

MICROSTRUCTURAL STABILITY AND CREEP DATA ASSESSMENT OF TENARIS GRADES 91 AND 911

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ABSTRACT

The availability of long term creep tests is mandatory to perform reliable data assessment for rupture up to 10^5 hours and more, which are very important for the designer of the components for high temperature service. An advanced characterization of the microstructures for the high chromium content steels is necessary to confirm and guarantee that such steels are not affected by unexpected breakdowns of the creep properties due to microstructure instability. This paper summaries the activities carried out on TenarisDalmine grades 91 and 911 in the last two decades to qualify a large range of products obtained also by different process routes. The results of the creep assessments of the two steels, compared also with the recent result issued by ECCC, confirm the performance of the TenarisDalmine products up to 10^5 hours and more, as confirmed also from the high microstructural stability of both steels.

KEYWORDS: 9-12%Cr steels, long term creep stability, microstructure evolution, Laves phase, creep data assessment

INTRODUCTION

In the last two decades the need of emission reduction has generate the design of new advanced power plant with higher efficiency. Consequently the pressure and temperature service conditions of components in the boilers and in the turbines are highly increased and more severe requirements on strength, corrosion resistance, fatigue and creep properties are requested for high temperature steels.

To face up these requirements, several new 9-12%Cr martensitic steels were developed and some of them, such as ASTM Grades 91, 92 and 911 are currently used in new Ultra Super Critical power plants up to 620°C.

TenarisDalmine and Centro Sviluppo Materiali (CSM) in the last 20 years have worked together to develop the production of tubes and pipes for boiler components: Grade 91 and 911 and more recently the production of Grade 92 for the high Cr steels and low alloyed Grades 23 and 24 for the waterwalls.

Tenaris experience on Grade 91 production started in 1985, when the first Italian heat of this steel was hot rolled and seamless tubes and pipes were manufactured. This activity was carried out within an European Coordinated Project sponsored by ECSC (European Coal and Steel Community) [1]. The production of Grade 911 started in TenarisDalmine in 1991 in the frame of the COST 501 Program, Round III [2].

TenarisDalmine has continuously increased and enlarged the tube and pipe production, through the optimisation of the process routes, the heat treatment procedures and the material properties of both Grades.

Over the years, the long term material properties in terms of strength and long term creep behaviour have been evaluated on the base of a large database to generate consistent assessment up to 10^5 hours and more.

Also the microstructural evolution of the steels was investigated by an extensive program of Transmission Electron Microscopy (TEM/STEM) analyses on aged samples, taken from broken creep specimens up to 100,000 hours and 64,000 hours, respectively for Grades 91 and 911.

The aim of this paper is to discuss and compare the results on microstructure evolution and creep behaviour of Grades 91 and 911.

PRODUCTION ROUTES

The chemical compositions of ASTM Grades 91 and E911 are shown in Table I.

The tubes and pipes are produced by TenarisDalmine in different mills according to their sizes; heavy wall pipes are produced by pilger mill. The industrial products comply with ASTM Standard (A213 and A335). Tubes and pipes of both Grades 91 and 911 are normalized in the range of 1040°C-1090°C and tempered in the range of 740°C-780°C, depending on components size.

Table I - Chemical composition range of ASTM Grades 91 and 911 (weight %)

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Nb	V	Al	W	N	B	
Grade 91	min	0.08	0.20	0.30	/	/	8.00	0.85	/	0.06	0.18	/	/	0.030	/
	max	0.12	0.50	0.60	0.020	0.010	9.50	1.05	0.40	0.1	0.25	0.04	/	0.070	/
Grade E911	min	0.090	0.10	0.30	/	/	8.50	0.90	/	0.060	0.18	/	0.90	0.04	0.0003
	max	0.130	0.50	0.60	0.020	0.010	10.50	1.10	0.40	0.100	0.25	0.040	1.10	0.09	0.0060

MICROSTRUCTURE

The CCT diagrams of Grades 91 and 911 are shown respectively in Figures 1 and 2.

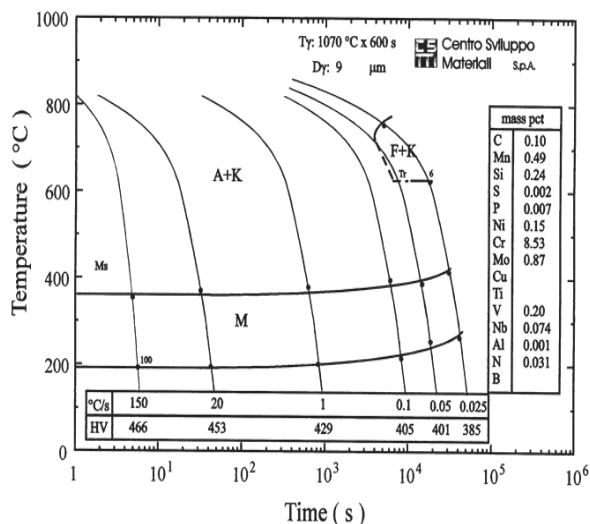


Figure 1 – CCT diagram of Grade 91

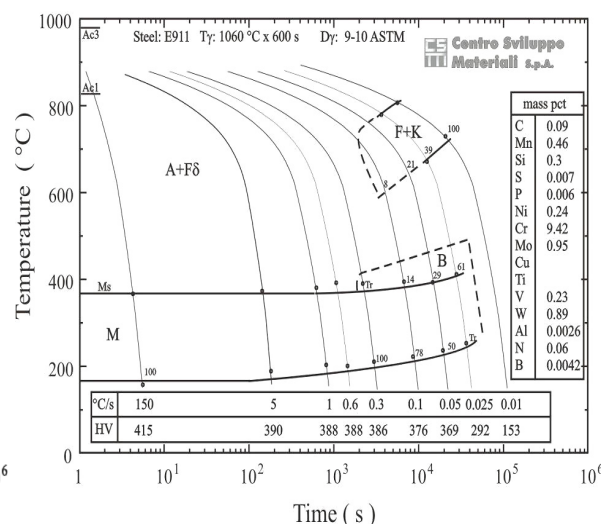
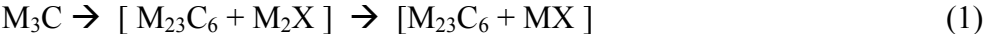


Figure 2 – CCT diagram of Grade 911

In both steels a martensitic microstructure is achieved by cooling from normalising temperature in a very wide range rates >0.2 °C/s. The microstructures are characterised by hardness values between 405-460 HV, depending on component thickness. In order to comply to ASTM and obtain a good compromise among creep resistance, toughness and ductility (i.e. cold formability), tubes and pipes were finished in normalized and tempered conditions. The normalizing treatment produces the desired martensitic microstructure and provides a good

carbide and nitride solubilisation into the matrix. With the subsequent tempering the martensite is recovered and the precipitation of $M_{23}C_6$ carbides and fine MX carbo-nitrides is promoted, according to the following precipitation sequence [3-6]:



The microstructures of Grade 91 and Grade 911 pipes after normalizing and tempering are respectively shown in Figure 3-a and 3-b. It can be observed that a small amount of delta-ferrite (δ -F) is present in 911 steel (<3%).

The quantity of δ -F which forms as a function of temperature was measured with laboratory heat treatments: the normalization at 1060°C gives the minimum amount of ferrite (Figure 4).

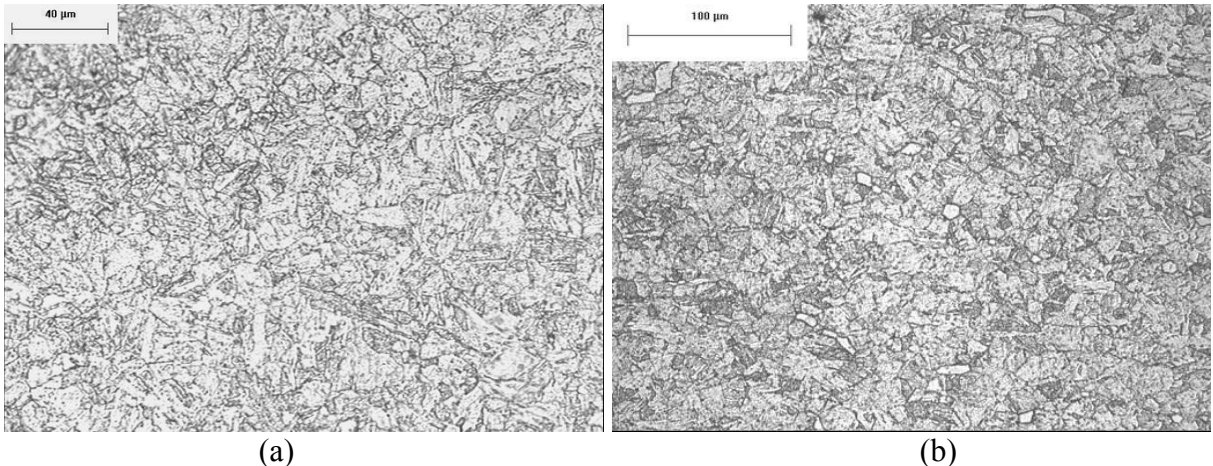


Figure 3 – Samples of (a) Grade 91 after 1070°C+780°C and (b) Grade 911 after 1060°C+780°C

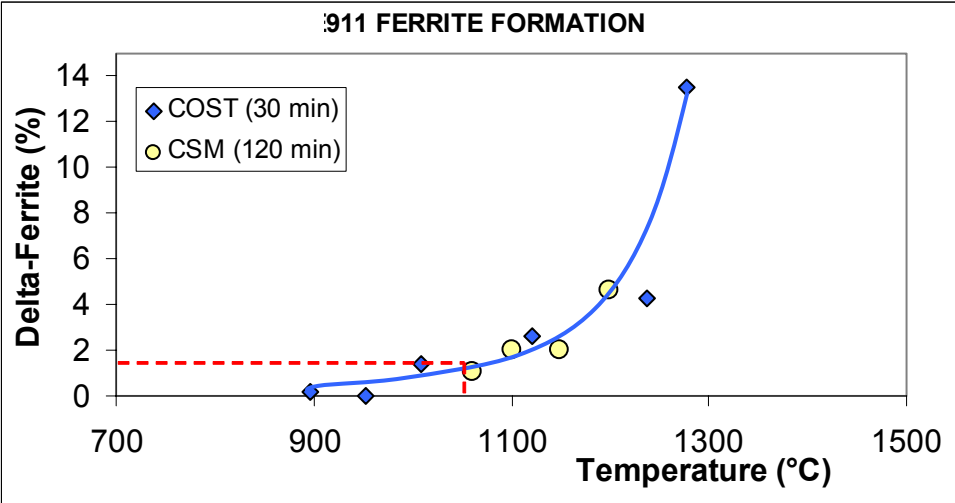


Figure 4 – Delta-ferrite fraction in 911 steel as function of temperature. Blue points are from COST experimentation (30 min holding time in furnace) [7]; yellow points are from CSM experimentation (120 min holding time)

MECHANICAL PROPERTIES OF AS-TREATED MATERIAL

The mechanical properties at room temperature of as-treated materials were investigated by tensile, hardness and impact tests. Typical values for both Grades are reported in Table II, in comparison with ASTM requirements. It is possible to observe that all the products sizes show very good mechanical properties and ductility.

Table II - Room temperature mechanical properties of some tubes and pipes of Grades 91 and 911 in comparison with ASTM requirements

Grade	Product dimension (ODmm x WTmm)	Y.S. (MPa)	U.T.S. (MPa)	Elong. (%)	Red. Area (%)	Impact Energy (J/cm ²)	Hardness (HV ₃₀)
91	38 x 4.6	499	702	20.5	32.5	225	219
	88.9 x 11.3	525	707	23	34	240	217
	219 x 31.7	504	695	22	36	252	214
	609 x 17.5	560	705	34	60	260	221
	ASTM A213-A335	>415	>585	>20	/	7	<265
E911	48.3 x 72	656	824	24.5	n.a.	n.a.	259
	285 x 55	543	728	25.4	66.4	235	224
	ASTM A213-A335	>440	>620	>20	/	/	<265

MECHANICAL PROPERTIES AFTER AGEING

Samples of Grades 91 and 911 pipes were long-term exposed at 625°C and 650°C in order to investigate the tensile and impact property loss at room temperature after 1,000, 3,000 and 10,000 hours. The ageing tests were performed using a laboratory furnace with a maximum temperature deviation of ± 4 °C.

From the results of the tensile tests at room temperature, summarised in Figures 5 and 6, the following conclusions can be drawn:

- the tensile properties of the two steels are very similar up to 10,000 ageing hours., even ultimate tensile strength (UTS) of Grade 911 after 10,000 hours at 625°C and 650°C is slightly higher than that of Grade 91;
- the tensile strength (UTS and YS) maximum reduction of after 1,000 hours is about 15%;
- After this initial decrease, the tensile properties remained quite constant during further ageing at 625°C and 650°C;

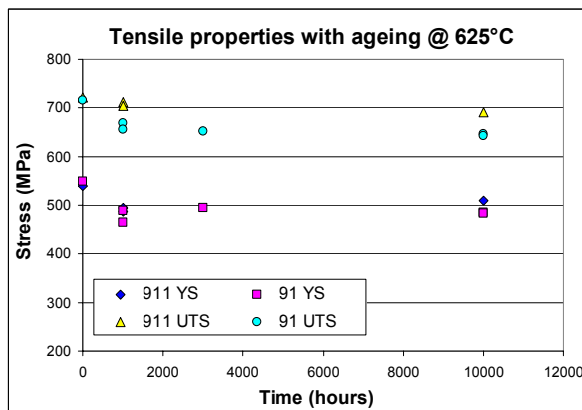


Figure 5

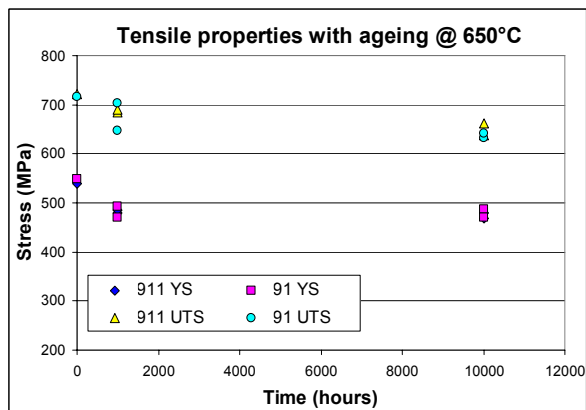


Figure 6

CREEP BEHAVIOUR

A wide creep test program was carried out on pipes and tubes of both Grades 91 and 911: isostress and isothermal tests have been performed in the temperature range of 500°C-700°C and a large database was generated during the last 20 years.

Tenaris Grade 91 database contains about 700 test results from tubes and pipes of more than 30 different heats, with outside diameter from 38 to 660 mm and wall thickness from 4.6 to 84 mm. The applied stresses range from 35 to 400 MPa and more than 6 million creep hours were accumulated. Several tests are still running and some of them have reached more than 70,000 hours with foreseen time to rupture over 100,000 hours. Up to now the longest creep test has time to rupture of 110,301h at 550°C with 150MPa stress. All data are completed by information about material pedigree: chemical composition, of heat treatment details and mechanical properties.

The database of Tenaris Grade 911 consists of about 100 data from COST 501 pipes and tubes for almost 750,000 creep hours (running tests included). Up to now the longest creep test has time to rupture of 64,065h at 575°C with 140MPa stress. Also for this material all data are completed by information about material pedigree.

Following European Creep Collaborative Committee (ECCC) Recommendations, the assessments of the creep-rupture data were performed and the Post Assessment Tests (PATs) were successfully passed [8-11].

The calculated creep-rupture curves of Grades 91 and 911 are respectively plotted in Figures 7 and 8 for main testing temperatures. The stresses for rupture at 10^5 hours of Grade 91 and Grade 911 are compared in Table III.

Due the availability of large and accurate database, it was possible to have reliable creep-rupture extrapolations at very long time: 600°C/78MPa/200,000h for Grade 91. It is important to notice that a reduction of creep-rupture strength in comparison to ECCC official extrapolation, dated 1995, was obtained for Grade 91. The difference is notable especially at 600°C. Tenaris Grade 91 database contains longer creep data than those used for extrapolations in 1995 by ECCC working group [12-13].

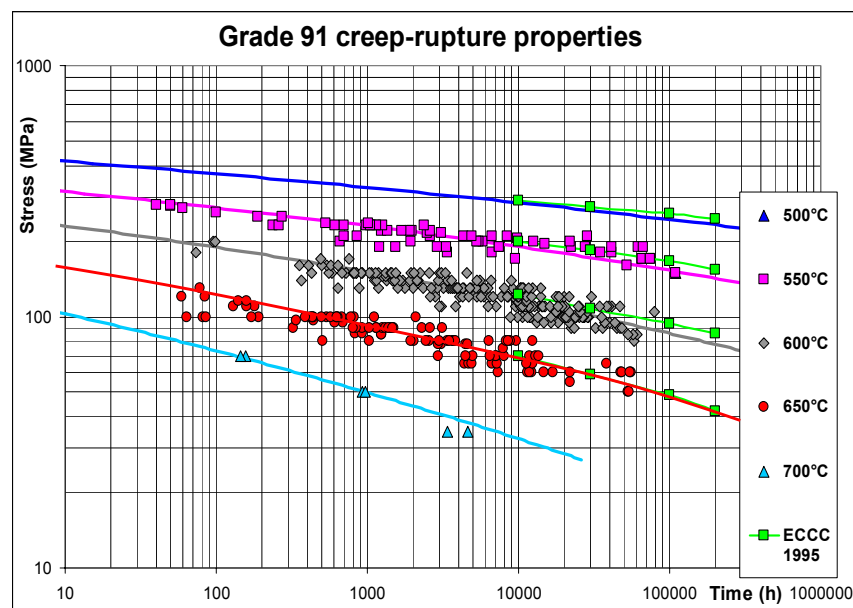


Figure 7 – Tenaris Grade 91 creep-rupture curves (main testing temperatures)

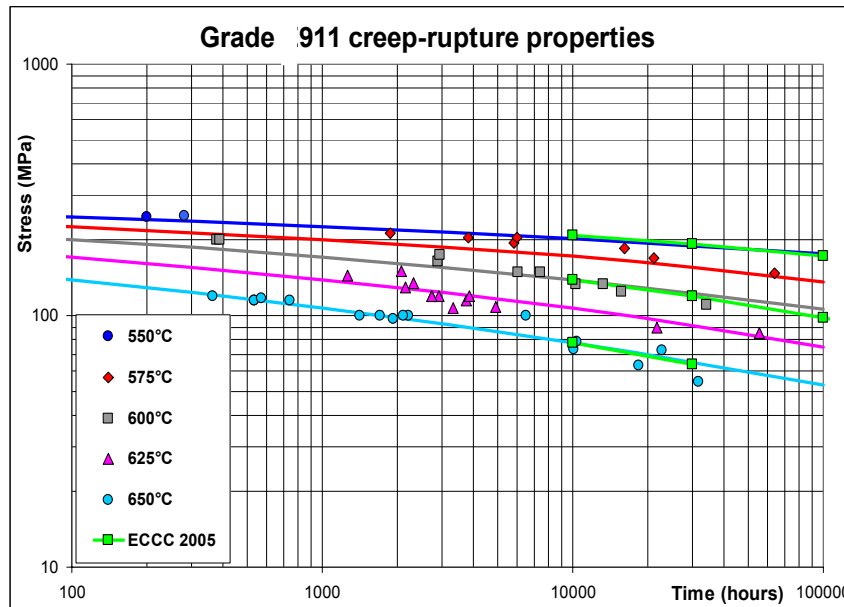


Figure 8 – Tenaris Grade 911 creep-rupture curves (main testing temperatures)

Table III – Predicted stresses to rupture for TenarisDalmine Grades 91 and 911 compared with 2005 ECCC new assessments

Stress values (MPa) to rupture into 10^5 hours				
Temperature (°C)	Grade 91		Grade 911	
	TenarisDalmine	ECCC assessment by CSM/VM [12]	TenarisDalmine	ECCC [13]
550	153	150	176	173
575	117	116	135	134
600	86	85	101	98
625	62	62	71	71
650	46	44	50	/

The creep ductility at rupture in terms of reduction of area and total elongation of both steels are plotted in Figure 9. The ductility decreases progressively with increasing temperature and exposure time, even if the reduction of rupture area of Grade 911 after very long time (~64,000 hours) is always higher than 20%.

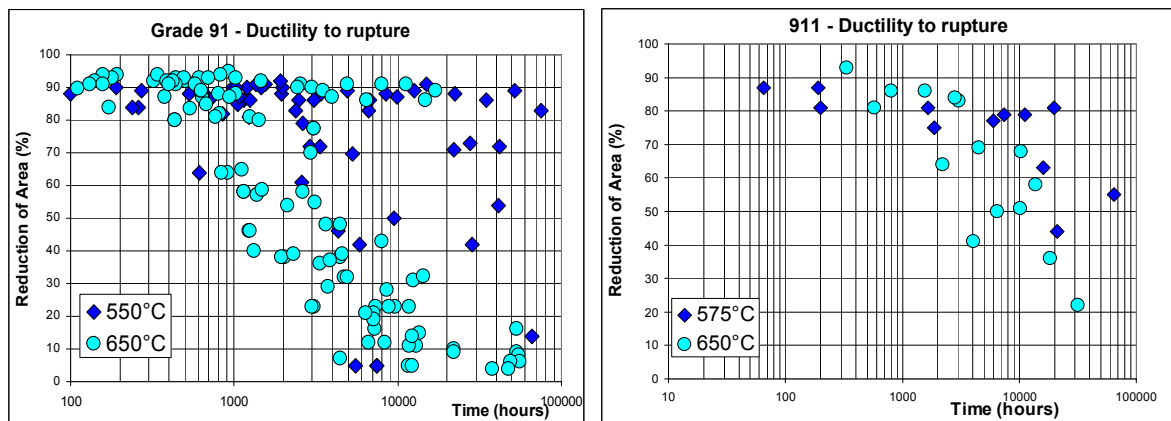


Figure 9 – Reduction of area and elongation to rupture of Grades 91 and 911

MICROSTRUCTURAL EVOLUTION

Both Grades 91 and 911 are generally used in normalized and tempered conditions, which determine the microstructure and the second phase precipitates. The most important carbides are of $M_{23}C_6$ type; these particles nucleate predominantly at prior austenite grain boundaries and along martensite lath boundaries. These carbides are present in high fraction and, together with intergranular MX carbonitrides precipitation into the matrix, promote precipitation strengthening of the steels and their high temperature properties.

The typical state of precipitation in Grade 911 are shown by TEM in Figure 10. After normalizing and tempering no Laves phase is present in the material.

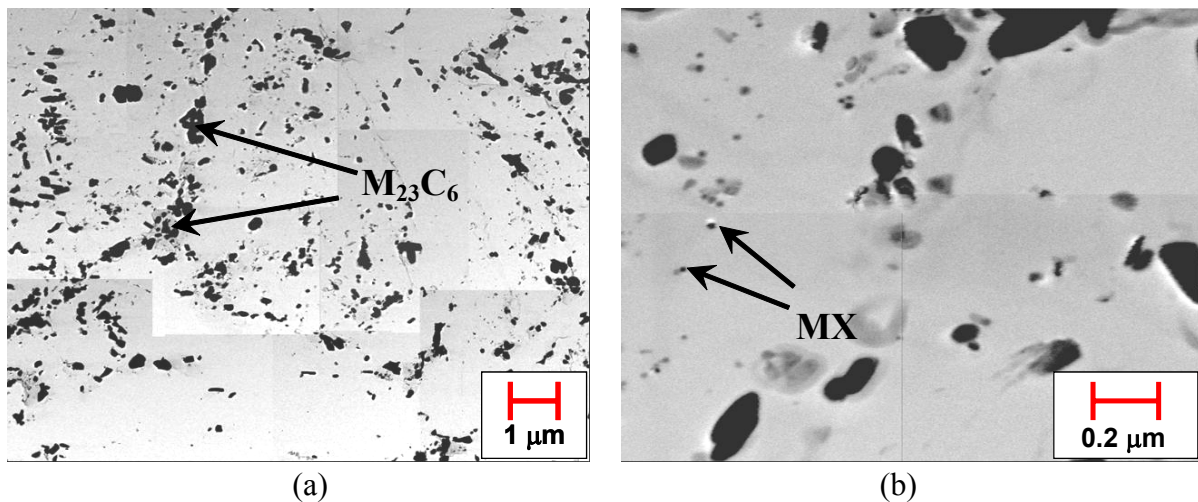


Figure 10 – TEM image of extraction replicas of 911 as-treated pipe: a) $M_{23}C_6$ carbides located at subgrains; b) fine MX carbo-nitrides

During high temperature exposure, $M_{23}C_6$ carbides coarsen, increasing their mean dimension; in the mean time precipitation and coarsening of Laves phase occurs. As a result, the solid solution strengthening is reduced, due to the dissolution of elements like molybdenum, tungsten and chromium [14-15]. CSM investigated the two degradation phenomena above mentioned by STEM examinations: the coarsening of precipitates and the nucleation and growing of Laves phase.

The coarsening of precipitates with increasing ageing time and temperature is clearly shown in Figure 11, where the precipitate size distributions (referring to MX, $M_{23}C_6$ and Laves precipitates) in five samples, submitted to different ageing conditions, are compared (as-treated, 550°C/110,000h; 600°C/58,439h; 650°C/38,079; 650°C/53,318h, characterized by different values of Larson-Miller Parameter, LMP).

A summary of the precipitation evolution in Grade 911 at 600°C and 650°C is shown in Figures 12 and 13, respectively, in comparison with the growth of precipitate phases in Grade 91 [16]. The kinetics of $M_{23}C_6$ carbides and MX carbo-nitrides are very similar in both steels at 600°C: no coarsening of MX carbides was observed and the mean dimension of $M_{23}C_6$ remained below 250 nm, even after a very long exposure and it is expected that they do not grow over. At 650°C the coarsening of the $M_{23}C_6$ is much higher for grade 911 than for grade 91.

Regarding the Laves phase the coarsening phenomena are similar at 600°C, with a fast increase of the dimension at 650°C for grade 911.

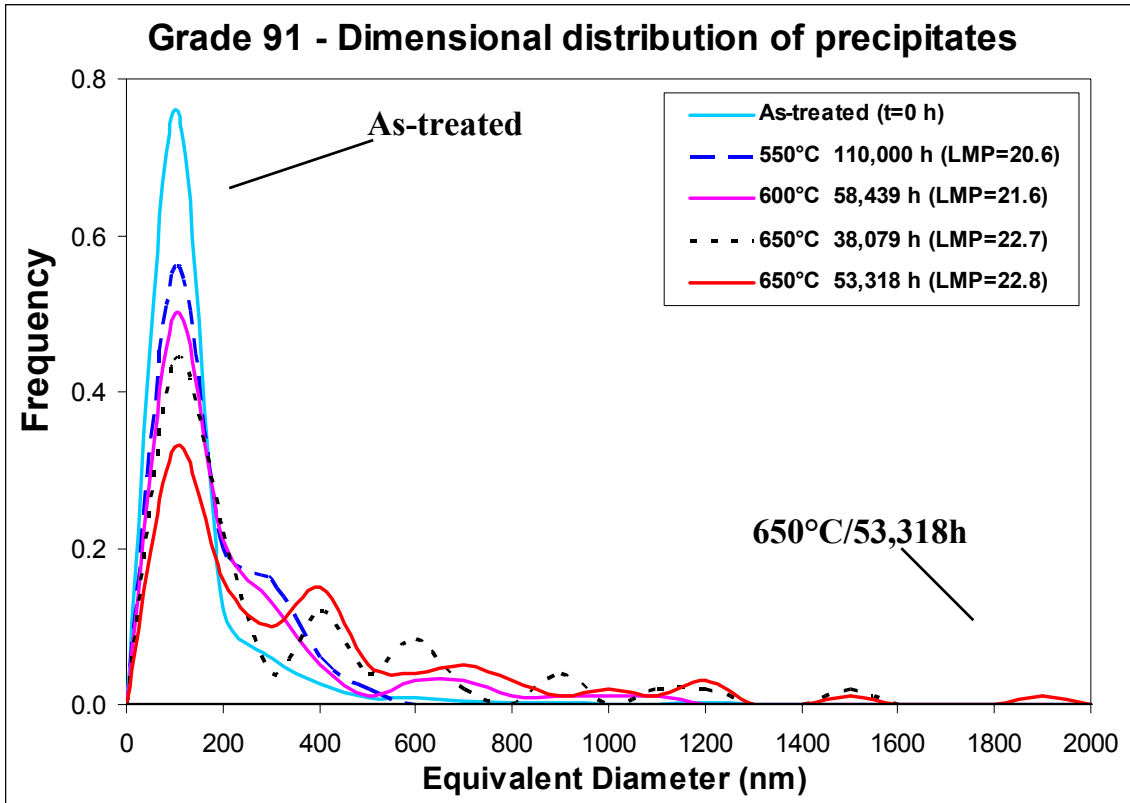


Figure 11 – Coarsening of precipitates during ageing

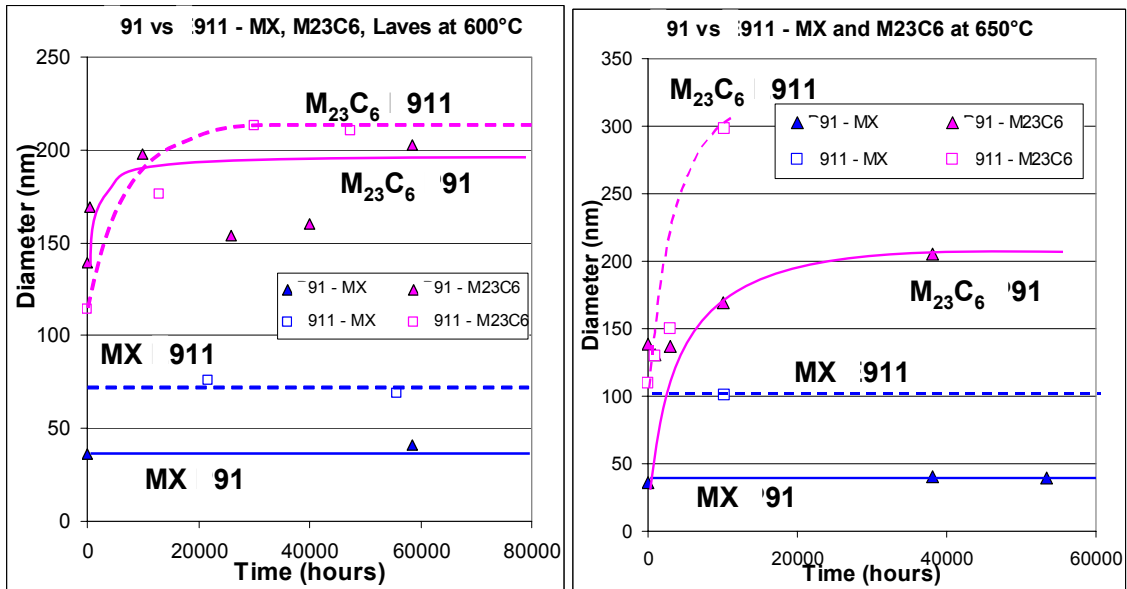


Figure 12 – Growth of MX and $M_{23}C_6$ precipitates in 911 and P91 at 600°C and 650°C

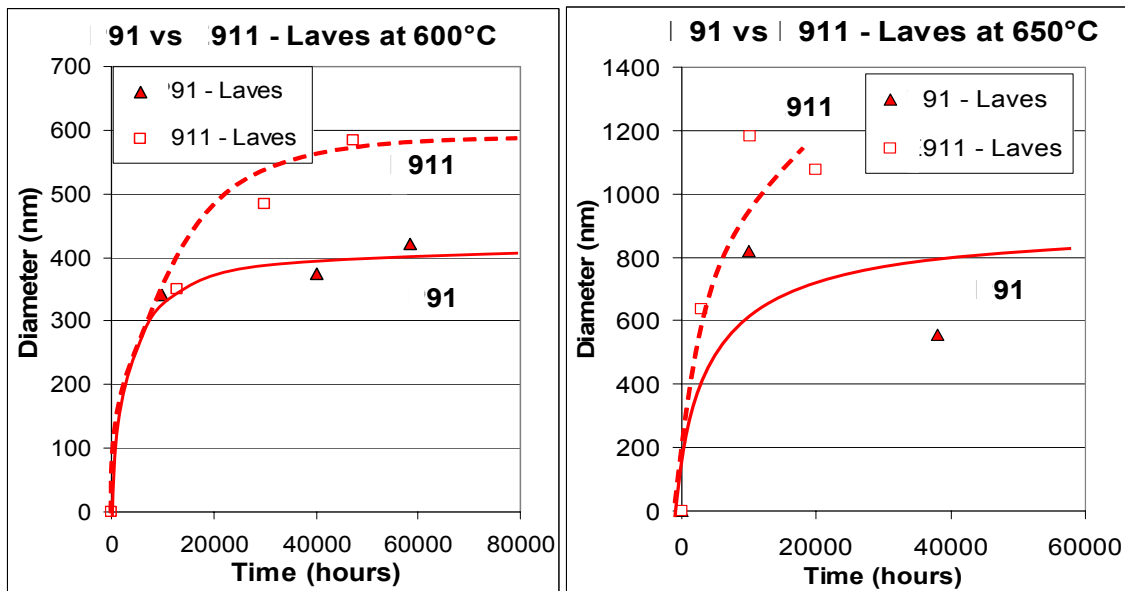


Figure 13 – Growth of Laves phase in 911 and 91 at 600°C and 650°C

DISCUSSION

The phase diagrams of grades 91 and 911, calculated by Thermocalc software, are shown in Figure 14a-b.

For both grades the $M_{23}C_6$ is the predominant phase up to about 820°C and MX is always present in the temperatures range 450-900°C.

The presence of Laves phase was experimentally detected at temperatures higher than 500°C and seems that the calculated phase diagram by Termocalc is better for grade 911.

The most relevant change observed in high CrMoV steels is the precipitation of the intermetallic Laves phase during ageing. The Laves phase was detected mainly at the subgrain boundaries and often was associated with carbides. At 625°C the nucleation of the Laves phase was observed just in the first 1,000 hours. The coarsening rate of this phase was very high: in Grade 911 at 650°C after 10,000 ageing hours the particles reached micrometric dimensions. The coarsening rate and size of Laves particles of the two steels are different, with a pronounced acceleration of coarsening of this phase in Grade 911. This can be explained by a smaller interdistance of Laves phase particles in Grade 911, due to a higher volume fraction and similar size respect to those observed in Grade 91, which accelerates the diffusion controlled growth.

This results is in line with the evaluation of the precipitates evolution obtained by Hald [3] on grade 91 and 92 both in term of particles dimension and growth as function of temperature, with a tendency for all these steels to reach a plateau. The availability in the future of creep specimens after 10^5 at different temperatures will be very helpful to confirm these tendencies.

The evolution of the precipitates can explain the reduction of mechanical properties in the first 1,000 hours as well as the reduction of ductility with increasing creep time and temperature. Similar results are obtained also for other 9-12%Cr steels. Nevertheless the flattening of the growing of $M_{23}C_6$ and Laves phase at 600°C is a guarantee that instability phenomena cannot occur for both steels.

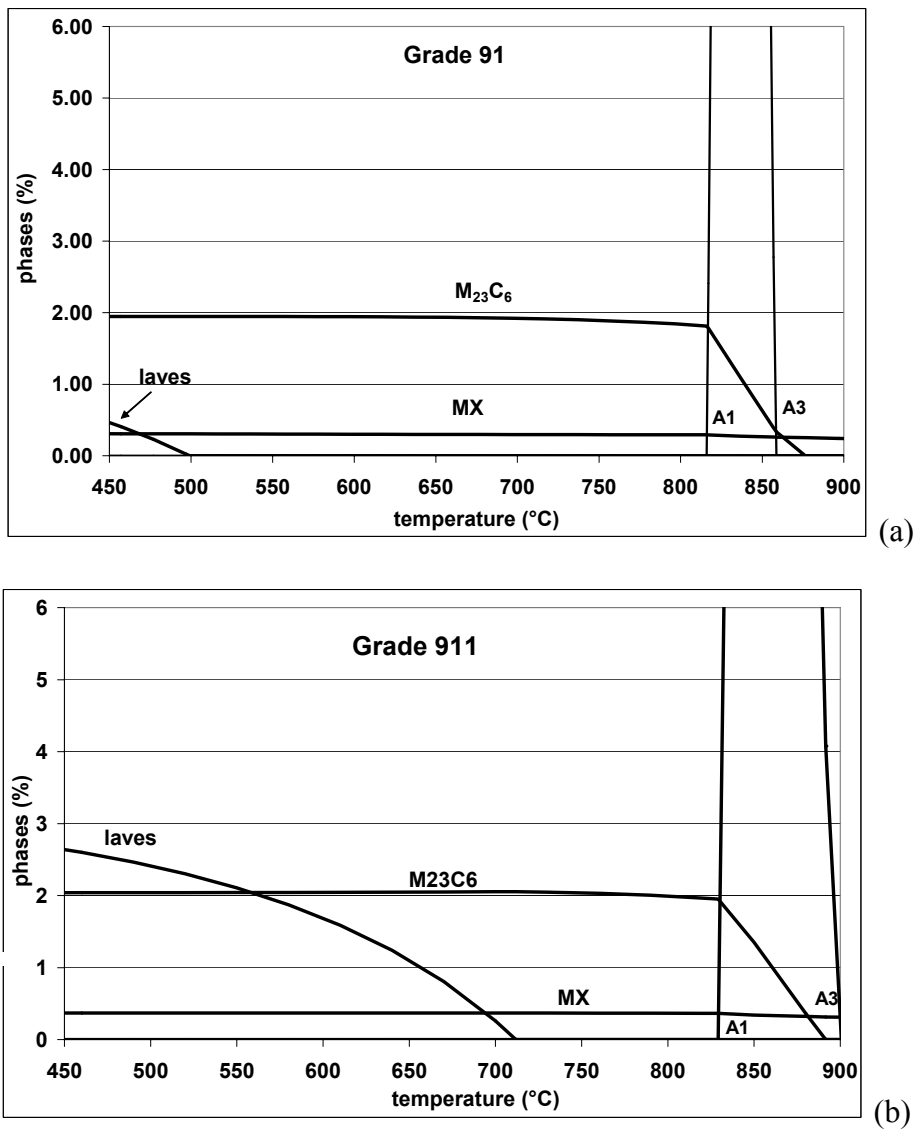


Figure 14 – Thermocalc diagram of
a) grade 91
b) grade 911

CONCLUSIONS

The creep resistance of Grade 911 was demonstrated to be always higher than the values assessed for Grade P91 at all temperatures, even if the differences are strongly reduced at 650°C. This is related to the addition of W, which promotes the precipitation of Laves phase.

The kinetics of $M_{23}C_6$ carbides and MX carbo-nitrides are very similar for both Grades 91 and 911 at 600°C, even after a very long exposure.

In 911 steel a larger coarsening of Laves phase than grade 91, which grows up to micrometric dimensions, was measured at 650°C, with the result of a loss in creep resistance and ductility after 10,000 hours. For this reason, while at 600°C the Grade 911 shows higher creep than Grade 91, at 650°C the creep strength of the two materials is very similar, due to the presence of large Laves particles: the assessed creep strength is 50MPa/10⁵h for Grade 911 and 46MPa/10⁵h for Grade P91.

Below 610°C the microstructural stability of both steels during service is guaranteed for very long times, without a relevant drop of the creep behaviours after 10-30,000 hours related to the nucleation and growth of Z-phase [3], which has been found in all the new 11-12% Cr developed in Europe and in Japan in the last 5-10 years and it is not predicted by the most thermodynamical model.

The coupling of large creep data base and analyses of microstructural evolution, generated by TenarisDalmine and Centro Sviluppo Materiali, for grades 91 and 911 guarantee the validity of the creep assessment up to 10^5 and 2×10^5 hours for grade 91, in agreement with previous and present assessment generated in the frame of ECCC activities.

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