Mitglied der Helmholtz-Gemeinschaft

Development of High Chromium Ferritic Steels Strengthened by Intermetallic Phases

B. Kuhn[1], M. Talik[1,2], L. Niewolak[1], J. Zurek[1], H. Hattendorf[3], P.J. Ennis[4], W. J. Quadakkers[1], T. Beck[1*], L. Singheiser[1]

[1]Forschungszentrum Jülich GmbH
Institute of Energy and Climate Research (IEK)
Microstructure and Properties of Materials (IEK-2)

[2]Czech Technical University, Praha, Czech Republic

[3]VDM Metals GmbH, Altena, Germany

[4]visiting Professor at University of Leicester, Leicester, United Kingdom

[*]now at: Technical University of Kaiserslautern, Institute of Materials Science and Engineering

The Role of Niobium in Advanced Ferritic Stainless Steels – Building a Sustainable Future
The Royal Society of Chemistry, Burlington House, Piccadilly, London, 15th July, 2015

Outlook

Motivation

- Worldwide energy demand
- The German “Energiewende” and what it means for material selection and development
- Steam oxidation resistance and creep strength: An antagonism?

High chromium ferritic steels strengthened by intermetallic phases

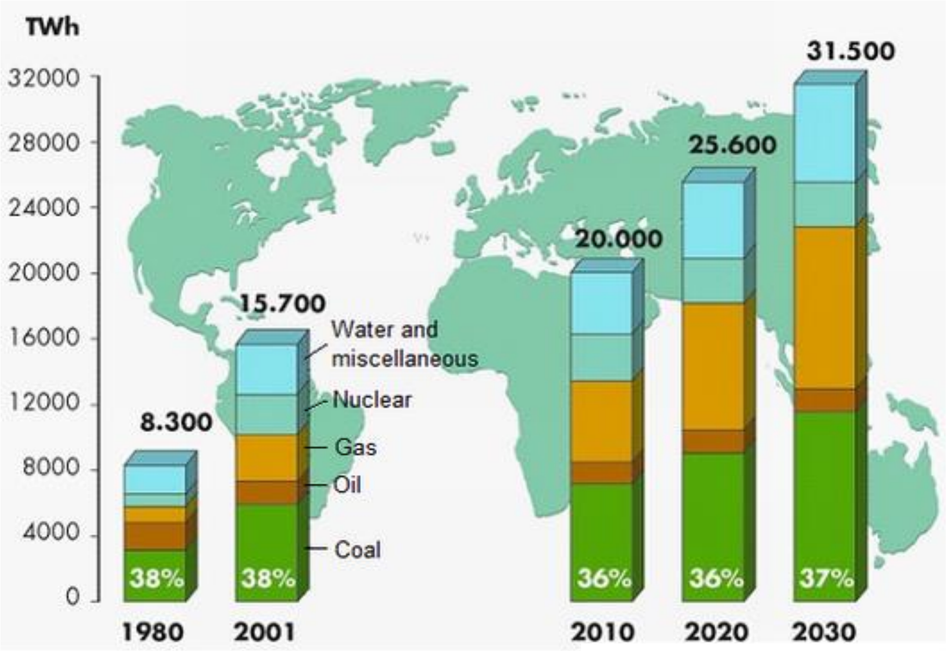
- Alloying philosophy, strengthening
- Hiperfor - High performance ferritic steels
- The role of Niobium for thermomechanical treatment, microstructure and mechanical properties

Conclusion and outlook

- Perspectives, development goals
- Partnerships

Motivation

Worldwide electric energy demand: A projection



Source: FZ Jülich, IEK-STE

- Until 2030 a rise in international energy demand by about 50 % is estimated.
- Improvement in generation efficiency is mandatory for resource protection and mitigation of emissions.
- A rise in operation parameters of thermal power plants is necessary!

Motivation

German “Energiewende” means…

… strongly increased requirement for control energy because of 40 GW of installed intermitting solar and wind power in 2013 (and growing). ➲

- load flexibility (low minimum load, strong gradients) with further
- increased efficiency

… enhanced thermal cycling capability is needed. ➲

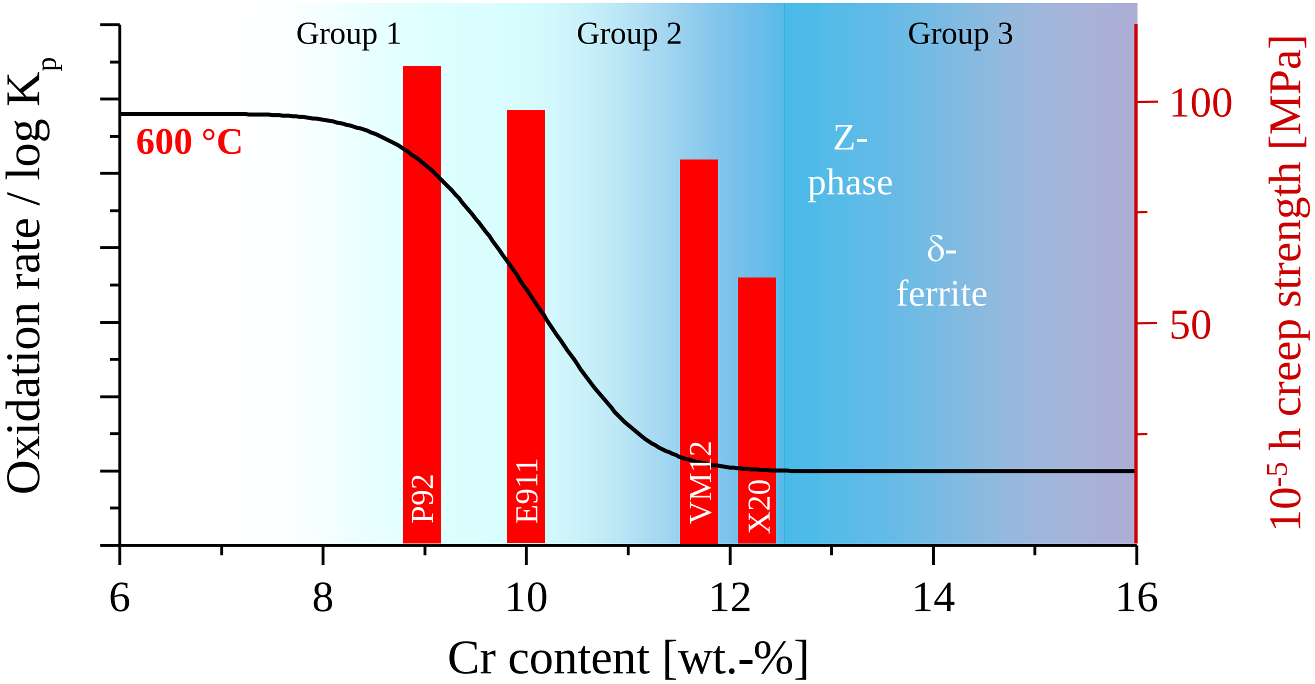
- frequent start-up and shut-down cycles
- longer and more frequent downtimes

… the processes will remain, but operation parameters will significantly tighten.

… new challenges for plant maintenance, design and material development..

Motivation

Steam oxidation resistance and creep strength: An antagonism?

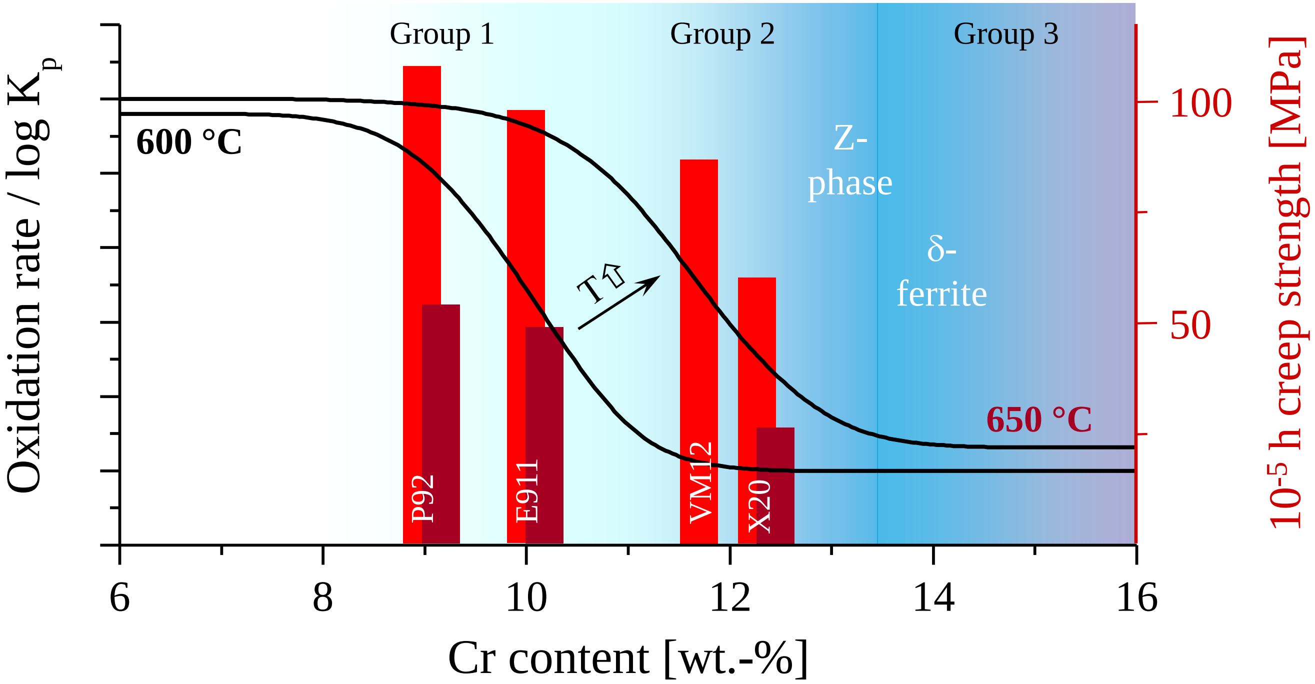


Steam oxidation resistance rises with Cr content, but

➲ *creep strength drops.*

Motivation

Steam oxidation resistance and creep strength: An antagonism?



Steam oxidation resistance rises with Cr content, but

- *creep strength drops.*
- *at higher T: Shift to higher Cr content necessary.*

- *An antagonism in case of creep strength enhanced ferritic-**martensitic** (CSEF) steels!*

Motivation

Materials for “cyclic” application – Ranking by properties

	ferritic-martensitic	austenitic	Nickel-base
TMF	?	- (TEC↑, λ↓)	- (TEC↑, λ↓)
HT-oxidation / -corrosion	- (Cr < 12)	+ (Cr > 15)	+ (Cr > 20)
Downtime-corrosion	- (Cr < 12)	+ (Cr > 15)	+ (Cr > 20)
Creep	O	+	+
“Technology”	+	O	O(?)
Cost	+	- (Ni > 10)	-- (Ni > 50)

Motivation

Materials for “cyclic” application – Ranking by properties

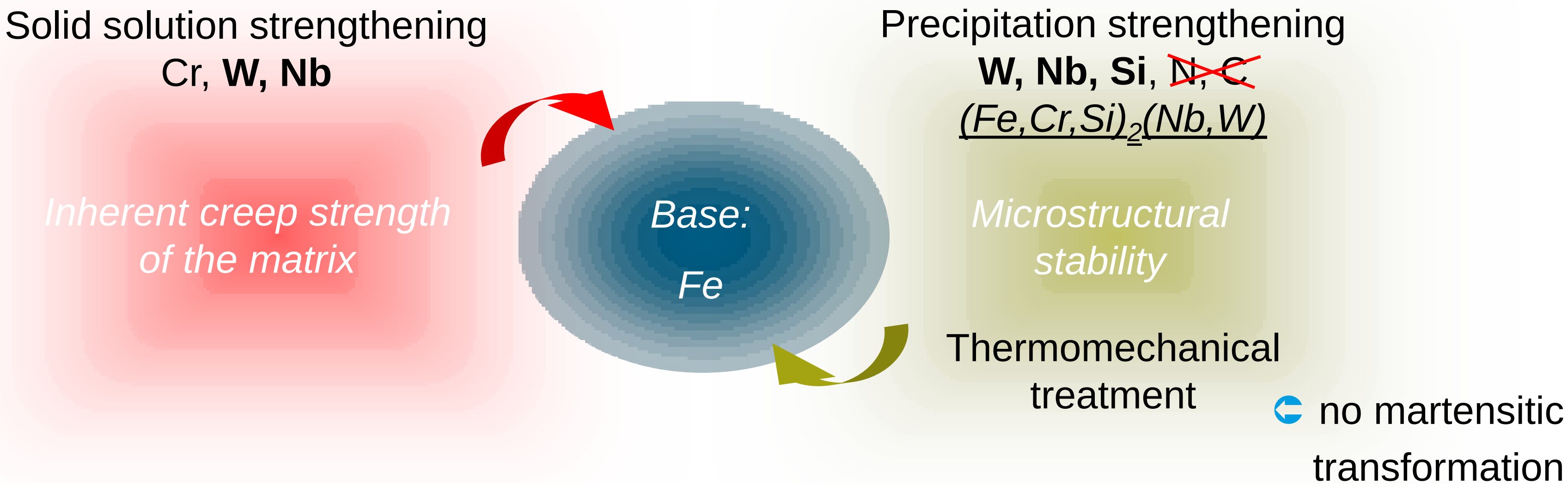
	ferritic-martensitic	austenitic	Nickel-base	ferritic
TMF	?	- (TEC↑, λ↓)	- (TEC↑, λ↓)	?
HT-oxidation / -corrosion	- (Cr < 12)	+ (Cr > 15)	+ (Cr > 20)	+ (Cr > 15)
Downtime-corrosion	- (Cr < 12)	+ (Cr > 15)	+ (Cr > 20)	+ (Cr > 15)
Creep	O	+	+	?
“Technology”	+	O	O(?)	?
Cost	+	- (Ni > 10)	-- (Ni > 50)	+

… an alternative ?

… for sure for science !

High chromium ferritic steels

Alloying philosophy



Solid solution strengthening
Cr, **W, Nb**

Inherent creep strength of the matrix

Base:

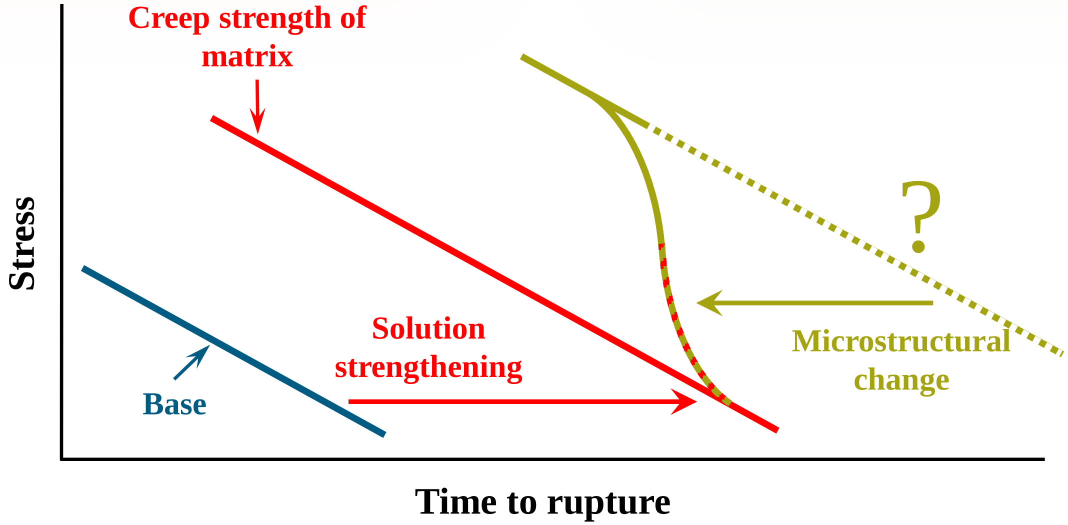
Fe

Precipitation strengthening
W, Nb, Si, ~~N, C~~
$(Fe,Cr,Si)_2(Nb,W)$

Microstructural stability

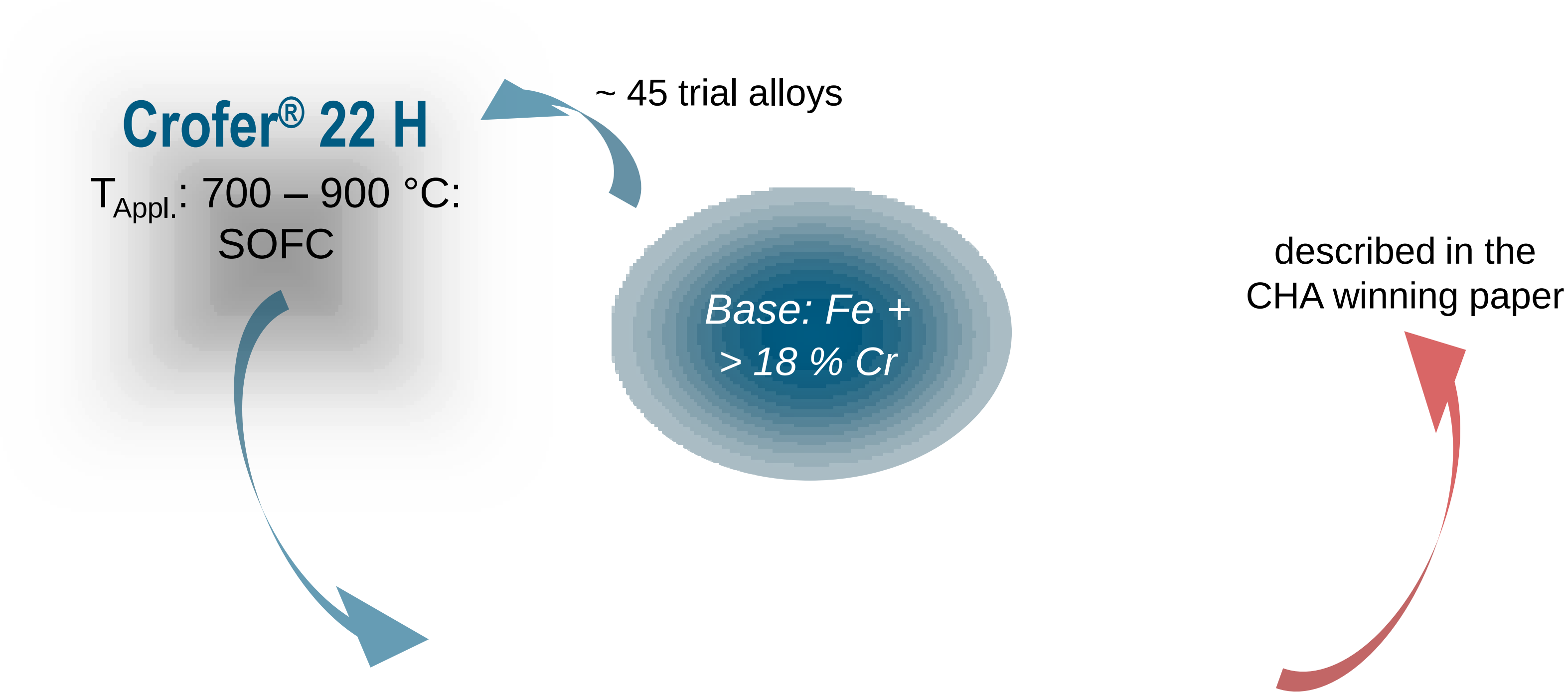
Thermomechanical treatment

⇐ no martensitic transformation



High chromium ferritic steels (CHA)

Alloying philosophy – Typical chemical compositions



Crofer® 22 H

$T_{\text{Appl.}}$: 700 – 900 °C:
SOFC

~ 45 trial alloys

Base: Fe +
> 18 % Cr

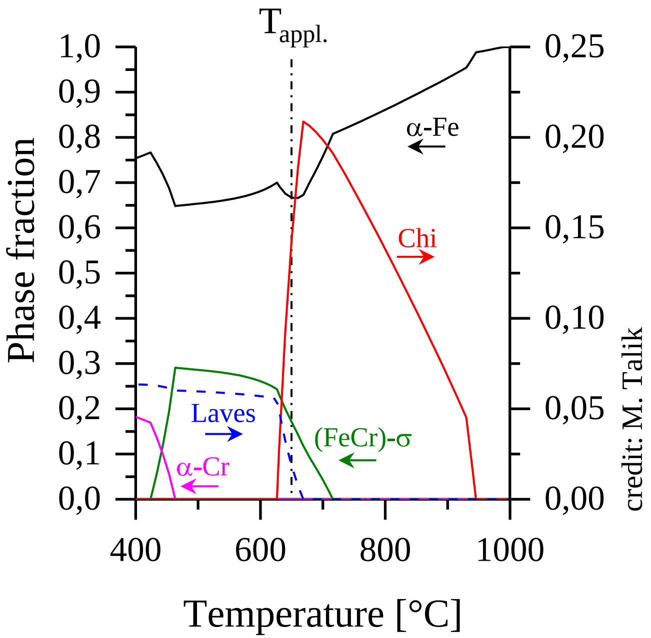
described in the
CHA winning paper

Group	Batch ID	C	N	Cr	W	Nb	Si	Mn	La	Ti
Crofer® 22 H	2.02W0.48Nb	0.002	0.007	22.32	2.02	0.48	0.24	0.43	0.06	0.06
"Zero Ti"	2.5W0.57Nb0Ti	0.004	0.008	22.95	2.5	0.57	0.20	0.46	0.03	0.004
"Zero Ti"	2.1W0.49Nb0Ti	0.002	0.004	23.08	2.1	0.49	0.24	0.45	0.12	0.003
"Low Cr"	18 Cr	0.002	0.005	18.50	1.98	0.51	0.24	0.44	0.12	0.057

High chromium ferritic steels

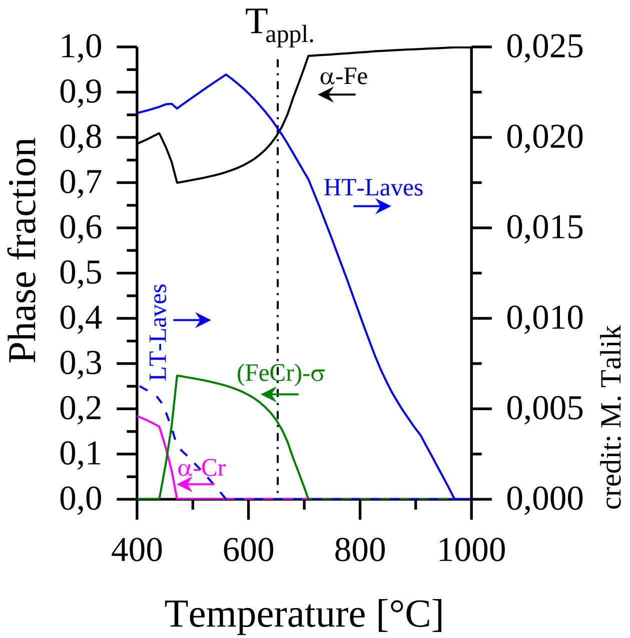
The specific role of Nb: Alloying, processing and application

7 W ➲ *$(Fe,Cr)_2W$ / Chi*



credit: M. Talik

2.5W0.57Nb0Ti ➲ *$(Fe,Cr,Si)_2(Nb,W)$ only*



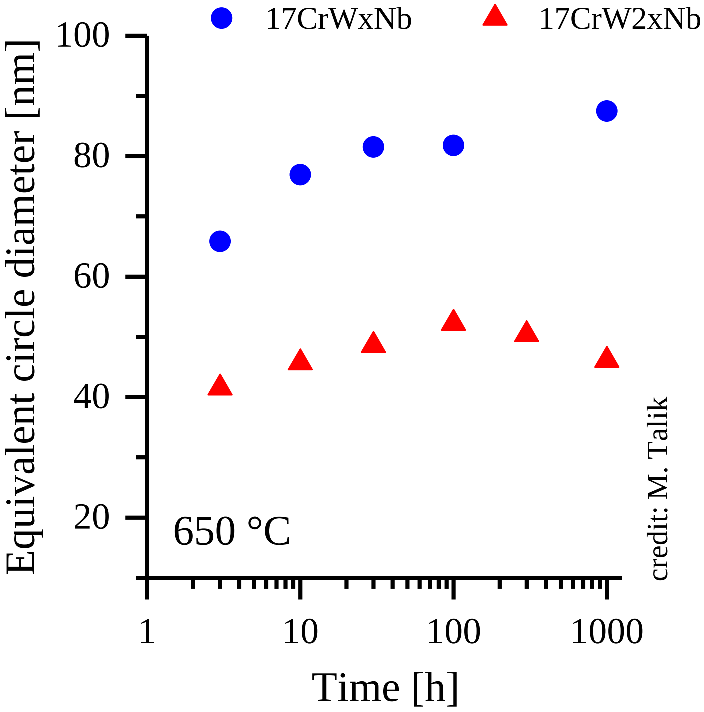
credit: M. Talik

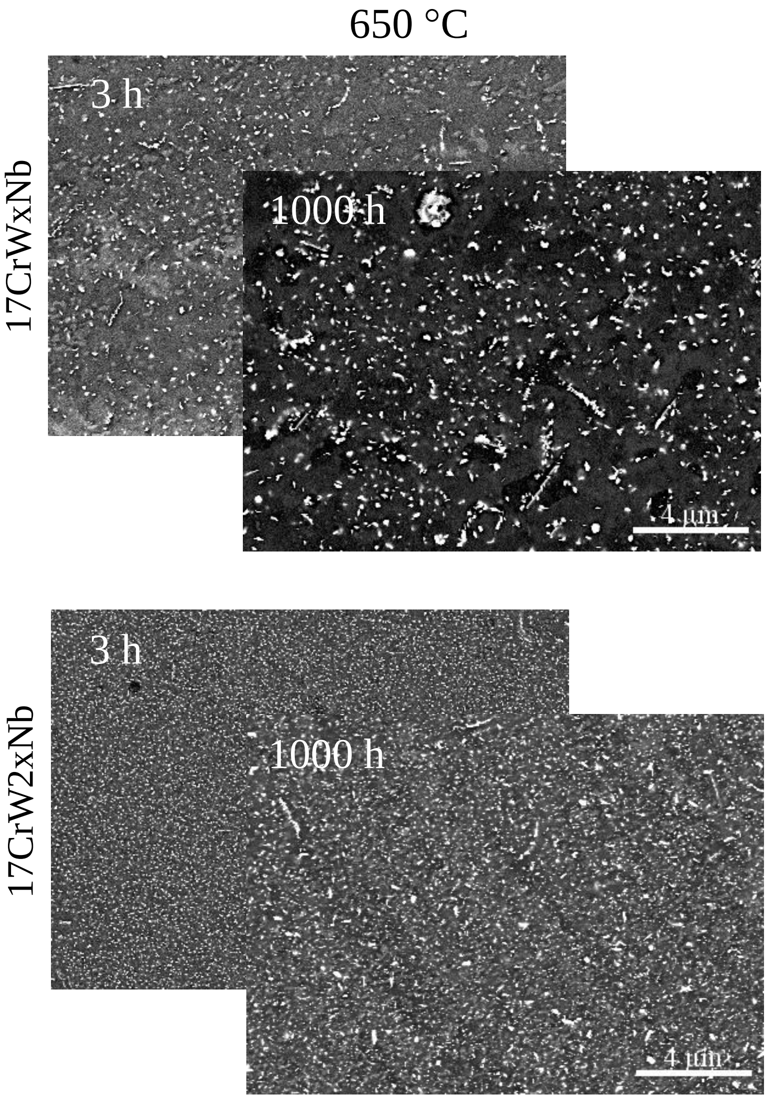
Niobium

- *“replaces” W, is incorporated into the Laves phase and refines it.*
- *boosts precipitation kinetics of the Laves phase*
  (Si seems to be incorporated into the $(Fe,Cr,Si)_2(Nb,W)$ phase only).
- *“forces” an HT-Laves phase with higher T_{Solvus} ➲ better long-term stability.*
- *no Chi-phase formation*

High chromium ferritic steels

The specific role of Nb: Alloying, processing and application



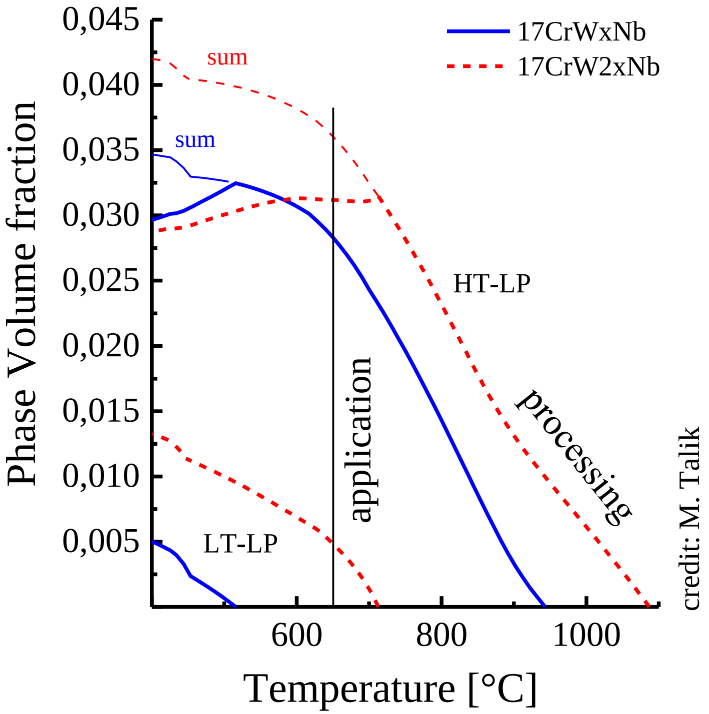


Increasing the Nb content

- *rises the Laves phase fractions,*
- *refines the particles and*
- *stabilizes them.*

High chromium ferritic steels

The specific role of Nb: Alloying, processing and application

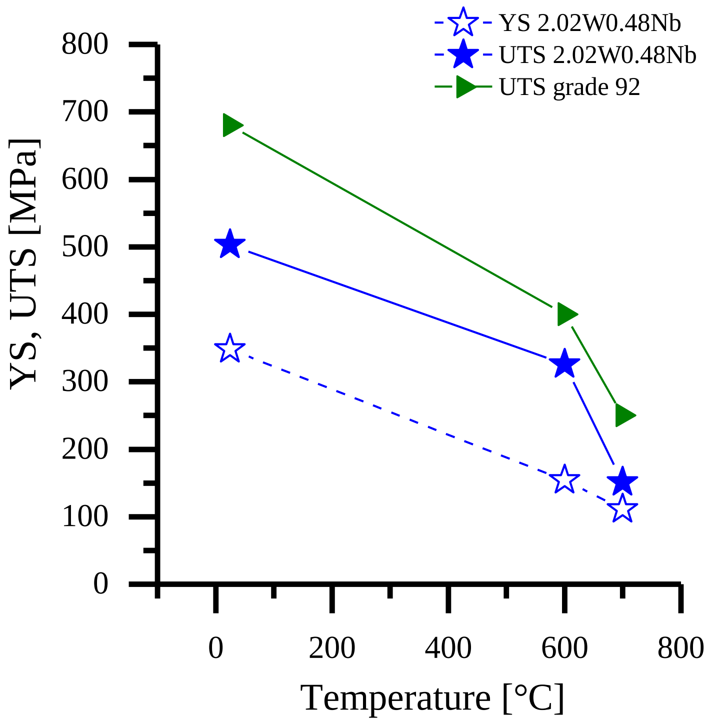


Increasing the Nb content

- *rises the Laves phase fractions,*
- *increases T_{Solvus} and for this reason*
- *has direct impact on processing, too.*

High chromium ferritic steels (CHA)

Properties: Tensile strength



No martensitic transformation!

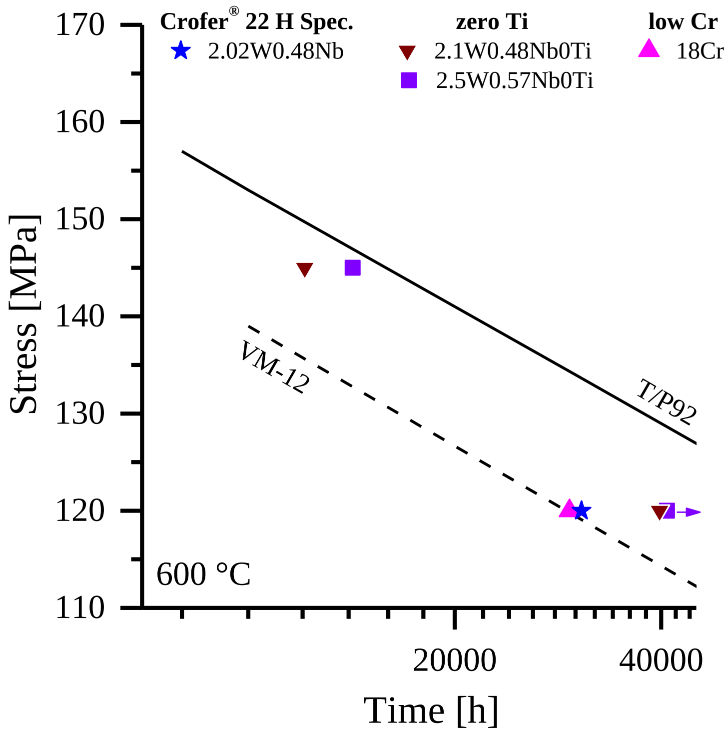
➲ *moderate tensile properties in comparison to 9 Cr CSEF grade 92*

➲ but: Can be altered by processing!

will be demonstrated in the following…

High chromium ferritic steels (CHA)

Properties: Creep resistance (600 °C)



at high stress (145 MPa):

- *Competitive to 9 Cr CSEF steel T/P92.*

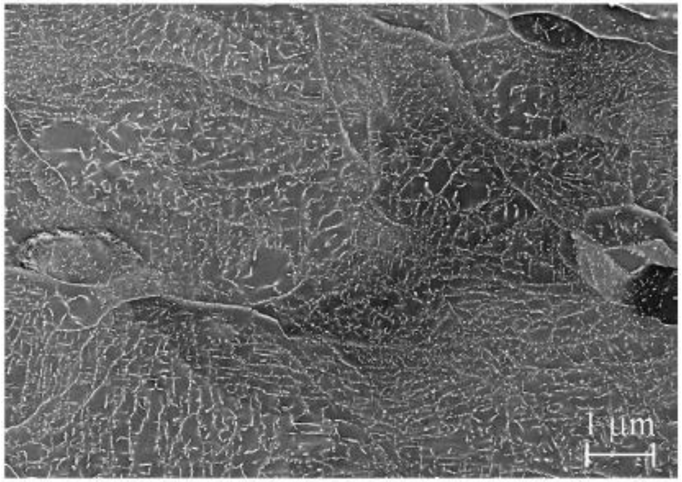
at intermediate stress (120 MPa):

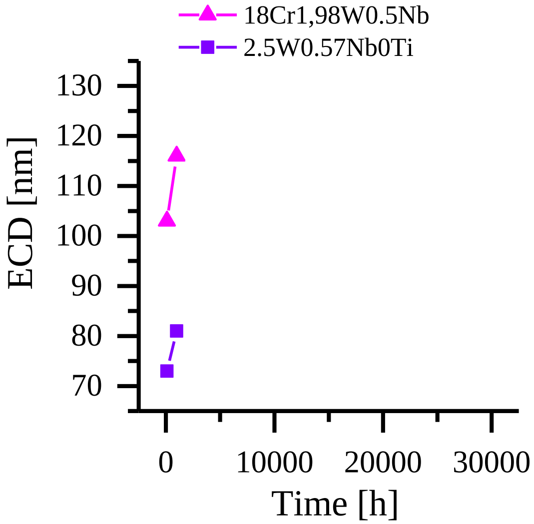
- *Competitive to 12 Cr CSEF steel VM-12.*
- *Reduction to 18 Cr does not have negative implications on creep strength.*
- *Alloys with enhanced W and Nb-contents perform better, because of higher volume fractions of strengthening Laves phase precipitates.*

High chromium ferritic steels (CHA)

Microstructure: Long-term precipitate stability (600 °C)

SEM: 2.5W0.57Nb0Ti
600 °C, 100 h





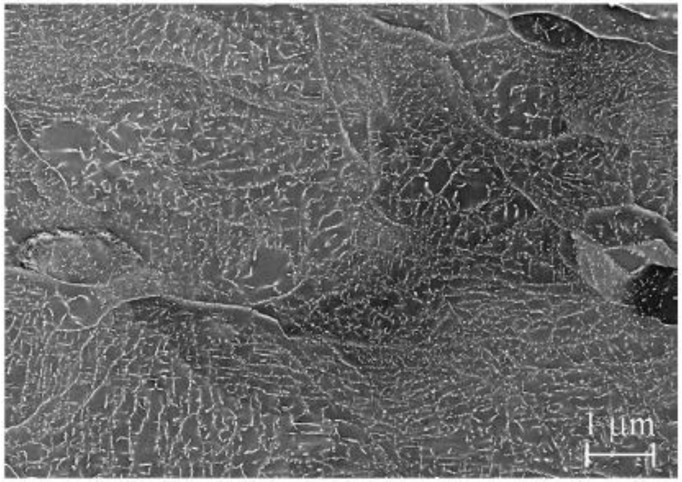
Laves phase particles

➲ *grow rapidly in the short-term (up to ~1000 h).*

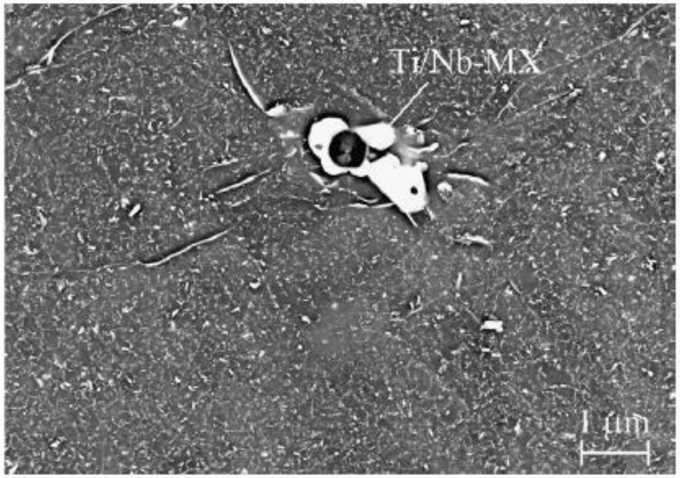
High chromium ferritic steels (CHA)

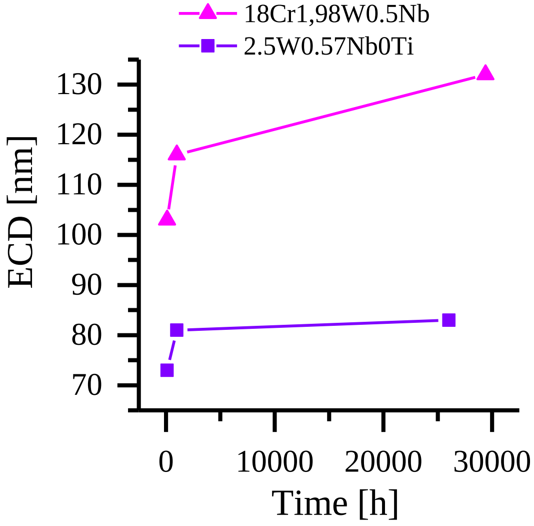
Microstructure: Long-term precipitate stability (600 °C)

SEM: 2.5W0.57Nb0Ti
600 °C, 100 h



SEM: 2.5W0.57Nb0Ti
600 °C, 26032 h, head section





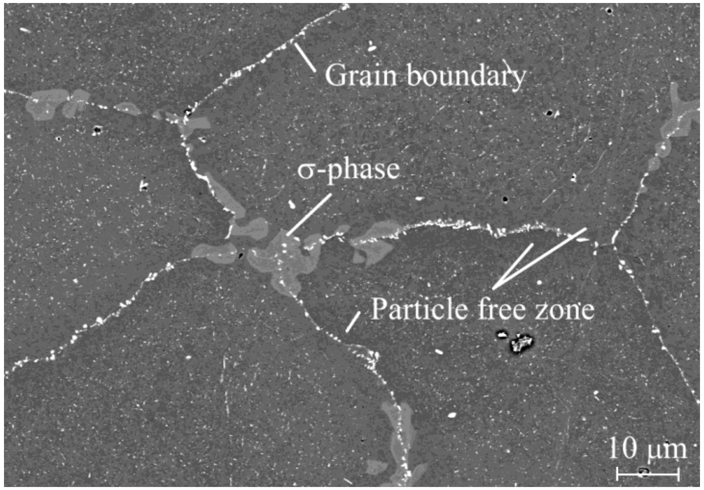
Laves phase particles

- *grow rapidly in the short-term (up to ~1000 h).*
- *coarsen slowly in the mid- and long-term.*
- *are stabilized by enhanced W and Nb-contents.*

High chromium ferritic steels (CHA)

Microstructure: Secondary phase formation – (Fe,Cr) σ-phase

SEM: 2.02W0.48Nb
600 °C, 28224 h, head section



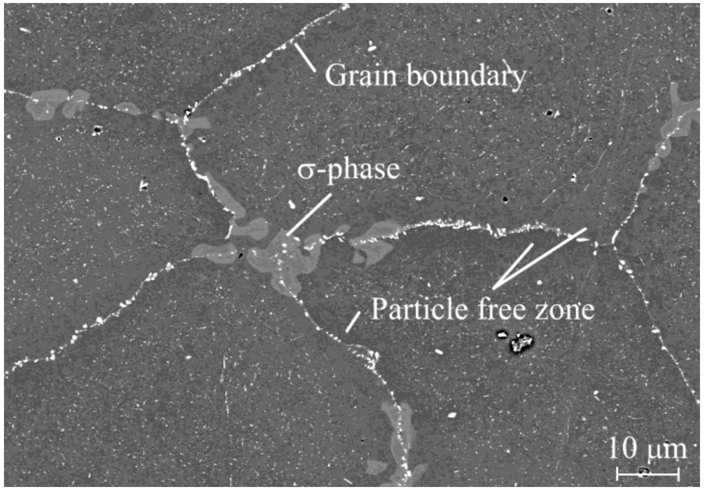
(Fe,Cr)-σ-phase at grain boundaries

- *might deteriorate ductility in the long-term.*
- *forms in all the* 22 Cr alloys.

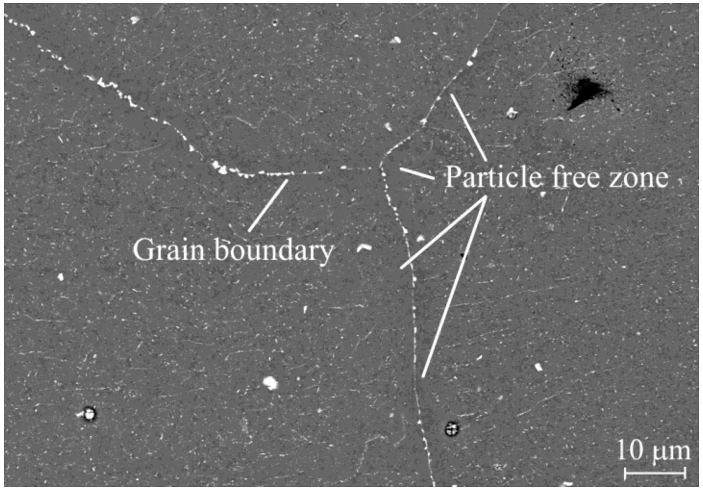
High chromium ferritic steels (CHA)

Microstructure: Secondary phase formation – (Fe,Cr) σ-phase

SEM: 2.02W0.48Nb
600 °C, 28224 h, head section



SEM: 18Cr
600 °C, 29395 h, head section



(Fe,Cr)-σ-phase at grain boundaries

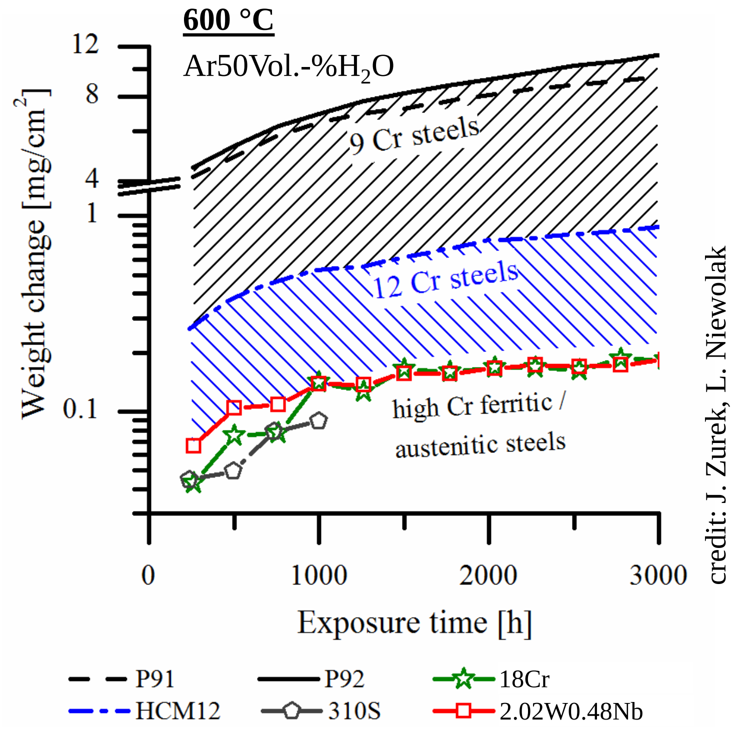
- *might deteriorate ductility in the long-term.*
- *forms in all the* 22 Cr alloys.

Reduction to 18 Cr does

- *mitigate formation of the (Fe,Cr)-σ-phase.*
- *not have negative impact on creep strength.*
- *What about steam oxidation resistance?*

High chromium ferritic steels (CHA)

Properties: Steam oxidation (600 °C)



credit: J. Zurek, L. Niewolak

- *mass gain rates appr. 1-2 orders of magnitude lower than 9-12 Cr CSEF grades*
- *comparable to high Cr austenitic grades*
- *cut in Cr content to 18 wt.-% does not negatively affect steam oxidation resistance*

High chromium ferritic steels

Preliminary conclusion

Ferritic steels strengthened by intermetallic phase particles offer

➲ *promising creep strength and*

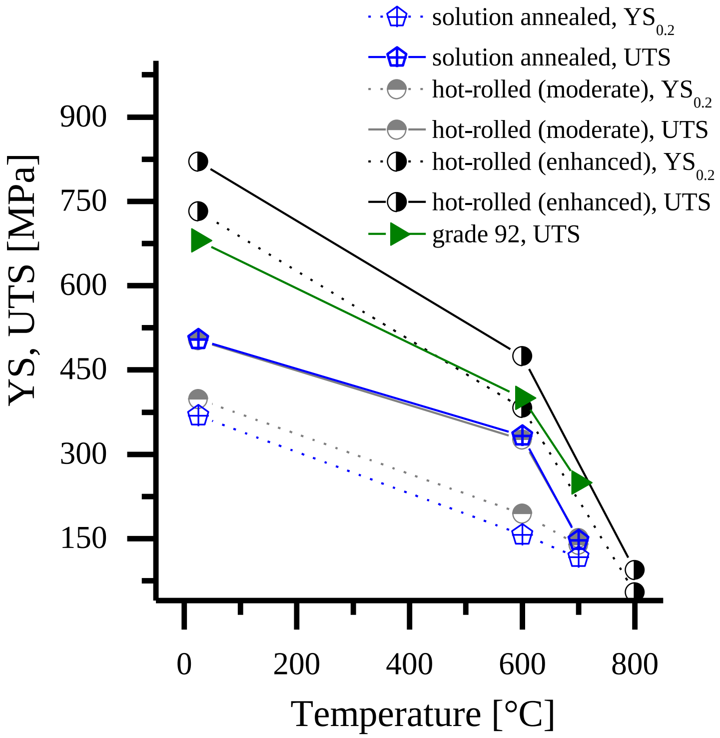
➲ *favorable steam oxidation resistance.*

Questions beyond:

- Further potential in compositional changes?
- Role of thermomechanical processing?
- Properties relevant to application (tensile, impact and creep strength, resistance to TMF, weldability)?

High chromium ferritic steels

Processing: Tensile strength

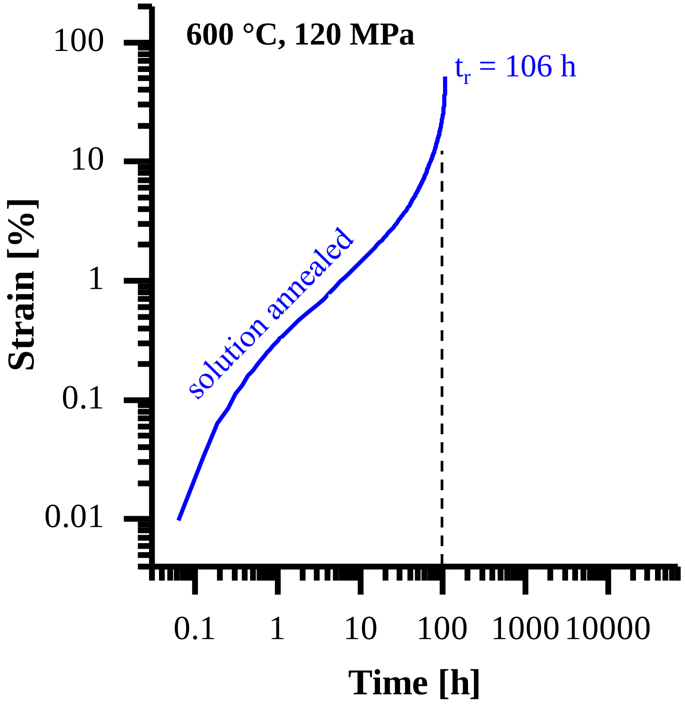


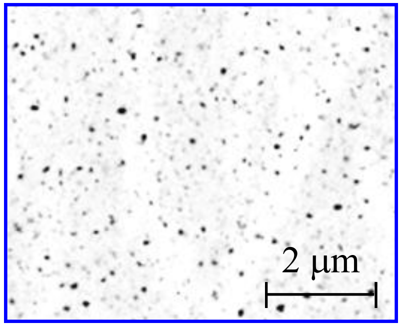
N	0.009
C	0.007
Mn	0.5
Si	0.25
Nb	0.5
W	2
Cr	22
Fe	R

- *hot-rolling parameters (TMT) govern tensile properties*
- *YS can be increased above UTS of solution annealed material in the whole temperature range* (elongation: 20 / 30 / > 50 % @ ambient / 600 °C / 700 °C +)
- *Tensile properties comparable to ferritic-martensitic grades are achievable!*

High chromium ferritic steels

Processing: Particle size and creep (600 °C)





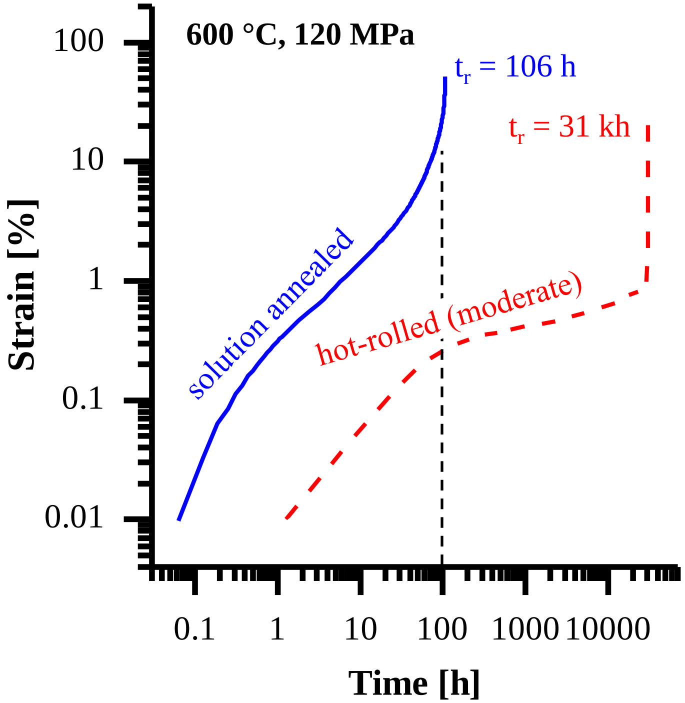
600 °C, 120 MPa,
106 h

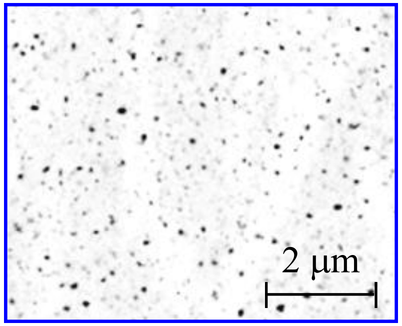
Initial state:
solution annealed
$HV_{0.1}$ ~ 200

N	0.009
C	0.007
Mn	0.5
Si	0.25
Nb	0.5
W	2
Cr	22
Fe	R

High chromium ferritic steels

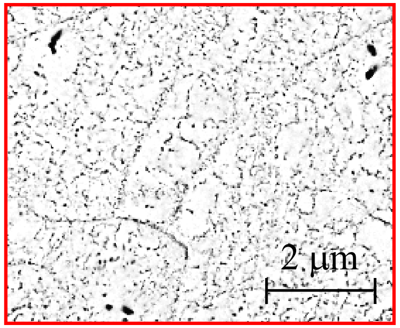
Processing: Particle size and creep (600 °C)





600 ˚C, 120 MPa,
106 h

Initial state:
solution annealed
$HV_{0.1}$ ~ 200



600 ˚C, 120 MPa,
100 h

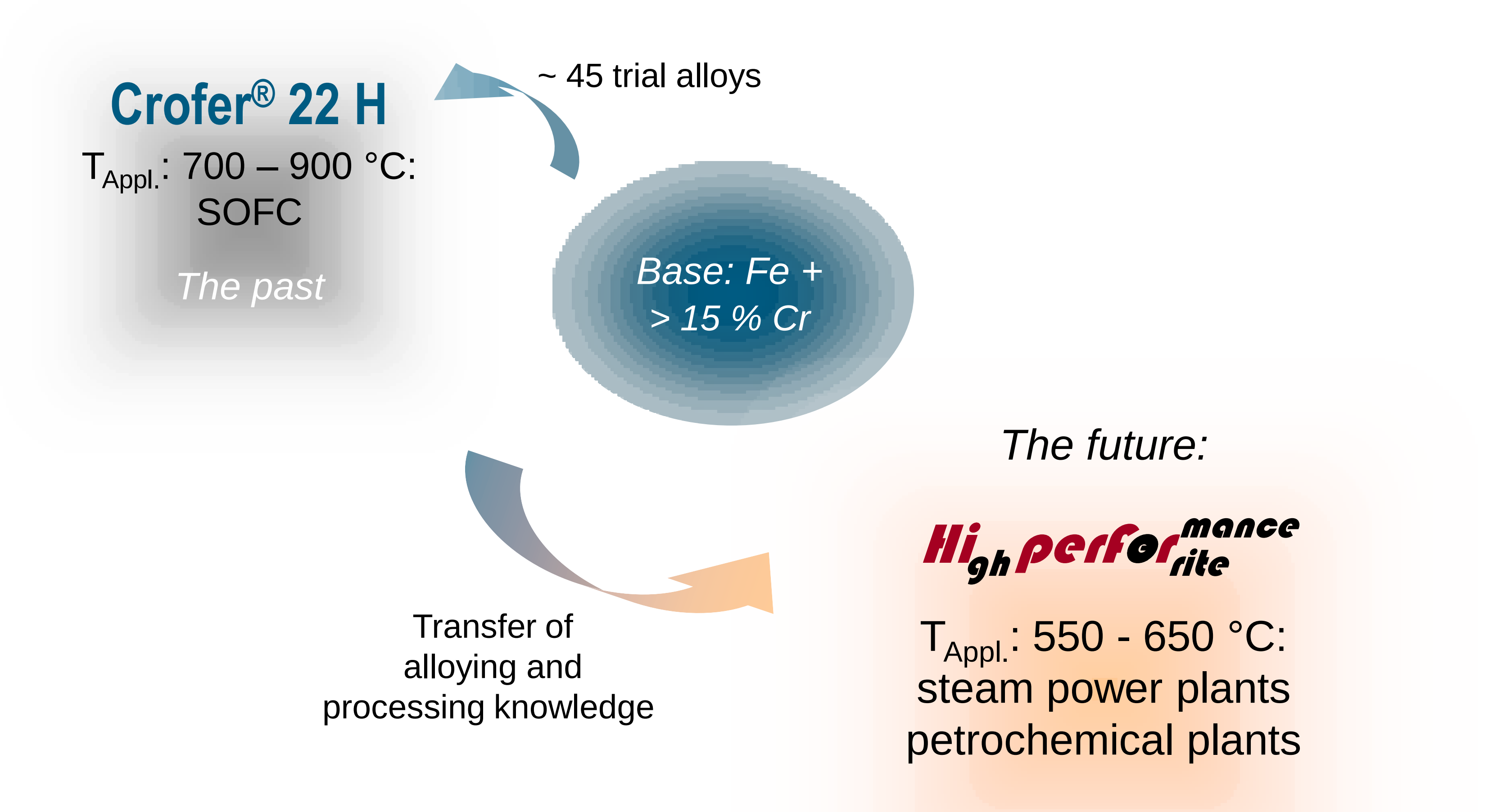
Initial state:
rolled (moderate)
$HV_{0.1}$ ~ 225

N	0.009
C	0.007
Mn	0.5
Si	0.25
Nb	0.5
W	2
Cr	22
Fe	R

- *TMT-state has an enormous effect on particle microstructure and thus on strength*
- *Freedom to adjust property profiles, but*
- *increased complexity!*

High performance ferrite

Alloying philosophy



Crofer® 22 H

$T_{Appl.}$: 700 – 900 °C:
SOFC

The past

~ 45 trial alloys

Base: Fe +
> 15 % Cr

Transfer of
alloying and
processing knowledge

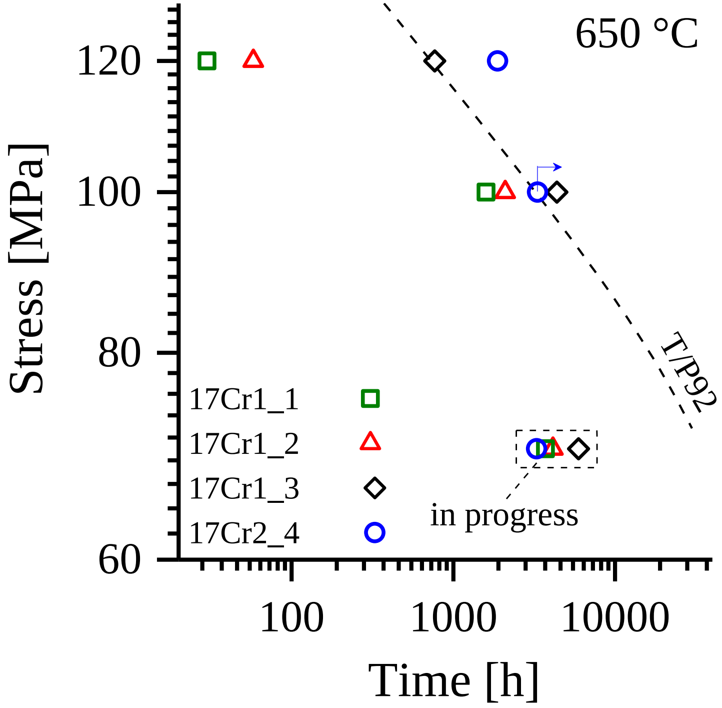
The future:

High performance ferrite

$T_{Appl.}$: 550 - 650 °C:
steam power plants
petrochemical plants

	Fe	Cr	W	Nb	Si	Mn	C	N
wt.-%	R	≤ 18	≥ 2.5	≤ 1	≤ 0.25	≤ 0.2	< 0.01	< 0.015

Creep (650 °C) – Hot-rolled condition



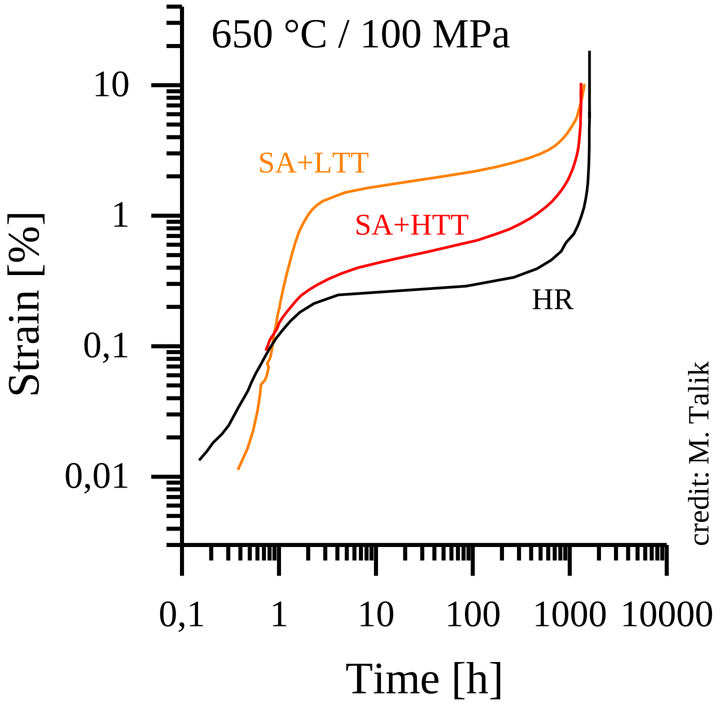
composition of the new “17Cr” batches (wt.-%):

Cr	W	Nb	Si	Mn	N	C
17	2.5	0.6	0.2	0.2	< 0.01	< 0.01

Advanced trial alloys combine

- *further reduced Cr content (17 Cr),*
- *enhanced W content (2.5 W) for increased Laves-phase formation,*
- *optimized rolling parameters and thus yield*
- *creep strength potential beyond CSEF grade 92*
- *without (Fe,Cr)-σ-phase embrittlement.*

Creep (650 °C) – Heat treatment



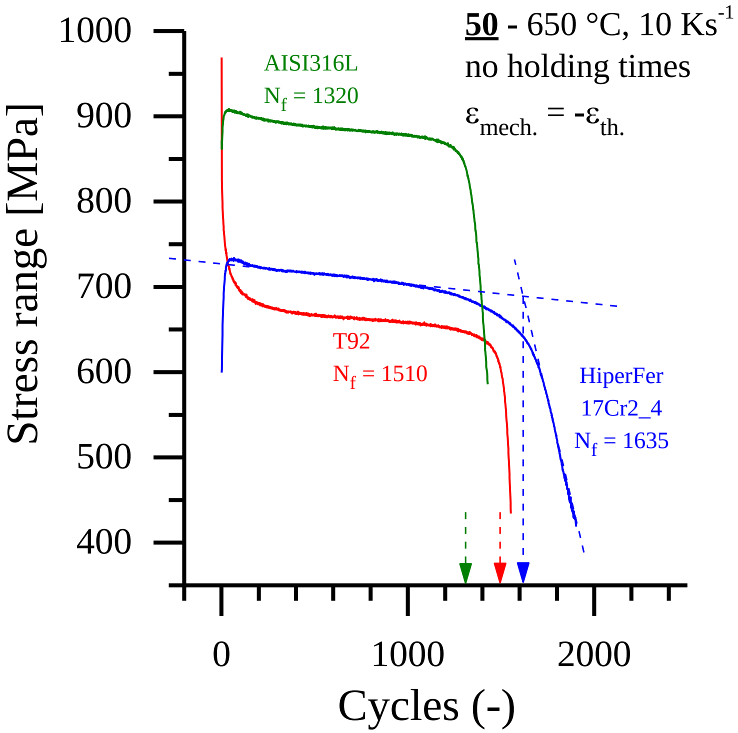
credit: M. Talik

same batch (17Cr1_1)
solution annealed (SA) plus

- low temperature treated (LTT) or
- high temperature treated (HTT)

- *Creep strength can be regained from the solution treated state by simple heat treatment.*
- *These heat treatments are effective in homogenizing hardness profiles after welding and do not harm creep strength of the hot-rolled material.*
- *Thermomechanical processing is not mandatory, but beneficial.*
- *Subject to further optimization.*

Thermomechanical fatigue



Ferritic-martensitic steel: *($\Delta\varepsilon_{mech.} \approx 0.79$ %)*

T92: N_f ~ 1510

➲ *not very "forgiving" after damage initiation*

Austenitic steel: *($\Delta\varepsilon_{mech.} \approx 1.12$ %)*

AISI316L: N_f ~ 1320

➲ *much higher stress range, "unforgiving"*

Ferritic steel: *($\Delta\varepsilon_{mech.} \approx 0.71$ %)*

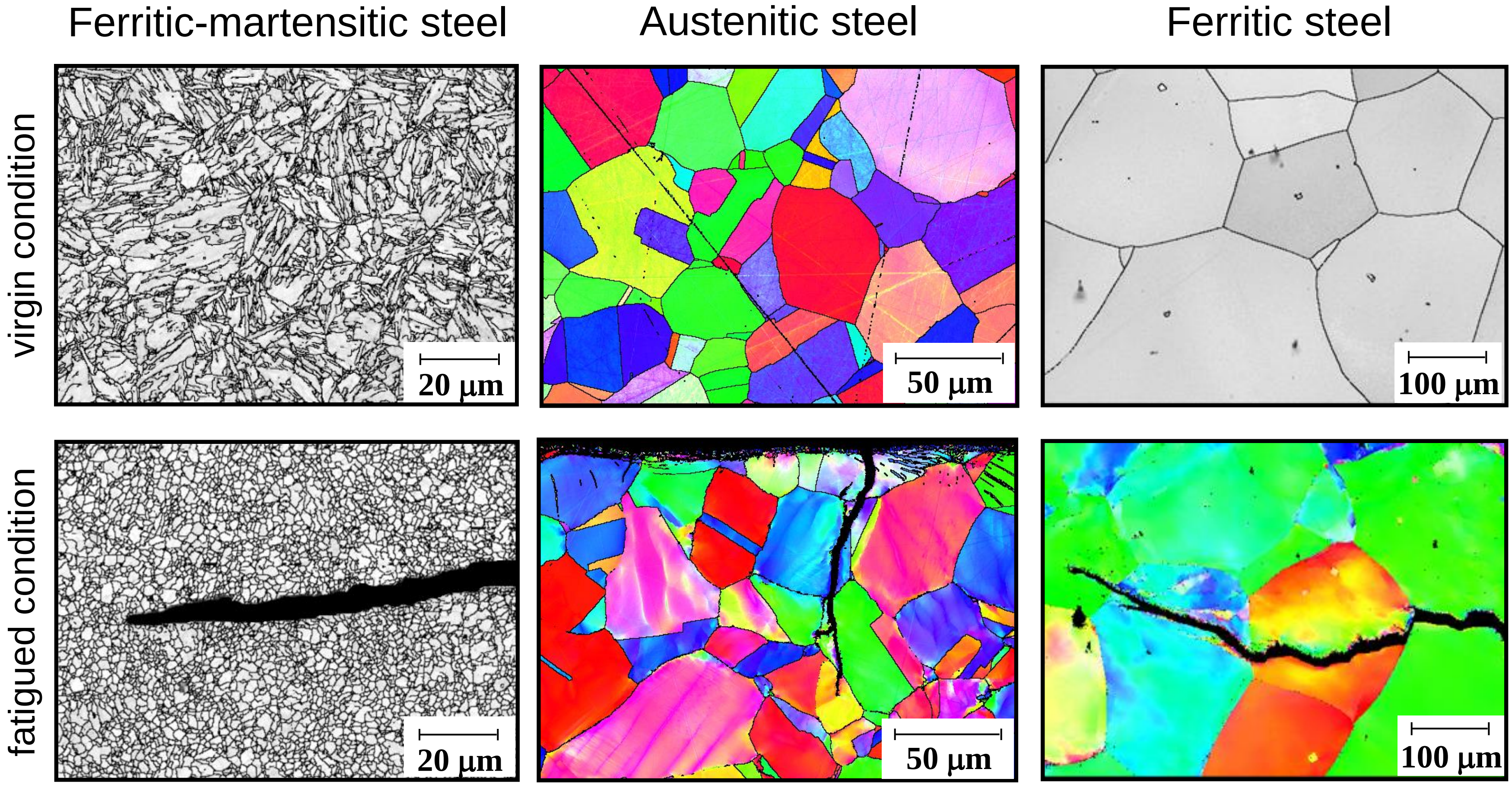
HiperFer 17Cr2_4: N_f ~ 1635

➲ *higher lifetime with*

➲ *higher stress range than T92 and*

➲ *good natured failure*

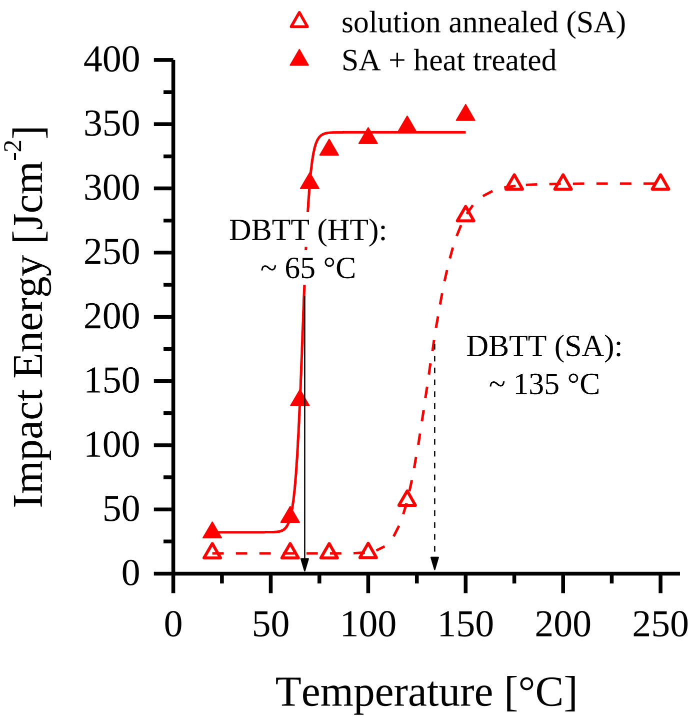
Thermomechanical fatigue – Microstructure stability



HiperFer ferritic steel combines

- ➲ *microstructural stability,*
- ➲ *low thermal expansion and high heat conductivity.*

Impact strength – Heat treatment and alloying



Impact strength can be increased by

- heat treatment alone or
- heat treatment and combined alloying

- *DBTT shift of -70 °C by heat treatment alone*
- *combined alloying gives another boost, but is not yet fully characterized*
- *subject to optimization*
- *to be implemented into lab scale production*

Hi gh perfor mance rite

Future applications

Hiperfor - grades for applications, where

- ease of processing,
- weldability and
- impact strength

play the major role:

➲ *Thin wall components (tube, sheet, …)*

Hiperforge - grades with optimized thermomechanical processing for applications, where

- weldability does not play a role,
- increased short-term / low temperature tensile properties

are beneficial:

➲ *Blading application*

- good stress relaxation properties

are desired:

➲ *Bolting application*

Recent work

New **Hiperfer** trial melts with

- doubled Laves phase content (~ 7 vol.-%) and thus enhanced mechanical,
- further improved impact strength and
- further decreased σ-phase stability range (< 550 °C)

were produced.

Matching SMAW electrodes were developed and first SMAW / TIG trial welds were produced by voestalpine Boehler Welding Gmbh (Germany) / ORNL (USA).

Optimization of **Hiperforge** trial steels concerning

- thermomechanical treatment (by rolling and / or forging) and
- heat treatment

is underway in cooperation with ORNL (USA) and RWTH Aachen (Germany).

➲ A lot of characterization work to come …

Acknowledgments

Thank you …

… to the (former) colleagues at Forschungszentrum Jülich:

M. Talik, J. Lopez Barrilao, L. Niewolak, J. Froitzheim, P. Huczkowski, W. J. Quadakkers, J. Zurek, C. Li, Z. W. Hsiao, N. Jing, W. Chen, Y. Wang, W. Lange, M. Braun, H. Esser, A. Moser, L. Lobert, H. J. Penkalla, E. Wessel, P. J. Ennis, T. Beck, L. Singheiser …

ORNL:

Y. Yamamoto, Y. Yang, P. Tortorelli

voestalpine Boehler Welding Germany:

M. Schmitz-Niederau, O. Trunova

RWTH Aachen, Institute of Ferrous Metallurgy:

H. H. Dickert, M. Schulte, A. Stieben, W. Bleck, G. Hessling

… and you for your kind attention !