A. NAGODE, L. KOSEC, B. ULE†, G. KOSEC

ISSN 0543-5846
METABK 50(1) 45-48 (2011)
UDC – UDK 669.14.018.298:669.18=111

REVIEW OF CREEP RESISTANT ALLOYS FOR POWER PLANT APPLICATIONS

Received – Prispjelo: 2010-02-19
Accepted – Prihvaćeno: 2010-09-19
Review paper – Pregledni rad

A paper describes the most popular alloys for power plant application as well as the most promising alloys for future application in that technology. The components in power plants operate in severe conditions (high temperatures and pressures) and they are expected reliable service for 30 years and more. The correct choice of the material is, thus, of a very importance. The paper describes the development as well as advantages and disadvantages of convenient ferritic/martensitic steels, ferritic/bainitic steels, austenitic stainless steels and the new alloys for the application at temperatures of 650 °C and more.

Key words: ferritic/martensitic steels, ferritic/bainitic steels, austenitic steels, okside dispersion strengthened (ODS) steels, power plant

Pregled slitina otpornih na puzanje za uporabu u energetskim postrojenjima. Članak opisuje najzastupljenije slitine za uporabu u energetici kao i slitine koje najviše obećavaju za uporabu u toj tehnologiji. Komponente u termoenergetskim postrojenjima rade u oštrim uvjetima (visoke temperature i tlakovi) i očekuje se da budu u radu 30 i više godina. Stoga je izbor materijala veoma važan. Članak opisuje razvoj te prednosti i nedostatke uobičajenih feritno/martenzitnih, feritno/bainitnih i austenitnih čelika kao i novih slitina za uporabu na temperaturama 650 °C i više.

Ključne riječi: feritno/martenzitni čelici, feritno/bainitni čelici, austenitni čelici, očvrsnuti disperzijom oksida (ODO) čelici, energetska postrojenja

INTRODUCTION

Creep resistant alloys designed for power plant applications like thick section boiler components, steam lines, turbine rotors and turbine castings must be reliable over long periods of time in sever environments. Besides high creep strength these materials must exhibit also other properties, i.e. good corrosion and crack resistance as well as good weldability.

The environmental impact and economics have forced a development of high efficiency and low emission systems of power plants. Namely, the increase in the thermal efficiency of power plant can be most effectively achieved by increasing the temperature and the pressure of steam entering the turbine. Hence, the new materials with better properties which can operate at these conditions have to be developed [1,2].

FERRITIC/MARTENSITIC 9-12 % CR STEELS

In last decades the ferritic/martensitic 9-12 % Cr steels have been most widespread for power plants application. For that purpose, this family of steels was firstly used in 1950´s when German alloy X20CrMoV12-1 was used for forged turbine components [4]. After the weldability problems were solved in 1957 this alloy was the most interesting for power plant application in continental Europe. Probably the most important step in development of 9-12 Cr steels was made in the middle of 70´s in previous century when 9Cr-1Mo-0.2V steel was developed in USA. This steel is by ASME known as P91 steel [3]. This steel exhibits much higher creep strength as X20CrMoV12-1 steel; however the last one has somewhat better corrosion resistance. P91 steel has low content of C and optimised content of V, Nb an N. Its composition has been used as a basic composition for further development of creep resistant alloys. Because of presence of V, Nb an N in this steel, the precipitation of MX (where X stands for C or N, while M for Nb, V) during tempering in heat treatment process as well as during later operation occurs. This precipitates act like obstacles for dislocation movement during creep. Nowadays, this steel is successfully used for temperatures up to 580 °C. Approximately at the same time in Japan were developing a new tungsten alloyed steel known as NF616 steel, or by ASME as P92 [4]. The basic concept was replacing part of Mo with approximately 1,8 % of W and addition of B. The addition of W causes solid solution strengthening as well as strengthening due to precipitation of Laves phase [5]. On the other hand, B is enriched in the $M_{23}C_6$ carbides during aging and creep, especially in the vicinity of prior austenite grain boundaries [6]. This reduces the coarsening rate

---

A. Nagode, L. Kosec, Faculty of Natural Sciences and Engineering, University of Ljubljana, Ljubljana, Slovenia. G. Kosec, Acroni d. o. o., Jesenice, Slovenia. B. Ule, IMT, Ljubljana, Slovenia.

of $M_{23}C_6$ carbides, which effectively stabilises the martensitic microstructure in the vicinity of prior austenite grain boundaries. Because of possible formation of BN precipitates it is necessary to lower the content of N in steel. Later, the pipe steel HCM 12A, which was approved by ASME under name P122 [7], has been developed. Besides W, this steel is also alloyed with Co. Co allows higher content of Cr in steel. Namely, it is known that higher concentration of Cr which is ferrite stabilising element can cause an occurrence of δ-ferrite during austenitisation. This phenomenon can be avoided by addition of austenite stabilising elements, for example: Cu, Ni or Co. While too high content of Ni can increase coarsening of $M_{23}C_6$ precipitates and thus is detrimental for creep strength [8], the addition of Cu or Co causes no problems. The developments of new steels have been continued in Europe. In the frame of Cost 501 program new alloy E911 for tubes and pipes was developed. In comparison to P92 this steel has a lower content of W since it has been found out that W can be detrimental to the stability of the microstructure of 9-12 Cr steels. Hence, the composition of E911 is based on 9 % Cr, 1 % Mo and 1 % W [4]. Figure 1 shows the maximum operating temperature in °C, based on a 10^5 h average stress rupture strength of 100 MPa.

The maximum service temperature increases with increasing complexity of the steel compositions.

It is expected that 9-12 % Cr steel could be also used to the temperatures close to 650 °C at which the Generation-IV reactors will operate. Thus, two steels, namely NF12 and SAVE12, respectively, are developing in Japan. Both of them contain 12 % Cr and approximate 0,1 % C. Content of Mo in these steels is additionally lowered, while the content of W is increased from 2,6 % to 3 %. However, the most important change according to the steels of previous generation is the content of Co. These two steels contain up to 3 % Co, which is used instead of Ni for austenite stabilisation. Ni is known that lowers the creep strength. SAVE12 steel also contains 0,04 % Nd and 0,07 % Ta. These two elements are added to form carbides. The 10^5 h creep rupture strength of NF12 and SAVE12 at 600 °C is 180 MPa [10-12].

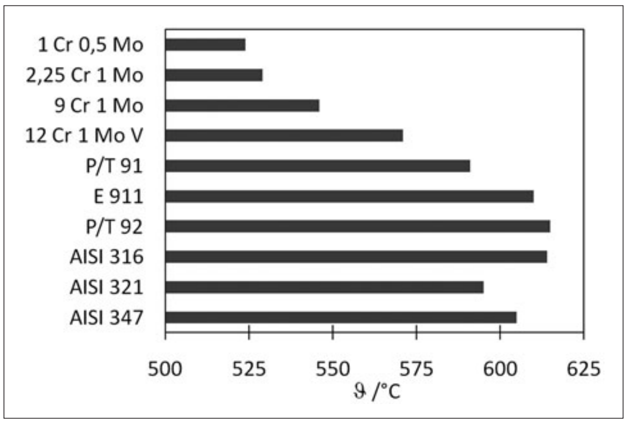

Figure 1 Stress rupture strengths of some power plants steels [9]

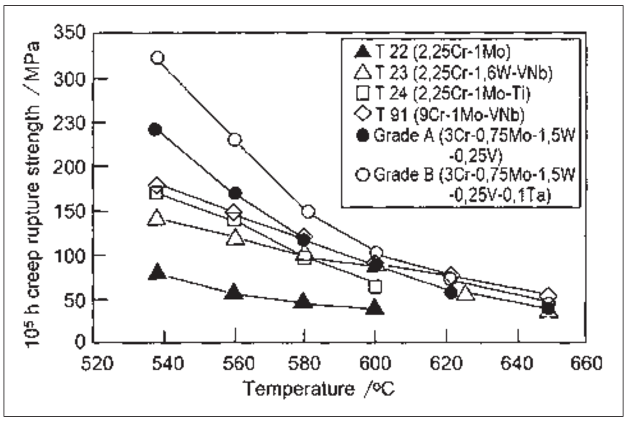

Figure 2 10^5 h creep rupture strength as a function of temperature of Grade A and B of 3 Cr-1,5W-0,75Mo-0,25V steel, comparing with T22, T23, T24 and T91 [16]

FERRITIC/BAINITIC STEELS

For the components like large water wall panel a heat treatment is very difficult. Thus, alloys which allow welding without post weld treatment has to be used. Since the standard material for water walls 1Cr-0,5Mo (ASTM T12, DIN 13CrMo44) does not longer meet the requirements of advanced boilers, the new ferritic/bainitic steels that satisfy all these requirements have been developed. One of them is T/P23 (2,25 Cr-1,6W-VNb steel, DIN 7Cr5WVNb9-6) which originates from Japan and the other is T/P24 (DIN 7CrMoVTiB10-10) which originates from Germany. The base composition for both steels was 2,25Cr-1Mo steel (ASTM T/P22, DIN 10CrMo9-10) [13, 14]. To enhance creep rupture strength, the elements V, Nb and N were added to form stable carbo-nitrides MX-type. In the case of T/P23 was added and the content of Mo was reduced [15]. The most recent success in low Cr bainitic steel is the development of 3Cr-3W(Mo) steels with higher creep strength than T/P22 steel and T/P23. Figure 2 shows the extrapolated 10^5 h creep rupture strength for T/P22, T/P23, T/P24 and 3Cr-1,5W-0,75Mo-0,25V without Ta (Grade A) and with 0,1 % Ta (Grade B) as a function of temperature. It can be seen that the creep rupture strength of Grade B steel is higher than T/P23 and T/P24 steels for entire test temperature range and also higher than T/P91 martesnitic steel up to 615 °C. Since Grade B contains 3 % Cr in comparison to P/T91 which contains 9 % Cr, Grade B has lower creep rupture strength at high temperature than P/T91. However, the grade A steel has higher creep rupture than T23 and T91 steels up to 600 °C [16].

AUSTENITIC CREEP RESISTANT STAINLESS STEELS

Austenitic stainless steels are essentially alloys of Fe-Cr-Ni which have austenitic microstructure at their room temperature. The addition of Cr improves corrosion resistance, however it is also known as a ferrite stabilising element. Thus, the addition of austenite stabilising elements is necessary for austenitic microstructure to be stable at room temperature. Nickel is the basic substitutional element used for austenite stabilisation [17].

In the evolution of austenitic steels Ti and Nb have been added to stabilise the steel from a corrosion point of view and to improve creep rupture strength. However, Cu additions increase precipitation strengthening by fine precipitation of Cu rich phase. Later developments of austenitic stainless steels have included an addition of 0,2 N and W for solid solution strengthening [18]. The highest creep strength is achieved in SAVE 25, but the fireside corrosion resistance of the alloy is controversial [19].

Austenitic stainless steels have been used as superheater tubes in harsh environments with temperature up to 650 °C at pressures of some 200 atm. However, austenitic stainless steels can only be used in power plant construction when their unfavourable physical properties do not impair the flexibility of the operation of the unit. For the thick section components such as headers and fittings in a main steam line, the use of austenitic steel is not appropriate, because the poor thermal conductivity and large coefficient of thermal expansion of these materials. For thick wall components martensitic steels would be much better choice [17].

THE ALLOYS FOR FUTURE POWER PLANTS

For the operation of power plants at temperatures above 650 °C the researchers try to develop new ferritic/martensitic steels. One of the newest is 9Cr-3,3W-0,2W-0,05Nb-0,05N-0,08C steel which contains 1 – 3 % Pd. This steel is strengthened by Ll_0-type ordered phase which formed coherently in the matrix [20]. The second example is ferritic steel with 15 % of chromium with a base composition of Fe-0,1C-15Cr-1Mo-3W-0,2V-0,05Nb-0,07N-0,003B was alloyed with up to an additional 3 % W and 3 % Co. In this way steel with very high creep strength attributed to non-identified precipitates was developed [21]. Also low-carbon 9Cr-3W-3Co-VNb steel with 0,05% N exhibits improved creep strength due to nano-sized MX carbonitrides along prior-austenite grain boundaries and lath boundaries [22]. Figure 3 shows the creep rupture data for 9Cr-3W-3Co-VNb steel with 0,05N-0,0002C (0,002C steel) and with 0,08C-0,0139B (0,0139B steel) in comparison to ferritic/martensitic P/T91 and P/T92 steels, ODS steel and new 9-12 % Cr steels, namely, NF 12 and SAVE12 steel. At 700 °C carbon-free martensite alloy Fe-11,0Ni-0,5Cr-10,0Mo-0,20Ti-0,12Al-0,005B shows excellent creep properties. However, all of these alloys are still in the testing phase.

For the temperatures beyond 650 °C the oxide dispersion-strengthened (ODS) ferritic steels have been also developing in the last few years. Since it exhibits good high temperature properties and radiation-resistance they have been considering in the planning for Generation-IV reactors as well as for the conventional power-generation industry [23]. The first ODS steels consist of low-carbon, high-chromium (12-17 % Cr) non-transformable ferrite matrix with high number density of small titania (TiO_2) and/or yttria (Y_2O_3) particles as the strengthening dispersion. The examples of such steels are DT2906 with a base composition of Fe-13Cr-1,5Mo-2,9Ti-1,8Ti_2O_2 and DT2203Y05 with a base composition of Fe-13Cr-1,5Mo-2,2Ti-0,9Ti_2O_3-0,5Y_2O_3. Improved creep strength at elevated temperatures is provided by a dispersion of fine titania and yttria particles and by χ-phase that forms at grain boundaries. In the newest ODS steels Mo is replaced with W and dispersion of yttria with lower concentration of Ti is used. One of the examples is 12YWT (12,29Cr-3W-0,39Ti-0,248Y_2O_3) [23].

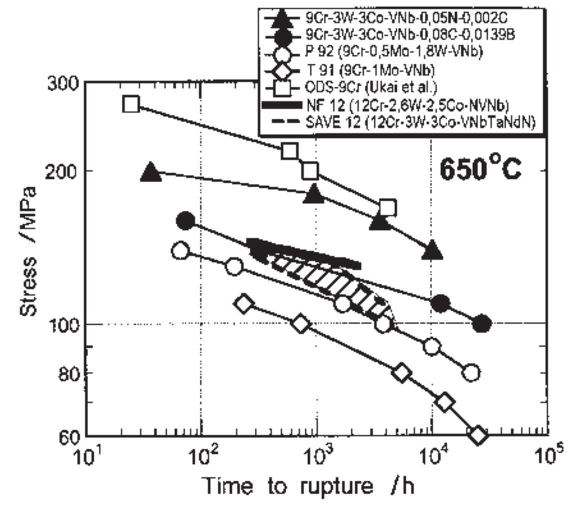

Figure 3 Creep rupture data for 0,002C and 0,0139B steels with 9Cr-3W-3Co-VNb base composition [16]

The problem of ODS steels lies in the anisotropy of mechanical properties because of the processing procedures used to form the steels [24]. In an effort to remove an isotropy a heat treatment at 1100 °C and higher is used. At this temperature a recrystalisation of the microstructure occurs. Creep rupture data for ODS-9Cr in comparison to some other creep resistant alloys is shown on Figure 3.

For steam power plants that operate at temperatures of 700 °C and higher nickel-base alloys have been developing [25]. In Europe development of materials for boilers and steam pipes for these temperatures is being carried out within AD700 project. The main goal is an increase in efficiency of power plants from around 47 % to around 55 % which would also decrease the carbon dioxide emission of almost 15 %. Most modern-day nickel based alloys have been developing from a relatively simple Ni20%Cr alloy. In order to achieve desirable creep properties of these alloys further strengthening through solid solution or dispersion strengthening is needed. Solid solution strengthening is achieved by addition of Mo, W, and Co. The examples of these alloys are alloys 230 and 617 which are relatively easy to weld and heat treated. However, the proof strength of these alloys is relatively low. Thus, the addition of Ti and Al in these alloys is a necessary to improve proof strength and creep strength due to the gamma prime precipitates. The example of such alloy is alloy 263. However, the additions of Ti and Al are limited because of the lowering the ductility due to the precipitates that can cause cracks in the heat effecting zone (HAZ). An alternative approach to precipitation strengthening is alloying with Nb, leading to more sluggishly precipitated gamma double prime. For better corrosion resistance is necessary to alloy with chromium, while an addition of iron lower the cost of nickel-based alloys. The examples of nickel-based alloys with significant content of iron are alloys 718 and 901 [25]. The main problems with Ni-based alloys would be the radiation embitterment.

Refractory metals (such as, Nb, Mo, Ta, etc.) have high melting temperature (> 200 °C), good creep resistance and good mechanical properties at temperatures above about 600 °C. Hence, they should be potent ional materials for high temperature applications [23]. Since they have poor oxidation rate and they are keen on radiation embitterment are not being considered for Generation-IV applications [26].

SUMMARY

The environmental protection and economics have been driving force for development new alloys with improved creep strength, better corrosion and crack resistance and good weldability. Thus, significant advances have been made in developing of creep resisting materials. The 10^5 h creep rupture strength of ferritic/martensitic steels at 600 °C has increased from about 35 MPa to 180 MPa in last few decades and the operating temperature is 50 °C – 100 °C higher. Besides ferritic/martensitic steels also ODS ferritic steels and nickel based alloys are also very promising for power plants operating at temperatures beyond 650 °C or even higher (700 °C). The efficiency of power plant would increase to around 55 % and the CO_2 emission would decrease for almost 15 %. The austenitic stainless steel, on the other hand, poses high corrosion resistance and mechanical properties at higher temperatures; however, due to the poor thermal conductivity and large coefficient of thermal expansion they are not appropriate for thick components.

REFERENCES

[1] K. Sawada, K. Kimura, F. Abe, Materials Science and Engineering, A358 (2003), 52-58.

[2] H.C. Furtado, L.H. de Almeida and I. Le May, Materials Characterization, 58 (2007), 72-77.

[3] V.R. Blum, J. Hald, W. Bendick, A. Rosselet, J.C. Vaillant, VGB Kraftwerkstechnik, 74 (1994), 641–652.

[4] J. Hald, Steel Research, 67 (1996) 9, 369–374.

[5] F. ABE, Key Engineering Naterials, 171-174 (2000), 395-42

[6] K. Spiradek, R. Bauer, G. Zeiler, Microstructural changes during the creep deformation of 9% Cr-steel in Materials for Advanced Power Engineering, D. Coutsouradis et. al., Eds., Kluwer Academic Publishers, Dordrecht, 1994, 251–262.

[7] Y. Sawaragi, A. Iseda, K. Ogawa, F. Masuyama, T. Yokoyama, in Proc. New Steels for Advanced Plant up to 620 °C. Edited by E. Metcalfe, London, 1995, EPRI, USA, 45–55.

[8] A. Strang, V. Vodarek, Scripta Materialia, 38 (1998), 101–106.

[9] P.J. Ennis, W.J. Quadakkers, 9–12 % chromium steels: Application limit and potential for further development in Parsons: 2000 Advanced Materials for 21st century turbines and power plants. A. Strang et. al., Eds., Book 736: The Institute of Materials, London, 2000, pp. 265–275.

[10] J. Bernetič, B. Bradaškja, G. Kosec, E. Bricelj, B. Kosec, F. Vodopivec, L. Kosec, Metallurgy, 49 (2010) 1, 29-32.

[11] R. Viswanathan, W. Bakker, Materials for Ultrasupercritical Coal Power Plants-Boiler Materials: Part I. Journal of Materials Engineering and Performance, 10 (2001), 81–95.

[12] R. Viswanathan, W. Bakker, Materials for Ultrasupercritical Coal Power Plants-Boiler Materials: Part II. Journal of Materials Engineering and Performance, 10 (2001), 96–101.

[13] J. Arndt, K. Haarmann, G. Kottmann, J.C. Vaillant, The T23/T24 Book, New Grades for Waterwalls and Superheaters, Vallourec & Mannesmann Tubes, 1998.

[14] B. Kosec, L. Kosec, J. Kopac, Engineering Failure Analysis, 8 (2001) 5, 355-359

[15] W. Bendick, J. Gabrel, B. Hahn and B. Vandenberghe, Int. J. Press. Vess. Pip. 84 (2007), 13-20.

[16] F. Abe, Current Opinion in Solid State and Materials Science 8 (2004), 305-311.

[17] T. Sourmail, Literature review - Precipitation in creep resistant austenitic stainless steels, Materials Science and Technology, 17 (2001), 1-4.

[18] A. Sundstrom, G. Chai, Heat resistant austenitic stainless steel, Patent No.: US 6,485,679 B1 (26.11.2002.).

[19] R. Wiswanathan, J. Sarver, J.M. Tanzosh, Journal of Materials Engineering and Performance, 15 (2006) 3, 255-274.

[20] M. Igarashi, Y. Sawaragi, In Proceedings International Conference of Power Engineering. Tokyo, 1997, vol. 2, 107–112.

[21] K. Kimura, K. Seki, Y. Toda, F. Abe, ISIJ International Supplement, 4 (2001), 121–129.

[22] M. Taneike, F. Abe, K. Sawada, Nature, 424 (2003), 294–296.

[23] K.L. Murty, I. Charit, Journal of Nuclear Materials, 383 (1-2) (2008), 189-195.

[24] S. Ukai, M. Harada, H. Okada, M. Inoue, S. Nomura, S. Shikakura, K. Asabe, T. Nishida, M. Fujiwara, J. Nucl. Mater., 204 (1993), 65–73.

[25] R. Blum, R.V. Vanstone, Materials development for boilers and steam turbines operating at 700 °C. In Parsons 2003: Engineering Issues in Turbine Machinery, Power Plant and Renewables. A. Strang, R. D. Conroy, W. M. Banks, M. Blacker, J. Leggett, G. M. McColvin, S. Simpson, M. Smith, F. Starr in R. W. Vanstone, Eds., Maney for the Institute of Materials, Minerals and Mining, 2003, 498–510.

[26] R. E. Gold, D. L. Harrod, J. Nucl. Mater., 85- 86 (1979), 805-815.

Note: The responsible translator for English language is Urška Letonja, University of Ljubljana.