Oxidation Phenomena in Advanced High Strength Steels

Project ZCO-62 International Zinc Association

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William Mao, Vahid Aghaei Lashgari, Wim G. Sloof

Delft University of Technology

Department of Materials Science and Engineering

Mekelweg 2, 2628 CD Delft, The Netherlands

Predicting mixed oxide formation

- In order to predict oxide formation in multi-element steel alloys a thermodynamic database is being developed that needs validation
- Oxidation experiments with Mn steels with Al, Si and Cr additions have been done
- The resulting oxide precipitates were analyzed
- A comparison with thermodynamic predictions is made
- Modelling of the formation of single oxides is done
- Modelling of the formation of mixed oxides is in progress

1.

Oxidation experiments with Mn Steel Alloyed with Al, Si and Cr

Mn steel alloys and annealing conditions

Sample (wt%)	C	Mn	Cr	Si	Al
A	0.103	1.7	-	0.049	0.002
B	0.099	1.8	0.53	0.25	0.003
C	0.101	1.8	1.02	0.26	0.019
D	0.102	2.8	0.55	0.25	0.005
E	0.177	1.8	-	0.15	0.95
F	0.202	1.8	-	0.97	0.90
G	0.104	1.9	-	0.94	0.017

Annealing atmosphere: N_2 with 5 vol.% H_2

Temperature (°C)	Time (min)	Dew point (°C)	P_{O2}	Code
950	60	-45	8.0×10^{-22}	1
950	60	-31	1.8×10^{-20}	2
950	60	-10	1.0×10^{-18}	3
950	60	+10	2.3×10^{-17}	4

Mn steel alloys and annealing conditions

Sample (mol%)	C	Mn	Cr	Si	Al
A	0.48	1.7	-	0.097	0.004
B	0.46	1.8	0.57	0.49	0.006
C	0.47	1.8	1.09	0.51	0.039
D	0.47	2.8	0.59	0.49	0.01
E	0.81	1.8	-	0.29	1.93
F	0.91	1.8	-	1.88	1.81
G	0.48	1.9	-	1.84	0.03

Annealing atmosphere: N_2 with 5 vol.% H_2

Temperature (°C)	Time (min)	Dew point (°C)	P_{O2}	Code
950	60	-45	8.0×10^{-22}	1
950	60	-31	1.8×10^{-20}	2
950	60	-10	1.0×10^{-18}	3
950	60	+10	2.3×10^{-17}	4

Activity of alloying element at 950 ° C, calculated with "Thermocalc"

Sample	C	Mn	Cr	Si	Al	Fe
A		1.2×10^{-2}	-	2.9×10^{-9}	2.4×10^{-8}	0.977
B		1.2×10^{-2}	5.3×10^{-3}	1.5×10^{-8}	3.8×10^{-8}	0.968
C		1.2×10^{-2}	1.0×10^{-2}	1.5×10^{-8}	2.4×10^{-7}	0.962
D		2.0×10^{-2}	5.6×10^{-3}	1.3×10^{-8}	6.6×10^{-8}	0.958
E		1.3×10^{-2}	-	1.3×10^{-8}	1.5×10^{-5}	0.947
F		1.1×10^{-2}	-	1.1×10^{-7}	1.9×10^{-5}	0.925
G		1.1×10^{-2}	-	7.2×10^{-8}	2.7×10^{-7}	0.957

Activities of all alloying elements smaller than that of Mn

2.

SEM cross-section analysis
Effect of dew point

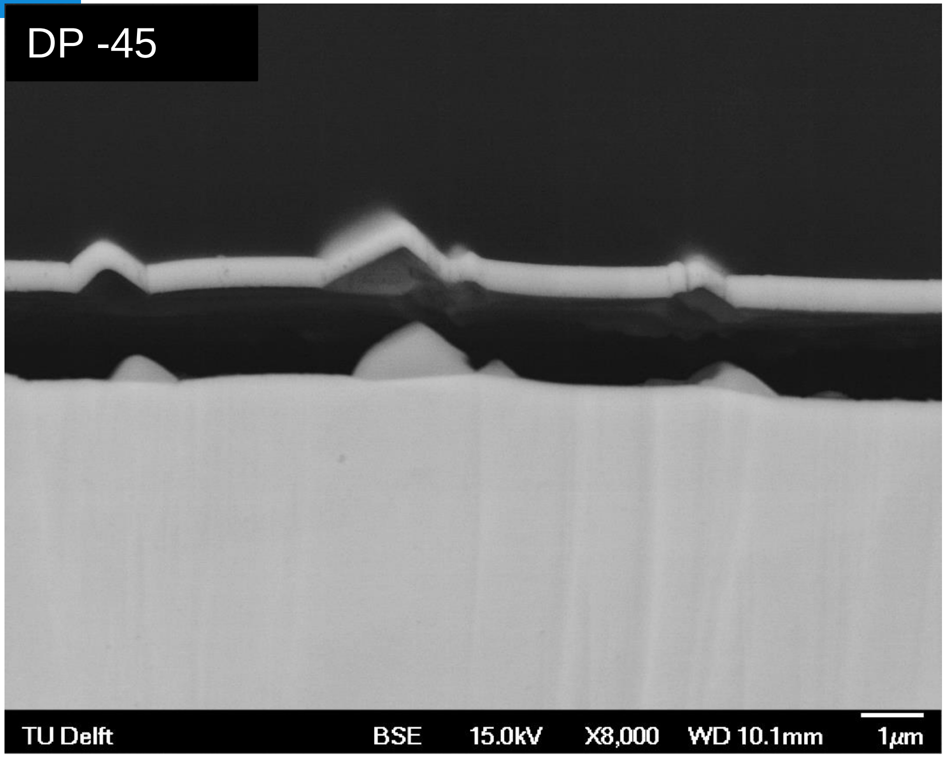
SEM cross-section observation: Fe-Mn

Annealing condition in N_2 with 5 vol.% H_2

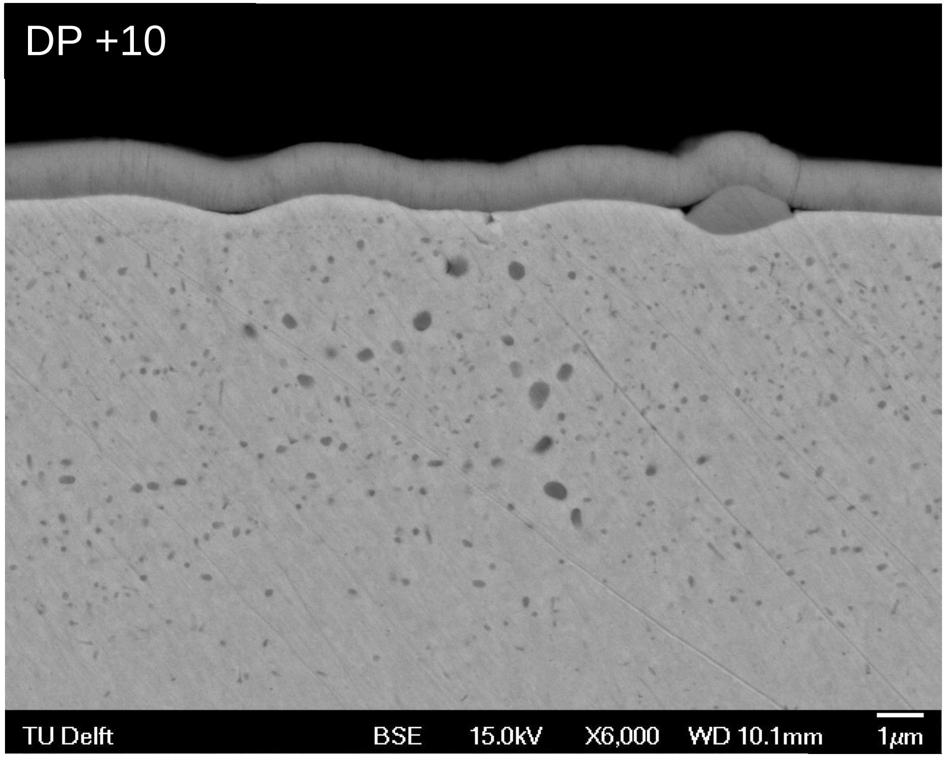
Dew point (° C)	Temperature (° C)	P_{O2}
-45	950	8.0×10^{-22}
+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample A	0.48	1.72	0.097	0.004



External MnO



Internal MnO

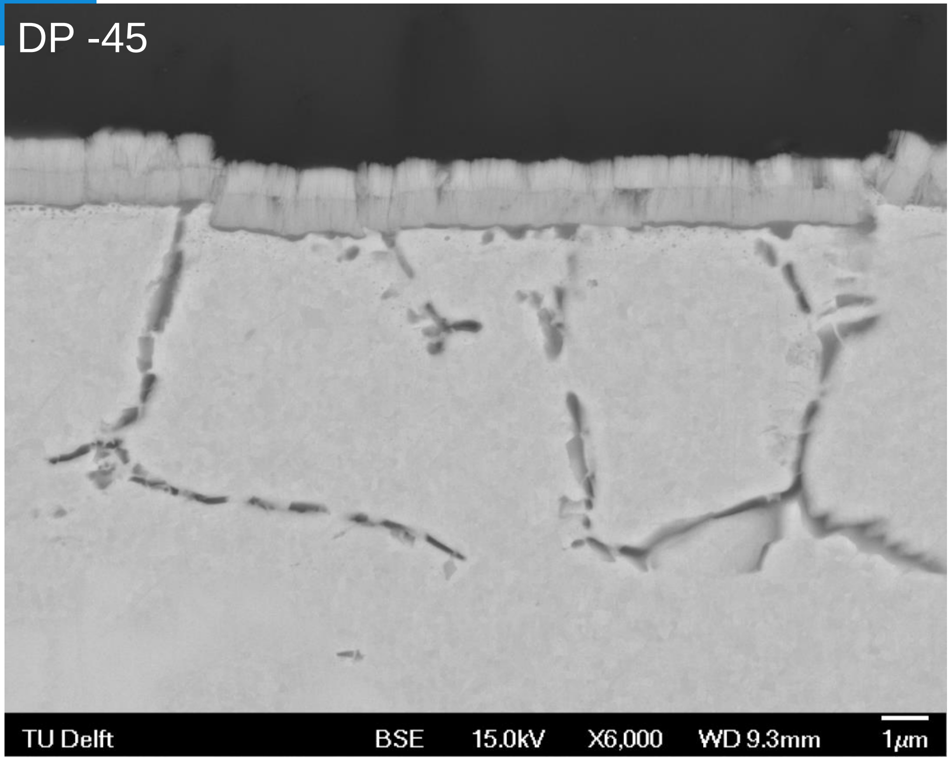
SEM cross-section observation: Fe-Mn-Si

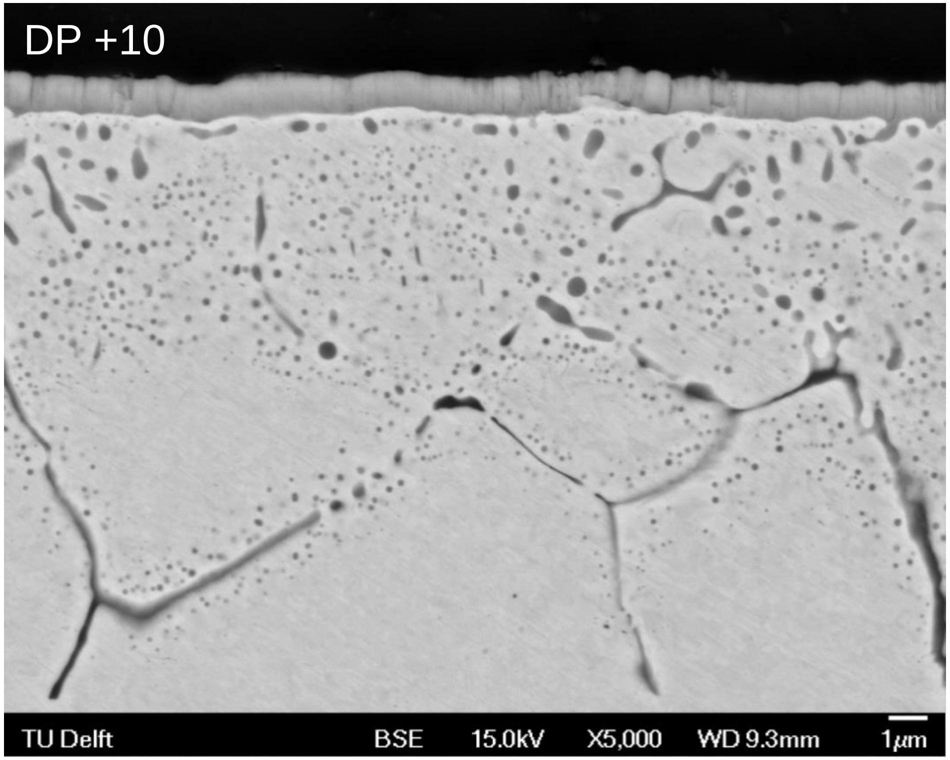
Annealing condition in N_2 with 5 vol.% H_2

Dew point (° C)	Temperature (° C)	P_{O2}
-45	950	8.0×10^{-22}
+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample G	0.48	1.91	1.84	0.03





Si promotes Mn_2SiO_4 formation along grain boundaries

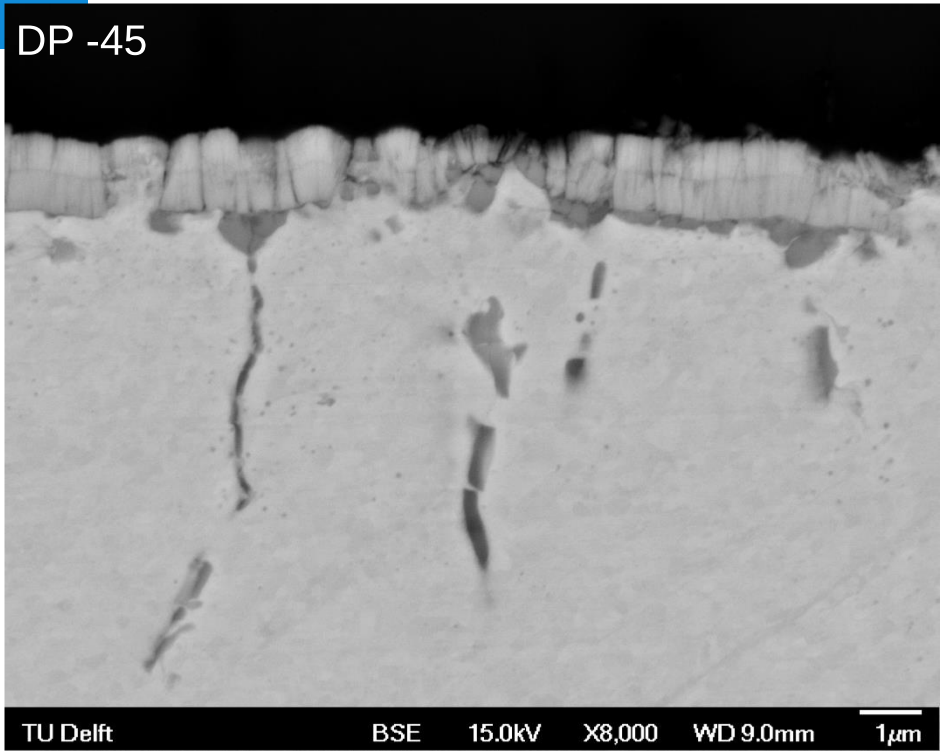
SEM cross-section observation: Fe-Mn-Cr-(Si)

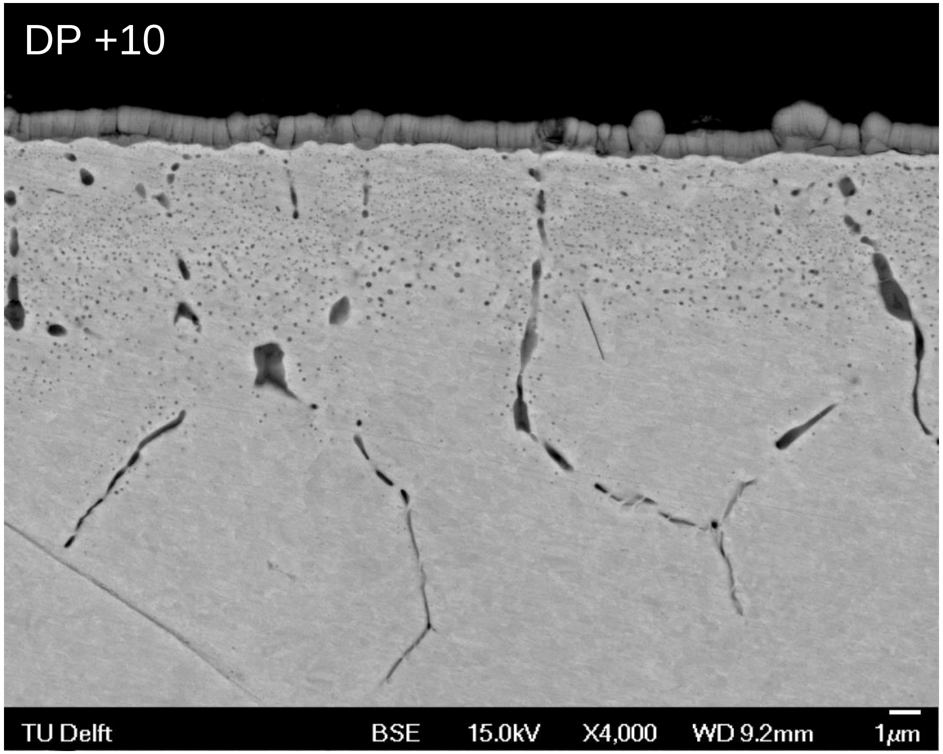
Annealing condition in N_2 with 5 vol.% H_2

Dew point (° C)	Temperature (° C)	P_{O2}
-45	950	8.0×10^{-22}
+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Cr	Si	Al
Sample C	0.47	1.82	1.09	0.51	0.039





Cr forms mainly internal $MnCr_2O_4$

Additional Si promotes Mn_2SiO_4 along grain boundaries

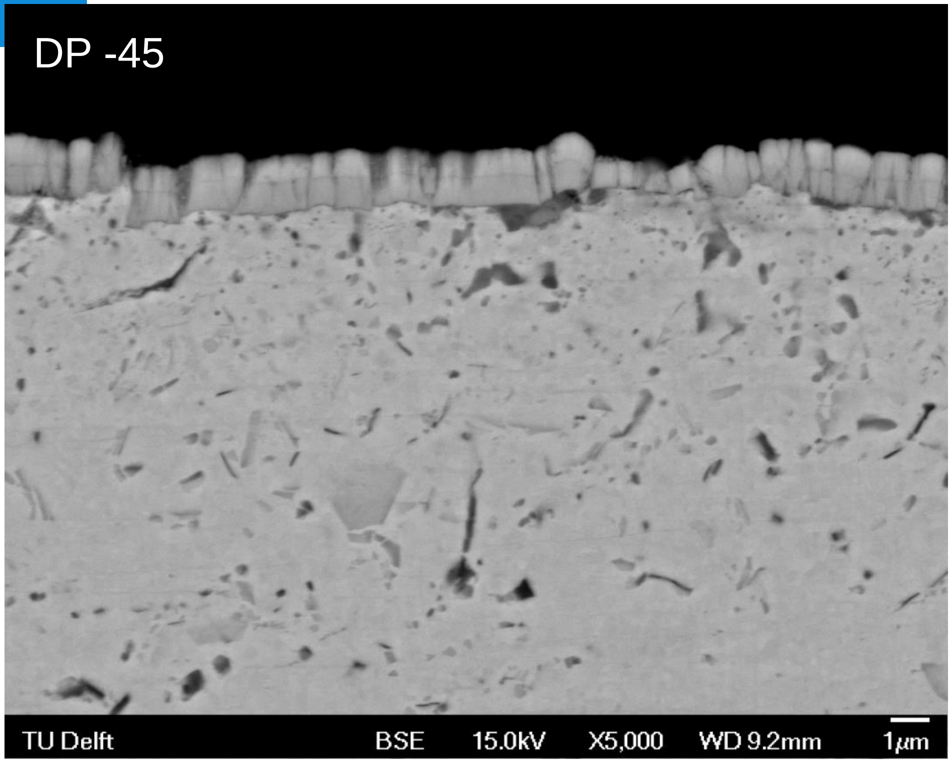
SEM cross-section observation: Fe-Mn-Al-(Si)

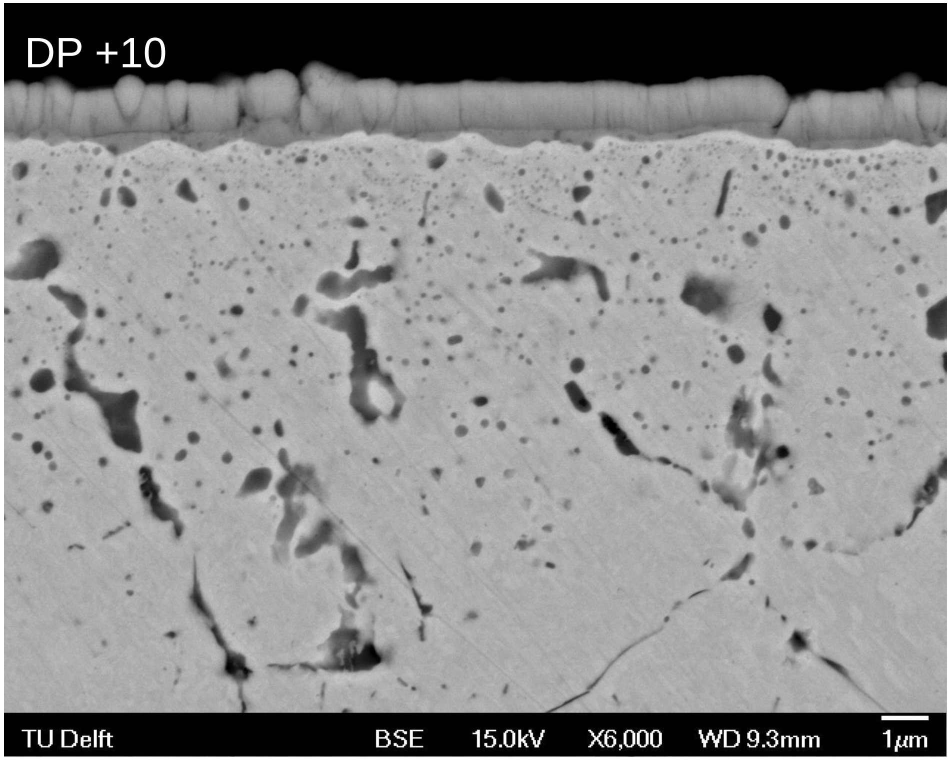
Annealing condition in N_2 with 5 vol.% H_2

Dew point (° C)	Temperature (° C)	P_{O2}
-45	950	8.0×10^{-22}
+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample E	0.81	1.8	0.29	1.93





At low DP AlN is formed, but suppressed with increasing DP

Al promotes formation of external MnO and formation of internal $MnAl_2O_4$

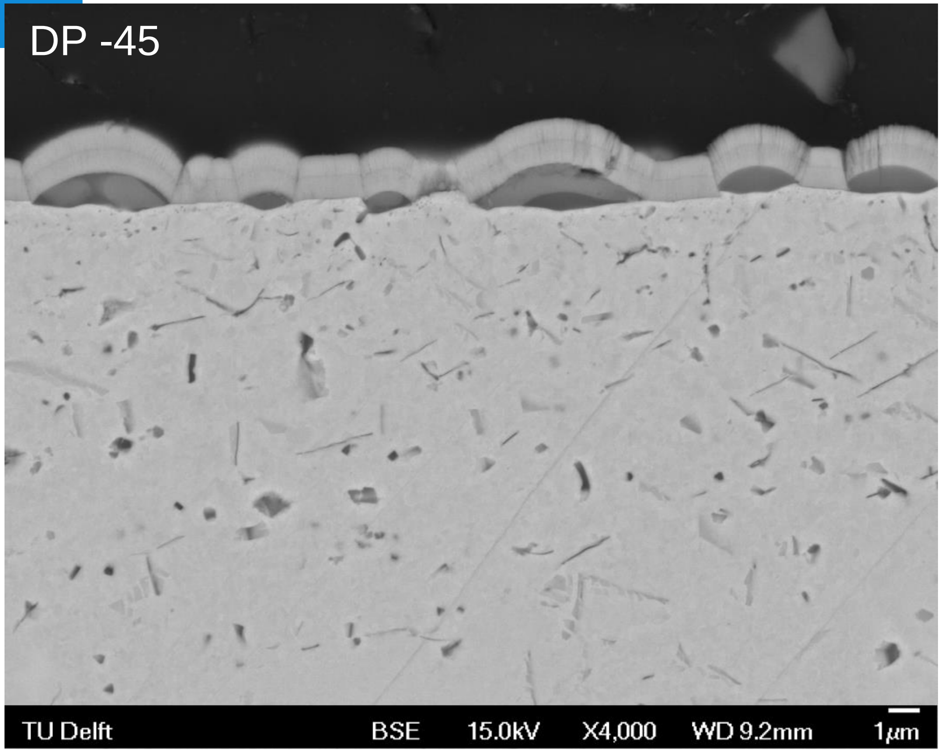
SEM cross-section observation: Fe-Mn-Al-Si

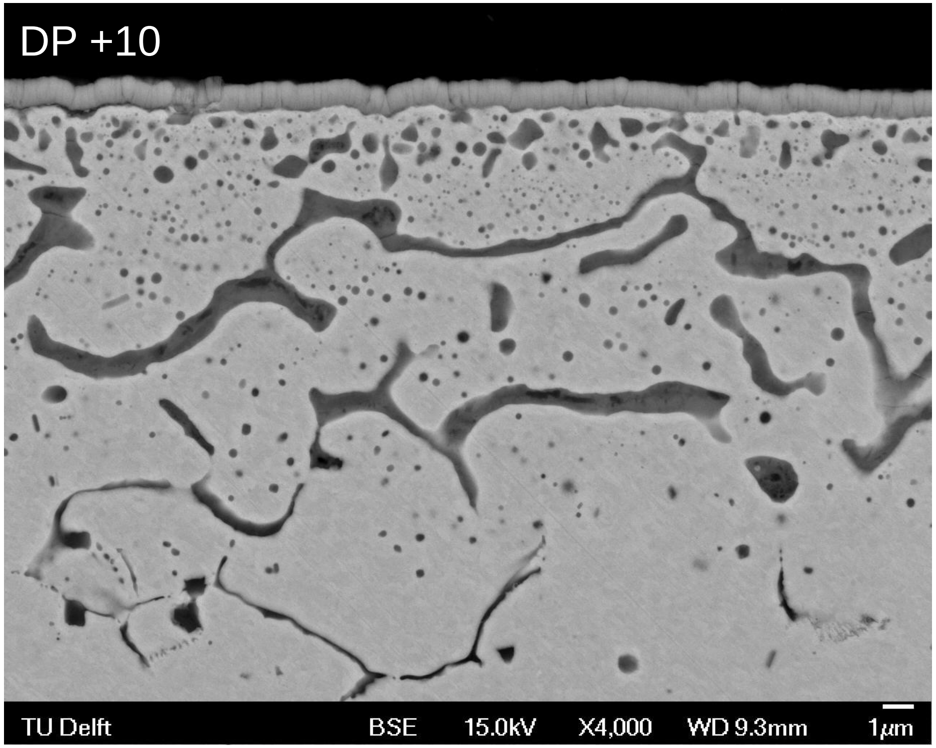
Annealing condition in N_2 with 5 vol.% H_2

Dew point (° C)	Temperature (° C)	P_{O2}
-45	950	8.0×10^{-22}
+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample F	0.91	1.78	1.88	1.81





Both $MnAl_2O_4$ and Mn_2SiO_4 are formed, inside grains as well as along grain boundaries

3.

XRD analysis & thermodynamic predictions of oxide formation

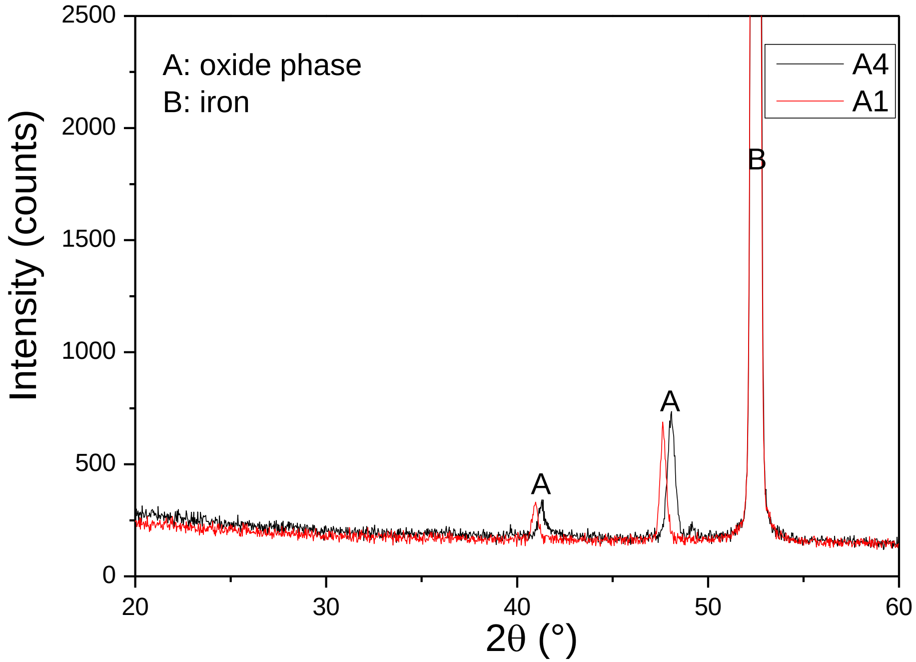
XRD analysis: Fe-Mn

Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
A1	-45	950	8.0×10^{-22}
A4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample A	0.48	1.72	0.097	0.004



Fe-Mn mixed oxide is formed:
A1: $Fe_{0.1}Mn_{0.9}O$
A4: $Fe_{0.4}Mn_{0.6}O$

The dew point for sample A4 is still lower than the critical value for the formation of FeO

The (Mn,Fe)O oxide phase has rock-salt crystal structure

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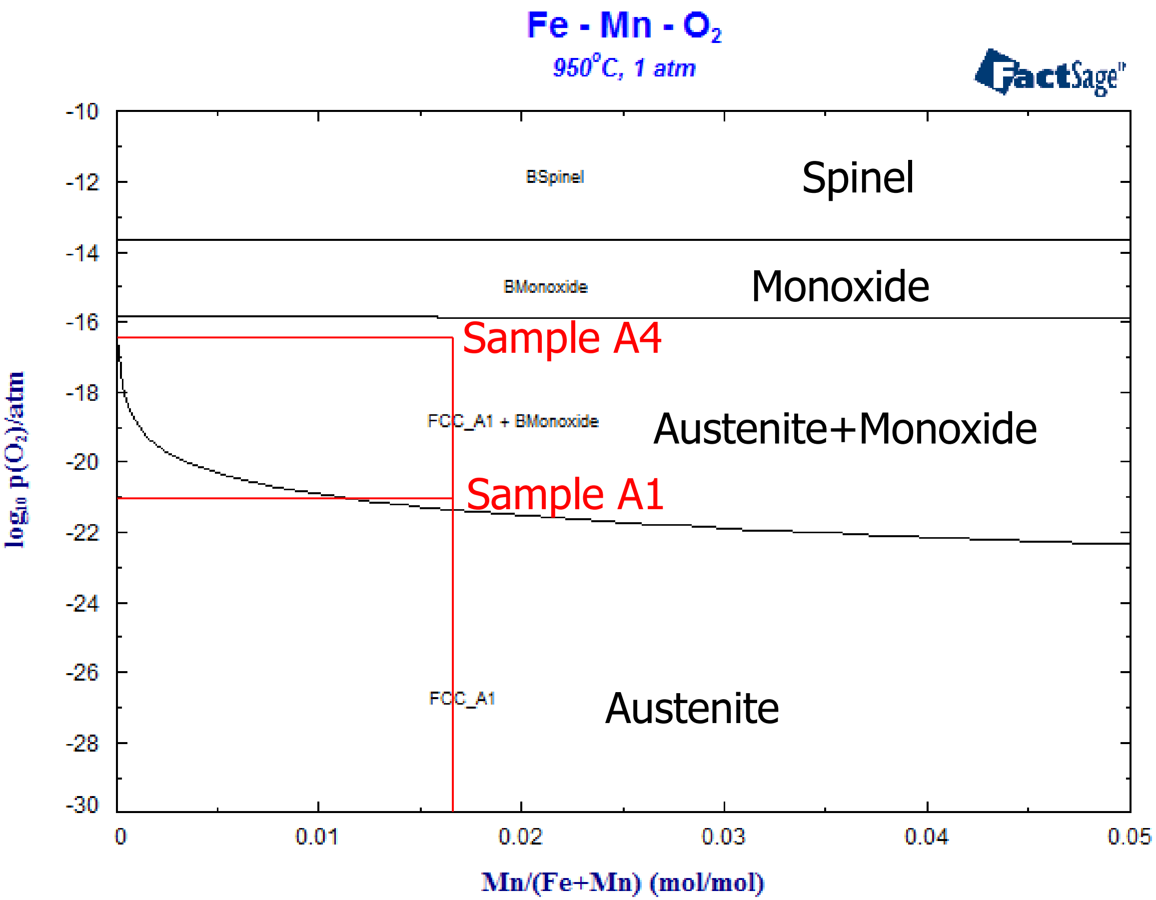
Prediction of oxides formation: Fe-Mn

Phase diagram of Fe-Mn alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution Phases selected in calculation: BSpinel, BMonoxide, FCC_A1

BSpinel is a solution of Fe_3O_4, $MnFe_2O_4$, $FeMn_2O_4$ with cubic crystal structure

BMonoxide is a solution of Fe_2O_3, FeO, MnO, Mn_2O_3 with rock-salt crystal structure

The amount of Fe in (Mn,Fe)O monoxide phase can be computed, which increases with dew point

XRD results agree with "Factsage" calculation

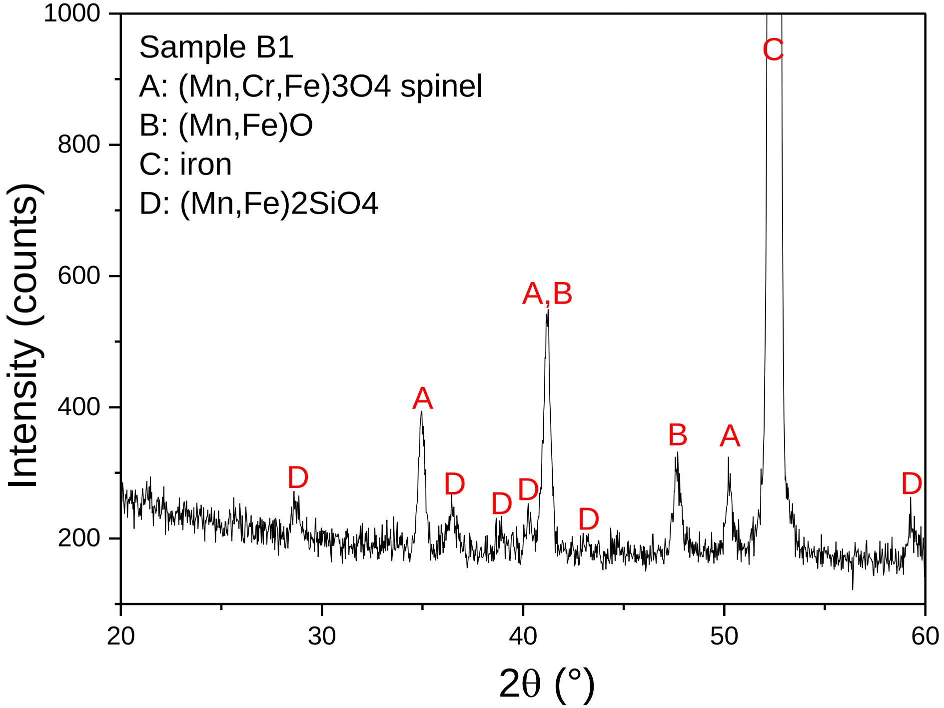
XRD analysis: Fe-Mn-Cr-(Si)

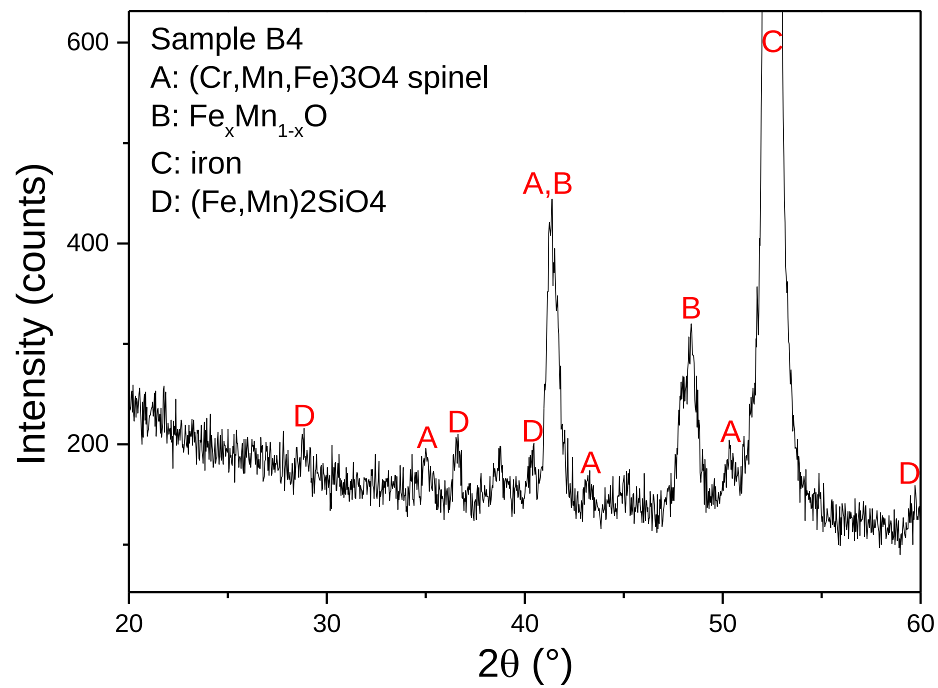
Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
B1	-45	950	8.0×10^{-22}
B4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Cr	Si	Al
Sample B	0.46	1.82	0.57	0.49	0.006





Addition of Cr leads to formation of $(Mn,Cr,Fe)_3O_4$ cubic spinel oxide

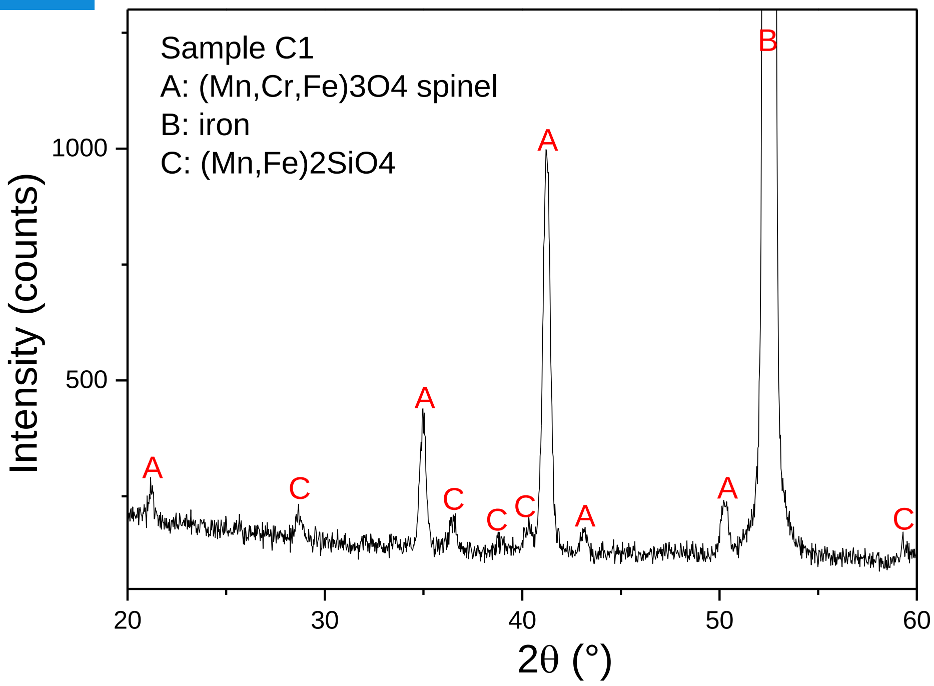
XRD analysis: Fe-Mn-Cr-(Si)

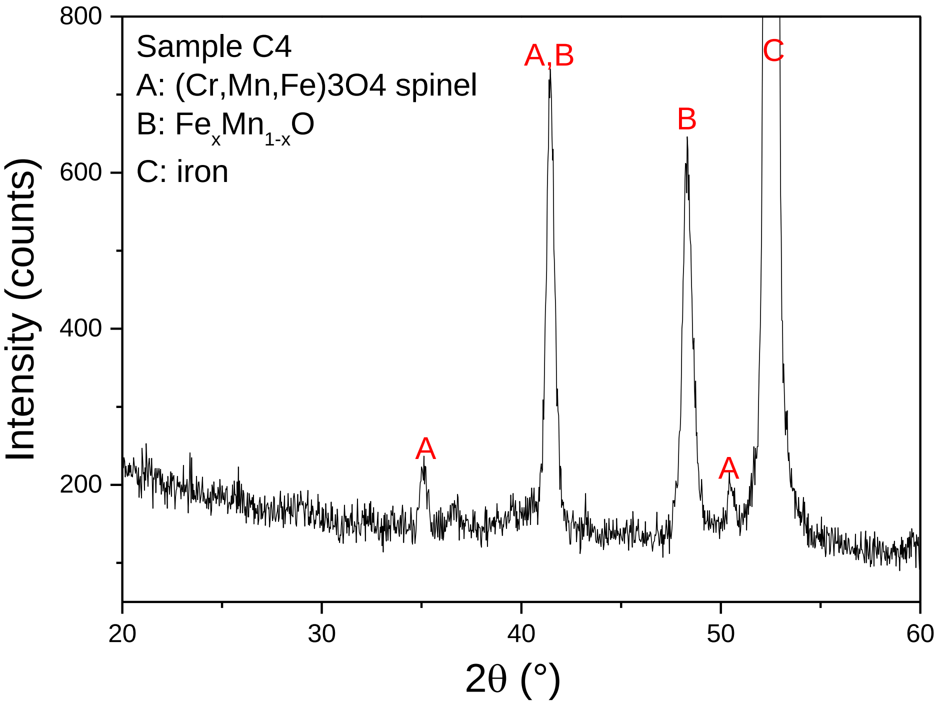
Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
C1	-45	950	8.0×10^{-22}
C4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Cr	Si	Al
Sample C	0.47	1.82	1.09	0.51	0.039





Again addition of Cr leads to the formation of $(Mn,Cr,Fe)_3O_4$ cubic spinel oxide
Higher Cr concentration does not change type of oxides formed

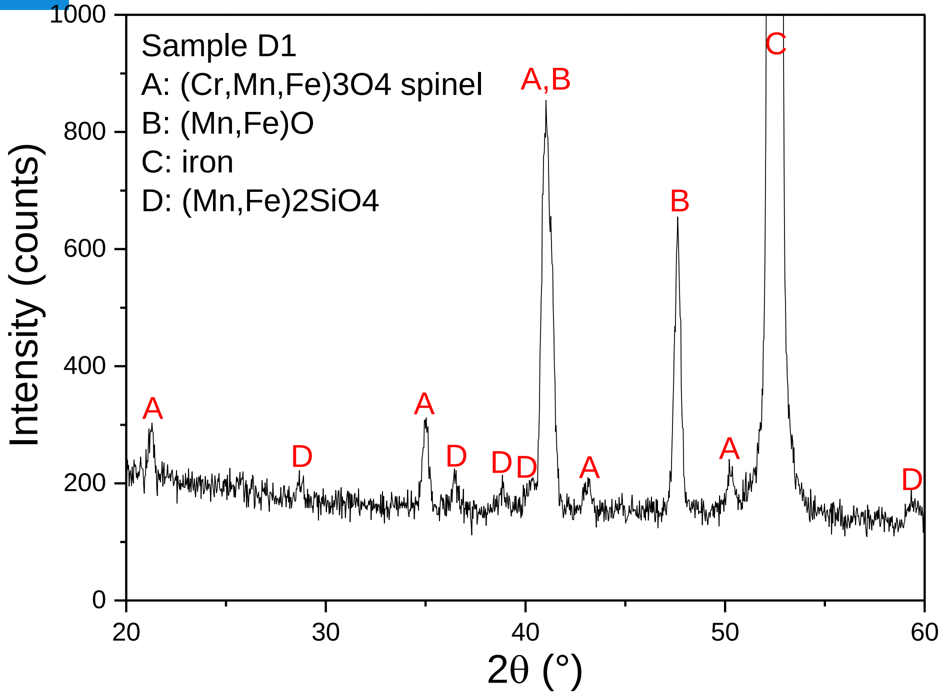
XRD analysis: Fe-Mn-Cr-(Si)

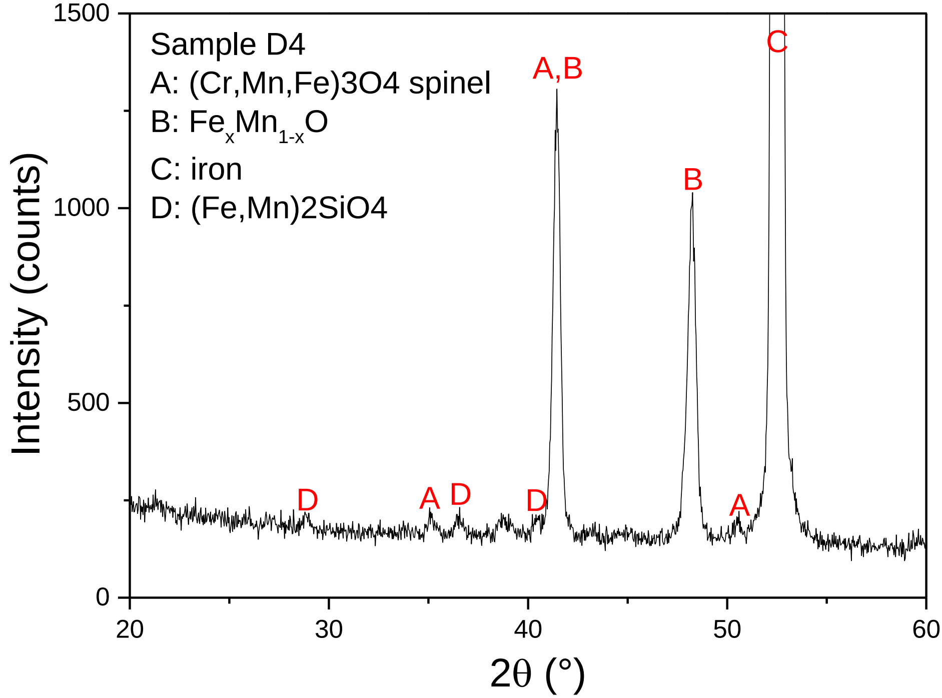
Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
D1	-45	950	8.0×10^{-22}
D4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Cr	Si	Al
Sample D	0.47	2.83	0.58	0.49	0.001



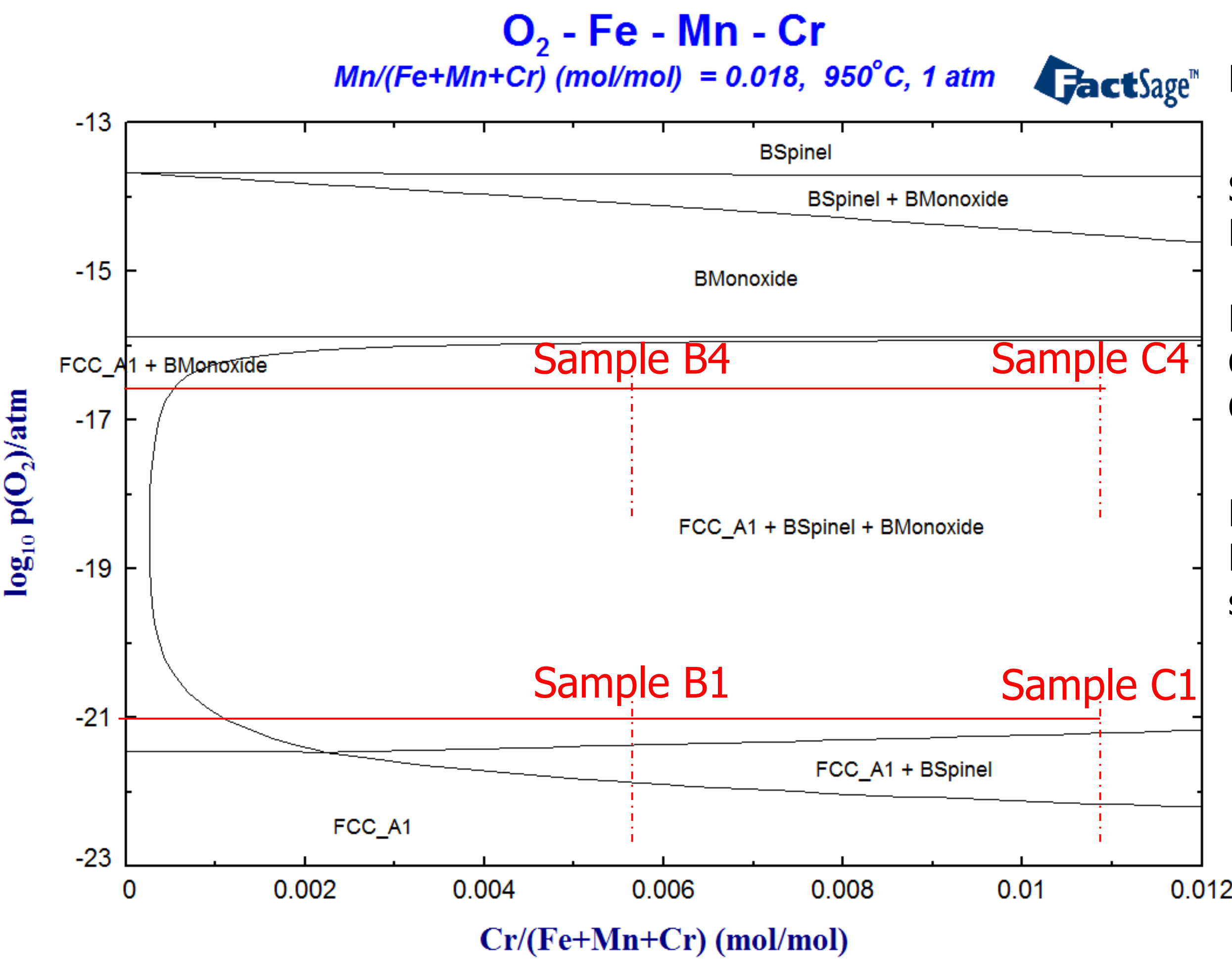


Again addition of Cr leads to the formation of $(Mn,Cr,Fe)_3O_4$ cubic spinel oxide

Higher Mn concentration does not change type of oxides formed

Prediction of oxides formation: Fe-Mn-Cr

Phase diagram of Fe-1.8Mn-Cr alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution phases selected in calculation: BSpinel, BMonoxide, FCC_A1

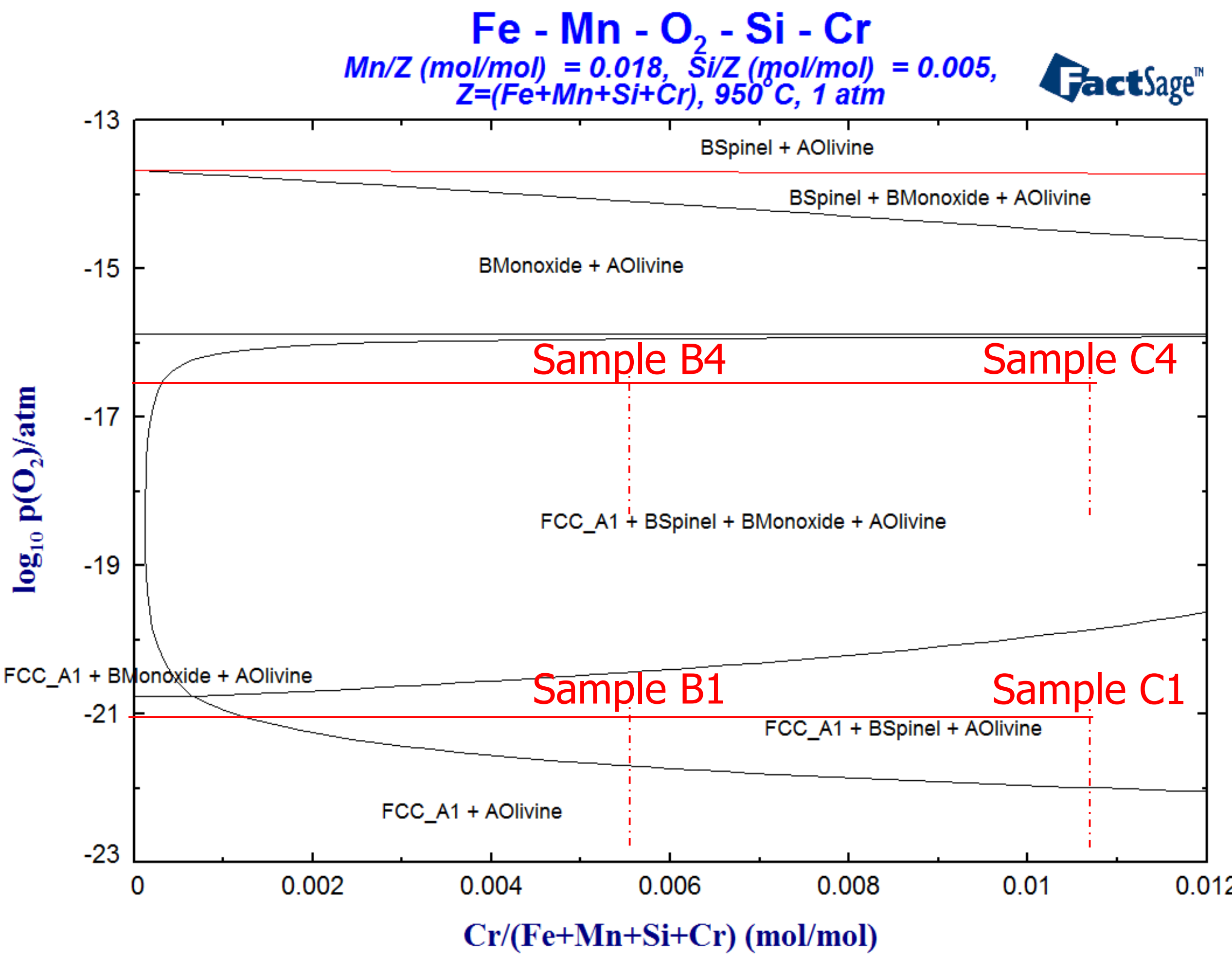
BSpinel is a solution of Fe_3O_4, $FeCr_2O_4$, $CrFe_2O_4$, $MnFe_2O_4$, $FeMn_2O_4$, $MnCr_2O_4$, $CrMn_2O_4$ wih cubic structure

BMonoxide is a solution of Fe_2O_3, FeO, MnO, Mn_2O_3, Cr_2O_3 with rock-salt structure

XRD results agree with "Factsage" calculation except sample C1, but the trend is correct

Prediction of oxides formation: Fe-Mn-Cr-Si

Phase diagram of Fe-1.8Mn-0.5Si-Cr alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution phases selected in calculation
BSpinel, BMonoxide, FCC_A1, AOlivine

Compound species selected:
Cr_2O_3, SiO_2

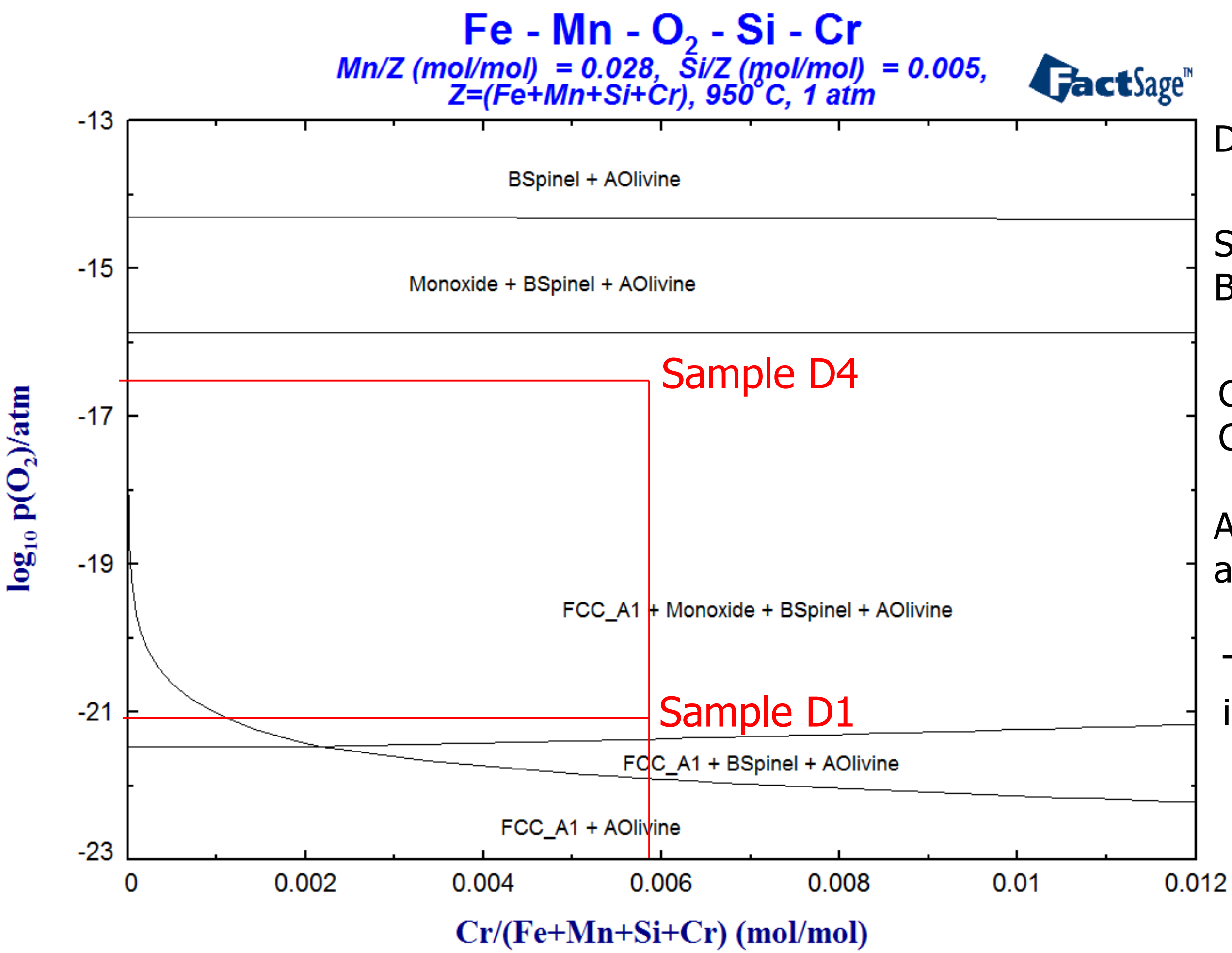
AOlivine phase is a solution of Fe_2SiO_4 and Mn_2SiO_4

The effect of Si is taken into account in calculation

XRD results agree with "Factsage" calculation except sample B1, but the trend is correct

Prediction of oxides formation: Fe-Mn-Cr-Si

Phase diagram of Fe-2.8Mn-0.5Si-Cr alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution phases selected in calculation: BSpinel, Monoxide, FCC_A1, AOlivine

Compound species selected: Cr_2O_3, SiO_2

AOlivine phase is a solution of Fe_2SiO_4 and Mn_2SiO_4

The effect of Si is taken into account in calculation

XRD results agree with "Factsage" calculation

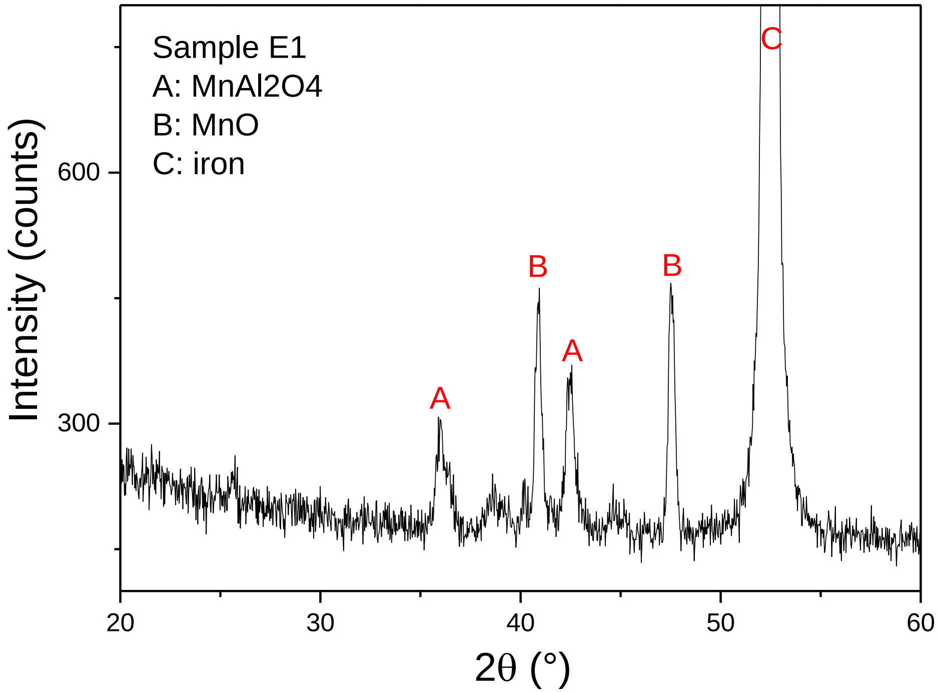
XRD analysis: Fe-Mn-Al-(Si)

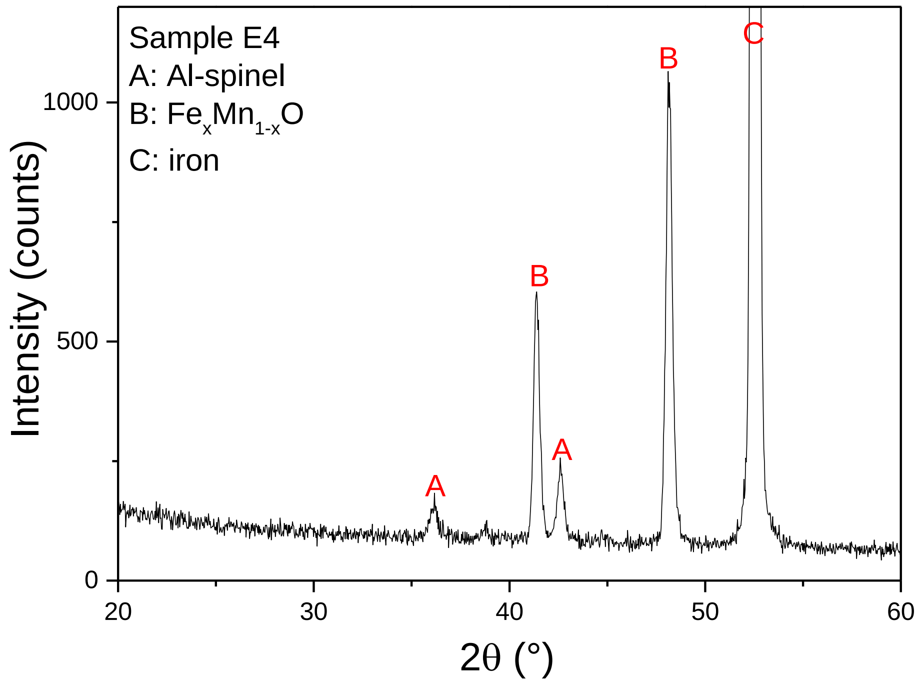
Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
E1	-45	950	8.0×10^{-22}
E4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample E	0.81	1.8	0.29	1.93

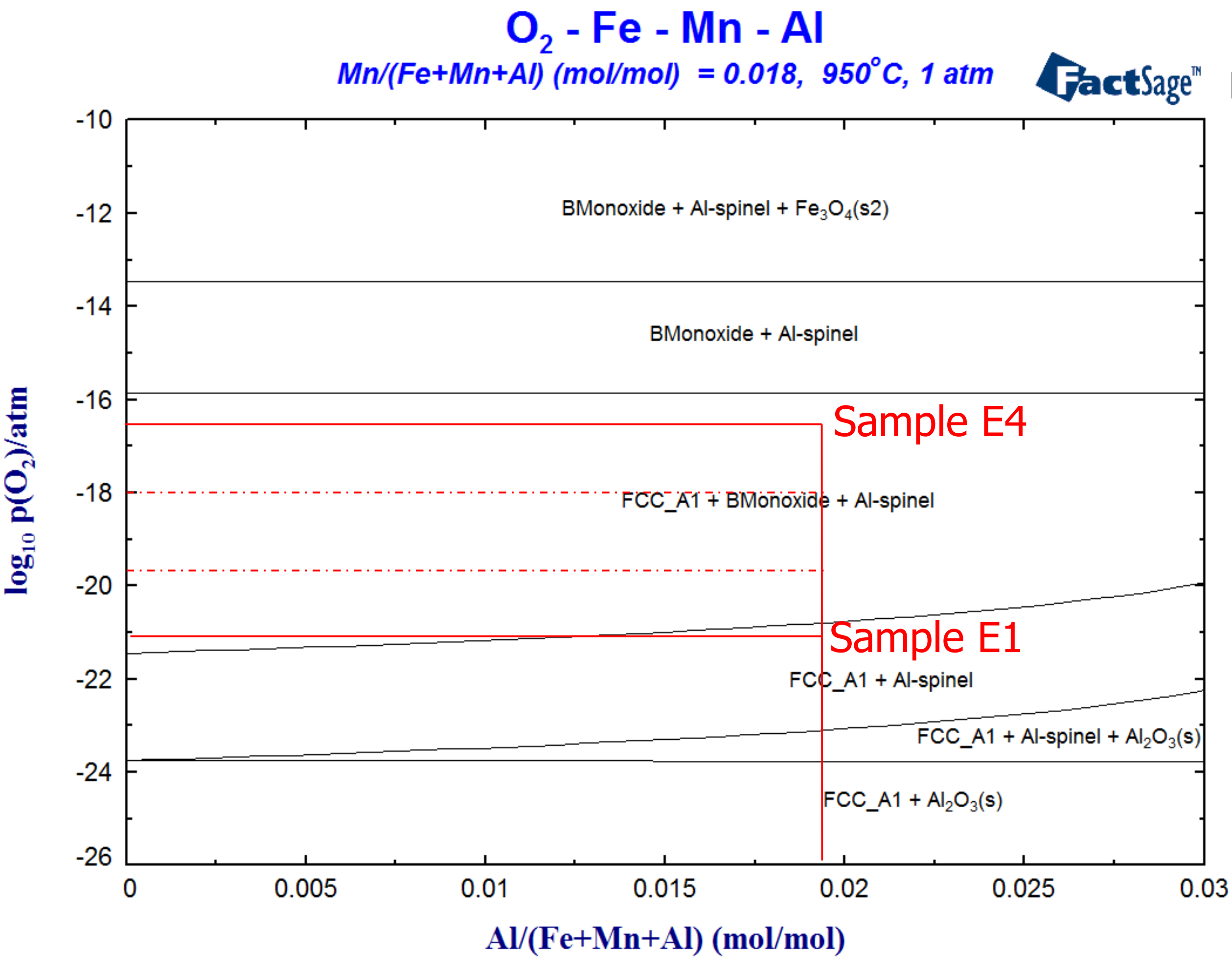




Addition of Al leads to formation of Al-spinel oxide

Prediction of oxides formation: Fe-Mn-Al

Phase diagram of Fe-1.8Mn-Al alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution phases selected in calculation:
Al-spinel, BMonoxide, FCC_A1

Compound species selected in calculation:
Fe_3O_4, Al_2O_3, $MnAl_2O_4$, $Al_2Fe_2O_6$, $FeAl_2O_4$, $Al_2Fe_2O_6$

Al-spinel is a solution of only $FeAl_2O_4$, $MnAl_2O_4$, Al_8O_{12}

For sample E1 only Al-spinel oxide is predicted

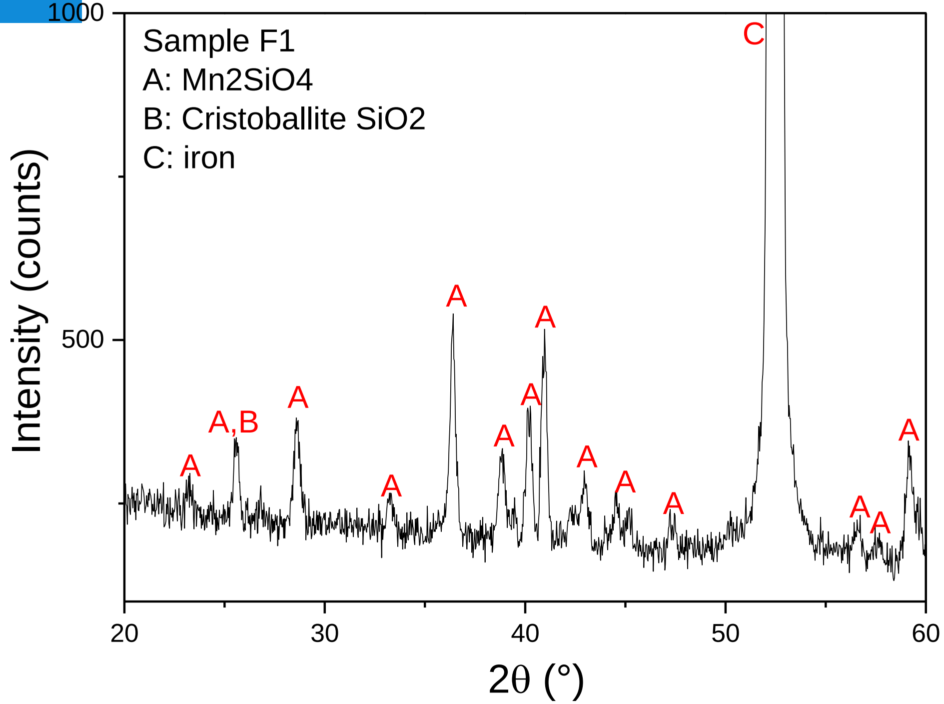
XRD analysis: Fe-Mn-Al-Si

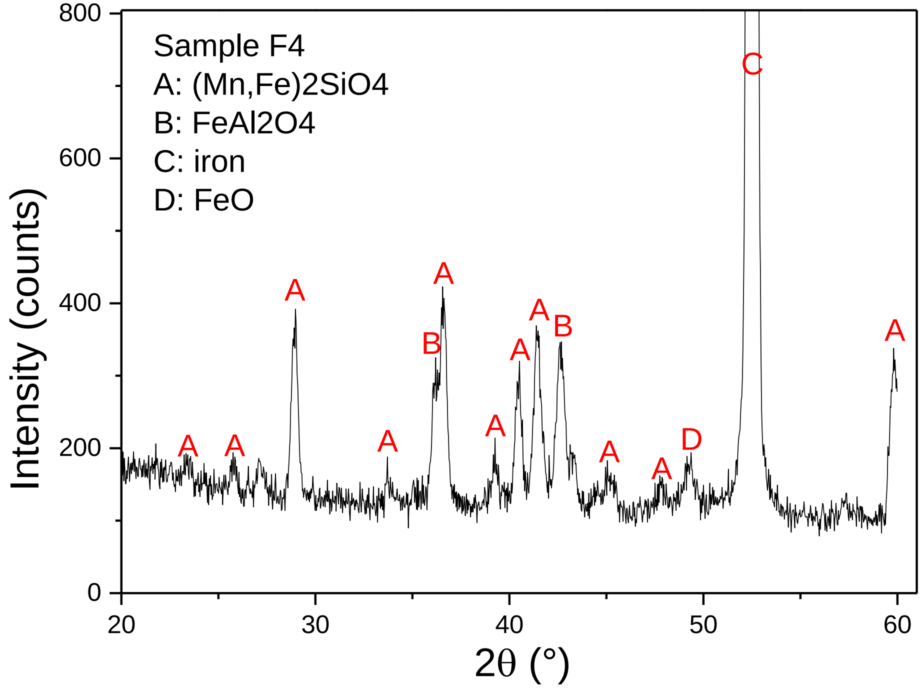
Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
F1	-45	950	8.0×10^{-22}
F4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample F	0.91	1.78	1.88	1.81



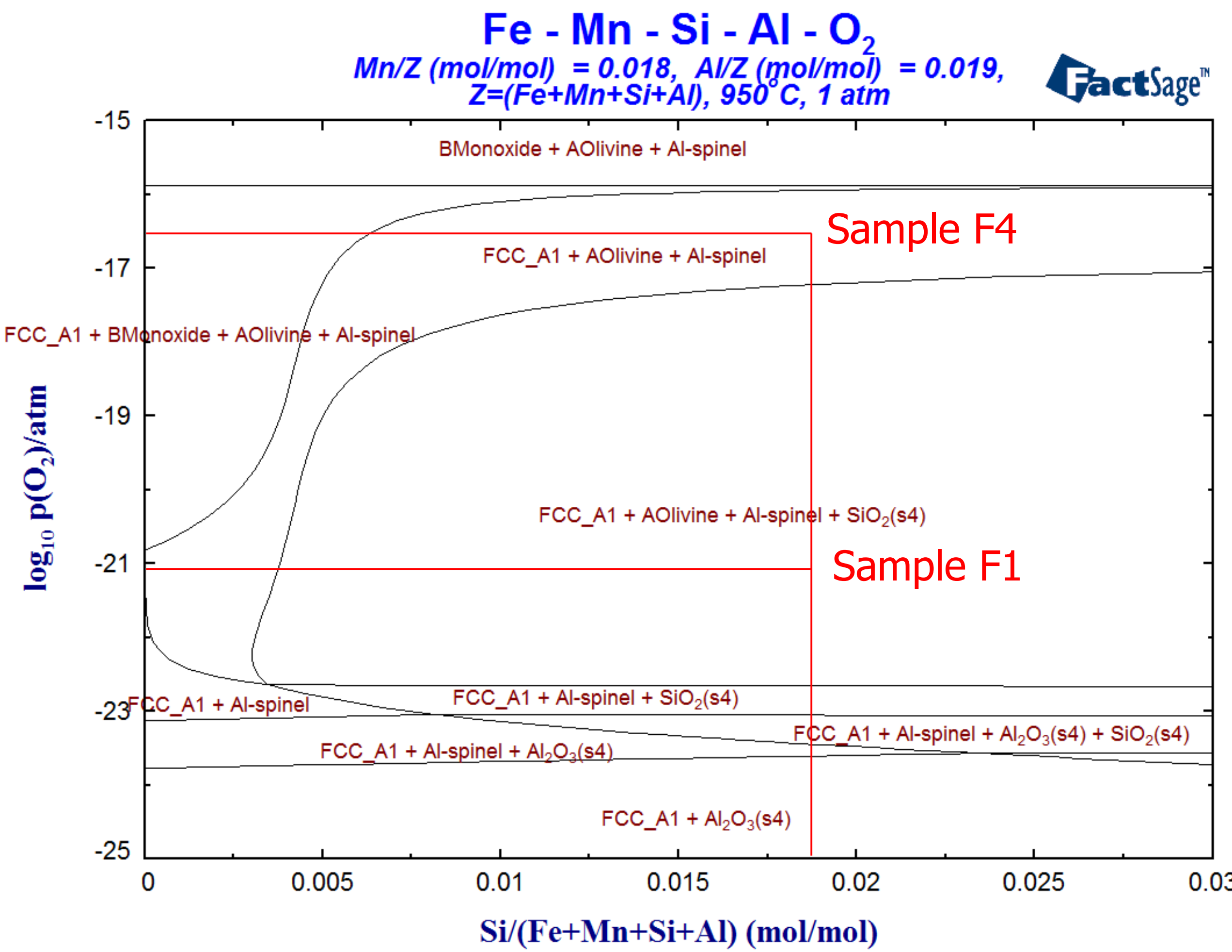


Addition of Si and Al leads to the formation of Mn_2SiO_4 and Al-spinel oxide, respectively

MnO is not formed

Prediction of oxides formation: Fe-Mn-Al-Si

Phase diagram of Fe-1.8Mn-Si-1.9Al alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution phases selected in calculation:
Al-spinel, BMonoxide, FCC_A1, AOlivine

Compound species selected:
SiO_2, Al_2O_3 from Ftoxid

AOlivine phase is a solution of Fe_2SiO_4 and Mn_2SiO_4

XRD results are generally in agreement with “Factsage” calculation

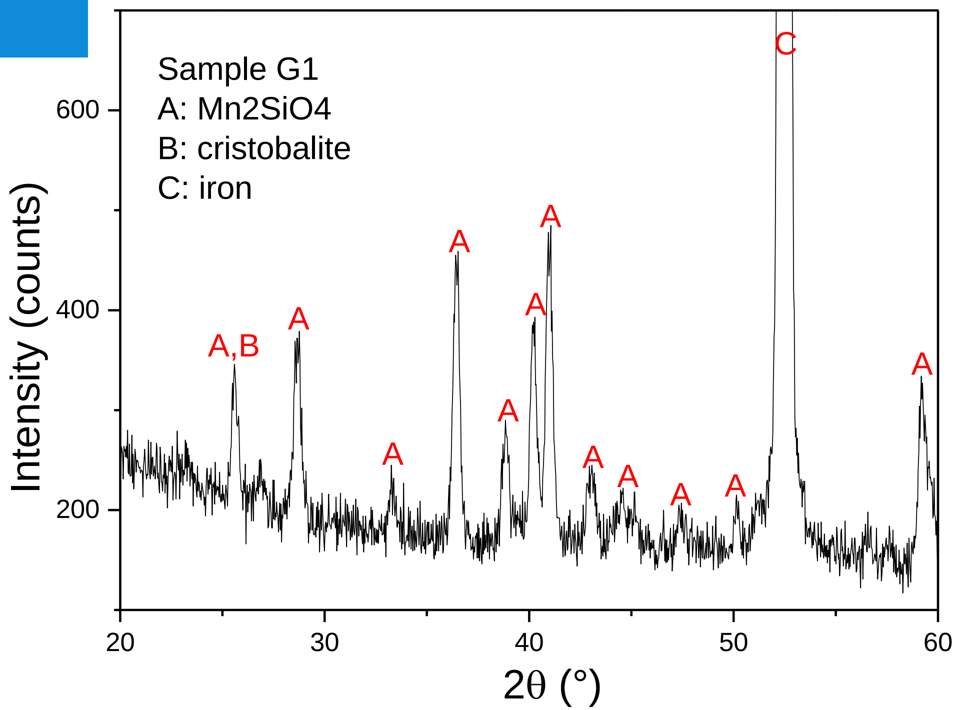
XRD analysis: Fe-Mn-Si

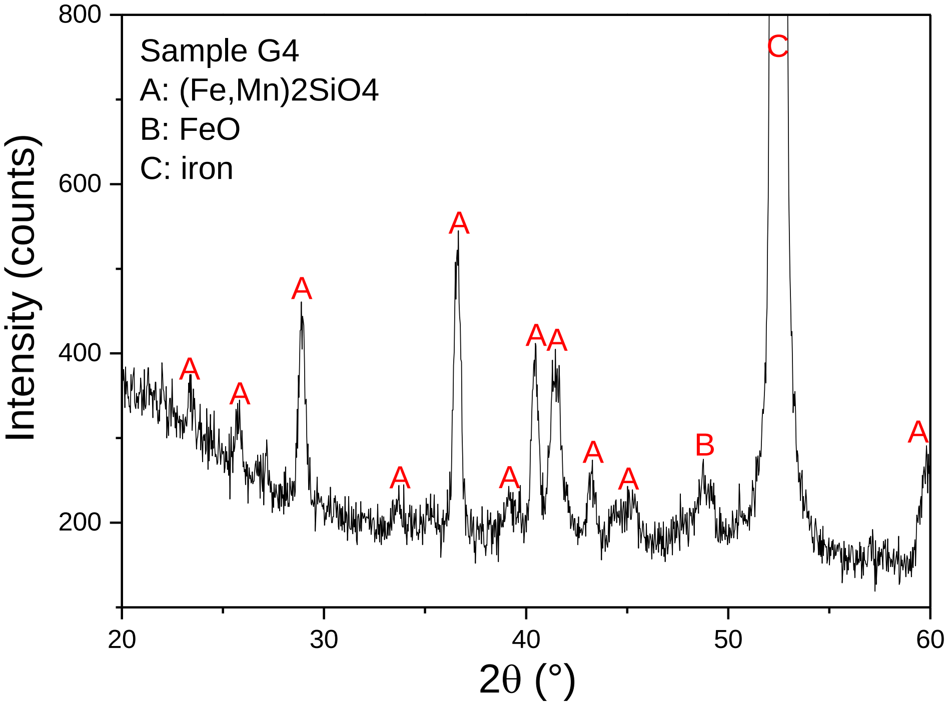
Annealing condition in N_2 with 5 vol.% H_2

Sample	Dew point (°C)	Temperature (°C)	P_{O2}
G1	-45	950	8.0×10^{-22}
G4	+10		2.3×10^{-17}

Sample composition (mol%):

	C	Mn	Si	Al
Sample G	0.48	1.91	1.84	0.03



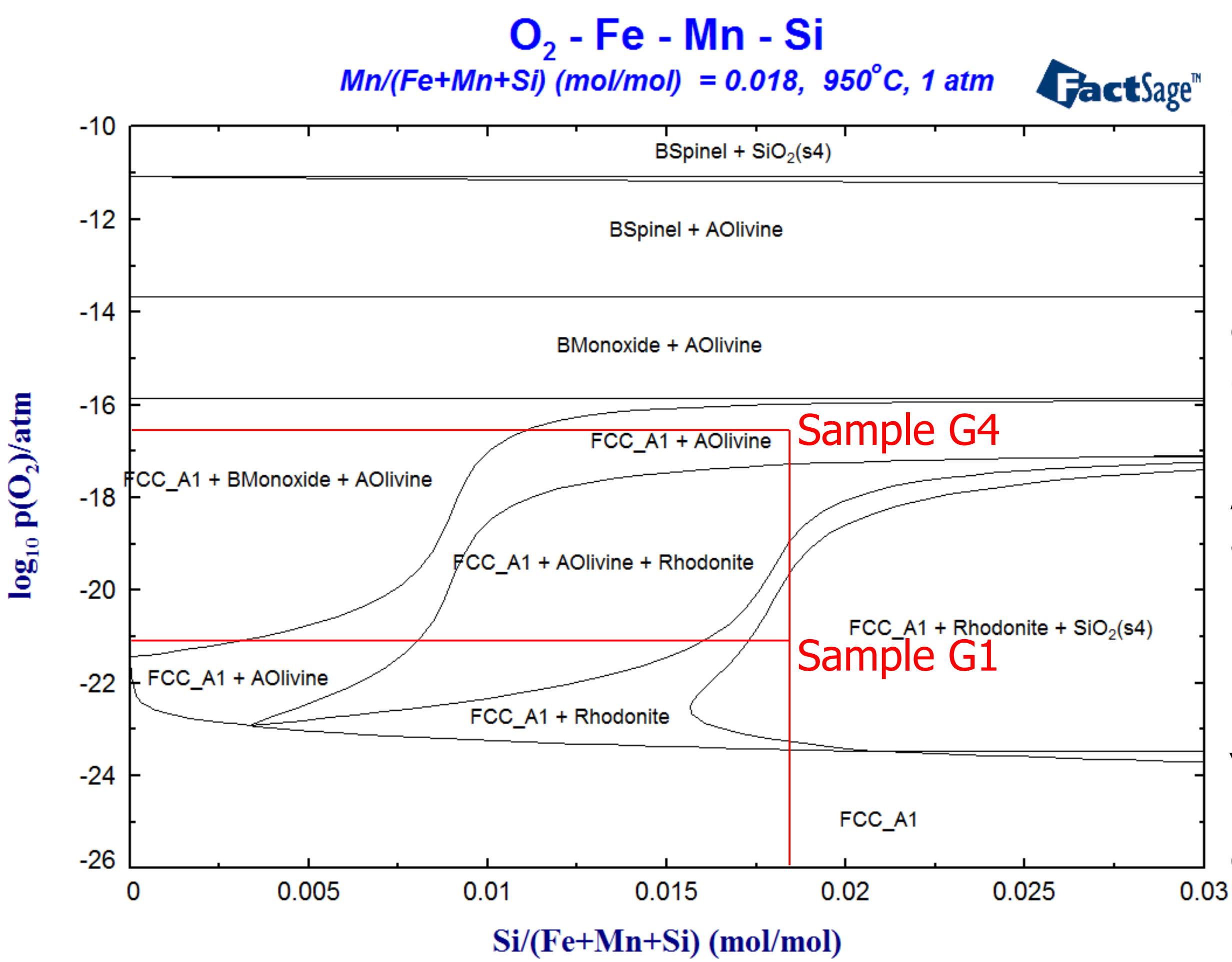


Si leads to formation of Mn_2SiO_4, and diffraction peaks of Mn_2SiO_4 shift to the right with increasing dew point

MnO is not formed

Prediction of oxides formation: Fe-Mn-Si

Phase diagram of Fe-1.8Mn-Si alloy in O_2 environment



Database: FactPS, Ftoxid, FSstel

Solution phases selected in calculation: BSpinel, BMonoxide, FCC_A1, AOlivine, Rhodonite

Pure solid phases selected in calculation: SiO_2, $MnSiO_3$, Mn_2SiO_4, $FeSiO_3$, Fe_2SiO_4, Mn_2O_3

AOlivine phase is a solution of Fe_2SiO_4 and Mn_2SiO_4

Rhodonite phase is a solution of $MnSiO_3$ and $FeSiO_3$

“Factsage” calculation also predicts Rhodonite, but it may not be formed due to kinetic reasons

Summary

- Oxidation mode changes from external oxidation to internal oxidation with increasing dew point (from -45 to +10 ° C)
- In Fe-Mn binary steel, the internal oxides formed are uniformly distributed, i.e. no grain boundary effect observed
- Oxides are formed along grain boundaries when Si is added to steel at both low and high dew points
- Oxide precipitates are not uniformly distributed when Si and Al are added to steel
- Al nitrides are formed internally when annealing in N_2 atmosphere; increasing of dew point suppresses formation of Al nitrides
- All oxides identified by XRD analysis are included in thermodynamic database
- Oxides predicted by thermodynamic calculations are generally in agreement with observed oxides

4.

Outlook

Outlook

- Completing analysis and characterization of oxidized multi-element steel alloys (oxide-phase identification, depth-profiles, external/internal oxidation, etc.
- Validating thermodynamic database for the prediction of the oxide formation (binary, ternary and mixed oxides)
- Developing theory to calculate the effect of 3rd elements on oxide precipitation in Fe alloys (solubility, diffusivity, etc)
- Expanding numerical model for selective oxidation: multi-element steel alloys

Contact

Wim G. Sloof: W.G.Sloof@tudelft.nl
Delft University of Technology
Department of Materials Science and Engineering
Mekelweg 2, 2628 CD Delft, The Netherlands