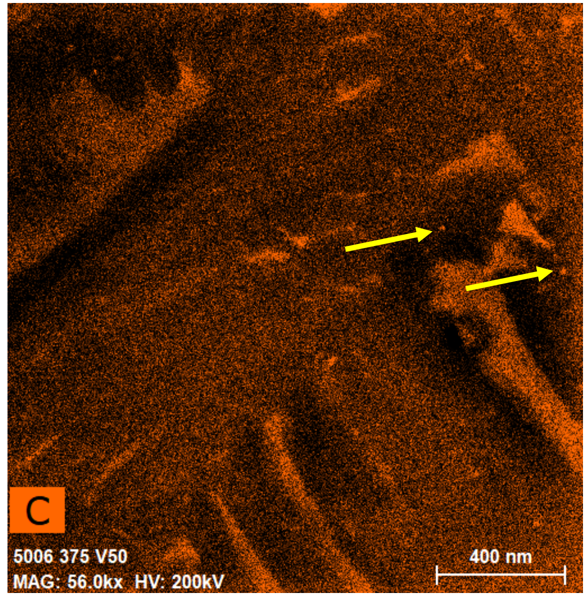


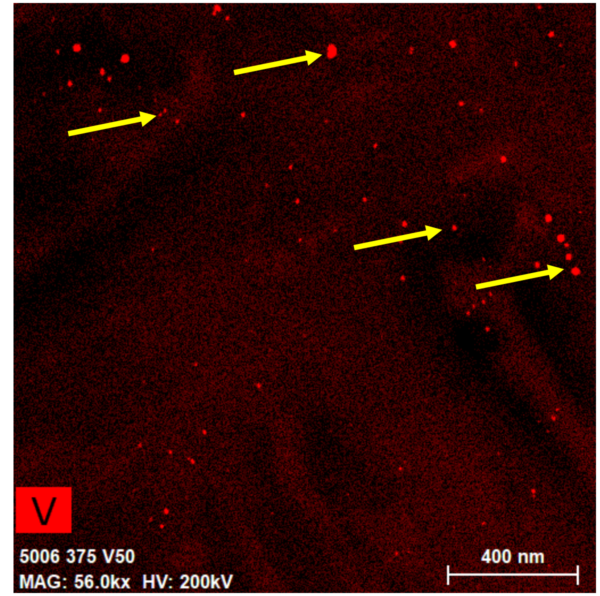


- TEM investigations (CanmetMATERIALS)
  - Tecnai Osiris 200 keV X-FEG (S)TEM / FEI FS1 EELS analysis system
  - EELS using a standards based second difference acquisition technique developed by the authors

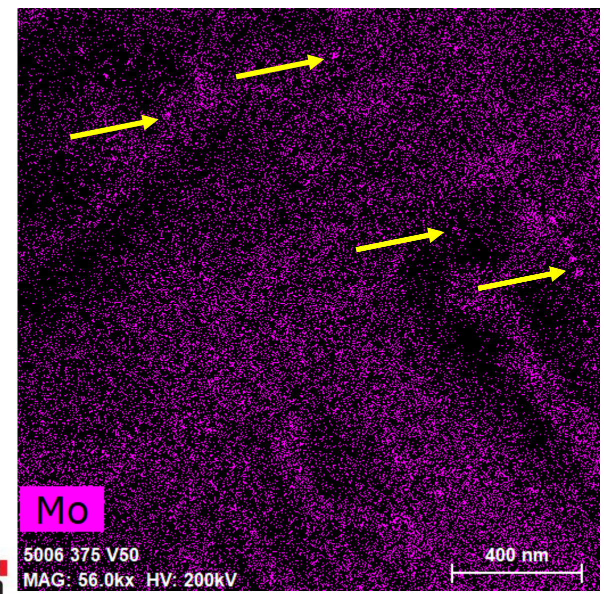
Results – TEM precipitation studies



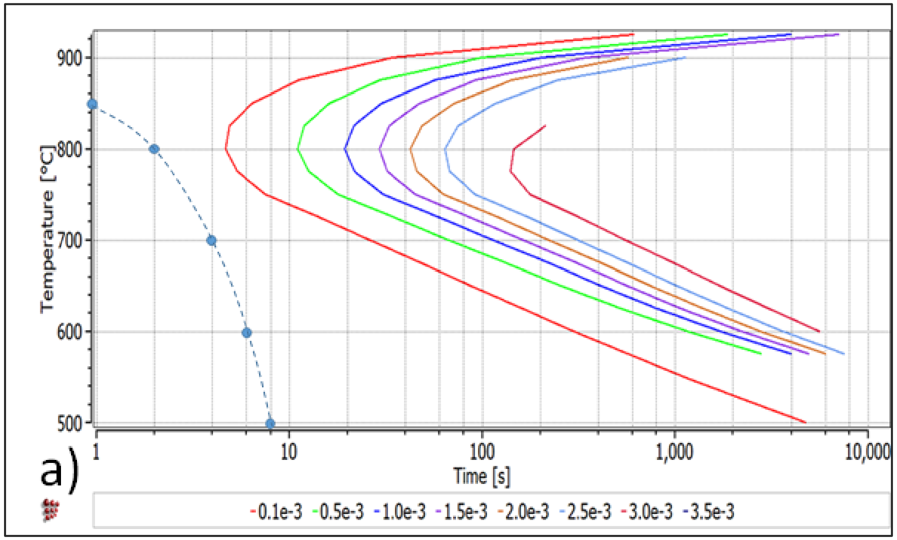


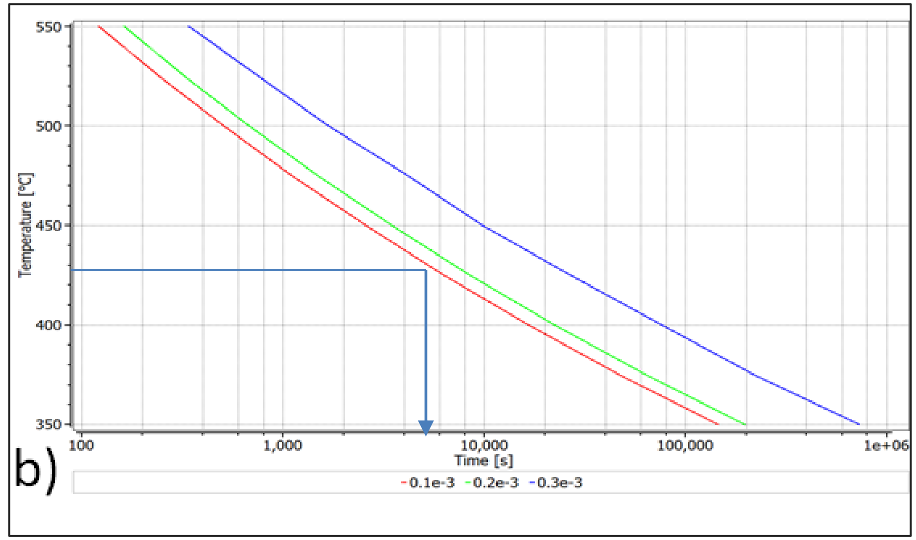


Most of the particles observed in *Ref*+V specimens transformed at 400°C and 430°C contained vanadium with small amounts of carbon and nitrogen being occasionally detected. However, at 375°C some of the particles contained V+Mo. Mo enrichment of V(C,N) is only significant at temperatures below 800°C, suggesting that these particles formed in ferrite



Results – kinetic precipitation modelling





a) V(C,N) PTT in *Ref+V* ferrite containing $1x10^{14}/m^2$ dislocations.
b) Low temperature PTT for V(C,N) in *Ref+V* bainitic ferrite containing $5x10^{14}/m^2$ dislocations

Kinetic modelling predicts that no V(C,N) should form for transformation times < 5000s

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