

I. Pikos, R. Kocurek, J. Adamiec

*Silesian University of Technology, Department of Material Science,
Faculty of Material Science and Metallurgy, Katowice, Poland
e-mail: izabela.pikos@gmail.com*

PERSPECTIVES OF MATERIALS FOR FIN TUBES

ABSTRACT

Modern design solutions of power boiler using the welded fin tubes for heat exchangers. Depending on thermal parameters (pressure and temperature), the heat transfer fluid and flue gas these constructions can be preheater, economizers or superheaters. Their use can significantly increase the energy efficiency of boilers. For the manufacture of welded fin tubes are used non-alloy steels and low-alloy C-Mo, C-Cr-Mo. Analysis of project assumptions supercritical blocks indicates that the range of conventional steel for power and martensitic steels has been depleted. Designing higher performance outlet of steam to 720°C and 35MPa requires the use of austenitic steels and nickel alloys. These materials are not easily available and not fully recognized, both technologically and in terms of materials, especially in the area of their weldability. In this work, performed the review of probably directions of development of materials for the finned tubes, with a particular focus on laser welding technology.

Key words: fin tubes, steel for energy, nickel superalloys, heat exchangers

INTRODUCTION

The development of modern energy industry is headed by ecological aspects, such as restrictions on the Earth's natural resources and reduction of flue gas emission. Despite the development of many branches of applying renewable energy, power plants using coal and gas are the largest share of the global market for power generation (including 81.1%) [1]. Activities aimed at protection of the environment have been formulated in the „Climate and Energy Package”, also called „3x20 Package”. It marks the Member States of the European Union following quantitative targets for the year 2020 [2]:

- reduce emissions of greenhouse gas by 20% compared to 1990,
- improve energy efficiency by 20%,
- increase the share of energy from renewable sources to 20%.

One of the preconditions for the implementation of the „3x20 Package” is to increase the share of energy from gas blocks and renewable energy sources and improve the efficiency of power plants, obtained by increasing the steam parameters. Use of renewable energy in EU countries are shown in Fig. 1.

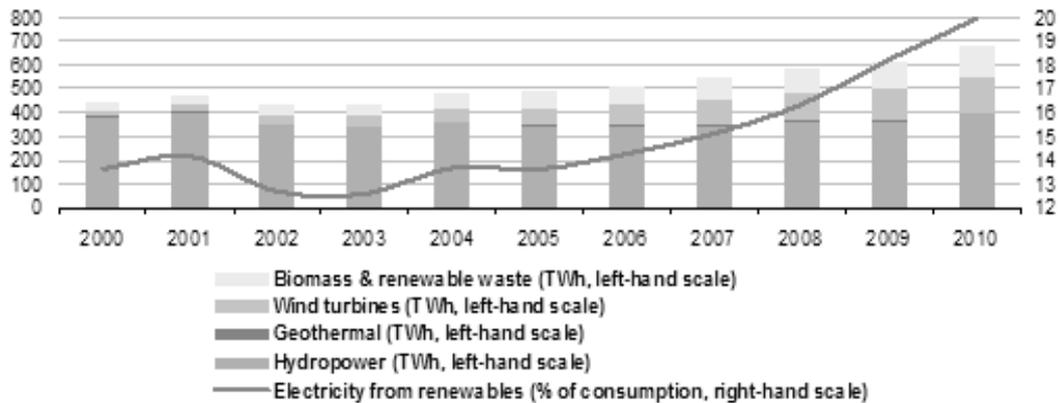


Fig. 1. Electricity generated from renewable energy sources in EU [3]

Modern solutions of gas blocks constructions use the welded finned tubes for heat exchangers. Depending on thermal parameters (pressure and temperature), of the heat transferring fluid and flue gas, these constructions can be applied as preheaters, superheaters or economizers (Fig. 2). Their use significantly increases the energy efficiency of boilers. Thermal efficiency of finned tubes is 2.5 times higher compared to the efficiency of smooth pipes and 1.5 times higher compared to the efficiency of tubes Favier.

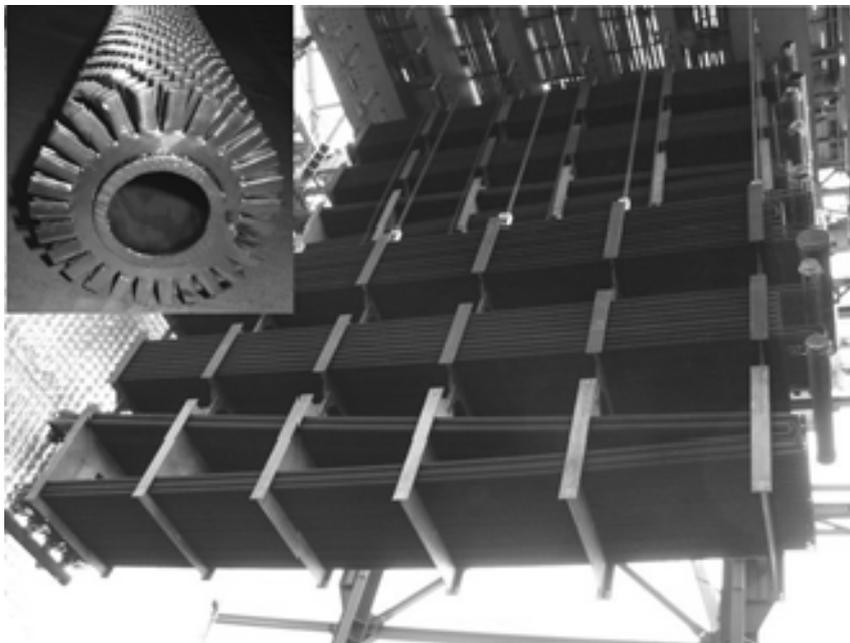


Fig. 2. Heat exchangers constructed of finned tubes used in gas boilers

Designing higher performance outlet of steam to 720°C and 35MPa requires the use of austenitic steels and nickel alloys. These materials are not easily available and not fully recognized, both technologically and in terms of materials.

MATERIALS USED IN THE ENERGY INDUSTRY

Materials used in the construction of boilers elements should have the appropriate strength properties i.e. $R_{0,2min}$ at 250MPa at 600°C, good creep resistance, $R_{Z/100000} \geq 140\text{MPa}$ at temperature of 620-650°C. Another requirement is resistance to the steam oxidation and to the hot corrosion in the environment of the liquid ashes. These materials should also have a structural stability, preserve plasticity and high impact strength, both as received condition and after a long period of use. Workability, formability and weldability are also important features [4,5]. The major materials used in the construction of boilers are ferritic steels with high content of chromium, austenitic steels and nickel superalloys. The mechanical properties of these materials have been collected from the producers information and showed in Fig. 3.

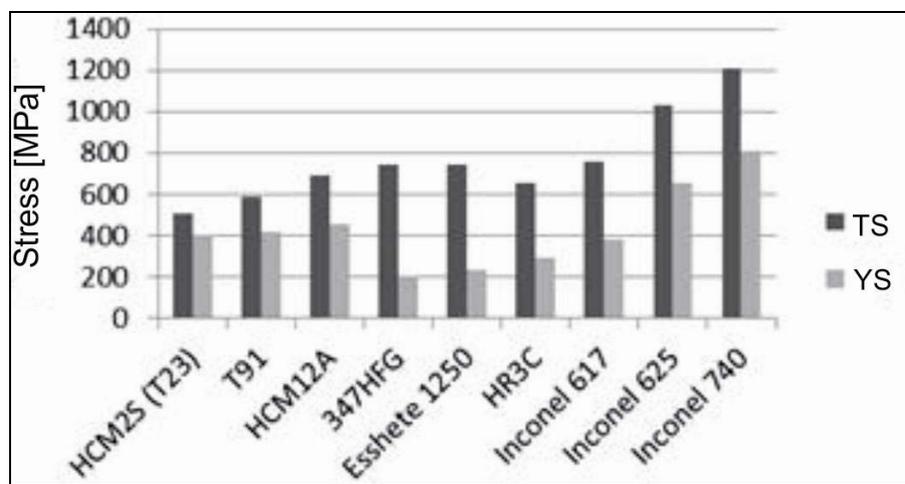


Fig. 3. The tensile strength and yield strength steels and nickel alloys used in the power industry (at temp. 20°C) [14-21]

The ferritic creep-resistant steels, which are martensitic and bainitic steels, can work at temperatures up to about 650°C. The principal alloying element that provides the corrosion resistance at high temperatures is 2-12% chromium. Steels containing 2% Cr, which are represented by T23 steel, are used mainly for parts working up to 550°C, like water wall panels. They are low-alloy bainitic steels. Among the martensitic steels containing 9-12% Cr, widely used grades P91 and P92, working at temperatures up to about 600°C. The advantageous properties of ferritic steels depends on the optimal selection of alloying elements. Solid solution strengthening, favorable in terms of creep resistance, is obtained by addition of Mo and W. The addition of elements such as vanadium and niobium, which have a tendency to create nitrides and carbides, determines a mechanism of precipitation strengthening. Principal precipitates formed in this steels are carbides $M_{23}C_6$ ($(Cr,Fe,Mo)_{23}C_6$), $MX((V,Nb)(N,C))$ and Laves phases $(Fe,Cr)_2(Mo,W)$. Boron is an element to prevent excessive coagulation and precipitate coarsening of carbides $M_{23}C_6$, especially near the boundaries of primary austenite, what contributes to the structural stability. Cobalt added to new grade of steel, working up to 650°C (NF12, SAVE12) is also an element which stabilizes and strengthens. During tempering effectively delays the recovery and favors the formation of fine secondary carbides, which positively affects for creep resistance [6-13].

Increase steam parameters of power boilers necessitated the development of materials working at temperatures above 620°C. Austenitic steels have good corrosion resistance,

satisfactory mechanical properties and resistance to creep also above this temperature. Major alloying elements in austenitic steels is nickel, is responsible for the stability of the matrix γ and addition of chromium responsible for the corrosion resistance. A problem in the long term withstand the elevated temperature is the tendency to separate at grain boundaries σ phase and rich in chromium and coagulated carbides $M_{23}C_6$. This phenomenon is particularly bad because of the significant decrease in ductility and the propensity to brittle cracking during use. Additionally, near the boundaries form depleted zone in chromium, it promotes the growth of intergranular corrosion. This disadvantage have forced steel makers to develop a grades of steel with improved high temperature properties [23].

Alloying carbonizer elements such as Ti (the steel type 321) and Nb (the steel type 347) and the addition of nitrogen lead to the formation of carbides, nitrides and carbonitrides of MX-type inside the grains, which effectively prevents the precipitate of $M_{23}C_6$ at boundaries and positively influences stabilization of the structure [23, 24]. From the perspective creep resistance, formed the nanoparticles (Nb, Cr, Fe) (C, N), for example Z-phase (CrNbN), characterized by a favorable morphology and a good stability at elevated temperature, increasing the strength properties. Manganese and nitrogen show a synergistic effect, stabilizing and facilitating the formation of carbonitrides in the austenite [25]. The addition of niobium is used, among others in steels Super 304H, TP347H, HR3C, Tempaloy A-1, NF709, Sanicro25 and SAVE25. Another addition of alloying, which effectively strengthens the solid solution is copper. Research has proven that in particles rich in copper are soluble in austenite matrix, effectively block the dislocation mobility and are stable during long-term operation at temperatures up to 650°C. Strengthened steels by the addition of copper are among other Super 304H, Tempaloy AA-1, SAVE25 and Sanicro25 [26, 27]. It has been proved that microalloying of boron and cerium have a positive influence on reduction the steady-rate creep determined thereby improve creep resistance alloy 347H [28].

The elements in power units of ultra-supercritical parameters, especially superheaters of primary and secondary steam, work at temperatures above 700°C and at pressures exceed than 35MPa. These conditions require the use of materials about particularly advantageous properties. Nickel superalloys are characterized by a microstructure consisting of matrix γ (FCC) strengthened precipitates the metastable phase γ' (Ni_3Nb), the phase γ' ($Ni_3(Ti,Al)$) and carbides MC, which provides a complex of the respective properties. High content of nickel and chromium provides good corrosion resistance in high temperature at fly ash containing sodium and potassium sulfates, so-called "hot corrosion", and resistance to oxidation in steam atmosphere. Molybdenum has a positive effect on creep resistance, and additions of titanium, zirconium and boron improves the weldability of the alloy [4]. Nickel based alloys are characterized by superior properties in comparison to steels, however, due to their prices are used in to the elements in the most difficult conditions.

Among the alloys of comparable tensile strength is slightly higher than the austenitic steels of the ferritic matrix. In austenitic steels is also smaller ratio $R_{0.2}/R_m$. Nickel based alloys, in particular grade Inconel 740, have significantly improved mechanical properties (Fig. 4). At a temperature of about 700 ° C, which is characteristic for ultra-supercritical boiler of operating parameters, Inconel 617 is almost three times the allowable stress as compared to austenitic steel Super 304H.

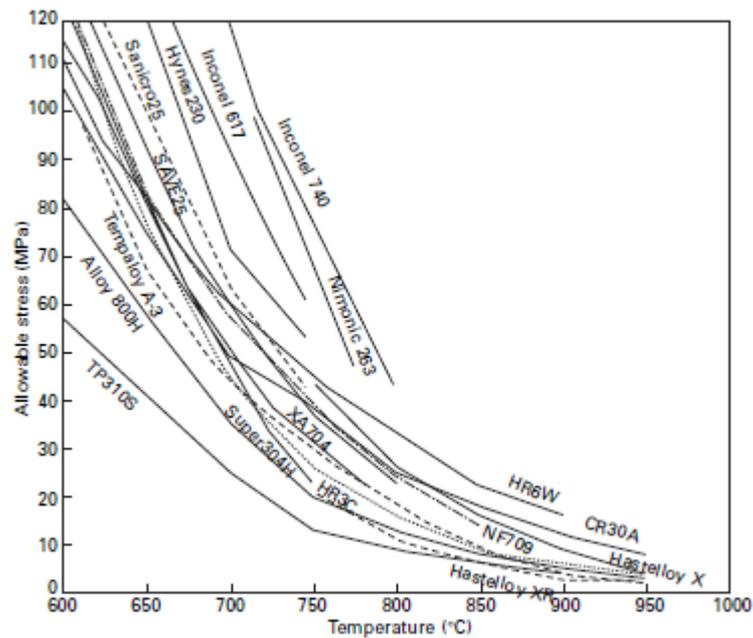


Fig. 4. Allowable stress in the materials [5]

In regards of creep resistance satisfactory properties at temperature 600°C have ferritic alloy steels. Time creep strength of steel HCM2S is 80MPa, the steel P91 is 94MPa and for steel HCM12A is 101MPa. Higher creep resistance at temperature 600°C resist the austenitic steel TP347HFG amount to 127MPa, for steel Super304H is 145MPa, whereas at temperature 700°C for grade of steels HR6W, SAVE25 and Sanicro25 90MPa. Nickel superalloys due to a favorable microstructure can be used at higher temperatures, the creep strength at 700°C exceed than 100MPa (Fig. 5) [5].

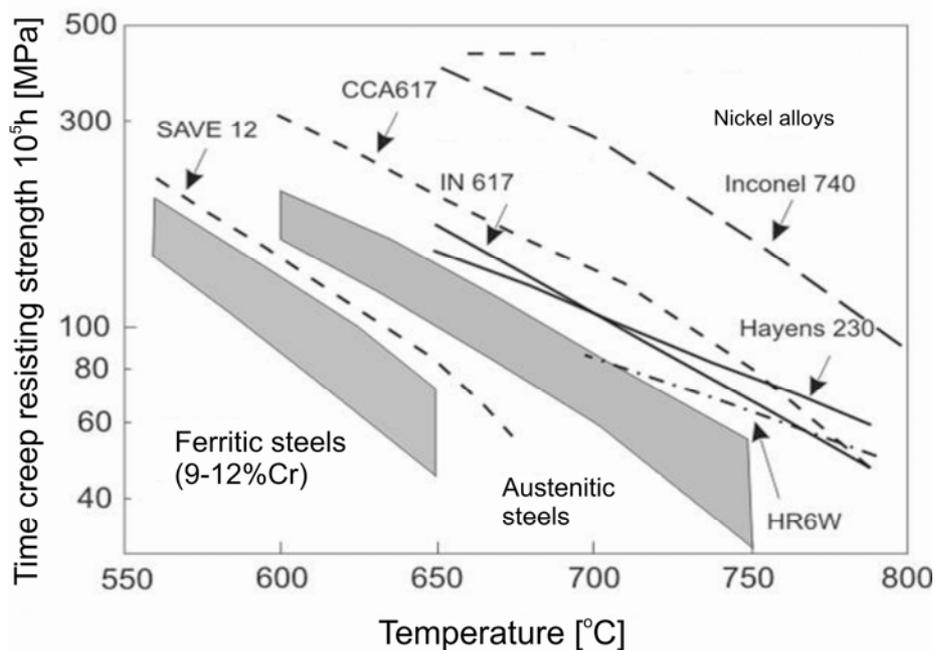


Fig. 5. Creep strength of materials used in the power industry [4]

MATERIALS USED FOR FINNED TUBES

For the manufacture of welded fin tubes are used non-alloy steels (e.g. P235) and low-alloy steels C-Mo, C-Cr-Mo in grades 15Mo3, 13CrMo4.4, 10CrMo9-10 acc. PN-EN 10216-2+A2:2007 and P91. As the material on the fin, is most often used ferritic steels such as DC01, DC03, DC04 (EN 10130) and 16Mo3 (EN 10028), X2CrTi12 (EN 10088-2). These steels are weldable steel group. Matching of materials which are used on finned tubes in the example of the waste heat boiler furnace gas, the working with thermodynamic parameters 148.6 kg/s/567°C/143.5 bar, is shown in Table 1.

Table 1. Materials used for finned tubes of the waste heat boiler furnace gas, the working with thermodynamic parameters 148.6 kg/s/567°C/143.5 bar

Module name (max. temperature of working [°C])	Temperature of medium [°C] inlet/outlet	Working pressure [bar]	Material of pipe / Material of fin
ECO (939)	171/354	260	16Mo3 / DC01A
Bank of steam tubes (897)	354	174	16Mo3 / DC01A
Superheater I part 1, 50% (482)	460	172	16Mo3 / DC01A
Superheater I part 2, 50% (536)	505	172	13CrMo4-5 / X2CrTi12
Superheater II part 1, 50% (576)	543	172	X10CrMoVNb9-1 / X2CrTi12
Superheater II part 2, 50% (623)	590	172	X10CrMoVNb9-1 / X2CrTi12
Superheater III (897)	614	172	X10CrMoVNb9-1 / Smooth pipe
Resuperheater I part 1, 50% (588)	513	40	13CrMo4-5 / X2CrTi12
Resuperheater I part 2, 50% (692)	551	40	10CrMo9-10 / X2CrTi12
Resuperheater II (780)	581	40	10CrMo9-10 / Smooth pipe

Analysis of project assumptions the supercritical units showed that the operating range of conventional steel for the power industry and martensitic steels has been out of working temperature at 650°C, due to the decrease in creep resistance and oxidation resistance. For heat exchangers working under supercritical and ultra-supercritical conditions recommends a new grades of austenitic steels and nickel superalloys. Evaluation of the mechanical properties with particular reference to the creep resistance and heat resistance indicates that a temperature of about 650°C should be used austenitic stainless steel e.g. X15CrNiSi25-21-10, X6CrNiTi18, X6CrNiNb18-10, and above this temperature nickel alloys use e.g. Inconel 600, Inconel 626, and Inconel 617.

For the sake of manufacturing finned tubes, particularly important feature of the materials used for fin tubes is their weldability. Austenitic steel are readily weld. However, it is essential to the maintenance of appropriate welding procedures to avoid problems such as hot cracking, intergranular corrosion and embrittlement due to the release of intermetallic phases. Recommended values are small linear energy and the use of additional cooling of the steel during welding. Generally, heat treatment is not required for welded joints, however, it is sometimes used to reduce the stresses in the joint, homogeneous structure and to minimize the segregation of alloying elements.

A precipitation hardened of nickel superalloys INCONEL characterized by a slightly inferior weldability because of the tendency to crack as a result of a complex state of internal stress during welding. Therefore it is recommended to use stress relieving after welding. Additives such elements as Cr, Mo, Fe, Co and Cu causes the weldability of nickel alloys is similar to austenitic steel. Additionally, the increased resistance to cracking and reduce the porosity of welded joints affected by Mn, Si, Nb, Al, Ti [29].

The test results of welding nickel superalloys and austenitic steel are positive. Fusion weld of superalloy Inconel 617 and the steel grade X15CrNiSi25-21, made with TIG method was characterized by a fully austenitic structure, and the study of impact fractures were of ductile. Welded joints in a static tensile test broke off in the base material. The use of a nickel superalloy filler material gave better mechanical properties of joint, than with the additive material in the form of steel [30].

Attempting to execute the mixed welded joints nickel/austenitic steel using laser technology have given positive results. Both of nickel superalloy and steel did not show changes in the structure and thus have not been hardened. Short periods of heating and cooling have a positive effect on hot cracking resistance. The porosity can be significantly reduced by using the protective gases. As an additional material may be used both as a nickel superalloy, and steel [31]. These results point to the desirability of the use of laser welding technology for the production of finned tubes.

SUMMARY

Modern industrial and commercial power plants are characterized by high reliability, high efficiency and minimal environmental impact. One of the applied solutions are steam-gas units with a gas turbine and a vertical or horizontal construction of the steam-water heat boiler. The use of the flue gas' enthalpy takes place in the arranged in series modular heat exchangers with finned tubes. They provide extended surface for heat transfer by convection to the working fluid (water) in order to heat or evaporate the water or generate the superheated steam. The application of finned tubes in subcritical and supercritical gas boilers significantly increases the efficiency of the system, and thus contributes to reduced fuel consumption and air pollution. The development of gas turbine technology can increase the efficiency from about 38% to 58-60% and increase temperature of the exhaust gas from 1250°C to 1400°C in ultra-supercritical boilers. It necessitates the application of austenitic steels and nickel alloys for finned tubes. Analysis of the currently used conventional materials (creep-resistant ferritic steel) and materials with enhanced creep strength and heat resistance (creep-resistant austenitic steels and nickel based alloys) indicated that X15CrNiSi25-21, X6CrNiTi18-10, X6CrNiNb18-10 and nickel alloys Inconel 600, Inconel 626 and Inconel 617 are materials with high application potential in finned tubes production.

ACKNOWLEDGEMTS

This work was supported by the project PBS1/A5/13/2012, Fri: "The technology of laser welding finned tubes of austenitic steel and nickel alloys intended for use in boilers for supercritical and ultra-supercritical" by NCBiR.

REFERENCES

1. Key World Energy Statistic 2012, International Energy Agency, <http://www.iea.org>.
2. Polish Energy Policy until 2030, Annex to Resolution No. 202/2009 of the Council of Ministers dated November 10, 2009.
3. <http://epp.eurostat.ec.europa.eu>.
4. Hernas A., Pasternak J., Brózda J., Moskal G.: Austenitic steels and nickel superalloys used in the construction of supercritical boilers and ultra-supercritical, Publisher SITPH, Katowice 2009.
5. Creep-resistant steels. F. Abe, T. Kern, R. Viswanathan [ed], Woodhead Publishing Ltd., New York, 2008.
6. Hald J.: Microstructure and long-term creep properties of 9–12% Cr steels. *International Journal of Pressure Vessels and Piping* 85(2008) 30–37.
7. Hernas A., Moskal G., Rodak K., Pasternak J.: Properties and microstructure of 12% Cr-W steels after long-term service. *Journal of Achievements in Materials and Manufacturing Engineering*, (1,2)2006 69-72.
8. Rodak K., Hernas A., Kielbus A.: Characteristics of new low-alloy steel T23 for power industry. Proc. 10th Jubilee International Scientific Conference Achievements in Mechanical & Materials Engineering, Gliwice, Cracow, Zakopane, Poland, 2001, pp. 483-486.
9. Dobrzański J., Zieliński A., Sroka M.: Microstructure, properties investigations and methodology of the state evaluation of T23 (2.25Cr-0.3Mo-1.6W-V-Nb) steel in boilers application. *Journal of Achievements in Materials and Manufacturing Engineering*, (32)2009 142-153.
10. Nagode A., Koces L., Ule B., Kosec G.: Review of creep resistant alloys for power plant applications. *Metalurgija* 50(2011) 45-48.
11. Zheng-Fei H.: Heat-resistant steels, Microstructure evolution and life assessment in power plants. [In] *Thermal power plants*, M. Rasul [ed.], Intech, Rijeka, 2012, pp. 196-226.
12. Onoro J.: Weld metal microstructure analysis of 9–12% Cr steels. *International Journal of Pressure Vessels and Piping* 83(2006) 540–545.
13. Viswanathan R., Bakker W.: Materials for ultra-supercritical coal power plants-boiler materials. *Journal of Materials Engineering and Performance* 10(2001) 81-95.
14. Arndt J., Haarmann K., Kottmann G., Vaillant J.C.: *The T23/T24 Book New Grades for Waterwalls and Superheaters*. Vallourec and Mannesmann Tubes, Chine, 2000.
15. P91/T91 Data Sheet, Thyssen Krupp Materials International http://www.s-k-h.com/media/de/Service/Werkstoffblaetter_englisch/Kesselrohre_ASTM/P91_T91_engl.pdf.

16. Material Data Sheet for HCM 12A, an Unclassified high-strength steel, including information regarding Fracture, Creep, Tensile, Elastic, Hardness, Density or mass, Thermal, Chemical composition, Heat treating, 1993.
17. http://www.smst-tubes.com/fileadmin/media/pdf_datasheets/.
18. Datasheet_DMV_347_HFG_20081118.pdf.
19. <http://www.smt.sandvik.com/en/materials-center/material-datasheets/tube-and-pipe-seamless/esshete-1250>.
20. <http://www.tubular.nssmc.com/product-services/specialty-tube/product/hr3c>.
21. <http://www.specialmetals.com/documents/Inconel%20alloy%20617.pdf>.
22. <http://www.specialmetals.com/documents/Inconel%20alloy%20625.pdf>.
23. <http://www.specialmetals.com/documents/Inconel%20alloy%20740.pdf>.
24. Nikulin I., Kipelova A., Kaibyshev R.: Effect of high-temperature exposure on the mechanical properties of 18Cr–8Ni–W–Nb–V–N stainless steel. *Materials Science and Engineering A* 554(2012) 61-66.
25. Lee B.S., Oh Y.J., Yoon J.H., Kuk I.H., Hong J.H.: J-R fracture properties of SA508-1a ferritic steels and SA312-TP347 austenitic steels for pressurized water reactor's (PWR) primary coolant piping. *Nuclear Engineering and Design* 199(2000) 113-123.
26. Vu The Ha, Woo Sang Jung, Jin Yoo Suh: Improved creep behavior of a high nitrogen Nb-stabilized 15Cr-15Ni austenitic stainless steel strengthened by multiple nanoprecipitates. *Metallurgical and Materials Transactions A* 42(2011) 3378-3385.
27. Cheng-yu Chi, Hong-yao Yu, Jian-xin Dong, Wen-qing Liu, Shi-chang Cheng, Zheng-dong Liu, Xi-shan Xie: The precipitation strengthening behavior of Cu-rich phase in Nb contained advanced Fe–Cr Ni type austenitic heat resistant steel for USC power plant application. *Progress in Natural Science: Materials International* 22(2012) 175-185.
28. Caminada S., Cumino G., Cipolla L., Venditti D., Di Gianfrancesco A., Minami Y, Ono T.: Creep properties and microstructural evolution of austenitic TEMPALLOY steels. *International Journal of Pressure Vessels and Piping* 87(2010) 336-344.
29. Yulai Xu, Heng Nie, Jun Li, Xueshan Xiao, Changchun Zhu, Junliang Zhao: Growth of creep life of type-347H austenitic stainless steel by micro-alloying elements. *Materials Science and Engineering A* 528(2010) 643-649.
30. Pilarczyk J.: *Engineers Handbook, Welding part 1*, Publisher of Science and Technology, Warsaw, 2003.
31. Shah Hosseini H., Shamanian M., Kermanpur A.: Characterization of microstructure and mechanical properties of Inconel 617/310 stainless steel dissimilar welds. *Materials Characterization* 62(2011) 425-431.
32. Dilthey U., Risch A.: Laser welding of stainless steel and stainless / low-alloy material combinations. *Welding in the World* 36(1995) 135-142.