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Database Development for Thermodynamic Simulation of Ta-based Z-Phase Formation in Martensitic Z-Steels

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INTRODUCTION

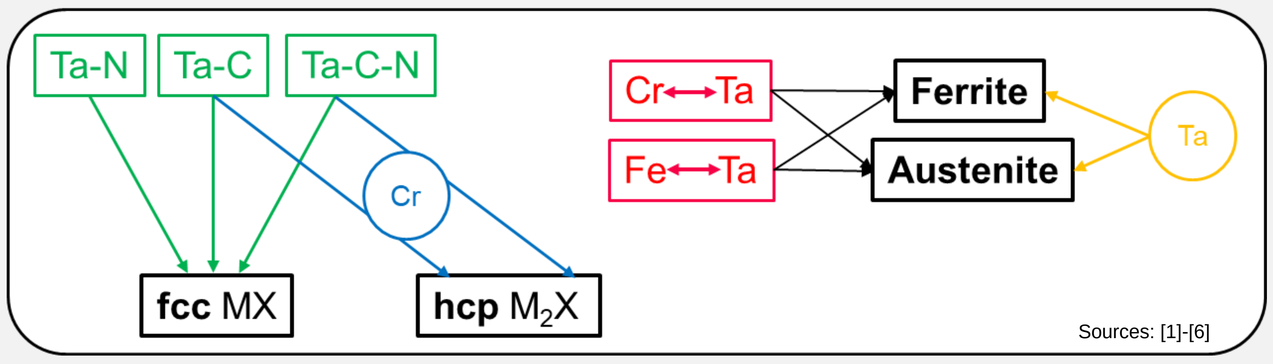
Z-steels are a new generation of creep-resistant martensitic 12% Cr-steels. They contain Tantalum, which causes an immediate transformation of precursor precipitates MX and M_2X into long-term stable and finely distributed Z-phase CrTaN. To simulate thermodynamic equilibrium and precipitation kinetics in MatCalc, further development of an existing CALPHAD steel database was realized, incorporating Ta and its interactions with matrix as well as particles. Tests of the database were conducted with 2 sample alloys (ZULC and Z6), leading to satisfactory results.

DATABASE AND SIMULATION SETUP

- Two **formation mechanisms of Z-phase**: Source: [8]

1.) Cr diffusing into **fcc** Ta(C,N) = MX 2.) Ta diffusing into **hcp** $Cr_2(C,N) = M_2X$

Database Setup:



Sources: [1]-[6]

Sublattice Model:

:Cr%,Fe:Nb,Mo,Ta,V:N%Va:

Input Parameters Equilibrium Simulation:

- Chemical composition

wt. %	Fe	Ni	Cu	Cr	W	Mo	Si	Mn	C	N	Co	Ta	B	V
ZULC	bal	0.50	-	11.79	2.90	-	0.30	0.48	0.005	0.033	7.30	0.39	0.004	-
Z6	bal	0.22	0.96	10.85	1.48	0.67	0.09	0.46	0.009	0.03	3.31	0.38	0.002	0.1*

Input Parameters Precipitation Kinetic Simulation:

- Heat treatment data
- Microstructural information
- Equivalent interface energy Z-phase

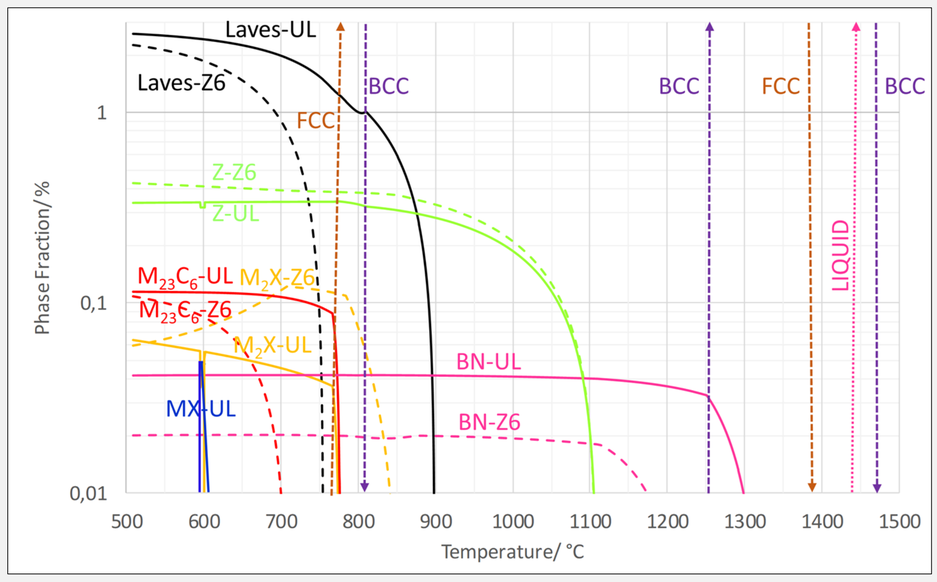
Input MatCalc		ZULC	Z6
Heat Treatm.	Hot Rolling	-	1064- 998°C
	Normalizing	1h@1150°C	1h@1100°C
	Tempering	24h@650°C	2h@650°C 2h@750°C
	Ageing	10^4h@650°C	10^4h@700°C
PAGS		114 µm	48 µm
Subgrain Size		0.56 µm (EBSD, P91)	
$\rho_{m,0}$ Martensite		$1.5 \cdot 10^{14}$ m^{-2} (TEM, P91)	
$\rho_{m,0}$ Austenite		10^{11} m^{-2}	

Input MatCalc	Value
Equivalent Interface Energy for Z-Phase	0.1 J/m^2
Minimum Nucleation Radius Z-phase	5 Å
Z-phase Shape Factor	0.128

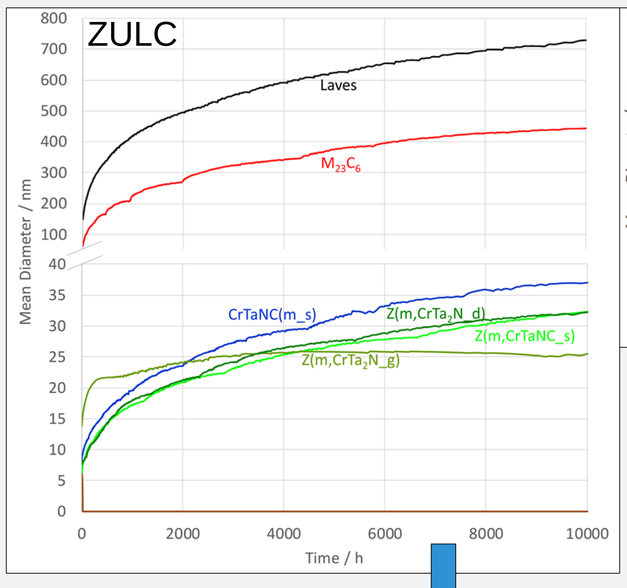
Sources: [7]-[14]

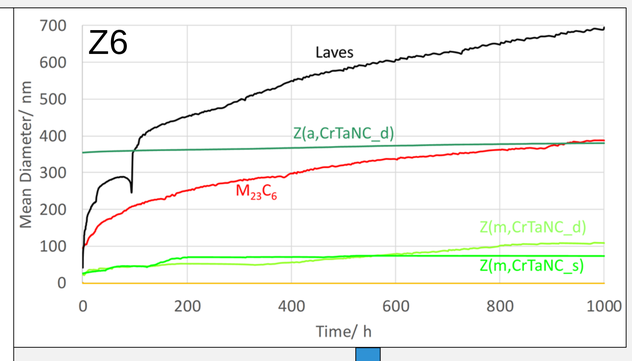
RESULTS

1.) PHASE FRACTION Equilibrium



2.) SIZES Precipitation Kinetics





As-rec. condition:
- Z(m,CrTaNC_s) Ø26 nm
- No MX

1000h @ 700°C:
- Ø73 nm of Z(m,CrTaNC_s)

As-rec. condition:
- Z-phase Ø61 nm (TEM)
- MX Ø34 nm (TEM)

1000h @ 700°C:
- Z-phase Ø79 nm (TEM)
- → Simulation 10 % close !

Source: [9]

As-rec. condition:
- Z-phase Ø6-14 nm
- MX Ø8 nm

10 000h @ 650°C:
- Z-phases with high phase fract.: Ø32 nm

As-rec. condition:
- MX Ø10-20 nm (TEM)
- Z-phase Ø10 nm (APT)

10 000h @ 650°C:
- Z-phase Ø48 nm (APT)
- → Simulation 30 % close !

Sources: [7],[8]

3.) CHEMISTRY Z-PHASE Precipitation Kinetics

ZULC

Simulated

MatCalc [at.%]	Cr	N	Ta
As-received	36.0	27.9	36.0
10^4h@650°C	35.9	28.1	35.9

Measured

APT [at.%]	Cr	N	Ta
As-received	33.6	26.9	30.2
10^4h@650°C	39.8	30.2	24.1

- As-rec. condition: good agreement
- Aged: too much Ta, but not enough Cr in simulation

Source: [10]

Z6

Simulated

MatCalc [at.%]	Cr	N	Ta	V
As-received	36.6	26.8	24.9	11.7
10^3h@700°C	36.5	27.1	25.6	10.9

Measured

TEM-EDX [at.%]	Cr	Ta	V
As-received	49.6	35.9	6.1
10^3h@700°C	52.1	36.6	2.0

- V is overrepresented in simulation at the expense of Ta

Source: [9]

CONCLUSIONS

ZULC
- Phase fraction of Z: app. 0.3 %
- Z-phase origin: 2/3 MX, 1/3 M_2X
- MX transform completely: ✖
- Agreement with measured Z size: 30 % close to APT (10^4h@650°C)
- Agreement Z composition & APT:
  - As-received: excellent
  - 10^4h@650°C: ↑Ta, ↓Cr

Z6
- Phase fraction of Z: app. 0.4 %
- Z-phase origin: all MX → due to V
- MX transform completely: ✔
- Agreement with measured Z size: 10 % close to TEM (10^3h@700°C)
- Agreement Z composition & EDX:
  - All conditions: ↑V

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