Advances in Materials Technology for Fossil Power Plants
Proceedings from the Eighth International Conference
October 11–14, 2016, Albufeira, Algarve, Portugal
https://doi.org/10.31399/asm.cp.am-epri-2016p1018

J. Parker, J. Shingledecker, J. Siefert, editors

DEVELOPMENT STATUS OF HIGH PERFORMANCE FERRITIC (HiperFer) STEELS

B. Kuhn*[1], M. Talik[1], J. Lopez Barrilao[1], L. Singheiser[1], Y. Yamamoto[2]

[1]Forschungszentrum Jülich GmbH
Institute of Energy and Climate Research – IEK-2, Germany
*Corresponding author e-mail: b.kuhn@fz-juelich.de

[2]Oak Ridge National Laboratory, Oak Ridge, TN, USA

ABSTRACT

High chromium **HiperFer** (**Hi**gh **per**formance **fe**rritic) materials present a promising concept for the development of high temperature creep and corrosion resistant steels. The institute for Microstructure and Properties of Materials (IEK-2) at Forschungszentrum Jülich GmbH, Germany develops high strength, Laves phase forming, fully ferritic steels which feature excellent resistance to steam oxidation and better creep life than state of the art 9-12 Cr steels. Mechanical strength properties of these steels depend not only on chemical composition, but can be adapted to various applications by specialized thermo(mechanical) treatment. The paper will outline the sensitivity of tensile, creep, stress relaxation and impact properties on processing and heat treatment. Furthermore an outlook on future development potentials will be derived.

KEYWORDS: HiperFer, Laves phase, thermomechanical treatment, tensile, creep, stress relaxation

INTRODUCTION

Advanced ferritic-martensitic (AFM) 9-12 wt% Cr steels with tempered martensite structure offer creep strength and corrosion resistance sufficient up to application temperatures of 600 - 620 °C [1, 2]. Beyond 620 °C the 9 wt% Cr materials cannot be used anymore, because of their limited steam oxidation resistance [2]. 12 wt% chromium AFM steels like SAVE 12 or NF 12 were developed to overcome this drawback, but these materials do exhibit a sigmoidal decrease in creep strength during long-term application [3], which is caused by the formation of the so called Z-phase - a complex Cr(V, Nb)N - at the expense of strengthening MX particles [4, 5]. However, an increase in chromium content is considered to be essential to ensure sufficient steam oxidation resistance [6, 7] up to temperatures of 650 °C and thus the development of AFM steels might probably be left at an irresolvable conflict of aims.

The novel high chromium HiperFer [8] fully ferritic steels of Forschungszentrum Jülich provide a promising way out of this technological dead end. Strengthening of these materials cannot be accomplished by MX particles, because of the lacking C and N solubility in fully ferritic matrices. Alloying by suitable amounts of niobium and tungsten ensures a combination of solid solution and intermetallic $(Fe,Cr,Si)_2(Nb,W)$ Laves particle strengthening [9], which enables creep strength potential beyond grade 92 and steam oxidation resistance superior to 12 wt% Cr AFM steels [8, 10] in combination with favourable thermomechanical fatigue resistance [8, 11]. Specialized (thermo)mechanical processing in production enables the mechanical properties to be tailored to a wide range of applications. This paper gives an overview of the development status reached so far and will outline future development and application potentials.

EXPERIMENTAL

Chemical Composition and Production of Trial Steels

The chemical compositions of the recent 17Cr1, 17Cr2 and 17Cr3 experimental steels are given in Table 1. The 17Cr2 and 17Cr3 melts featured a slightly lower content of manganese. All the batches were produced by vacuum induction melting of high purity elements by the Institute of Ferrous Metallurgy (IEHK) and rolling to a final plate thickness of 16 mm at the Institute of Metal Forming (IBF) at RWTH Aachen University, Germany. Five rolling pass schedules (marked by "_1", "_2", "_3", "_4" and "_5"), featuring variations in temperature and deformation within the last rolling pass, followed by air cooling or water quenching, were applied to produce plate materials of differing stored dislocation density. The "model 1" alloy [8] was prepared by VDM Metals GmbH by vacuum melting. Rolling was performed down to a final sheet thickness of 2.5 mm followed by water quenching which accomplished and maintained maximum dislocation strengthening.

Table 1: Chemical compositions (wt.-%)

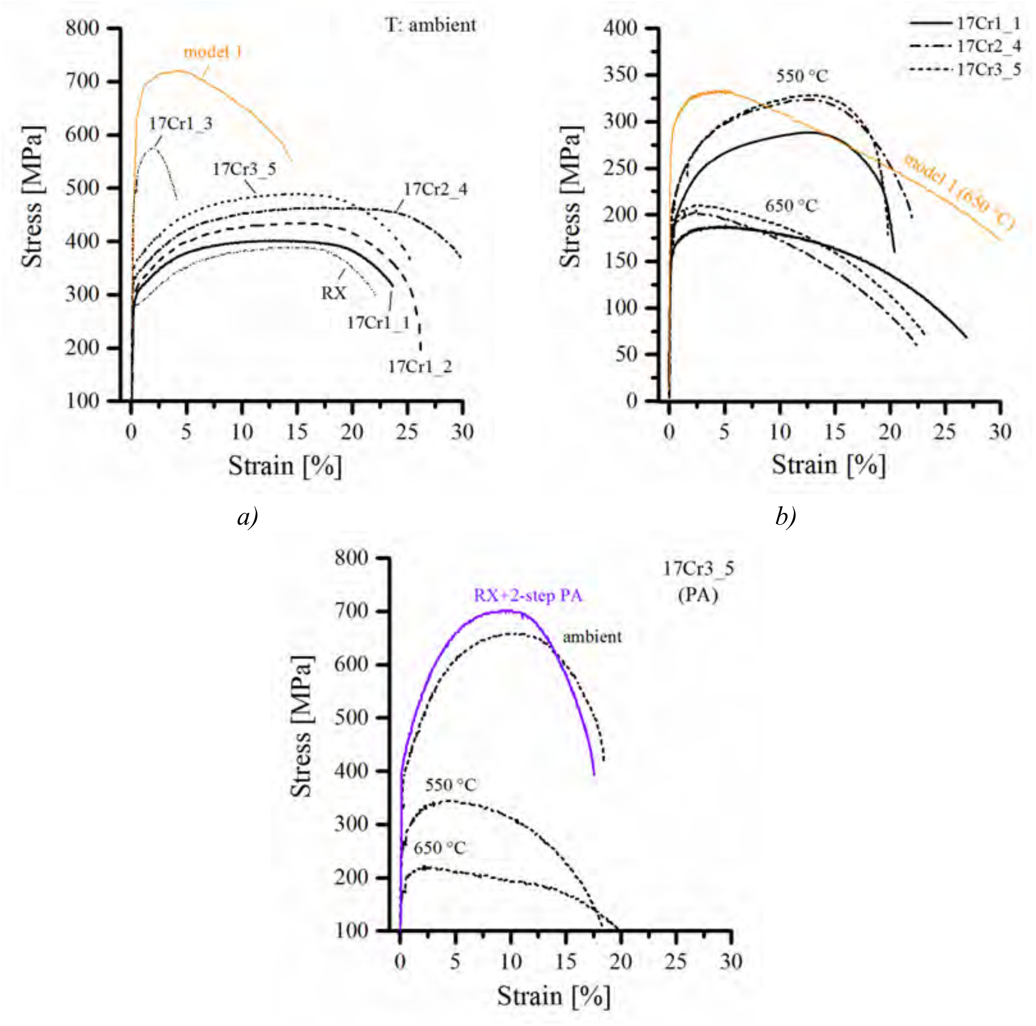
	Batch-ID:	C	N	Cr	Mn	Si	Nb	Fe	W
HiperFer	17Cr1	<0.01	<0.01	16.8	0.45	0.23	0.56	R	2.41
	17Cr2	<0.01	<0.01	17.0	0.19	0.27	0.58	R	2.45
	17Cr3	<0.01	<0.01	17.1	0.18	0.25	0.60	R	2.40
model	1	0.002	0.007	22.32	0.43	0.27	0.48	R	2.02

The (hot) tensile experiments were performed in an electromechanical Instron 1362 testing machine with 10 kN load capability, equipped with a 3-zone resistive furnace and a high temperature extensometer. Strain rates of $10^{-3}s^{-1}$ (at ambient temperature, according to DIN EN 10002-1) and $8{,}33\cdot10^{-5}s^{-1}$ / $8{,}33\cdot10^{-4}s^{-1}$ (elastic / plastic range at elevated temperatures, according to DIN EN 10002-5) were applied. Dead weight loaded lever arm type machines, equipped with 3-zone resistive furnaces, were utilized in testing of creep specimens with a gauge length/diameter of 30/6.4 mm. Furthermore flat, dog-bone shaped sheet specimens with gauge dimensions of 10 mm in length and 2.5 mm in thickness were applied in some tensile experiments. A temperature accuracy of +/- 1.5 °C was ensured in all the isothermal high temperature experiments by type S thermocouples, attached to the gauge sections of the specimens. Thermomechanical fatigue (TMF) tests were executed at solid round specimens with a gauge length/diameter of 15/7 mm, according to the European Code-of-Practice for Strain Controlled TMF Testing [12], utilizing a servohydraulic fatigue testing system with inductive heating. A Zwick 50 J miniature hammer was utilized in impact testing of 27 mm · 3 mm · 4 mm KLST specimens (60 ° notch, 1 mm depth, R = 0.1 mm, distance between anvils: 22 mm). A conversion function was established by comparison of DIN V and KLST impact energy results of solution annealed material, following the procedure outlined by Schill et al. [13].

RESULTS AND DISCUSSION

Impact of (thermo)mechanical processing on tensile strength

High yield strength helps in increasing the resistance of materials for blading application to high cycle fatigue damage by keeping a high extent of strain within the elastic range during deformation.



a) *b)*

c)

Fig. 1: Stress-strain curves of the model 1, 17Cr1, 17Cr2 and 17Cr3 trial steels, taken at (a) ambient temperature from material with increasing rolling deformation, (b) at elevated temperatures and (c) with precipitation heat treatment (17Cr3_5 only) and after recrystallization and precipitation heat treatment (RX+2-step PA)

Because fully ferritic steels do not undergo martensitic transformation upon cooling their intrinsic tensile strength is low in the recrystallized state (curve “RX”, cf. Fig. 1a: YS0.2: 285 MPa, UTS: 391 MPa). This can be counterbalanced by tailored thermal or thermomechanical processing: A strong impact of the initial thermomechanical treatment state on the minimum creep rate of ferritic steels was reported in [8]. This behavior was caused by changes in dislocation density, which varies by changes in the applied rolling parameters. This does not only affect the minimum achievable creep rate, but has a significant effect on tensile strength, too (cf. Fig 1a). The "model 1" curve, measured at rolled 2.5 mm sheet material, reaches ambient temperature offset yield/ultimate tensile strength values of 632/720 MPa and represents the benchmark for the optimization of thermomechanical processing towards future, thick section, semi-finished, slab and billet material for the production of high strength components.

Table 2: Tensile strength values in dependence on (thermo)mechanical treatment history

	ambient		550 °C		650 °C	
	$YS_{0.2}$ [MPa]	UTS [MPa]	$YS_{0.2}$ [MPa]	UTS [MPa]	$YS_{0.2}$ [MPa]	UTS [MPa]
17Cr1_1	298	401	185	282	160	186
17Cr1_2	314	433	185	289	160	202
17Cr1_3	508	575	-	-	160	188
17Cr2_4	332	461	210	323	170	202
17Cr3_5	361	488	210	328	175	210
17Cr3_5(PA)	401	662	267	343	177	222
17Cr3* (RX+2-step PA)	449	702	-	-	-	-
model 1	632	720	-	-	246	330

** named "17Cr3", because RX (recrystallization) wiped out rolling schedule _5*

In comparison to the as-rolled 17Cr1_1 material (298/401 MPa) this equals to a rise of appr. 210/180 %. With increasing deformation (within the last rolling pass) from rolling parameter set "_1" to parameter set "_5" the ambient temperature tensile strength values of the HiperFer 17Cr plate materials monotonically rise (Fig. 1a) from 285/400 MPa to 358/488 MPa. Optimization is complex, because a proper balance of dislocation strengthening and sufficient ductility has to be settled. While the stepwise increase of tensile strength was successful from the 17Cr1_1 to the 17Cr1_2 material, the 17Cr1_3 batch failed because of lacking ductility. Parameter set "_4" combines a further rise in strength with proper ductility. Rolling schedule "_5", which is an evolution of set "_4", guides the future way towards achieving benchmark strength values in thick section material with reasonable cutback in ductility.

The results displayed in Fig. 1b demonstrate that dislocation strengthening is effective at elevated temperatures, too. The advanced processing parameter sets "_4" and "5" lead to a moderate gain in tensile properties in comparison to the "_1" rolling schedule at 550 and 650 °C. Again, the "model 1" steel ($YS_{0.2}$/UTS at 650 °C: 246/330 MPa) sets the benchmark by reaching the 550 °C performance of the "_4" and "_5" materials at 650 °C.

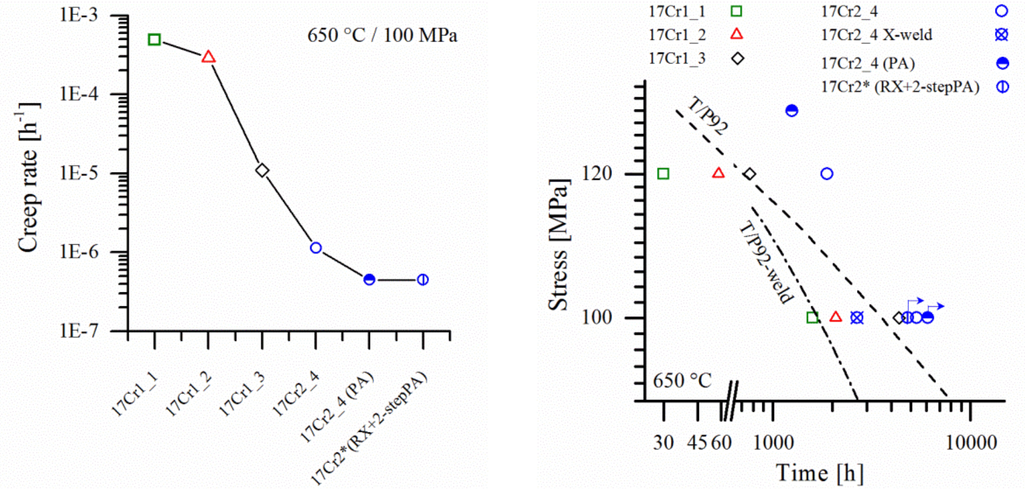
The experimental results outlined so far were all measured at materials without precipitation annealing prior to tensile testing. Additional precipitation heat treatment thus is a viable measure to achieve further increased tensile performance (Fig. 1c). Precipitation treatment rises the strength of the rolled 17Cr3_5 batch up to 401/662 MPa (as-rolled state: 361/488 MPa, equaling to an increase of appr. 10/35 %, Fig. 1b) at ambient temperature. At higher temperature this effect is less pronounced.

Strong dependence of the mechanical properties on thermomechanical processing would greatly restrict utilization of the proposed steels to applications where component production and plant construction do not cause significant microstructural alterations, i.e. to components which have not be welded. A 2-step heat treatment, which restores the tensile properties of recrystallization annealed material (Fig. 1c: RX+2-step PA), was developed to overcome this limitation and clears the path towards widespread application in power engineering.

A comprehensive overview of all the tensile testing results is given in Table 2. The results demonstrate that strongly increased tensile strength can be accomplished either by intelligent mechanical processing (with or without subsequent precipitation heat treatment) or by specialized 2-step heat treatment in case of recrystallized material. It may furthermore be stated, that heat treatment is mainly effective in increasing the ultimate tensile strength. If greatly enhanced yield strength is desired smart (thermo)mechanical processing becomes necessary and subsequent precipitation heat treatment may result in further, moderate increase of performance and stabilization towards elevated temperature.

Creep and stress relaxation properties, weldability

Creep experiments carried out at the “model 1” steel, amongst others of comparable chemical composition, demonstrated a remarkable dependency of the minimum achievable creep rate on thermomechanical treatment history [8]. The same prevails for the 17Cr trial materials in relation to the applied processing parameters.



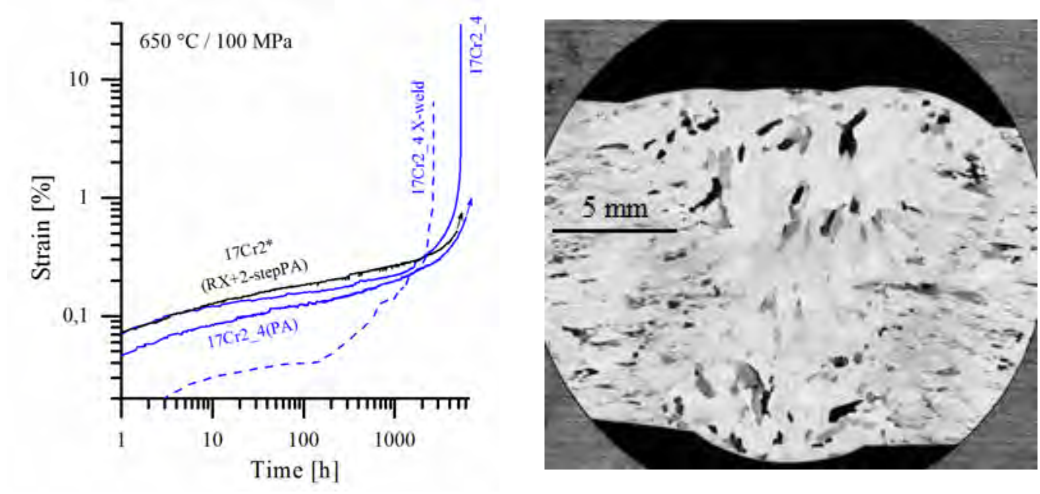
a) b)

Fig. 2: Minimum creep rates (a) and creep life (b) plots of various trial steels referring to the applied processing schedule and heat treatment (named “17Cr2”, because RX wiped out rolling schedule _4; T/P92 data taken from [14]; arrows: experiments in progress)*

With increasing rolling deformation the minimum creep rate monotonically drops in 100 MPa experiments carried out at 650 °C (Fig. 2a). The same relation holds in terms of creep life, especially at high (120 MPa) and intermediate (100 MPa) testing stresses (Fig. 2b): While the mildly processed 17Cr1_1 and 17Cr1_2 materials failed comparatively early after 1594 and 2092 h, the 17Cr1_3 steel ruptured after 4387 h and the 17Cr2_4 variant after 5337 hours (@100

MPa). At high stress (120 MPa) the relation is even more pronounced, but the tendency of the testing results obtained so far may suggest, that it fades out below a stress level of approximately 90 MPa at 650 °C. Below this stress level / beyond this exposure time the thermomechanical treatment history is supposed to have no significant influence on creep rupture life anymore. Low stress (70 MPa) experiments of all the outlined variants are in progress to prove this assumption and reached times of appr. 6500 hours so far.

Precipitation heat treatment prior to operation was effective in improving the short-term tensile strength. For this reason it was considered as a measure to reach optimized creep life, too. First creep experiments have been initiated on precipitation annealed material. Fig. 3a displays creep curves of selected 100 MPa experiments carried out at 650 °C on the as-rolled 17Cr2_4, additionally precipitation annealed 17Cr2_4(PA) and recrystallized and 2-step heat treated 17Cr2*(RX+2-stepPA) materials.



a)

b)

*Fig. 3: a) Creep curves of selected material variants and a GTAW weld (experiments marked with an arrow are still in progress; * named "17Cr2", because RX wiped out rolling schedule _4) and b) cross-sectional view of a GTAW weld of as-rolled 17Cr2_4 material*

Compared to the as-rolled 17Cr2_4 material the 100 MPa 17Cr2_4(PA) creep specimen yielded lower minimum creep rate (Fig. 2a). The experiment is still in progress after 6091 h (expected rupture time ~ 7200 h) and thus already surpassed the as-rolled 17Cr2_4 material. At 130 MPa this variant reached a creep rupture lifetime of 1255 h (cf. Fig. 2b). It may thus be stated, that additional precipitation heat treatment enables further increase in creep strength. All of the failed specimens reached creep rupture elongations in the range from 25 – 30 % and can be considered to be creep ductile for this reason. The current status of the experiments carried out at recrystallized material does not allow final conclusions on rupture life yet, but after 2-step heat treatment its creep response (Fig. 2a, b and 3a: 17Cr2*(RX+2-stepPA)) may combat that of the rolled and precipitation treated (17Cr2_4(PA)) material.

First trial gas tungsten arc welds (GTAW) of as-rolled 17Cr2_4 plate material were produced by Oak Ridge National Laboratory (USA) applying compositionally matched filler metal (Fig. 3b) and yielded promising creep results without any post-weld heat treatment carried out ("17Cr2_4 X-weld" in Fig. 3a). Optimization of the welding consumable and the welding parameters is in progress.

Resistance to stress relaxation is an important property of materials for bolting application. Fig. 4 presents stress relaxation curves of the "model 1" and the 17Cr2_4 steels in comparison to ferritic-martensitic grade 92. Starting from an initial stress of 250 MPa a remaining stress level of 115 MPa after 600 hours of relaxation at 600 °C is the benchmark value to reach for evolving materials [15]. With remaining stresses of ~100 and ~30 MPa after less than 200 hours the 17Cr2_4 and grade 92 steels fail to reach this criterion, but the "model 1" steel precisely meets the target and demonstrates the potential of fully ferritic steels in an adapted thermomechanical processing state. Precipitation heat treated 17Cr3_5 material (Fig. 4: 17Cr3_5(PA)) closely resembles the relaxation curve of as-rolled 17Cr2_4, but reaches a higher level of residual stress close to the required 115 MPa.

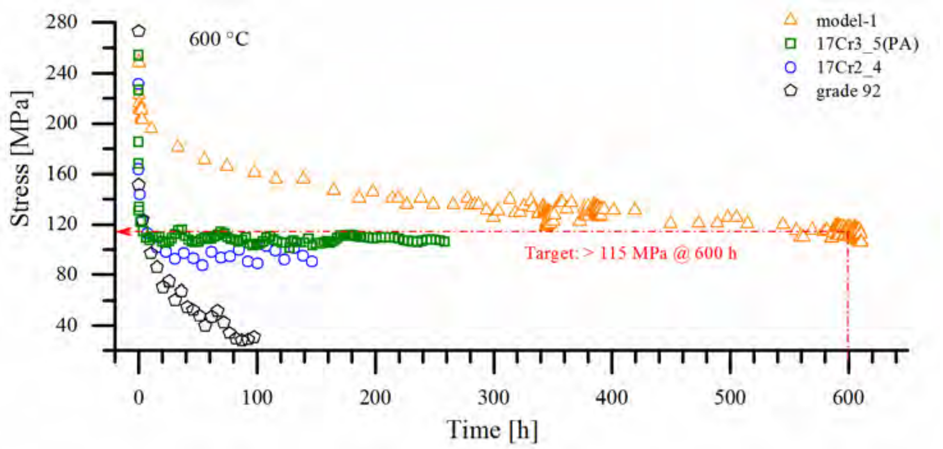


Fig. 4: Stress relaxation of the "model 1", the HiperFer 17Cr2_4 and 17Cr3_5(PA) steels and ferritic-martensitic grade 92 (600 °C, initial stress level: 250 MPa)

Impact strength

According to the technical rules EN 10216 / VdTÜV533 minimum impact energy values of 27/41

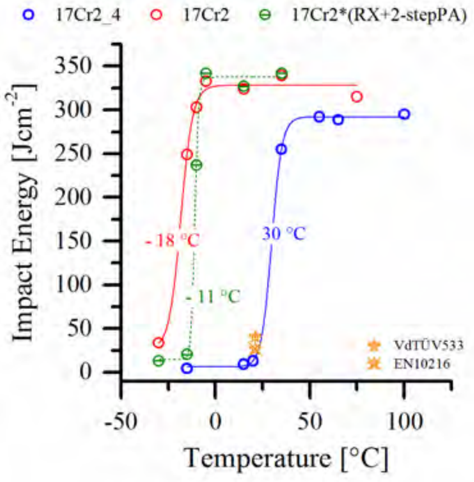


Fig. 5: Impact strength variation of as-rolled (17Cr2_4), recrystallized (17Cr2) and recrystallized and 2-step heat treated (17Cr2(RX+2-stepPA)) material*

Jcm^{-2} are mandatory at ambient temperature. The impact strength of ferritic stainless steels is generally considered to be problematic, but if proper processing and heat treatment is applied this is not the case for HiperFer steel. Fig. 5 displays brittle to ductile transition curves of the as-rolled (17Cr2_4), recrystallized (17Cr2) and recrystallized and 2-step heat treated (17Cr2*(RX+2-stepPA)) variants. The rolled 17Cr2_4 steel still remains slightly below 27 Jcm^{-2}, but with optimized rolling this limitation is likely to be overcome in the future. With a DBTT of -11 °C the 17Cr2*(RX+2-stepPA) material combines viable impact properties and promising creep and short-term tensile strength (Fig. 1c, 2b and 3a).

SUMMARY, OUTLOOK AND CONCLUSION

Fully ferritic HiperFer steels combine superior steam oxidation [10] and wet corrosion resistance with improved thermomechanical fatigue resistance [8, 11]. Regarding thermodynamic calculations further potential in long-term creep resistance is deducible from systematic variations in alloy composition. Recently produced advanced experimental alloys for this reason feature an, in comparison to the 17Cr1 to 17Cr3 materials, approximately doubled volume fraction and increased thermodynamic stability of the strengthening Laves phase particles.

The recent experimental results, obtained at the 17Cr HiperFer trial alloys, indicate that these improved trial steels may be suitable for low stress (i.e. piping) application without thermomechanical processing. Concerning weldability this is considered to be an essential advantage in pipework construction. Because such alloys do not undergo α to γ transformation upon cooling they should be essentially free from Type4 cracking issues. The creep results obtained from early GTAW welds were promising without applying any post-weld heat treatment. Furthermore first trial shielded metal arc welds (SMAW; produced by voestalpine Böhler Welding, Germany) of as-rolled plate material, applying matching stick electrodes, were prepared. Mechanical testing of this type of weld is in progress.

Based on either optimized thermomechanical treatment in production or heat treatment after recrystallization annealing tensile, creep and impact strength of HiperFer steels can be specifically adjusted to a broad range of tubing and piping applications. Further potential regarding resistance to stress relaxation is accessible by targeted processing of thick-section semi-finished material by rolling and / or forging to clear the way for turbine blading and bolting applications.

ACKNOWLEDGMENTS

The authors would like to express their gratitude for open discussions and great ideas concerning the production and processing of the 17Cr base materials to A. Stieben and M. Schulte at the Institute of Ferrous Metallurgy (RWTH Aachen University, Aachen, Germany). Financial support of the German Ministry of Education and Research and support of VDM Metals GmbH with the experimental model 1 alloy is gratefully acknowledged. Part of the current research was sponsored by the Crosscutting Research Program, Office of Fossil Energy, U.S. Department of Energy (Y. Yamamoto)

REFERENCES

[1] F. Abe, T.-U. Kern, R. Viswanathan: Creep resistant steels; Woodhead Publishing Limited 2008, ISBN: 978 1 84569-401-2, pp. 546-570

[2] R. Viswanathan, W. Bakker; J. Mater. Eng. Perform. 10 (2001), pp. 81-95 http://dx.doi.org/10.1361/105994901770345394

[3] F. Abe: Bainitic and martensitic creep-resistant steels; Current Opinion in Solid State and Materials Science; Volume 8, Issues 3–4, June–August 2004, pp. 305–311

[4] H.K. Danielsen, J. Hald, Energy Mater. 1 (2006), pp. 49-57, http://dx.doi.org/10.1179/174892306_99732

[5] H.K. Danielsen, J. Hald, VGB Power Tech. 5 (2009), pp. 68-73, http://www.vgb.org/vgbmultimedia/Forschung/danielsen_pt09_05.pdf

[6] Shreir's Corrosion. Editors: Bob Cottis, Mike Graham, Rob Lindsay, Stuart Lyon, Tony Richardson, David Scantlebury, Howard Scott. Fourth Edition (2010), Vol. 1, pp. 407-456

[7] I. G. Wright, R. B. Dooley; In: International Materials Reviews 55 (3), 2010, pp. 129-167

[8] B. Kuhn, M. Talik: HiperFer - High Performance Ferritic Steels; Proceedings of the 10th Liége Conference on Materials for Advanced Power Engineering, September 13th – 17th, 2014, Liége

[9] J. Lopez Barrilao, B. Kuhn, E. Wessel: Microstructure and Intermetallic Particle Evolution in Fully Ferritic Steels; Proceedings of the 8th International Conference on Advances in Materials Technology for Fossil Power Plants; this publication

[10] B. Kuhn et al.: Development of high chromium ferritic steels strengthened by intermetallic phases; Materials Science and Engineering A 594 (2014), pp. 372-380

[11] B. Kuhn, M. Talik, J. Lopez Barrilao, L. Singheiser: Microstructure stability of ferritic-martensitic, austenitic and fully ferritic steels under fluctuating loading conditions; Proceedings of the 1st 123 HiMat Conference, June 29th – July 3rd, 2015, Sapporo, Japan

[12] P. Hähner, E. Affeldt, T. Beck et al. Validated Code of Practise for Strain Controlled Thermomechanical Fatigue Testing (2006) http://www.tmf-workshop.bam.de/en/tmf_media/eur22281en.pdf

[13] R. Schill, P. Forget, C. Sainte Catherine: Correlation between Charpy-V and Subsize Charpy Test Results for an Un-Irradiated Low Alloy RPV Ferritic Steel, http://www.gruppofrattura.it/ocs/index.php/esis/ECF13/paper/view/8423/4871

[14] ECCC Datasheets, 2015, ASTM Grade 92

[15] Personal email communication with Dr. T.-U. Kern, Siemens Energy Sector, Mühlheim a. d. Rur, Germany