ADVANCED HIGH CHROMIUM FERRITIC STEELS FOR BOILER COMPONENTS OPERATING AT HIGH TEMPERATURE

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Abstract - **In the last 15 years Dalmine and Centro Sviluppo Materiali (CSM) have worked together to develop the high Chromium ferritic steels for tubes and pipes to manufacture high temperature boiler components used in new high efficiency power plants.**

The activities started in 1985 with the development of P/T91 process and metallurgy, in the frame of ECSC project, followed, in 1994, by the evolution of P/T91 with the addition of 1% W. This new European steel called E911 was introduced during the COST 501 European Programme to improve the high temperature mechanical properties.

This paper describes the process routes and compares the mechanical and creep behavior of the two grades as well as the evolution of microstructure and precipitates after aging.

Keywords - **high chromium ferritic steel, creep, microstructure evolution, boiler material.**

I. INTRODUCTION

The development of the family of 9-12%Cr martensitic steels for power generation components has been a significant feature in the 1980s. However, the basic compositions of 9Cr1Mo have been widely used for many years. The driving force for new developments has been the need to increase the temperature and pressure of the steam circuit.

The Steel Grade P91, which has the base composition of 9%Cr 1%Mo with additions of niobium, vanadium and nitrogen, developed in the ORNL Research Laboratories, has provided a platform for further developments in Japan (Naoi *et al.*,1995; Sawarahi *et al.*, 1995). In Europe, a new steel called E911 derived from the Grade 91 (9Cr1MoNbVN) with the addition of 1% W was developed in the frame of the programme COST 501 Round III WP11.

The aim of this paper is to present the work carried out by Dalmine and CSM to develop and qualify P91 and E911 in terms of mechanical properties and microstructure evolutions (Di Gianfrancesco *et al.*, 1996).

II. MATERIALS

External qualified suppliers manufactured ingots of the two grades: Cogne for P91, UES (United Engineering Steel, UK) for E911.

The chemical compositions are shown in Table I. Dalmine has manufactured the pipes with the following process route:

- ingot heating at 1300°C;
- partially boring on a horizontal press;
- piercing;
- rolling at the pilger mill;
- heat treatment (Grade E911 = normalizing 1060°C/air + tempering 760°C; Grade 91 = normalizing 1040°C/air + tempering 740°C);
- finishing operations;
- machining.

A. Characterization of the as treated material

The E911 transformation temperatures have been evaluated by dilatometer. As shown in Table II they are higher than for steel P91.

Grade	C	Si	Mn	P	S	Cr	Mo
P91	0.10	0.45	0.50	0.019	0.002	9.12	0.96
E911	0.11	0.20	0.35	0.007	0.003	9.16	1.10
	Ni	Nb	V	Al	W	N	
P91	0.05	0.060	0.21	0.004	-	0.040	
E911	0.23	0.068	0.23	0.007	1.0	0.072	

Table I: Chemical composition of steels (wt %).

Material	A_{c1} (°C)	A_{c3} (°C)
P91	815	865
E911	841	948

Table II: Transformation temperature.

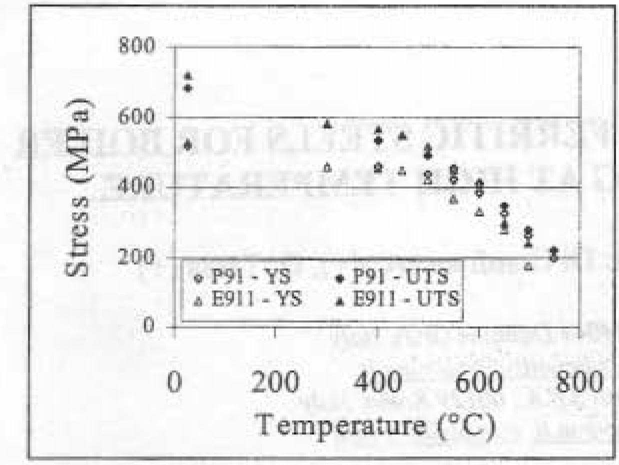


Fig.1: Tensile properties of the P91 and E911 pipe versus temperature.

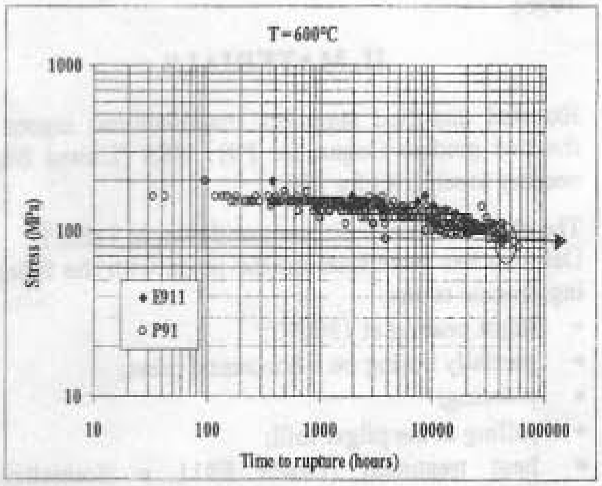


Fig. 2: Isothermal curves of Grade 91 and 911 pipes at 600°C.

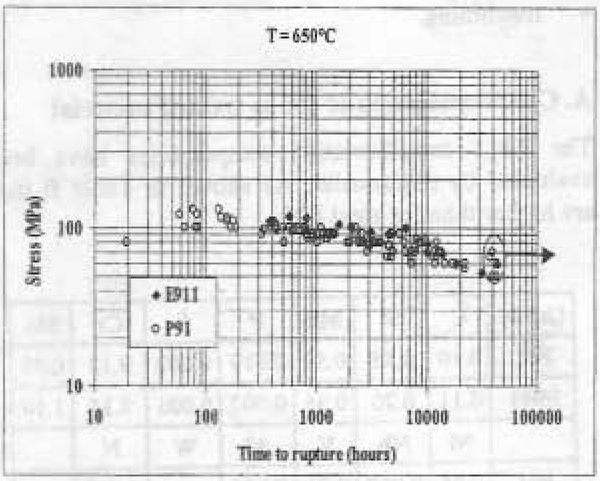


Fig.3: Comparison of E911 and P91 creep behavior at 650°C.

The tensile properties from room temperature up to 700°C are shown in Fig. 1 for both the steels.

B. Creep tests

Creep tests have been carried out on pipes in the range 550 - 650°C. Creep rupture tests have now reached

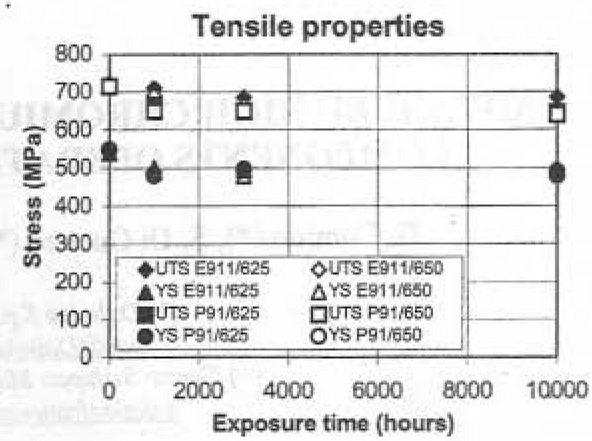


Fig. 4: Effect of exposure time on tensile properties of E911 and P91.

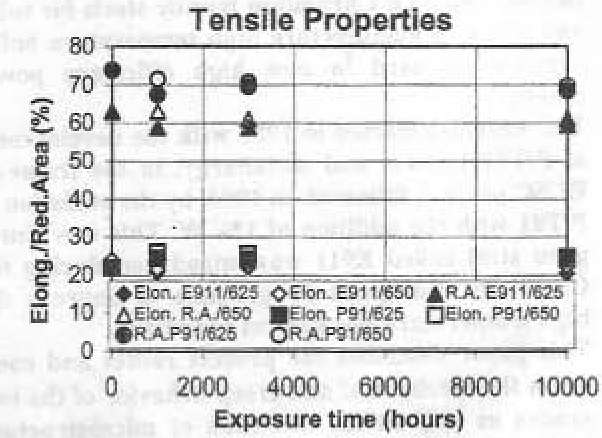


Fig. 5: Effect of exposure time on ductility of E911 and P91.

40000 hours for E911 and P91 at 650°C. The oldest creep specimen still running for P91 at 550°C has reach 89000 hours. Figs 2 and 3 show a comparison between the behavior of E911 and P91 pipes at 600°C and 650°C respectively.

The ductility of both materials decreases just a little after 15000 hours for the specimens tested at higher temperature, but in any case, up to now the elongation to rupture is still more than 17 % and the reduction of area is more than 50%. The lowest values of the reduction of area were found at the highest test temperature (650°C).

C. Mechanical Testing of Aged Materials

Grade E911 and P91 materials have been subject to a long-term exposure in order to evaluate the variation in tensile and impact properties at room temperature. This has been made after an isothermal exposure of the materials at 625 and 650 °C up to 1000, 3000 and 10000 hours made by an electrical laboratory furnace showing a maximum temperature deviation in the chamber of ± 4 °C. The results of the tests are summarized in Figs 4-7.

The results of the long-term exposure show:

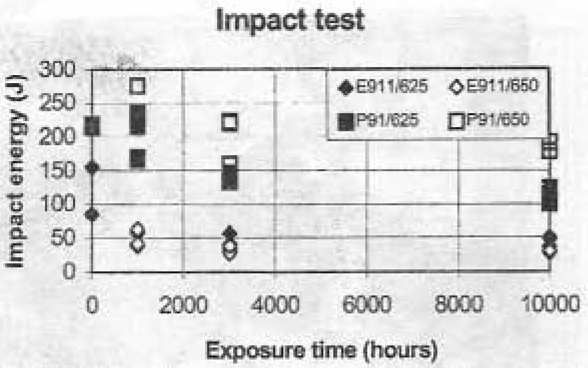


Fig. 6: Effect of exposure time on absorbed energy of E911 and P91.

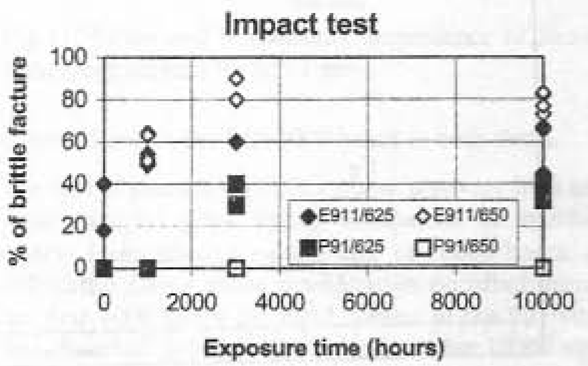


Fig. 7: Effect of exposure time on brittle Fracture of E911 and P91.

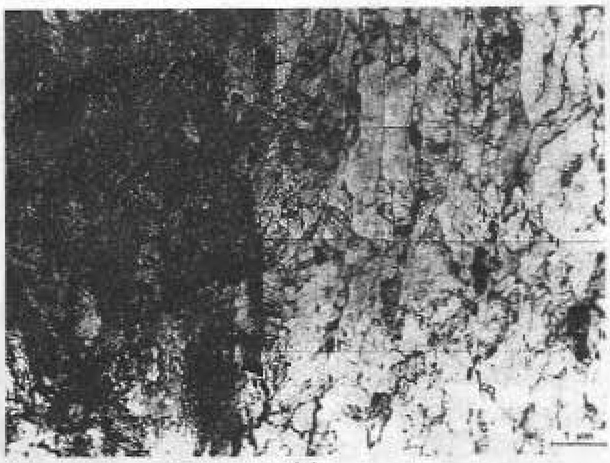
- a 10% maximum reduction of the tensile properties after 1000 hours (Fig. 4),
- a constant values of ductility (Fig. 5),
- a strong reduction of the impact properties during the first 3000 hours of exposure (Fig.6) with an increase of % of brittle fracture (Fig.7).

After the same long-time exposure, steel P91 shows a similar trend in term of tensile properties, but impact properties of P91 keep always better than E911.

D. Microstructural Evolution

STEM investigations on thin foils under the as received and aged conditions, have been performed on both steels E911 and P91. The aim was to characterize the evolution of the tempered martensite and to determine the different types of second phase, the dimensional distribution of different types of precipitate and their composition evolution with ageing treatment. Quantitative analysis on automatic image analysis system, X-ray diffraction and EDS microanalyses have been carried out by extraction replicas. The microstructures of the as treated materials are presented in Fig. 8.

Fig. 9 show an evident recovery process due to formation of subgrains, with a reduction of the dislocation density, that replace gradually the original martensite laths. The rate of the recovery process, rather similar



(*a*)

(*b*)

Fig.8: TEM microstructure (scale, 1 μm) of as received materials: (*a*) P91 steel, (*b*) E911.

for both the steels at 625°C, is faster for E911 steel at 650°C, in which the transformations of martensite laths to subgrain is complete after 1000 hours.

Nevertheless the retained high dislocation density is connected with a stable microstructure also in the more aged structures.

In all the samples, the MX type carbide or carbonitride rich in vanadium and niobium were observed primarily precipitated on dislocations inside the subgrains, although it was difficult detect them because of their very small dimensions. They are rather stable in terms of composition and size with increasing ageing time. The $M_{23}C_6$ carbides detected in all the samples are observed predominantly on subgrain boundaries. Both steels show the coarsening of the $M_{23}C_6$ carbides, with an increase of the size from an original value of 200 nm up to 400 nm after 10000 hours of ageing at 650°C. The extensive quantitative microanalysis in-

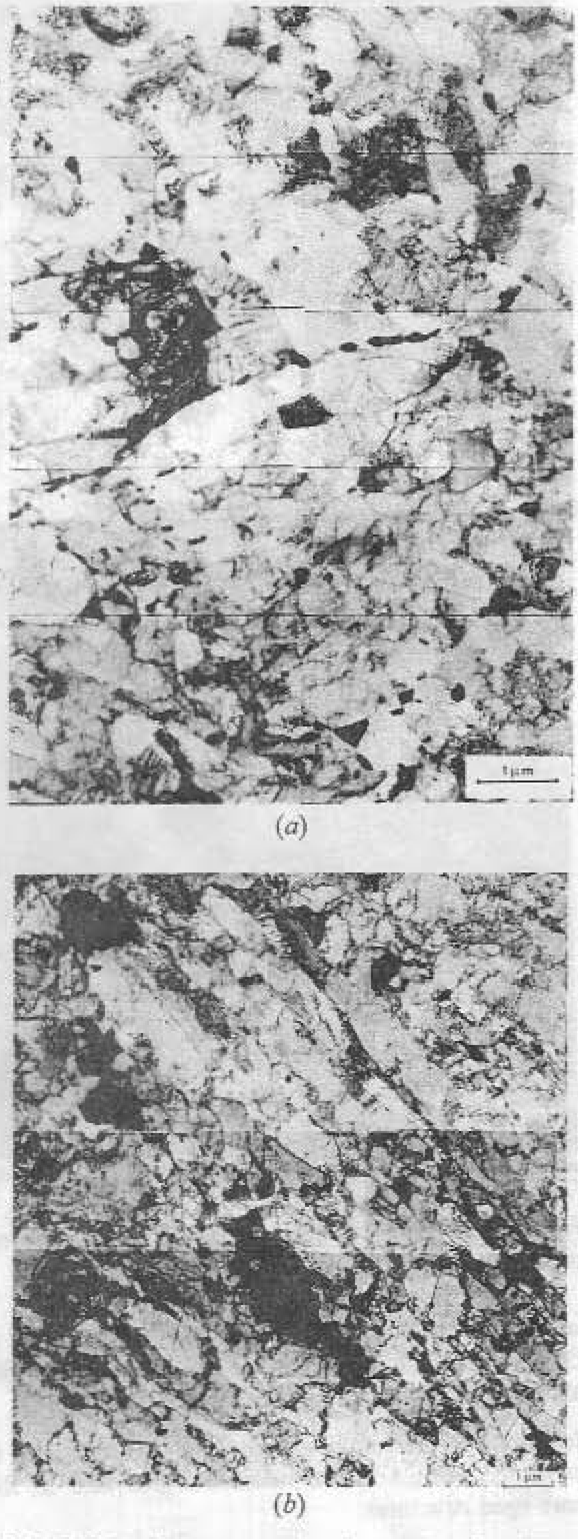

(a)
(b)

Fig.9: TEM microstructure (scale, 1 μm) of aged materials at 650°C steel for 10000 hours: a) E911, b) P91 steel.

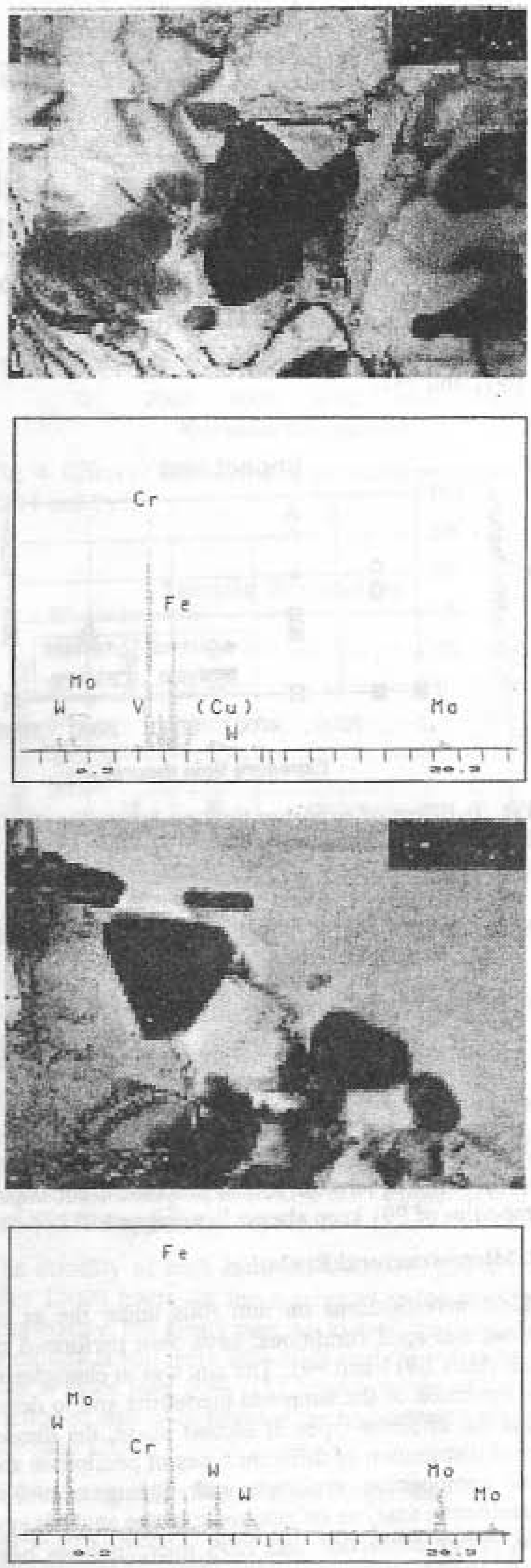


Fig.10: $M_{23}C_6$ and Laves phase particles with EDX spectrum in grade P91 and E911 steels.

vestigation shows that the relative amount of Fe, Cr, Mo and W in the $M_{23}C_6$ carbides varied as a function of the carbide size. Particularly the Mo content increased with the size, and a tendency to an enrichment in Cr appears with increasing the ageing time. An EDX spectrum of $M_{23}C_6$ carbides in P91 and E911 steels respectively is shown in Fig.10.

The precipitation of the intermetallic Laves phase $(Fe,Cr)_2(Mo,W)$ during ageing represents the most relevant microstructure change. The particles of Laves phase are localised at the subgrain boundaries and often these precipitates are associated with $M_{23}C_6$ carbides. At 625°C the nucleation of the Laves phase is

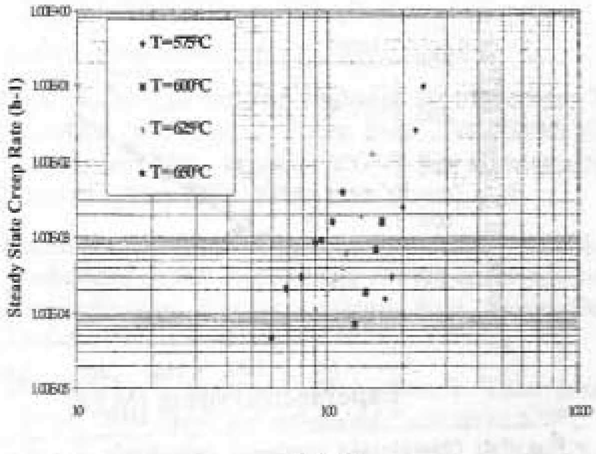


Fig.11: Stress and temperature dependence of steady state creep rupture for E911 steel.

observed just in the first 1000 hours in both steels.

The rate of coarsening of this phase was very high and these particles grow up to dimensions of approximately 1 μm after an ageing time of 10000 hours. At 650°C the Laves phase precipitation occurred during the first 1000 hours for E911, where in the P91 steel was observed only after 3000 hours. After 10000 ageing hours the Laves phase in both steels reached micron sizes. In Fig 10 the typical EDX spectra of Laves phase particles in P91 and E911 steels are shown.

III. DISCUSSION

The stress dependence of the minimum creep rate (Fig. 11) can be described by a well-known equation of the form

$$\varepsilon_s = A\sigma^n e^{-\frac{Q}{KT}} \qquad (1)$$

where A and n are constants at given temperature, σ is the applied stress and Q represents the apparent activation energy. The value of the mean stress exponent n is related to the operating mechanism of creep deformation. This equation can be used for the estimation of Q and n separately for low stress and high stress domains and the values calculated for E911 are reported in Table III.
The stress exponent n, calculated by means of all the data, decreases with increasing temperature. The observed values are ranging between 15 at 575°C and 5 at 650°C.

The activation energy calculated by Eqn. (1) gives a Q value of 552 KJ/mol. The values of Q and n calculated in the present work on E911 steel agree with found values for P91 steel reported in (Slenicka *et al.*, 1994). Nevertheless two distinct domains of the stress dependence of creep rate are observable in agreement with the case of precipitation strengthened low alloy and modified Cr steels (Slenicka *et al.*, 1994; Nishimura *et al.*, 1994; Foldyna *et al.*, 1996). This behavior

	Low and High stress domains	High stress domain $\sigma \geq \sigma_{z(T)}$	Low stress domain $\sigma \leq \sigma_{z(T)}$
T (°C)	n	n	n
575	14.9	19.0	7.5
600	7.0	12.4	3.3
625	7.8	13.7	5.1
650	6.2	9.7	5.0
Q (KJ/mol)	552	912	458

Table III: Calculated mean value of stress exponent n and apparent activation energy for E911 steel.

is also confirmed in E911 steels and the calculated n and Q values for both the domains are reported in Table III. According to literature the value of $n = 19$ for high stress domain and $n = 5$ for low stress domain have been determined. With increasing temperature the low stress domain becomes more important and the difference between two domains is smoother. The activation energies calculated in the low and high stress domains are respectively of 458 and 912 KJ/mol. The differences in n and Q are thought to result from the different dislocation process operating at high and low stress. As reported in literature at high stress regions the dislocations can overcome particles of secondary phases by Orowan mechanism while at low stress a climb mechanism is predominant (Foldyna *et al.*, 1996).

The dependence of n and Q on temperature and stress can be related to the microstructure evolution during the creep that is principally the precipitation of Laves phase and the particle coarsening. The precipitation of Laves phase in the first period of creep exposure that increases the strengthening due to the precipitation give a reason of the high n and Q found values. The particle coarsening, correlated to a long time exposure at high temperature, becomes the predominant effect at low stress. The resulting strengthening loss can explain the reduction of n and Q.

The procedure used for the assessment of the creep rupture data to extrapolate up to time to rupture of 10^5 hours is based on the Larson Miller parametric equation:

$$P_{LM} = f(\sigma) = T(°K)(C_{LM} + \log t_r) \qquad (2)$$

where C_{LM} is a constant, t_r is time to rupture. The procedure used is based on the assumption that the stress dependence of P_{LM} can be described by a polynomial stress dependence in the form:

$$\log(\sigma) = a + b(P_{LM}) + c(P_{LM})^2 + d(P_{LM})^3 + e(P_{LM})^4, \qquad (3)$$

By using all the experimental data, at high and low stress domains, the calculated C_{LM} for the E911 and P91 steels are respectively 31.9 and 31.3. In Fig. 12

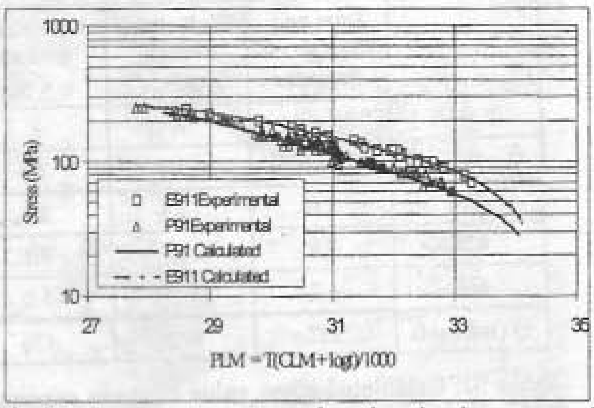


Fig.12: Creep rupture strength estimation by means of LM parametric equation.

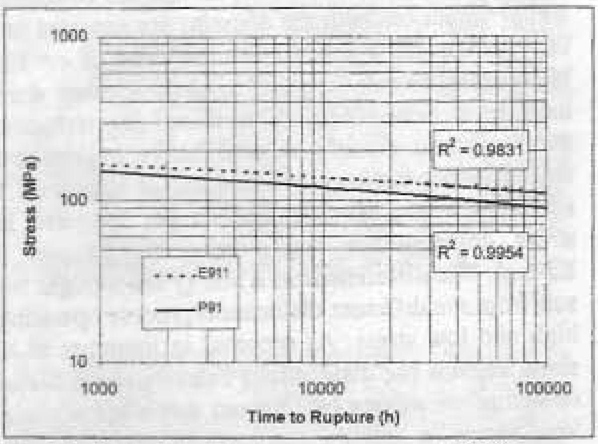


Fig. 13: Calculated isothermal curves at 600°C.

the results of creep tests in the form of stress to Larson-Miller parameter is shown.

By using the above values of the constant C_{LM} a preliminary extrapolation of the base material creep results with the data at this moment available, shows at 600°C a stress of 105 MPa to have the rupture in 10^5 hours, instead of 94 MPa for the P91, with a possible increase of about 10 Mpa. In Fig. 13 the isothermal curves at 600°C are reported for the both P91 and E911 for comparison. As suggested by (Foldyna *et al.*, 1996) the prediction of long-term stress rupture should be more correct if the constant C_{LM} is calculated taking into account only the experimental results obtained at low stress domains. In effect the data for E911 steel are not yet enough to give a reasonable extrapolation by taking in account only the low domain stress data.

In Fig.14 a very good agreement is shown between calculated stresses and the experimental values to obtain similar time to rupture.

The higher resistance of E911 steel is related to the addition of W, which is completely in solid solution in the ferrite only for short time tests. The presence of Laves phase, that produces a loss of Mo and W in the ferrite, is normally connected with a loss of creep strength due to the precipitation of this intermetallic phase. The creep results for E911 at 625°C and 650°C

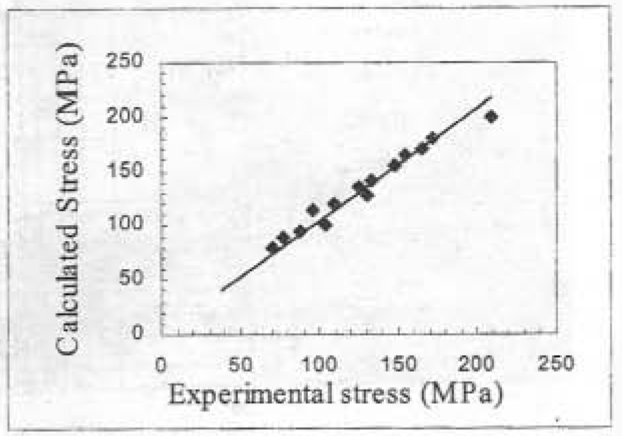


Fig. 14: Correlation between calculated and experimental creep rupture stresses.

and after 1000 when the Laves phase is just precipitated show a higher creep resistance of this steel with respect to the P91 steel. As suggested by Hald (1995, 1996), the highest creep resistance cannot be associated with the solution strengthening of W but it is due to the beneficial effect of the precipitation of Laves phase that increase the total volume fraction of secondary phases and can contribute to the precipitation strengthening.

The loss of ductility observed after time to rupture of 15000 hours particularly at 650°C can be associated to the increased size of these precipitates that grow up to dimensions at around 1μm.

IV. CONCLUSIONS

The mechanical properties such as tensile, hardness toughness and creep rupture strength have been discussed for the new steel Grade E911, in comparison with the Grade P91.

The tensile and creep rupture properties of E911 appears to be higher than the values measured on P91. E911 presents however a limited loss of ductility for creep test at 650°C after time to rupture of 15000 hours that can be associated with the coarsening of Laves phase, as suggested by the results of the microstructure analysis. By considering that this steel has been developed for application temperature of 600°C, where the coarsening process is slower than observed at 650°C, the microstructure stability of E911 steel can be guaranteed in terms of precipitation state.

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