IMPaCT

EPSRC Centre for Doctoral Training in Innovative Metal Processing (IMPaCT)

Understanding the effects of deep cryogenic treatment on precipitation behaviour in En31 bearing steel

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- Cryogenic treatment
- Stages of tempering in Fe-C alloys
- Kinetics of thermal decomposition of Fe-C martensite

Experimental methodology

Results and Conclusions

- Effects of deep cryogenic treatment on precipitation behaviour
- Effects of varied austenitising temperatures with deep cryogenic treatment

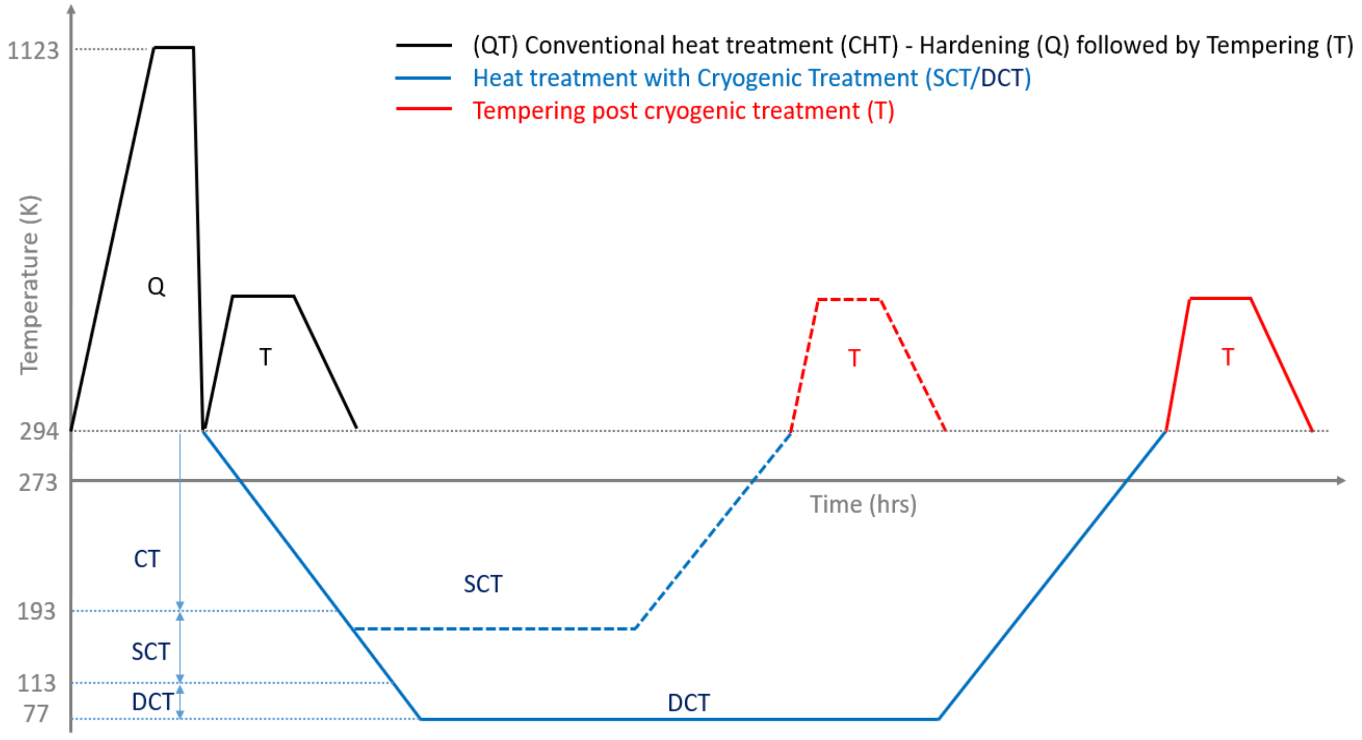
Further Work

Cryogenic treatment (1)

- In-depth research began c.1980's, with advances in computer controlled technology
- Utilises phase transformations at cryogenic temperatures to provide improved mechanical and tribological properties
- Usually performed after quenching but prior to tempering, as a supplementary step to a conventional heat treatment (CHT)
- Industrial use concerted around tools, bearings, gears
- Process conducted industrially using a 'cryo-chamber' or 'cryo-processor' with LN_2

Cryogenic treatment (2)

- Three main stages: cooling, soaking, heating
- Three main treatment temperature regimes, by which cryogenic treatments are classified:
  - Cold treatment (CT) ≥ 189K
  - Shallow cryogenic treatment (SCT) 189 – 113K
  - Deep cryogenic treatment (DCT) 113 – 77K
- The latter, DCT, is the one of interest here and commercially



Cryogenic treatment (3)

Advantages

- Increased dimensional stability
- Increased hardness
- Increased wear resistance
- Even reports of increased fatigue life

Disadvantages

- Mechanisms of microstructural change not currently well understood
- Contradictory results in literature
- Most commonly treated are tool steels, containing high quantities of alloying elements
- Long process times (DCT ~24 hrs)
- Not a 'one-process suits all'

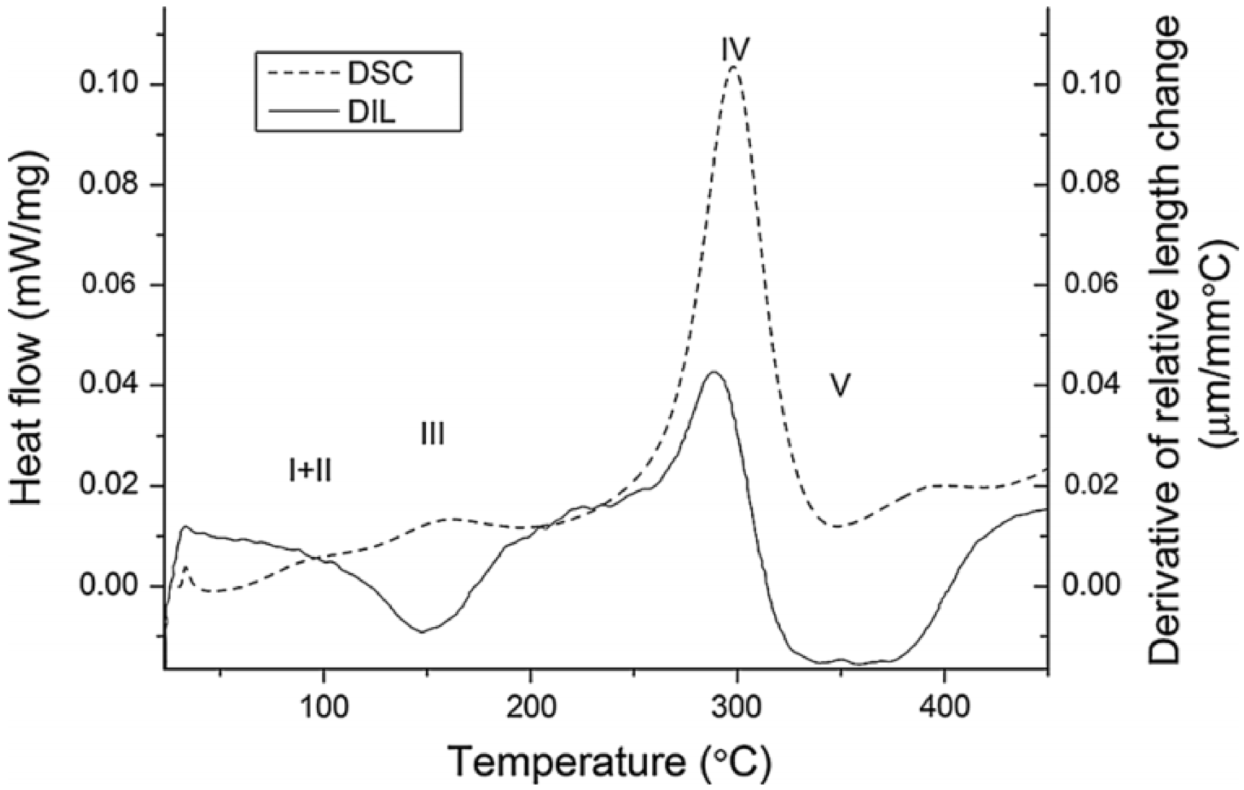
Cryogenic treatment (4)

Mechanisms of microstructural change in hardenable Fe-C alloys

- Conversion of retained austenite γ_{RA} to martensite α'
- Increased dispersion and number of secondary carbides
- ‘Low-temperature conditioning’ of RT formed martensite
- Formation of nano-sized precipitates

Stages of tempering in martensitic Fe-C alloys

Stage	Occurrence	Expected temperature range (K)
I & II	Pre-precipitation processes (segregation of carbon and its subsequent arrangement)	< 373
III	Formation of transition carbides (η, ϵ)	353 - 473
IV	Decomposition of retained austenite γ_{RA} to cementite and ferrite (θ and α)	513 – 593
V	precipitation of cementite θ	533 - 623



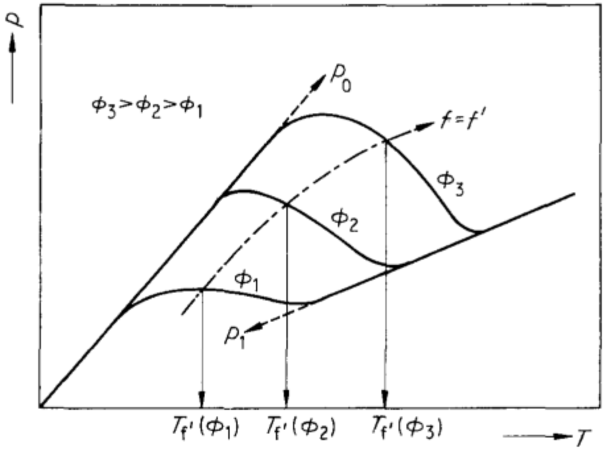
Preciado, M. & Pellizzari, M. (2014) J Mater Sci, 49, 8138-8191.
Cheng. L et al., (1988) Met Trans A, 19A, 2415-2426.

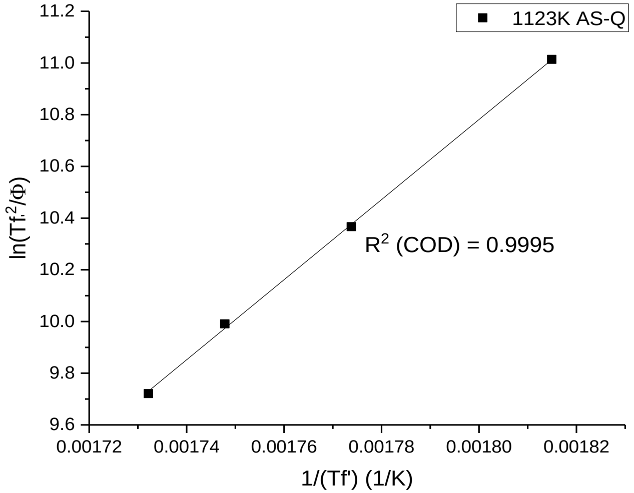
Kinetics of thermal decomposition of martensite during tempering

- Activation energies of the stages of tempering determined by a Kissinger-like analysis:

$$\ln\left(\frac{T_{f'}^2}{\phi}\right) = \frac{1}{T_{f'}}\frac{E_a}{R} + C$$

  - R = Universal Gas constant (J mol^{-1} K^{-1}) , E_a = activation energy (J mol^{-1}), ϕ = heating rate (K min^{-1})
  - $T_{f'}$ = temperature of which a certain fraction of the phase transformation is complete, usually taken as the maxima of the phase transition studied
- Isochronal annealing





Mittemiejer, E.J. (1992) J of Mat Sci. 3977-3987.

Rationale for this research

- Effects of prior austenitising conditions on deep cryogenic heat treatment yet to be clinically analysed
- Most hardened steels applied in the tempered state – lots of studies on the tempering of Fe-C alloys, but the effects of an industry standard DCT cycle on subsequent tempering behaviour yet to be evaluated
- Views to optimise DCT cycles for specific applications and desired properties

Experimental methodology

Material

- En 31 bearing steel (AISI 52100, DIN 100Cr6)

Heat Treatment

- 3 sets of austenitised samples. 30 mins at one of 1123 K, 1223 K, 1323 K
- All subsequently oil quenched
- As-quenched (AS-Q) Control samples vs quenched + DCT samples (Q + DCT)

Deep cryogenic treatment

- Cryogenic Treatment Services Ltd, Newark-On-Trent (-2020)
- 24 hrs soaking at 93 K, cooling and re-heating to 93 K at rates <1 K min^{-1}

Element	Wt.%
C	0.95 – 1.10
Cr	1.20 – 1.60
Mn	0.40 – 0.70
Si	0.10 – 0.35
S	0.050 max
P	0.040 max
Fe	Remaining

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Experimental methodology

Characterisation

- **This study**

- DSC
- Microscopy (SEM)
- XRD (pre-DCT)
- Mechanical tests – Vickers hardness testing

- **Future**

- Dilatometry – further study precipitation behaviour
- Tribology – wear tests
- XRD (post DCT)
- Neutron diffraction

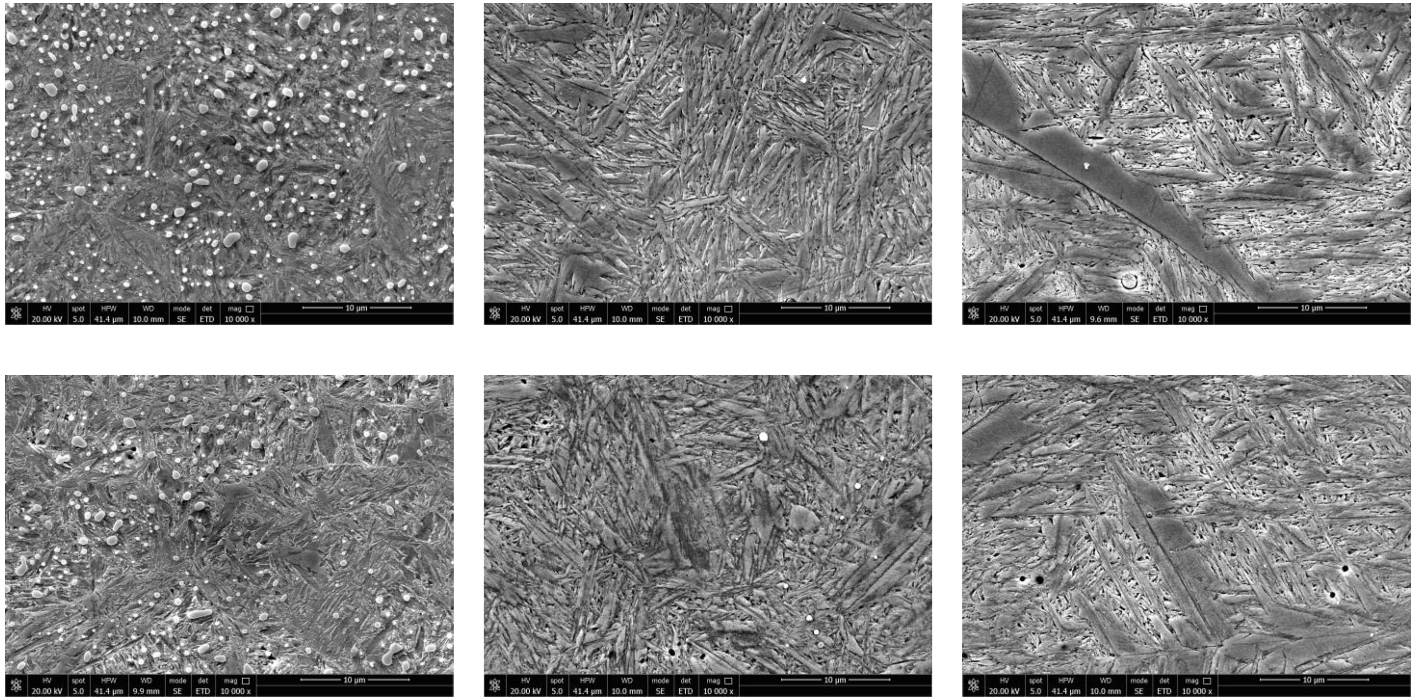
Results – Microstructures

Austenitising temperature **1123K** **1223K** **1323K**

AS-Q structures

↓

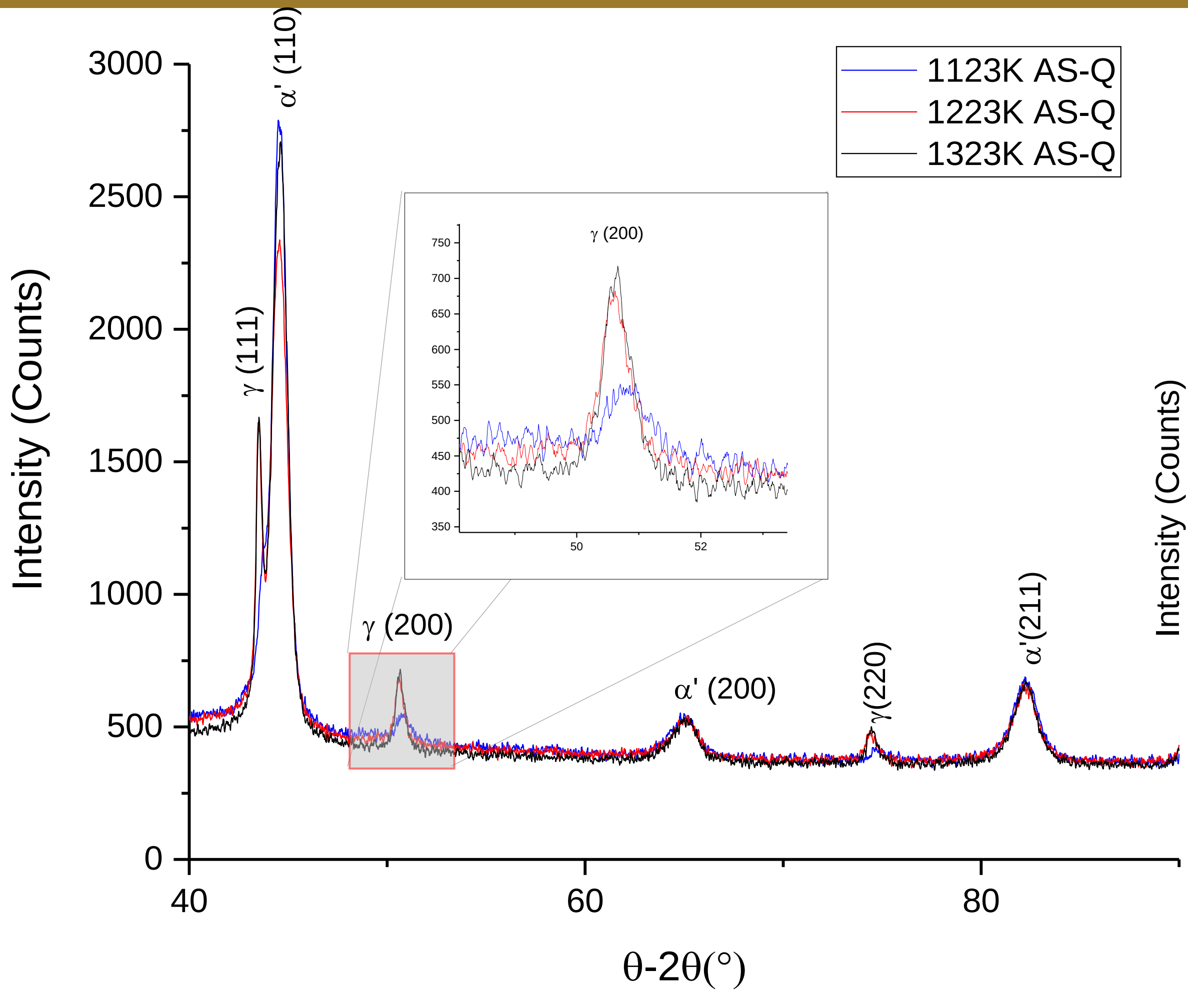
Q + DCT structures

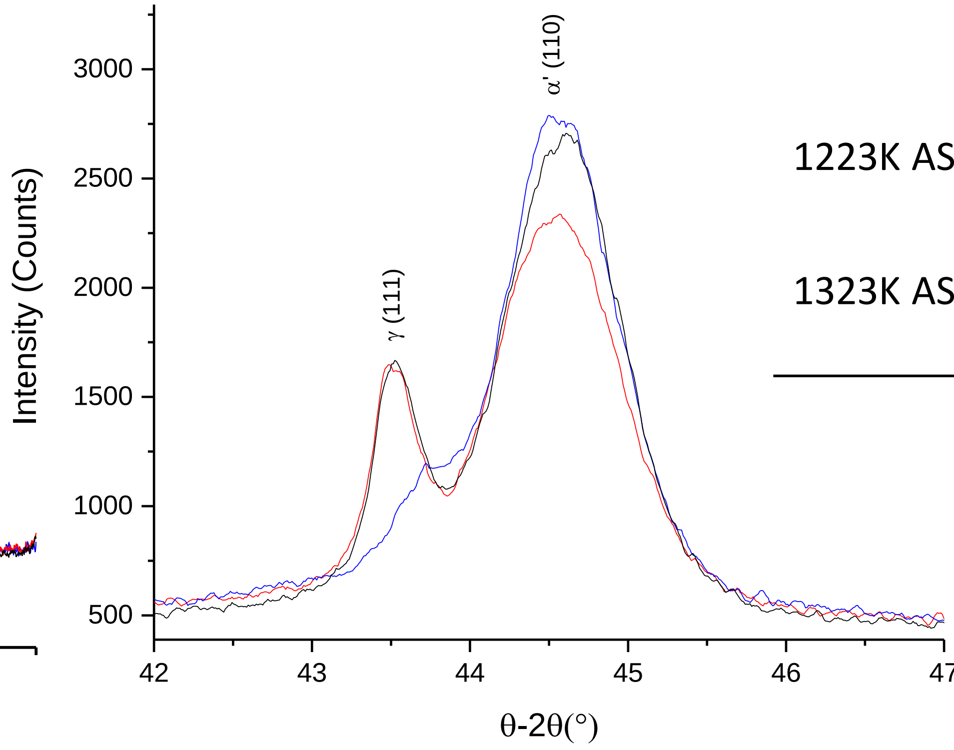


Etchant: 2% Nital

Etchant: 4% Picral

Results – XRD

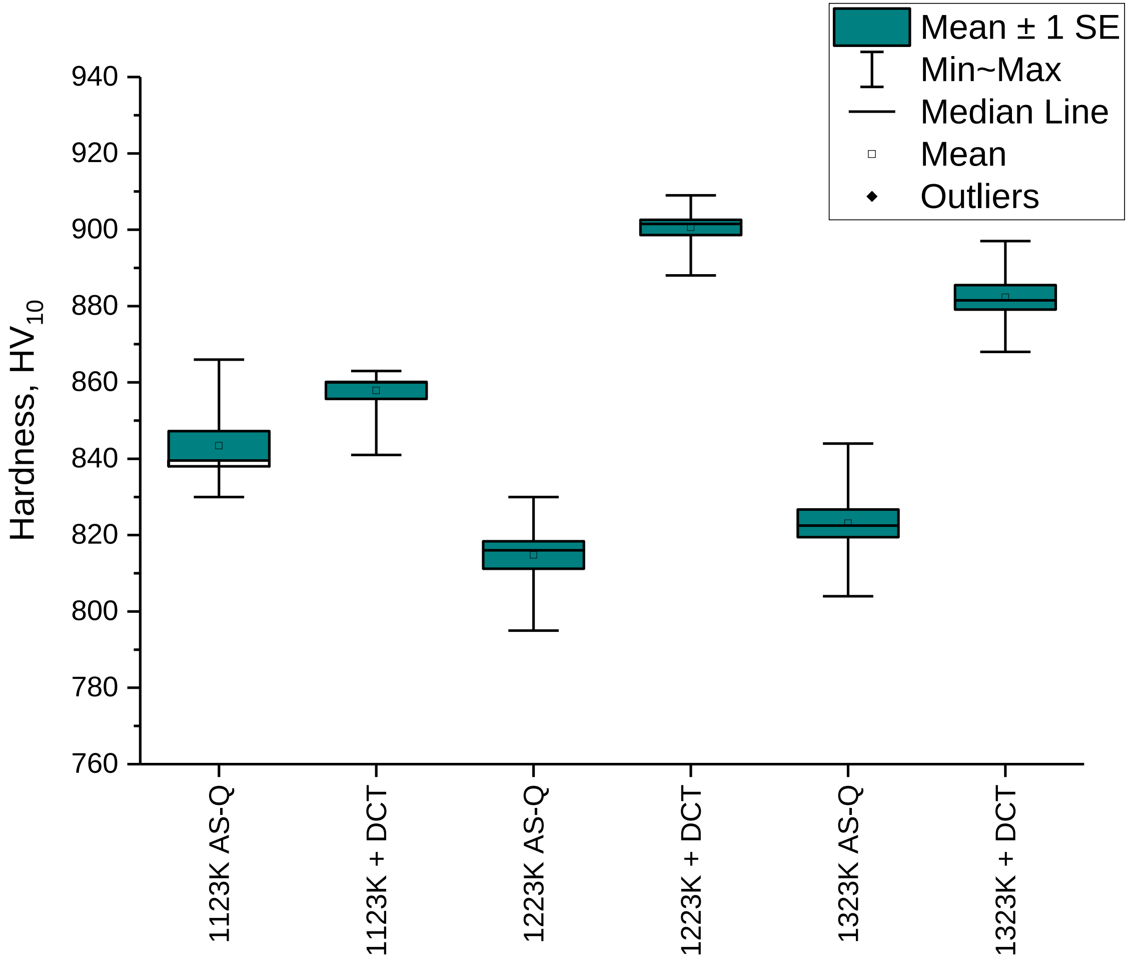




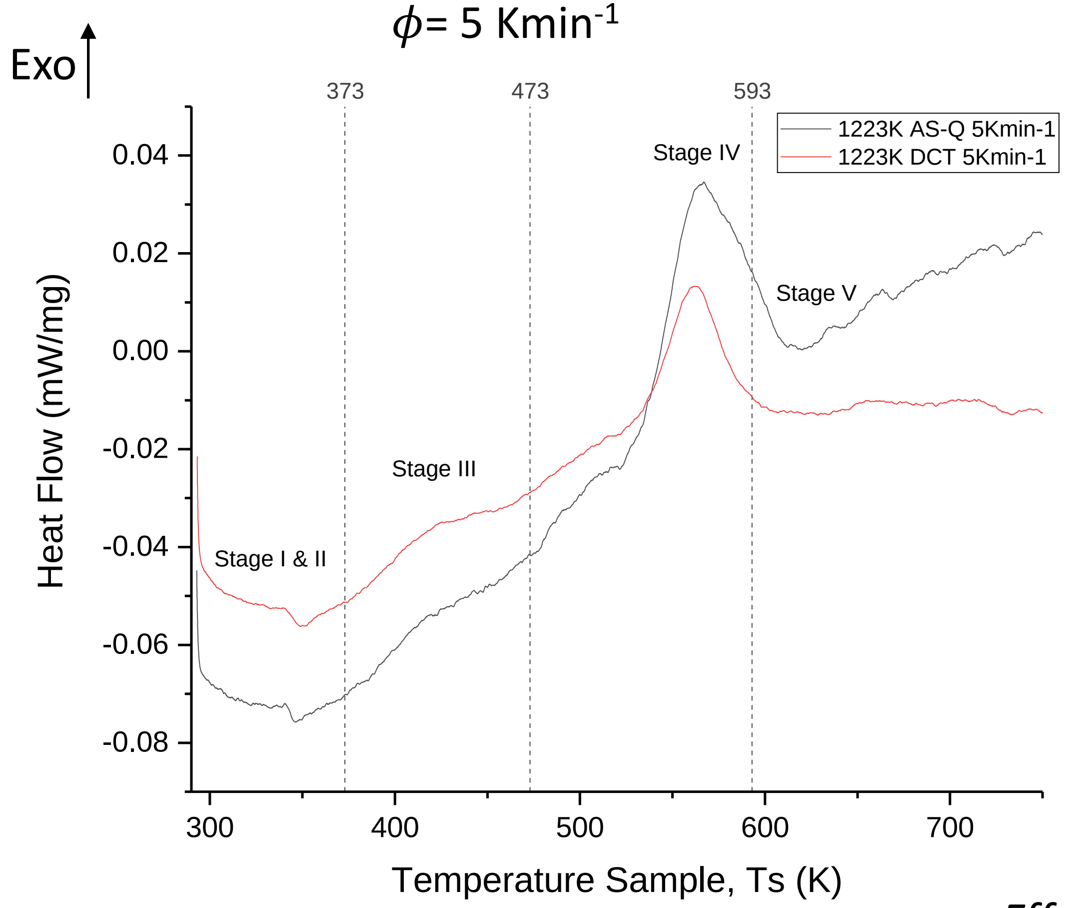
Sample	Phase	Wt.%
1123K AS-Q	α'	83.5
	γ_{RA}	12.6
	Fe_3C	3.9
1223K AS-Q	α'	69.8
	γ_{RA}	30.2
1323K AS-Q	α'	78.6
	γ_{RA}	21.4

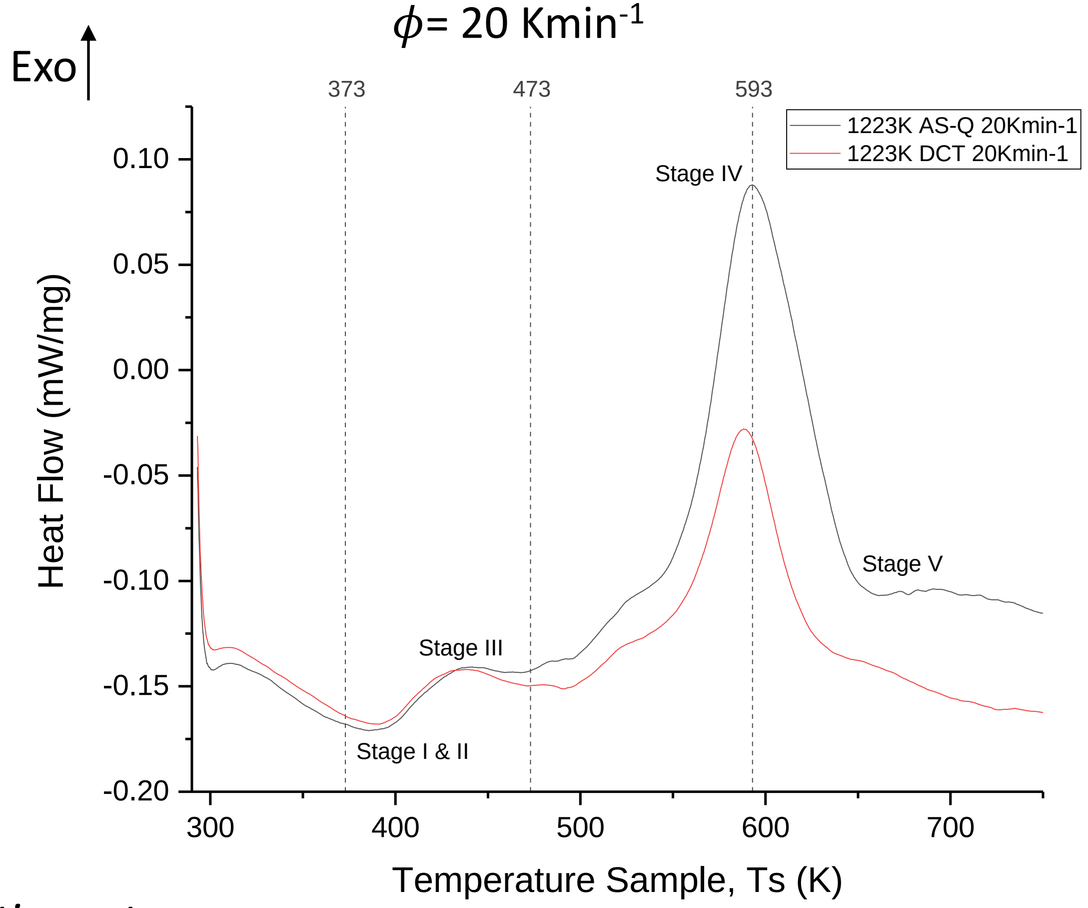
Results – Macro-hardness

- 10 measurements for each sample, HV10
- Relatively large SD due to domain of grains encountered (austenite, martensite)
- 1123K samples experienced mean increase in hardness of 1.72% with DCT
- Mean hardness of 1223K austenitised samples increased by 10.53% with DCT and 1323K samples by 7.19%
- More analysis required on whether γ_{RA} to α' is responsible or conditioning of RT formed α' at DCT temperatures



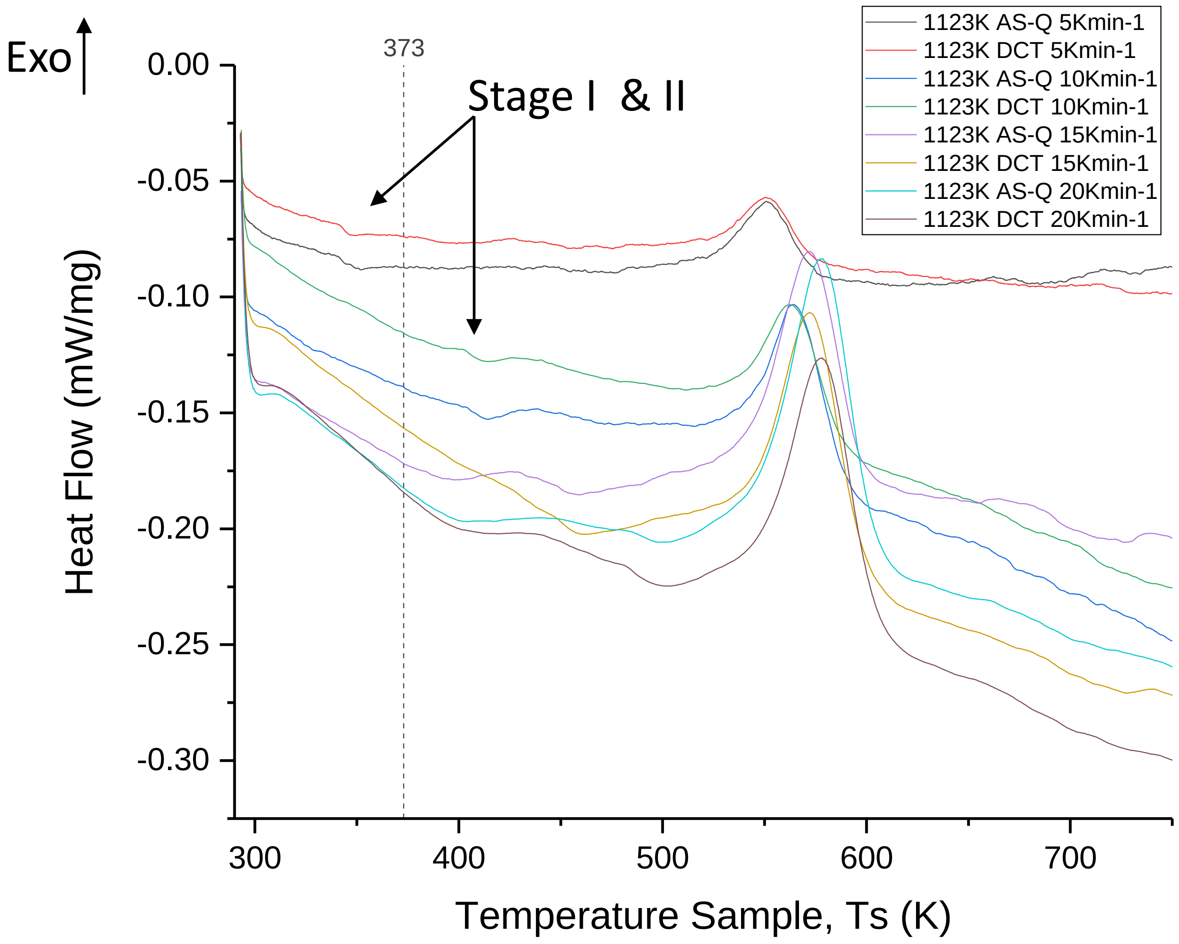
Results – Calorimetry 1223K Samples

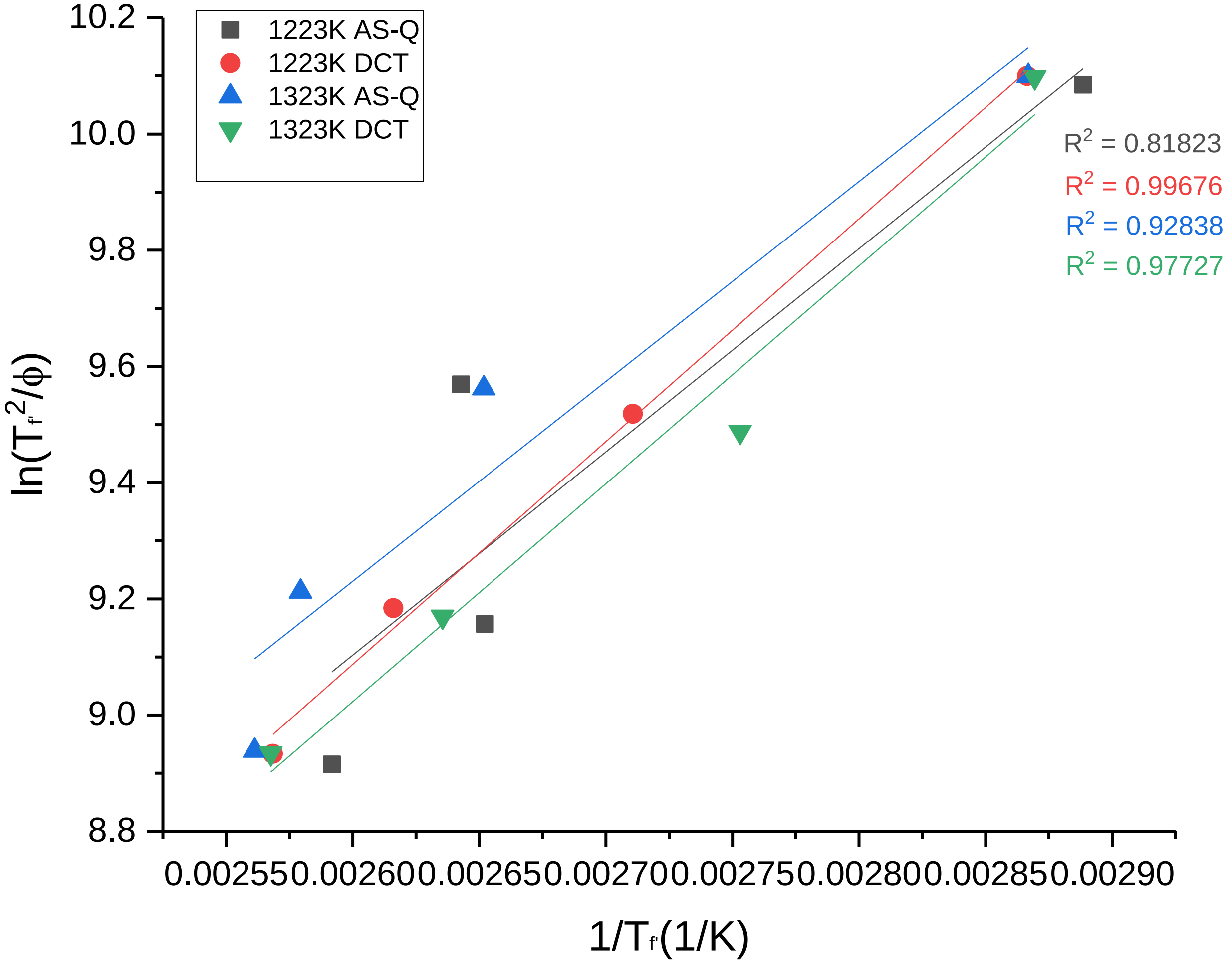




Effect of heating rate

Results – Calorimetry – Stage I & II





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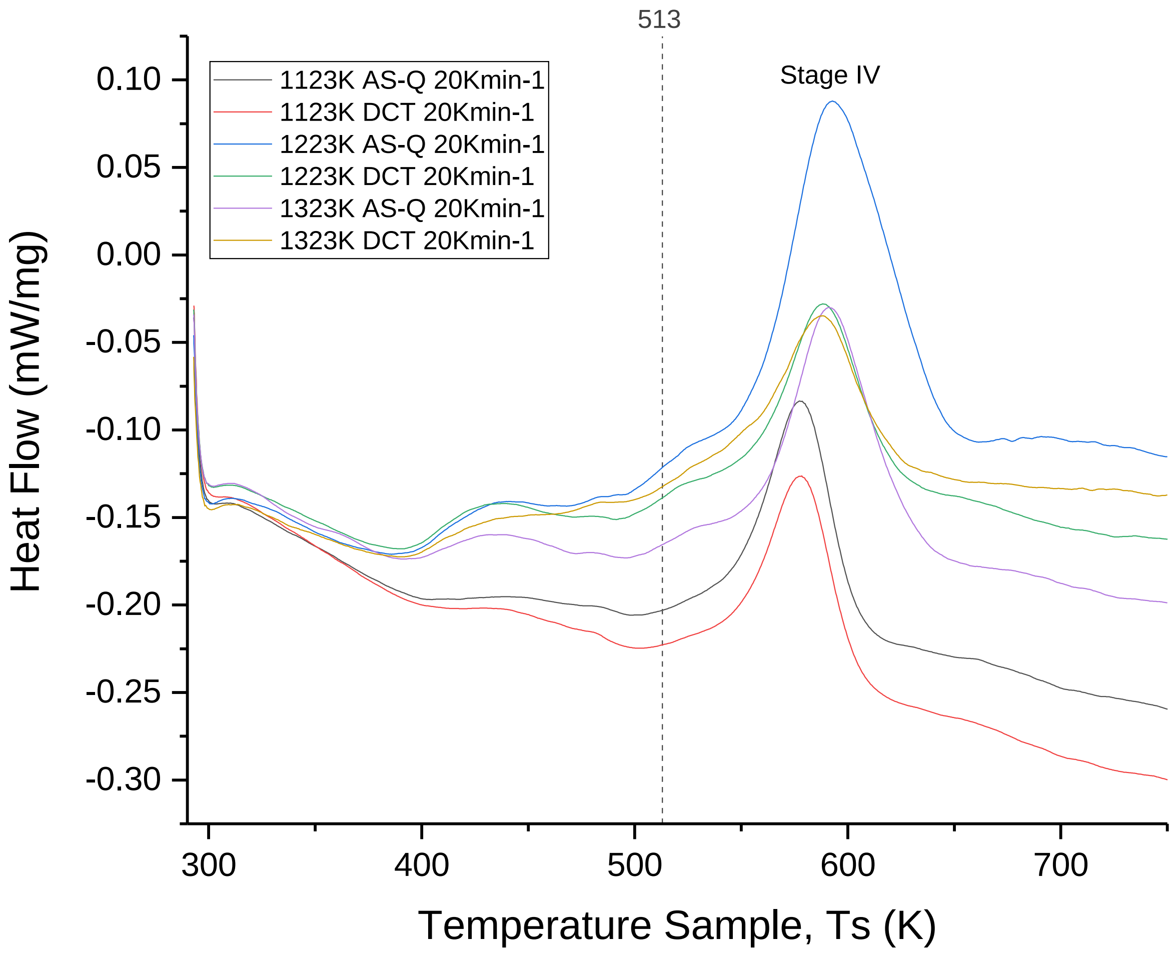
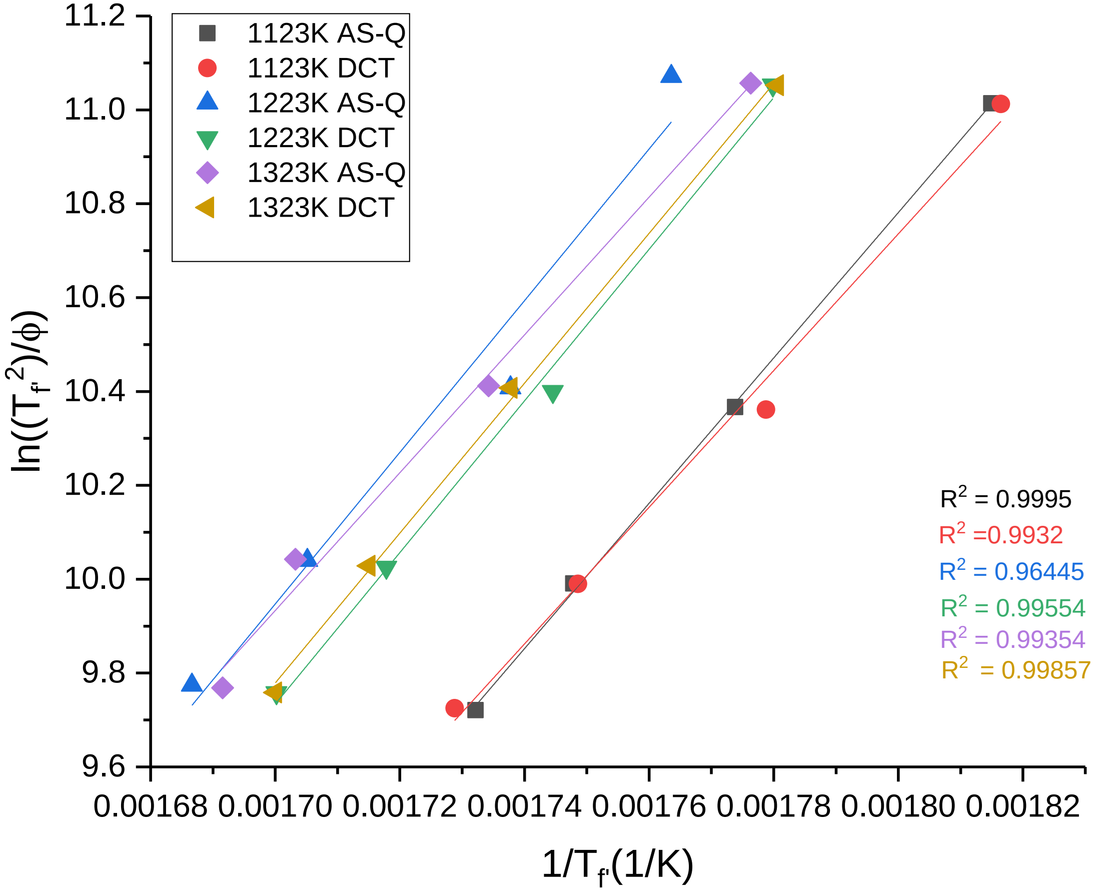
Results – Calorimetry – Stage IV





Results – Kinetic analysis

		Activation energies, E_a ($\mathbf{kJmol^{-1}}$)						
Stage	**Occurrence**	***Literature Values***	**1123K AS-Q**	**1123K Q+DCT**	**1223K AS-Q**	**1223K Q+DCT**	**1323K AS-Q**	**1323K Q+DCT**
I & II	Pre-precipitation processes (segregation of carbon and its subsequent arrangement)	*83 & 79 [1]* *55 - 78 [2]* *111 & 80 [3]*	**-**	**-**	**29**	**32**	**29**	**31**
III	Formation of transition carbides (η, ϵ)	*111 [1]* *89-99 [2]*	To be inferred from dilatometry					
IV	Decomposition of retained austenite γ_{RA} to cementite and ferrite (θ and α)	*132 [1 & 3]* *115-134 [2]*	**129**	**121**	**134**	**134**	**122**	**133**
V	precipitation of cementite θ	*203 [1 & 3]* *185-282 [2]*	To be inferred from dilatometry					

[1] Cheng. L et al., (1988) Met Trans A, 19A, 2415-2426. [2] Preciado, M. & Pellizzari, M. (2014) J Mater Sci, 49, 8138-8191. [3] Van Genderen M.J. et.al., (1996) Met and Mat Trans A, 28A, 545-561.

Conclusions

- DCT does not transform all retained austenite γ_{RA} to martensite α' but has converted some of the phase when compared to AS-Q samples evidenced by DSC
  - Post-DCT XRD required to evaluate quantify extent of transformation during DCT
- Hardness improvements suggestive of retained austenite γ_{RA} to martensite α', but further metallography needed for verification
- Activation energies determined for stage I & II during tempering show poor linear regressions – broad DSC signals and fast heating rates
  - DCT treated samples present a higher activation energy than AS-Q samples austenitised at 1223K and 1323K, suggesting less favourable sites available for C atoms to segregate to in DCT samples
- Stage III analysed by calorimetry but broad transformation peaks hinder accurate identification of the position of $T_{f'}$ – dilatometry required
- Activation energies determined for stage IV (decomposition of γ_{RA}) agree well with literature values and the value of diffusion of C in austenite (128 kJ mol^{-1}) [1]
  - DCT of 1123K austenitised samples reduced activation energy required to decompose austenite, suggestive of increased transition carbides, 1223K & 1323K DCT samples activation energy increased suggestive of austenite stabilisation
- Stage V (precipitation of cementite from transition carbides) not observed during calorimetry – dilatometry required

1. Preciado, M. & Pellizzari, M. (2014) J Mater Sci, 49, 8138-8191.

Future Work

- **Calorimetry**
- Study enthalpies of transitions
- **Dilatometry**
  - Effects of a DCT (93 K 24 hrs) cycle studied by dilatometry
  - Length changes during the stages of tempering help elucidate precipitation stages
  - Compliment DSC results
- **In-situ XRD**
  - Diffraction studies in-situ after a DCT (93 K 24 hrs) cycle
  - RT to 673 K to investigate changes in strain state, lattice parameters and phases
- **In-situ Neutron Diffraction**
  - Neutron diffraction at ISIS Engin-X (postponed May 2020 & March 2021)
  - Again track changes in strain state, lattice parameters and phases

The End

Thank You

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