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Microstructure and mechanical properties of HR3C austenitic steel after service

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ABSTRACT

Purpose: The purpose of the investigations was to determine changes in the microstructure and mechanical properties of HR3C creep resisting austenitic steel after service.

Design/methodology/approach: The investigations were performed on test specimens taken from a part of the steam superheater tube. The range of the investigations included: microstructural investigations - light and SEM microscope; analysis of precipitates - carbide isolates; investigations of mechanical properties - hardness measurement, static tensile test, impact test.

Findings: The precipitation processes at the grain boundaries lead to increase in intergranular corrosion of the HR3C steel resulting in loss of grains in the structure. The impact strength testing on test specimens with reduced width may result in overestimation of crack resistance of the material after service.

Research limitations/implications: The comprehensive analysis of precipitation processes requires TEM examinations. Finding the correlation between the impact strength determined on standard vs. non-standard test specimens with reduced width.

Practical implications: The obtained results of investigations are used in industrial practice for diagnosis of pressure parts of power boilers. Test procedures developed based on comprehensive materials testing conducted under laboratory conditions are used in upgrading and design of pressure parts of steam boilers. The results of investigations are also the element of database of the materials characteristics of steels and alloys as well as welded joints made of them working under creep conditions developed by the Institute for Ferrous Metallurgy.

Originality/value: The results and analysis of the investigations of microstructure and mechanical properties of HR3C steel after service under actual boiler conditions are presented.

Keywords: HR3C steel; Microstructure; Mechanical properties

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PROPERTIES

1. Introduction

Due to their structure and chemical composition, the austenitic steels are characterised by a different set of mechanical and physical properties from that in the ferritic-matrix steels used so far in the power engineering, as the austenitic steels show both higher creep and heat resistance. Hence, these steels can work at up to 650-700°C. However, they are characterized by unfavourable physical properties, such as higher thermal expansion coefficient and lower thermal conductivity coefficient. The creep-resisting austenitic steels have been used mainly in power units operated with steam superheaters [1,2].

Similarly to ferritic steels, the development of austenitic steels was mainly the result of the optimisation and modification of chemical composition of the currently used steels [1-4]. One of the new grades of creep-resisting austenitic steels that have been introduced into the energy sector is HR3C steel. This steel resulted from the modification of chemical composition of TP301 steel, which involved the increase in chromium content up to approx. 25% and nickel content up to approx. 20% and the introduction of niobium and nitrogen elements into its composition. High chromium and nickel content in HR3C steel ensures high resistance to corrosion and oxidation at high service temperature, while the introduction of niobium and nitrogen elements into the steel provides fine-dispersion MX carbonitride and Z-phase (NbCrN) precipitates during service. These precipitates provide this austenitic steel with high creep resistance [5,6].

The previous studies on HR3C steel were mainly related to the effect of microstructure on strength properties and impact resistance of the aged steel [7,8] and changes in the microstructure and properties following the creep process [9], whereas this paper presents the results of investigations of microstructure and mechanical properties of HR3C steel after service under actual boiler conditions.

2. Material and methodology

The investigation concerned 25Cr - 20Ni - Nb - N (HR3C) creep resisting austenitic steel. Test specimens were taken from the pipeline section of 45mm x 5.7mm, which was operated for approx. 26.000 hours at 540°C. Chemical composition of the examined steel determined with SpectroLab K2 spark spectrometer is presented in Table 1.

The microscopic examinations were carried out on metallographic sections, etched with Mi19Fe reagent, with light microscope Axiovert 25 (OM) and scanning electron microscope Jeol 6610LV (SEM). Phase composition of the precipitates was determined by the carbide isolate method with PANalytical Empyrean X-ray diffractometer by using filtered cobalt radiation in configuration with Pixcel detector. The range of investigations on mechanical properties included: Vickers hardness measurement under the indenter load of 30 kG (294.3 N) - Future - Tech FM - 7 hardness tester, static tensile test using flat test specimens with initial measuring width b_o = 10 mm - Zwick / Roell Z100 testing machine, impact test on non-standard Charpy-V test specimens with width reduced to 2.5 mm. The investigations of mechanical properties were carried out at room temperature, in accordance with the applicable standards.

3. Description of achieved results of own researches

3.1. Microstructure of HR3C steel after service

In the after-service condition (Fig. 1), the examined steel revealed the austenitic microstructure with visible annealing twins and numerous precipitates. The grain size determined by comparative method was 5.5 according to the scale of standards [12]. A characteristic feature of the examined steel was the existence of numerous niobium-rich primary carbides with band-like arrangement in places (Fig. 2). These precipitates were observed both inside the grains and at the grain boundaries. The large particles of this type, as shown by own experience, including, but not limited to [13], are the niobium-rich NbC primary precipitates. The presence of these particles in the microstructure is a characteristic feature of creep-resisting austenitic steels containing the addition of niobium in their chemical compositions [5,11,14]. The size of these precipitates (average diameter of the order of a few micrometers) makes them not affect the increase in precipitation hardening of austenitic steels. Their main function is to inhibit the generation of $M_{23}C_6$ carbides by binding carbon atoms.

Table 1.
Chemical composition of the examined steel, %wt.

C	Si	Mn	P	S	Cr	Ni	Nb	N
0.08	0.49	1.15	0.014	0.004	25.39	19.79	0.30	0.18

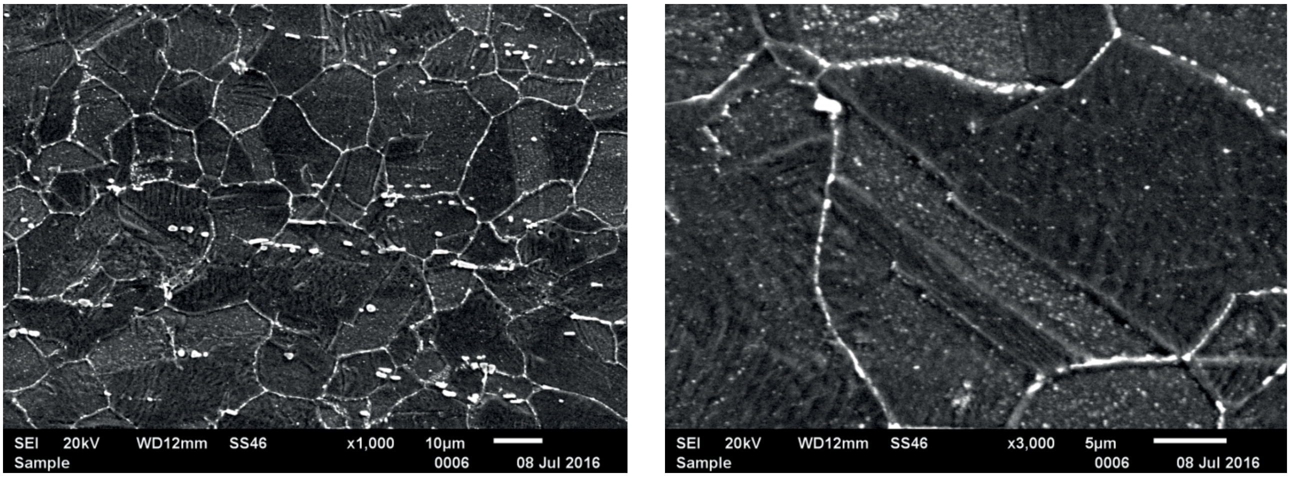

Fig. 1. Microstructure of HR3C steel after 26.000 h service, SEM

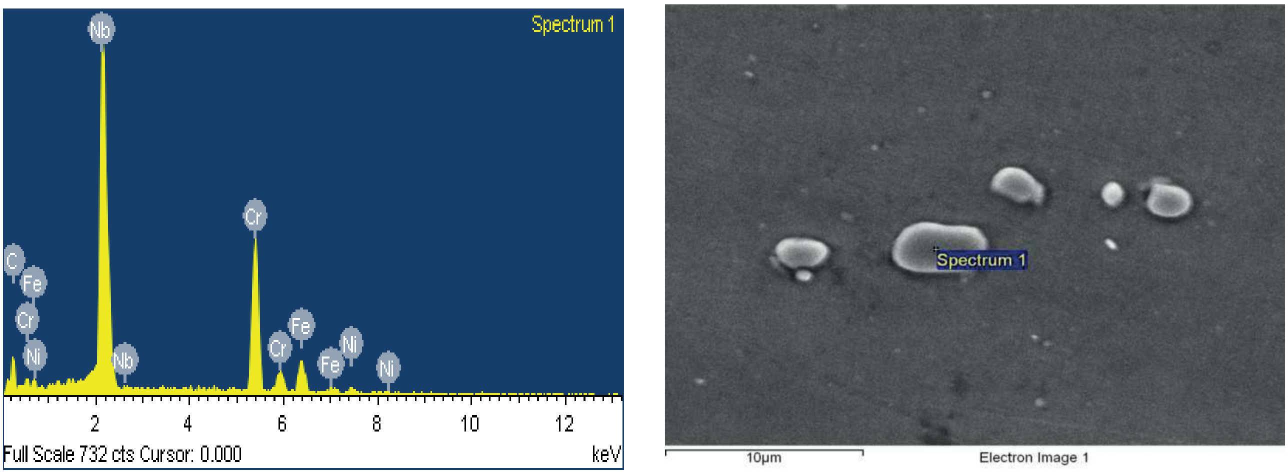

Fig. 2. EDX analysis of primary precipitates in HR3C steel

The NbC primary carbides in austenitic steels are treated as disadvantageous precipitates because there is a substantial likelihood that the nucleation and growth of creep voids may occur at their carbide/matrix interface [3,15]. In addition to large NbC primary carbide particles, numerous small precipitates inside the grains and numerous precipitates at the grain boundaries, forming the so-called continuous network of precipitates in places, were observed in the microstructure of the examined steel. Single fine particles were observed at the twin boundaries (Fig. 1b), but also twin boundaries with no precipitates were visible.

The phase analysis of particles by isolate method revealed, in addition to NbC carbides, the existence of NbCrN precipitates and $M_{23}C_6$ carbides in the examined steel (Fig. 3).

In contrast to 9-12% Cr martensitic steels, the NbCrN-Z phase secondary precipitates in austenitic steels are advantageous, as they have significant effect on the increase in precipitation hardening of these steels, thus contributing to the enhancement in strength properties, hardness and creep resistance during service [3,5,6]. The Z phase precipitates inside the grains in a finely dispersed form. In accordance with the Orowan mechanism, this provides an effective reduction and inhibition of free dislocation movement. The high thermodynamic stability of these precipitates results in a very slow increase in their size [3,16,17].

The chromium-rich $M_{23}C_6$ carbides, as it is commonly assumed, are the first secondary precipitates that occur in the microstructure of austenitic steels. The $M_{23}C_6$ carbides were revealed in 304H steel as early as after one-hour creep at 600-650°C [18].

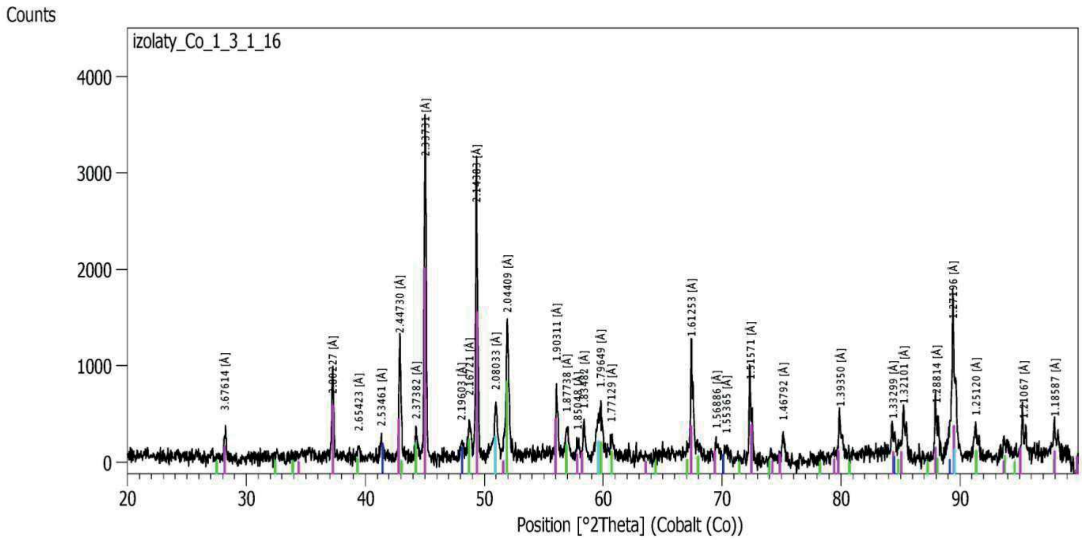

Fig. 3. Diffractogram of isolates extracted from HR3C steel

The privileged sites of $M_{23}C_6$ carbide precipitation are grain boundaries, which are characterise by high degree of coincidence Σ or high misorientation angle Θ. The other area where $M_{23}C_6$ carbides may precipitate is non-coherent and coherent twin boundaries [5,16,18]. The short time of service shows that $M_{23}C_6$ precipitates observed at the grain boundaries in the examined steel are boundaries non-coherent with the matrix. Single $M_{23}C_6$ carbides can also be observed inside the grains. The ratio of carbides precipitated inside the grains to those precipitated at the grain boundaries is 7:93 [20]. Due to their low thermodynamic stability, the $M_{23}C_6$ carbides tend to coagulate during service and form the so-called continuous network at the grain boundaries. This not only affects the very fast decrease in impact strength of austenitic steels, but also results in the formation of near-boundary areas with reduced chromium contents [13,21]. The decrease in chromium concentration in the near-boundary areas contributes to the increase in tendency to intergranular corrosion of austenitic steels. This leads to the loss of grains, which was observed in the microstructure of the examined steel (Fig. 4).

The literature data [3,7,9] also show that in addition to the primary NbC precipitates in the microstructure of HR3C steel after ageing/creep, the secondary precipitates of NbX carbonitrides are observed too. Similarly to the Z-phase precipitates, the fine dispersion NbX particles precipitated inside the grains contribute to the reduction in mobility of dislocations.

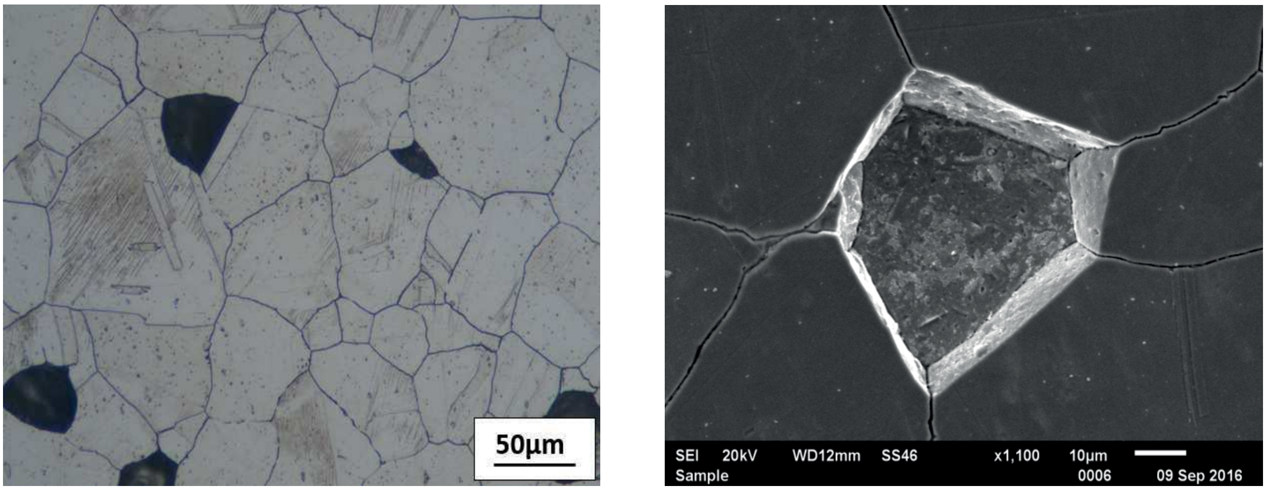

Fig. 4. Lost austenite grains in the examined steel

Phase analysis of the precipitates in the examined steel did not reveal the existence of intermetallic phases, for example Sigma, Laves, G phases etc., which is primarily the result of low temperature and relatively short time of service.

In the as-received condition, HR3C steel is characterised by austenitic microstructure with precipitates of primary NbC carbides [7,9]. The research [20] shows that in the microstructure of HR3C steel in the as-received condition, apart from large primary NbC carbides, also the fine-dispersion precipitates of Z phase - NbCrN can be observed.

3.2. Properties of HR3C steel after service

The properties of the examined steel after service including requirements are shown in Table 2.

The investigations of mechanical properties demonstrated that the steel after 26.000 h service was characterised, in relation to the requirements, by approx. 50MPa higher tensile strength and by ~80MPa higher offset yield point, while the plastic properties expressed as elongation met the required minimum. The literature data [3,8] show that strength properties of HR3C steel may increase during service. High values of yield point and tensile strength of the examined steel (Table 2) show that they probably increase during service. The growth of these properties may be the result of precipitation of fine dispersion Z-phase particles and probably of secondary NbX carbonitrides inside the grains. In the opinion of the authors, the impact strength of HR3C steel equal to KV300/2.5, as determined on test specimens with width reduced to 2.5 mm, is significantly overestimated and does not correspond to the real one.

The examinations [22] showed that reduction in width of the impact test specimen from 10 mm to 2.5 mm for C45 steel resulted in apparent increase in the impact strength KV by 60%. The notch in the Charpy-V test specimen of 0.25 mm in radius makes a triaxial state of tensile stress occur under the notch and spread in a small volume of the material under its edge. On the other hand, the reduction in thickness of the impact test specimen affects the change in the state of stress at side walls, which results in the occurrence of characteristic "shear lips" with ductile fracture mechanism. Similar effects will occur under the notch and in the hinge area. The foregoing results in overestimation of the obtained value of crack resistance for the examined steel, the more so that it was demonstrated in [3,7,20] that the impact strength of this type of steel decreases rapidly to ~20J after a short time of ageing. The researchers associate this effect with the precipitation processes of $M_{23}C_6$ carbides and sigma phase at the grain and twin boundaries and the coarse-grain structure with grain size of 3-4 according to the ASTM scale. Numerous precipitates were observed in the microstructure of the analysed steel which had negative impact on the cohesion of grain boundaries and contributed to changing the cracking mechanism from ductile to brittle intercrystalline [7,8,20].

4. Conclusions

- The operation of HR3C steel contributed mainly to the precipitation processes of: Z phase (NbCrN) and $M_{23}C_6$ carbides and maybe NbX carbonitrides.
- The low, as for austenitic steels, operating temperature resulted in the intensive precipitation process at the grain boundaries. The precipitation and growth of $M_{23}C_6$ carbides at the grain boundaries contributes to the sensitisation of the examined steel, which results in grain loss.
- For thin-walled tubes, where it is impossible to take standard impact test specimens, there is a need to develop a crack resistance assessment procedure for these materials.
- The obtained results show the need to exercise some caution in operation of the steam superheater elements made of HR3C steel.

Table 2.
Properties of HR3C steel after service

	YS, MPa	TS, MPa	El., %	KV300/2.5, J	KCV300/2.5, J/cm^2	KV_c*	HV30
Examined steel	372	707	30	13	65	52	230
Requirements according to [23]	min. 295	min. 655	min. 30		min. 85 J**		-

* - $KV_c = (10 \times KV_p)/w$; KV_p – impact strength obtained on non-standard test specimen; J, w - non-standard test specimen width; mm [24]
** - impact strength KV of standard test specimen.

References

[1] A. Zieliński, Austenitic steels for boiler elements in USC power plant, Journal of Achievements of Materials and Manufacturing Engineering 57 (2013) 68-75.

[2] A. Zieliński, G. Golański, M. Sroka, J. Dobrzański, Estimation of long-term creep strength in austenitic power plant steels, Materials Science and Technology 32/8 (2016) 780-785.

[3] Ch. Chi, H. Yu, X. Xie, Advanced Austenitic Heat-Resistant Steels for Ultra-Super-Critical (USC) Fossil Power Plants, Alloy steel - properties and use, InTech Publisher, 2011, 171-201.

[4] J. Liu, D. Jiao, C. Luo, Microstructural evolution in austenitic heat-resistant cast steel 35Cr25Ni12NNbRE duration long-term service, Materials Science and Engineering A 527 (2010) 2772-2779.

[5] T. Sourmail Precipitation in creep resistant austenitic stainless steel, Materials Science and Technology 14 (2001) 1-14.

[6] B. Peng, H. Zhang, J. Hong, J. Gao, H. Zhang, J. Li, Q. Wang, The evolution of precipitates of 22Cr-25Ni-Mo-Nb-N heat-resistant austenitic steal in long-term creep, Materials Science and Engineering A 527 (2010) 4424-4430.

[7] B. Wang, Z.-D. Liu, S.-Ch. Cheng, Ch.-M. Liu, J.-Z. Wang, Microstructure evolution and mechanical properties of HR3C steel during long-term Aging at high Temperature, Journal of Iron and Steel Research International 21/8 (2014) 765-773.

[8] J.Z. Wang, Z.D. Liu, H.S. Bao, S.C. Cheng, Evolution of precipitates of S31042 heat resistant steel during 700°C aging, Journal of Iron and Steel Research, International 20/10 (2013) 113-121.

[9] A. Iseda, H. Okada, H. Semba, M. Igarashi, Long term creep properties and microstructure of SUPER304H, TP347HFG and HR3C for A-USC boilers, Energy Materials 2/4 (2007) 199-206.

[10] A. Zieliński, J. Dobrzański, M. Sroka, Changes in the structure of VM12 steel after being exposed to creep conditions, Archives of Materials Science and Engineering 49/2 (2011) 103-111.

[11] M. Sroka, A. Zieliński, Matrix replica method and artificial neural networks as a component of condition assessment of materials for the power industry, Archives of Materials Science and Engineering 58/2 (2012) 130-136.

[12] PN-EN ISO 643:2012 Steels - Micrographic determination of the apparent grain size.

[13] G. Golański, A.K. Lis, J. Słania, A. Zieliński Microstructural aspect of long term service of the austenitic TP347HFG stainless steel, Archives of Metallurgy and Materials 60 (2015) 2091-2094.

[14] Ch. Solenthaler, M. Ramesh, P.J. Uggowitzer, R. Spolenak, Precipitation strengthening of Nb-stabilized TP347 austenitic steels by a dispersion of secondary Nb(C,N) formed upon a short-term hardening heat treatment, Materials Science and Engineering A 647 (2015) 294-302.

[15] J. Erneman, M. Schwind, H.-O. Andrén, J.-O. Nilsson, A. Wilson, J. Ågren, The evolution of primary and secondary niobium carbonitrides in AISI 347 stainless steel during manufacturing and long-term ageing Acta Materialia 54 (2006) 67-76.

[16] A.F. Padilha, P.R. Rios, Decomposition of austenite in austenitic stainless steels, ISIJ International 42/4 (2002) 325-337.

[17] Y.H. Zhou, Ch.X. Liu, Y.Ch. Liu, Q.Y. Guo, H.J. Li, Coarsening behavior of MX carbonitrides in type 347H heat-resistant austenitic steel during thermal aging, International Journal of Minerals, Metallurgy and Materials 23/3 (2016) 283-293.

[18] H. Tanaka, M. Murata, F. Abe, H. Irie, Micro-structural evolution and change in hardness in type 304H stainless steel during long-term creep, Materials Science and Engineering A 319/321 (2001) 788-791.

[19] J.K. L. Lai, A Review of precipitation behaviour in AISI Type 316 stainless steel, Materials Science and Engineering 61 (1983) 101-109.

[20] B. Peng, H. Zhang, J. Hong, J. Gao, Q. Wang, H. Zhang, Effect of aging on the impact toughness of 25Cr-20Nr-Nb-N steel, Materials Science and Engineering A 527 (2010) 1957-1961.

[21] K. Kaneko, T. Futunaga, K. Yamada, N. Nakada, M. Kikuchi, Z. Saghi, J.S. Barnad, P.A. Midgley, Formation of $M_{23}C_6$ - type precipitates and chromium -depleted zone in austenite stainless steel, Scripta Materialia 65 (2011) 509-512.

[22] G. Stradomski Methodology problems of using PN - EN ISO 148-1:2010 standard, Proceedings of the 15th International Scientific Conference, New Technologies and Achievements in Metallurgy, Material engineering and productions engineering, Częstochowa, 2014, 378 -381.

[23] Data Sheet HR3C Nippon Steel & Sumitomo Metal 2013.

[24] PN-EN 10216-2 Seamless steel tubes for pressure purposes - Technical delivery conditions. Non - alloy and alloy steel tubes with specified elevated temperature properties.