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Microstructural Evolution of T91 in High Temperature Conditions and under Combined Effect of Stress and Temperature

Andrea Tonti ^{1,*} , Daniela Lega ², Alessandra Antonini ², Antonello Alvino ², Loriana Ricciardi ¹ and Luana Campanile ¹

¹ INAIL-DIT-Sezione VI Supporto Tecnico UOT Via Roberto Ferruzzi, n.38/40, 00143 Roma, Italy

² INAIL-DIT-Laboratorio III Sicurezza delle Attrezzature Centro Ricerca Area Casilina Via del Torraccio di Torrenova, 7, 00133 Roma, Italy

* Correspondence: a.tonti@inail.it

Abstract: ASTM A213 T91 steel is widely used in power plants and petrochemical industry for long-term service components. Due to its high resistance to creep, thermomechanical fatigue and corrosion, the use of grade 91 steel allows usual plant service parameters to be raised up to ultra-supercritical conditions (600 °C, 300 bar) so that performances are remarkably increased. The strongest factors that affect performances are the time of exposure, the temperature and the applied stress: such parameters can dramatically decrease the service life of a plant component. The improved mechanical properties of grade 91 are strictly related to its specific microstructure: a tempered martensite matrix with fine precipitates embedded in. Two typologies of secondary phases are present: $M_{23}C_6$ carbides (where $M = Cr/Fe/Mo/Mn$) and finely dispersed MX-type carbonitrides (where $M = V/Nb$ and $X = C/N$). This study is focused on the microstructure evolution of grade 91 steel under creep conditions. First, three sets of laboratory-aged specimens heated in oven at 550 °C, 600 °C and 650 °C were examined; the exposure time was up to 50,000 h. Furthermore, the influence of stress on the microstructure in two sets of samples was evaluated: a first batch of specimens cut from an ex-service tube of a petrochemical plant (over 100,000 h of service at 580 °C and 19–25 bar) and a second set of samples coming from another ex-service tube under ultra-supercritical conditions (605 °C, 252 bar) in a power plant. The microstructures were characterized by optical, scanning electron and transmission electron microscopy and the results were compared to the literature. Some interesting trends were evidenced, in terms of secondary phases precipitation and coarsening, as well as martensite recovery. Furthermore, the applied stress seems to influence size and number of Laves phase particles.

Keywords: ASTM T91; microstructure evolution; aging; precipitates; Laves; carbides



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1. Introduction

Grade 91 steels were developed during the 1970s and 1980s and they constitute one of the most used materials in ultra-super-critical (USC) plants with service temperatures and pressures up to 600 °C and 300 bar, respectively.

These steels are an improvement of the pre-existing alloys (grade 9) by the addition of Nb, V and N. The good mechanical properties of grade 91 steels are determined by a microstructure consisting of tempered martensite with a fine precipitation of carbides and carbonitrides [1,2]. Standardized by ASME in 1983 for pipes and in 1984 for boilers, over the past 25–30 years they have been used especially in the USA and Japan. Since they have only spread to Europe in the last 15 years, the service experience is still rather limited. Degradation mechanisms of grade 91 steels are different from those shown by the previously largely used low alloy steels. Furthermore, conventional techniques for evaluating residual life used for low alloy steels, such as the use of replicas [3–5], appear almost inadequate.

For this reason, then, the evaluation of the material performances and the residual life for long-term use in power plants is a very hard topic for researchers, especially concerning creep resistance. In the last 15–20 years several studies have been carried out on the evolution of the microstructure and damage mechanisms [6–12]. The microstructure of tempered martensite and finely dispersed carbides can be obtained after an accurate heat treatment, that is normalizing and tempering. As a result of normalizing, martensite is formed and then, during tempering, the number of dislocations is reduced, the ferritic sub-grains are formed and the dispersion of precipitates, consisting of Chromium-rich carbides $M_{23}C_6$ ($M = Cr, Mo, Fe, Mn, V$) and MX carbonitrides ($M = Nb, V; X = C, N$), is achieved. During service, several important modifications that may reduce the grade 91 creep resistance, occur in the martensite matrix: [13–18]

- increase in the size of the $M_{23}C_6$ carbides;
- martensite recovery;
- precipitation and coarsening of new phases (Laves and Z).

The latter phenomenon, in particular, has important consequences. The Laves phase is an intermetallic that is formed during service [2,14,17,18]. Its average chemical composition is Fe_2Mo , Fe_2W , $(Fe/Cr)_2$ (W, Mo) with some Si and P. Laves particles are mainly found along the prior austenitic grain boundaries (PAGB) next or into the pre-existent $M_{23}C_6$ carbides. Z Phase is also a secondary phase, that is not present in the as cast material. Its chemical composition is $CrNbN$ or $Cr(Nb,V)N$ and it precipitates during service as a consequence of Cr diffusion into the MX carbonitrides [2,14,19]; the carbonitride MX lattice shifts from cubic to tetragonal. MX carbonitrides enriched in Cr are called hybrid particles and they are precursors of the Z phase. These hybrid particles are constituted by an inner region, with a chemical composition typical of the MX ($Nb + V > 70\%$), and an external region with a chemical composition similar to Z ($Fe + Cr \approx V + Nb$, with $30 < Fe + Cr < 40\%$) [19].

In order to evaluate the microstructural changes that occur in high Cr steels, a study of the microstructural damage of the grade 91 steel is presented in this paper; this study was carried out both on laboratory-aged specimens and on ex-service materials. In particular, the effects of both temperature and aging time were monitored on the morphological evolution of the microstructure and on the composition and dimension of the secondary phases. Particular attention was paid to the formation and growth of Laves and Z phase. The creep resistance was also investigated: creep damage is mainly caused by dislocations movement, a phenomenon that increases significantly during service. A decrease in the volume fraction of precipitates, an increase in particles size and a depletion of strengthening elements in the solid solution are factors that heavily promote dislocation movement. So, the analysis of particles (chemistry and occurrence) and the measurement of their average diameter have been deeply investigated in this paper.

2. Materials and Methods

Samples were taken from two normalized (1070 °C) and tempered (760 °C) industrial tubes, made by ASTM A 213 grade T91, to perform laboratory aging treatments. Their dimensions (outer diameter x wall thickness) were 38.1 mm × 4.6 mm and 88.9 mm × 11.3 mm, respectively. Samples were artificially aged according to laboratory conditions reported in Table 1. The target was to collect data about aging at least in the range 0–100,000 h, since this is the average service life defined by materials standards such as EN 10028 or ASME SA 213. At the present time the samples are still in the oven. Available data range between 0 and 50,000 h. After each aging interval, a tube cross section was cut from the aged sample and used to make both extraction replicas and metallographic specimens, to perform microstructural and secondary phases characterization. The obtained results were compared to the literature results [6,7] from aging experiments on steels whose chemical composition was within the range set by the appropriate ASTM standard (A213 T91).

Table 1. The times and temperatures chosen for laboratory experiments of T91 aging.

T (°C)	3000	5000	10,000	20,000	25,000	30,000	40,000	45,000	50,000
550		✓	✓	✓		✓	✓		
600	✓	✓	✓	✓	✓	✓	✓	✓	✓
650	✓	✓	✓	✓	✓	✓	✓	✓	✓

Microstructural characterization of aged samples was carried out with a Leica Reichter optical microscope (Leica, Wetzlar, Germany), equipped with Image Pro Plus as image analysis software. Secondary phases analysis was performed by a TEM-FEG Jeol 3200 FS (Jeol, Peabody, MA, USA) on extraction replicas and Scanning Electron Microscopy/Automatic Imaging Analysis (SEM-AIA) was carried out using a Jeol JSM 6480 (Jeol, Peabody, MA, USA) on metallographic specimens. Fields chosen for the metallographic analysis were acquired in the center of tubes thickness.

A second set of samples was made from two ex-service materials, named S1 and S2, respectively. S1 was a reformer tube that operated with naphtha and H₂ as process fluids for 116,000 h at 580 °C and 19–26 bar; S2 was a tube that operated 43,000 h in a power plant at 605 °C, 252 bar with steam as process fluid.

Microstructural characterization of samples from ex-service materials was carried out with a Nikon Eclipse ME600 optical microscope (Nikon, Tokyo, Japan) and with a Field Emission Scanning Electron Microscope (FEG-SEM) Zeiss Ultra Plus (Zeiss, Oberkochen, Germany) equipped with EDS X-MAX 506480 (Oxford Instruments Abingdon-on-Thames, UK). Dimension analysis of secondary phases was performed by Scandium software (Scandium 5.2, Olympus Soft Imaging Solutions GmbH, Munster, Germany).

Chemical analysis of materials was carried out with a ThermoFisher ARL 3460 (Thermo Fisher Scientific, Waltham, MA, USA) optical emission spectrometer.

Small punch creep tests were performed, according to EN 10371:2021 standard [20], by a SPUTT 500 machine, setting 480 N load and 580 °C temperature.

3. Results and Discussion

The chemical analysis of the steels examined in this study is reported in Table 2, compared with ASTM A213 standard [21].

Table 2. Results of chemical analysis of the steels used in this study. Material from aging experiments has been named as “aged”; the steels from ex-service materials have been named as “S1” and “S2”, respectively.

	C	Si	Mn	P	S
ASTM A213	0.07–0.14	0.20–0.50	0.30–0.60	≤0.020	≤0.010
aged	0.114	0.25	0.32	<0.005	<0.005
S1	0.115	0.37	0.35	0.012	0.006
S2	0.099	0.38	0.42	0.014	0.007
	Cr	Mo	Nb	V	N
ASTM A213	8.0–9.5	0.85–1.05	0.06–0.10	0.18–0.25	0.03–0.07
aged	8.4	0.87	0.07	0.21	0.04
S1	8.4	0.96	0.09	0.20	0.05
S2	8.9	0.96	0.08	0.25	-

In Tables 3–5, the average diameter D and the occurrence frequency F_R of each class of secondary phases examined by TEM extraction replica from T91 steel specimens after aging experiments are reported. F_R is a frequency number relative to the total analyzed particles and it can be defined as the percent ratio between the number of spotted particles of a single class of precipitates and the total number of particles detected in the examined field.

Table 3. Average diameter (D) and occurrence frequency (F_R) of each class of precipitates found in grade 91 steel specimens treated at 550 °C at increasing aging time.

	Precipitate	Aging Time (Hours)					
		0	5000	10,000	20,000	30,000	40,000
average diameter D (nm)	$M_{23}C_6$	145	123	274	167	133	174
	MX	48	37	62	45	44	39
	Laves	-	-	327	333	203	347
	Z-phase hybrid	-	-	42	-	72	-
occurrence frequency F_R (%)	$M_{23}C_6$	49	53	56	43	45	40
	MX	51	47	21	45	49	49
	Laves	-	-	17	12	5	11
	Z-phase hybrid	-	-	6	-	1	-

Table 4. Average diameter (D) and occurrence frequency (F_R) of each class of precipitates found in grade 91 steel specimens treated at 600 °C at increasing aging time.

	Precipitate	Aging Time (Hours)								
		0	3000	5000	10,000	20,000	25,000	30,000	40,000	50,000
average diameter D (nm)	$M_{23}C_6$	145	152	117	245	231	289	174	150	185
	MX	48	51	47	43	41	40	59	54	45
	Laves	-	-	126	517	535	528	485	383	448
	Z-phase hybrid	-	-	-	102	28	34	150	-	-
occurrence frequency F_R (%)	$M_{23}C_6$	49	77	54	55	51	49	34	35	32
	MX	51	23	34	23	38	31	58	62	57
	Laves	-	-	12	14	4	11	7	3	11
	Z-phase hybrid	-	-	-	8	7	9	1	-	-

A deeper size analysis of precipitates was performed also on massive specimens by SEM/AIA on a large number of fields and particles. The experimental results, compared to literature [6,7], referred to $M_{23}C_6$ carbides, MX carbonitrides and Laves phase are reported in Figures 1–3, respectively. For Laves phase, moreover, the area fraction F_A of particles is shown in Figure 4. F_A is calculated as the percent ratio between the total area of all Laves particles found in the field and the whole area of the field itself.

The typical microstructure of as cast grade 91 steel is a martensite matrix surrounded by $M_{23}C_6$ carbides at prior austenitic grain boundaries (PAGB) and MX carbonitrides embedded into the matrix. The average diameters found for $M_{23}C_6$ and MX precipitates are 145 nm and 48 nm, respectively. Though $M_{23}C_6$ carbides show scattered data, a trend can be assumed: a moderate coarsening occurs during the first 10,000 h, then a size reduction can be observed and finally there is a new minor coarsening. The literature data seem to

yield similar evidence, since Cipolla [7] found that the coarsening of $M_{23}C_6$ carbides is minimal. After 100,000 h of aging, in fact, the mean diameter does not exceed 300 nm and no appreciable variation in chemical composition is found, suggesting that the temperature cannot be considered the only growing factor for $M_{23}C_6$ carbides.

Table 5. Average diameter (D) and occurrence frequency (F_R) of each class of precipitates found in grade 91 steel specimens treated at 650 °C at increasing aging time.

	Precipitate	Aging Time (Hours)								
		0	3000	5000	10,000	20,000	25,000	30,000	40,000	50,000
average diameter D (nm)	$M_{23}C_6$	145	145	128	166	321	234	241	206	166
	MX	48	52	43	40	67	61	67	59	45
	Laves	-	-	-	-	-	-	48	850	-
	Z-phase hybrid	-	-	-	115	50	-	212	137	-
	Z-phase	-	-	-	-	-	414	-	-	-
occurrence frequency F_R (%)	$M_{23}C_6$	49	64	50	53	56	50	39	45	34
	MX	51	36	50	46	40	48	59	53	64
	Laves	-	-	-	-	-	-	0.5	1	-
	Z-phase hybrid	-	-	-	1	4	-	1.5	1	-
	Z-phase	-	-	-	-	-	2	-	-	-

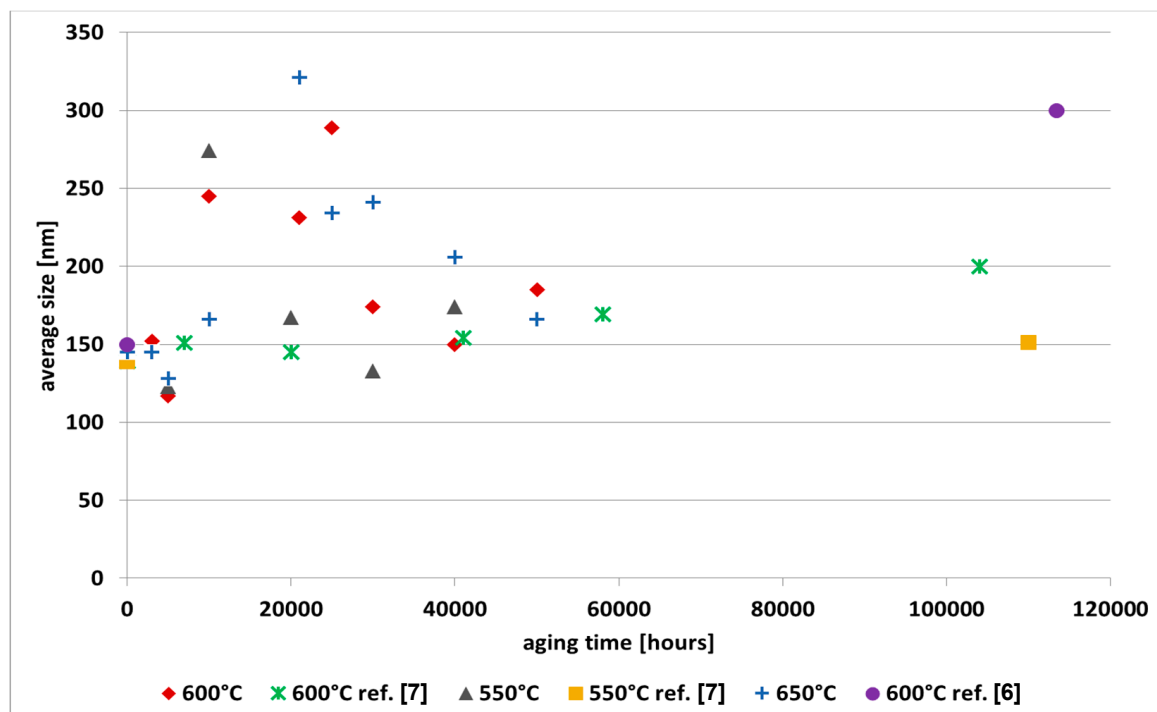


Figure 1. Evolution of average size (calculated as average diameter) of Cr-rich carbides $M_{23}C_6$ in grade 91 specimens aged at 550, 600 and 650 °C, respectively, compared to data found in literature.

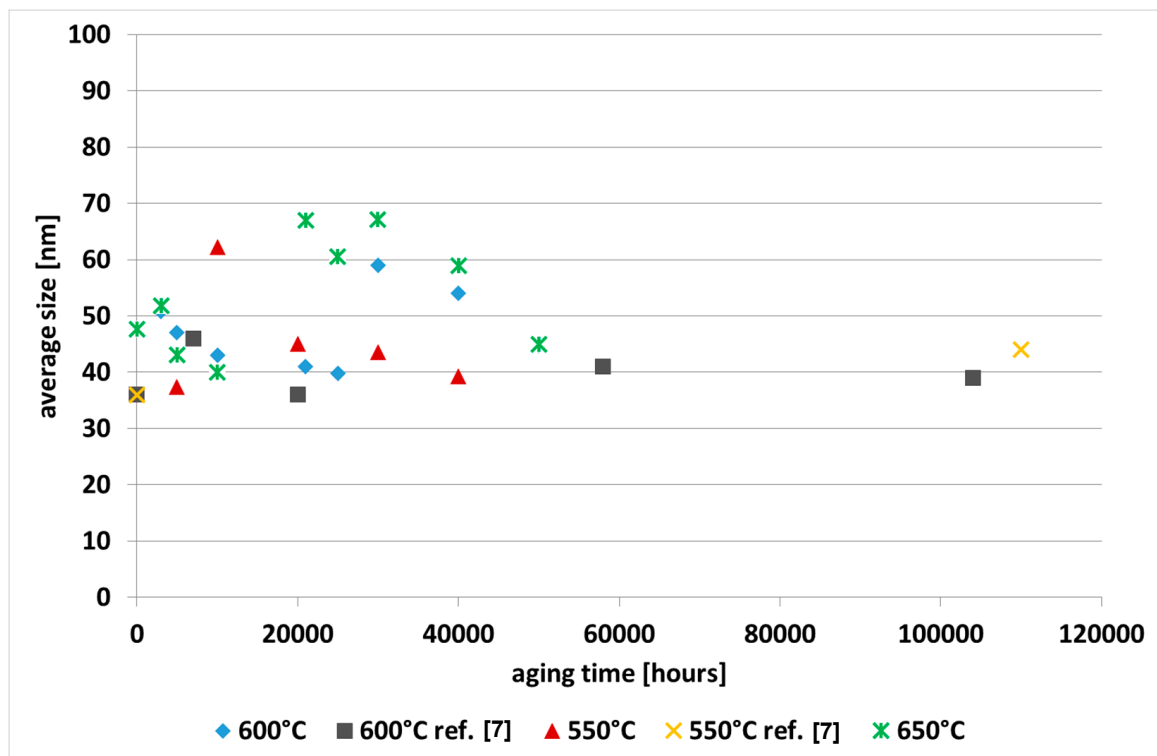


Figure 2. Evolution of average size (calculated as average diameter) of MX carbonitrides in grade 91 specimens aged at 550, 600 and 650 °C, respectively, compared to data found in literature.

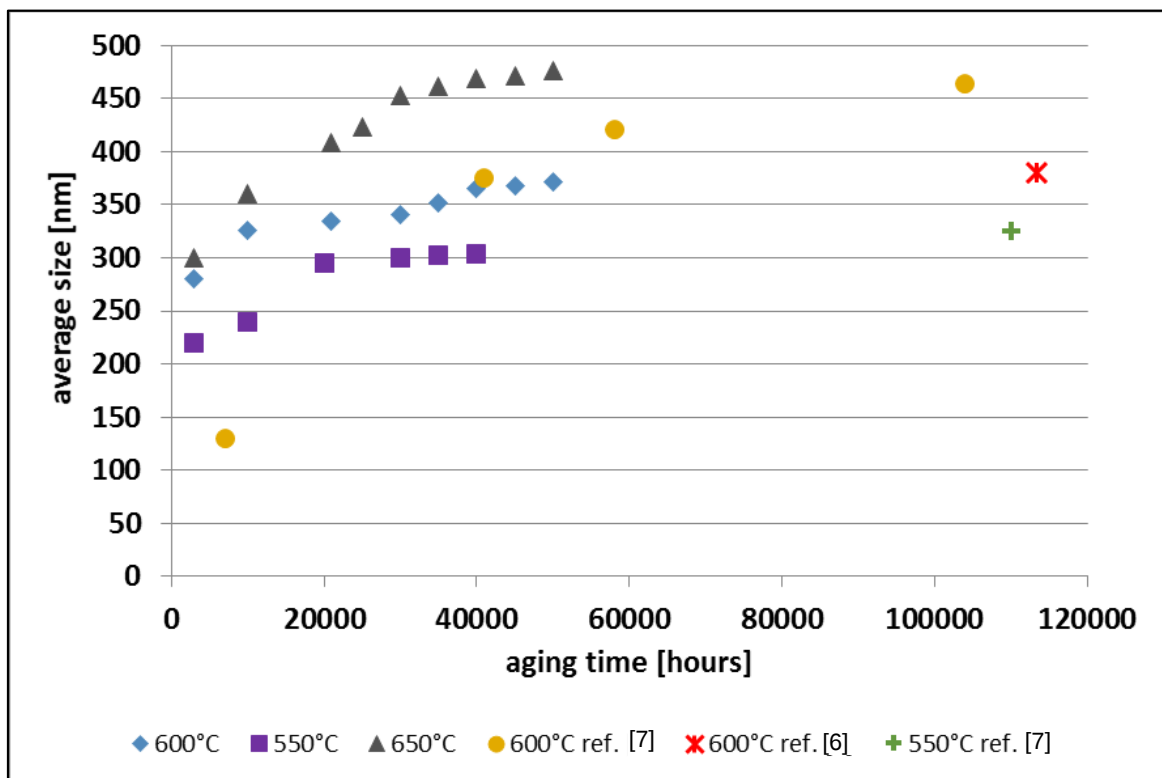


Figure 3. Evolution of average size (calculated as average diameter) of Laves phases in grade 91 specimens aged at 550, 600 and 650 °C, respectively, compared to data found in literature.

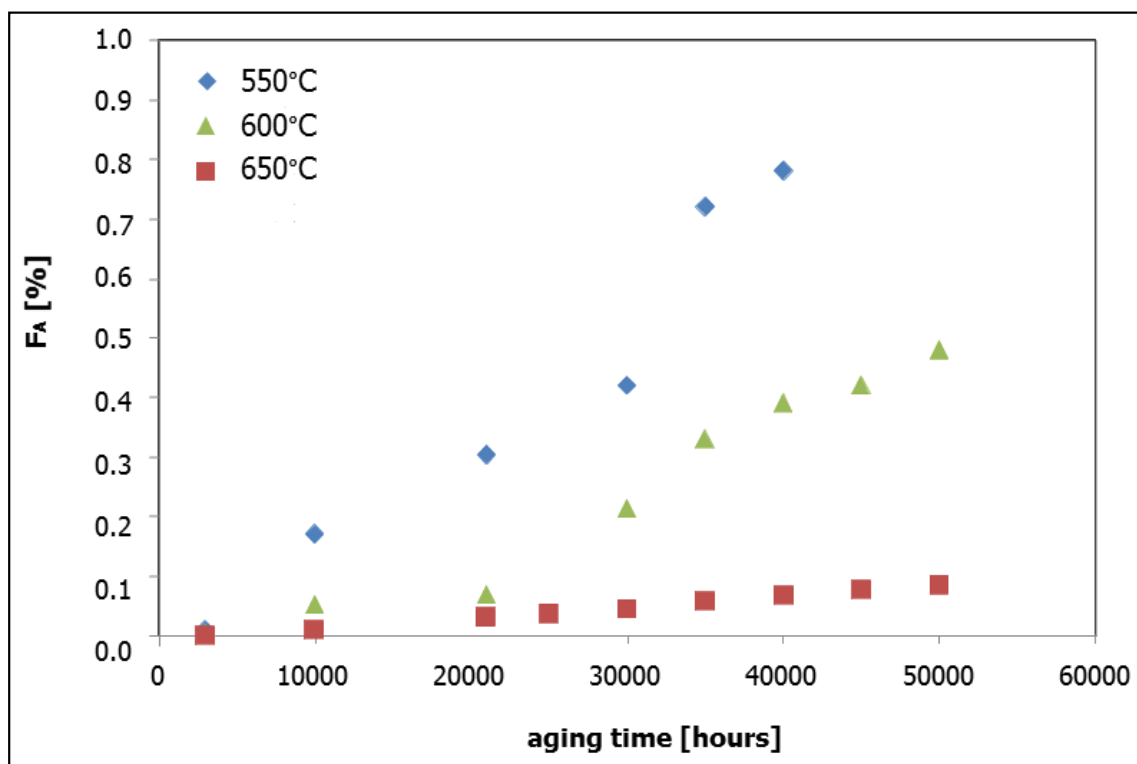


Figure 4. Evolution of percent area fraction F_A of Laves phases in grade 91 specimens aged at 550, 600 and 650 °C.

An explanation to this trend can be found in Laves phase formation: this precipitate nucleates into Cr-rich carbides and consumes chromium, reducing the metal available for carbides growth. So, when the Laves start to precipitate, the carbides coarsening is strongly reduced.

Data collected about MX carbonitrides are quite scattered, and no appreciable trends can be easily deduced; nevertheless, it can be assumed that this class of particles does not undergo variations in size, since after 100,000 h of aging the mean diameter is lower than 50 nm. They nucleate during tempering process and are almost unaffected by aging. The literature data [7] seem to confirm this evidence.

Nucleation and coarsening of Laves phase appear to be directly related to the aging time as well as to the temperature of exposure. Depending upon the experiment temperature, in fact, particles start to precipitate after 5000–10,000 h and grow until their average diameter reaches 300–450 nm, after 30,000–40,000 h of aging. This trend has been also described in the literature [6,7]. Laves particles nucleate and coarsen into the chromium-rich carbides $M_{23}C_6$ and, as reported by some authors [22,23], seem to be preferential sites for stress concentration; they are, in fact, suspected to trigger cavitation in high chromium steels, especially if they nucleate at PAGB. It is of note that Laves precipitation is dramatically reduced at temperatures higher than 600 °C, because these particles start to be soluble in the matrix approximately at 600–650 °C.

Small amounts of hybrid precipitates, identified as Z-phase precursors, were detected. A progressive enrichment of Chromium in MX particles can be identified as the originating factor. Appreciable amounts of Z-phase were not found, except in one specimen aged for 25,000 h at 650 °C. A similar trend has also been described by Cipolla [7], who assumed that Z-phase is not a damage factor for grade 91 steel because it is prevented to precipitate by kinetic factors, though such phase could be considered thermodynamically stable. Sawada described a very different trend since he found a massive Z-phase precipitation on grade 91, as well as an appreciable decrease in MX carbonitrides [22,24–26]. This evidence, however, could be not totally in contrast with results found in this paper, because the steel

that Sawada examined was normalized for a lower time than recommended by technical standard. The evidence found in Sawada's study could be addressed to a non-homogeneous dispersion of MX precipitates: it is known, in fact, that such particles, if large and grouped at PAGBs, can trigger Z-phase precipitation in high chromium steels [22–26].

In order to better assess the influence of temperature and stress on the evolution of microstructure in grade 91 steels, a metallographic study was carried out on two ex-service materials, named S1 and S2, respectively. The microstructure of steel from S1 shows recovered martensite [27] (Figure 5). Some precipitates have been detected and characterized: Laves, MX carbonitrides, Cr-rich carbides $M_{23}C_6$ and Z-phase precursors; Table 6 reports the average diameter and the occurrence frequency F_R of each class of precipitate. F_R is a frequency number relative to the total analyzed particles and it can be defined as the percent ratio between the number of spotted particles of a single class of precipitates and the total number of particles detected in the examined field.

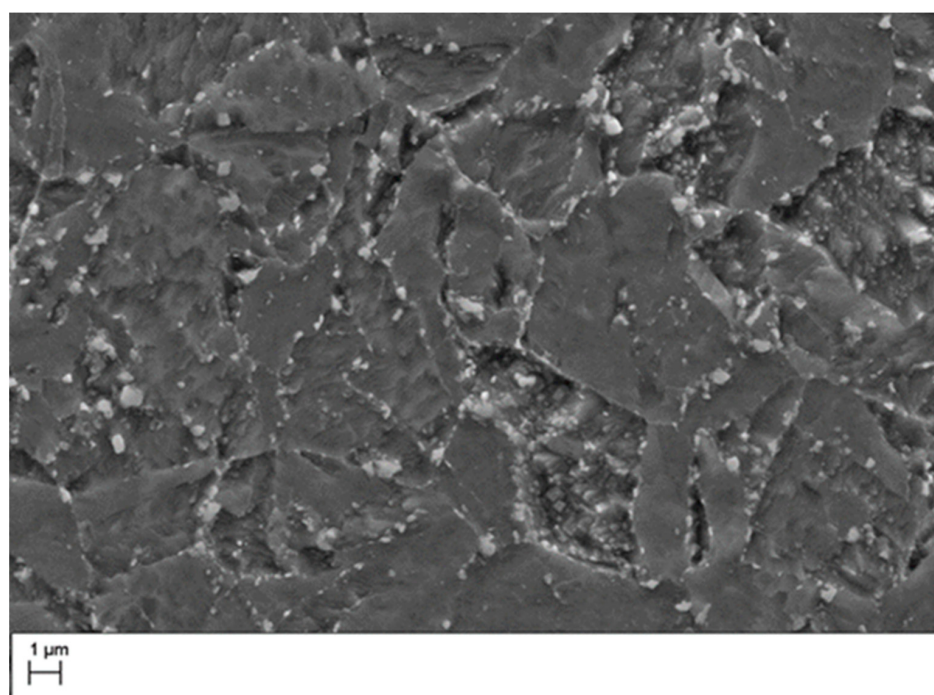


Figure 5. Microstructure of metallographic specimen from S1 tube. FEG-SEM micrograph, cross section. Etching: Vilella 20 s. No cavities are detectable. The secondary phases can be spotted as bright particles.

Table 6. Average diameter (D) and occurrence frequency (F_R) of each class of precipitates found in grade 91 steel from S1.

	D (n)	F_R (%)		D (n)	F_R (%)
$M_{23}C_6$	167	52	Laves	241,6	13
MX	42	17	Hybrid	96,5	18

Figures 6 and 7 show size distribution of Laves and $M_{23}C_6$. It is worth noting that the average sizes of Laves and $M_{23}C_6$ particles are very similar to the diameter found in samples aged at 600 °C. The tube S1, in fact, was an ex-service tube, working at a quite low pressure, so that no heavy precipitate evolution could be expected. Nevertheless, a somewhat appreciable amount of hybrid Z-phase precursors was detected, since their occurrence frequency F_R is higher than that found for Laves phase. The average diameter of hybrid particles was approximately 100 nm.

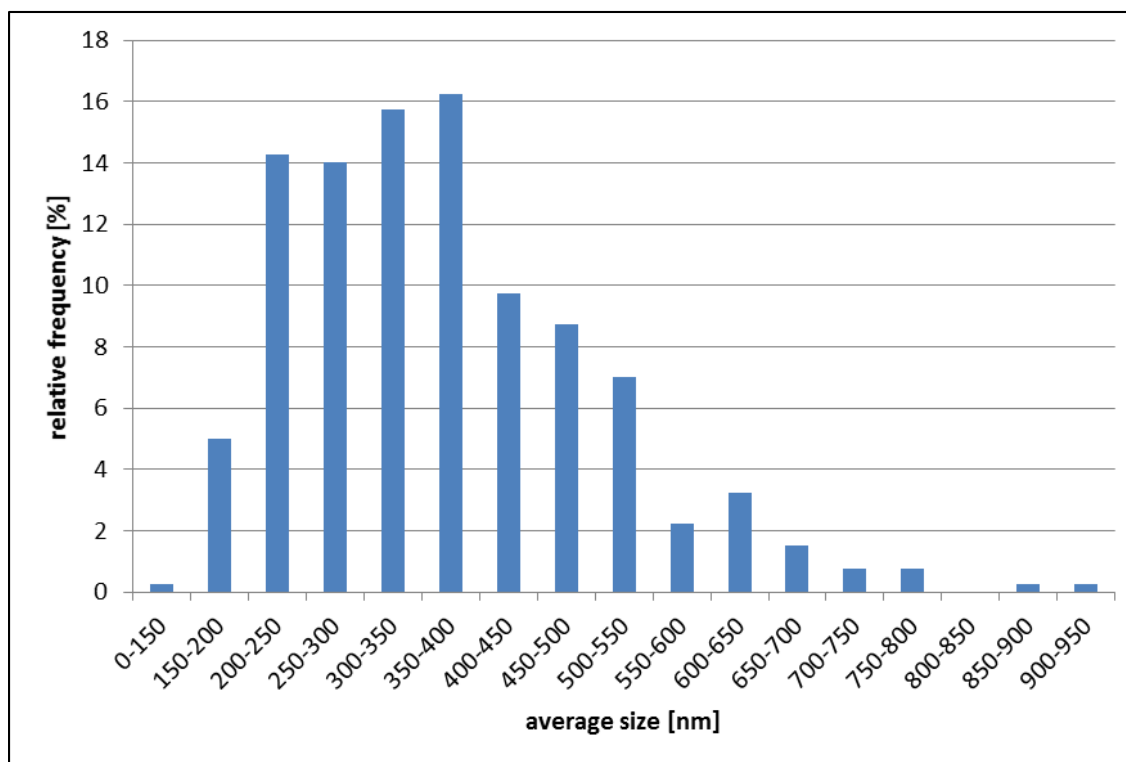


Figure 6. Average size distribution (calculated as average diameter) of Laves phase in steel specimens from S1.

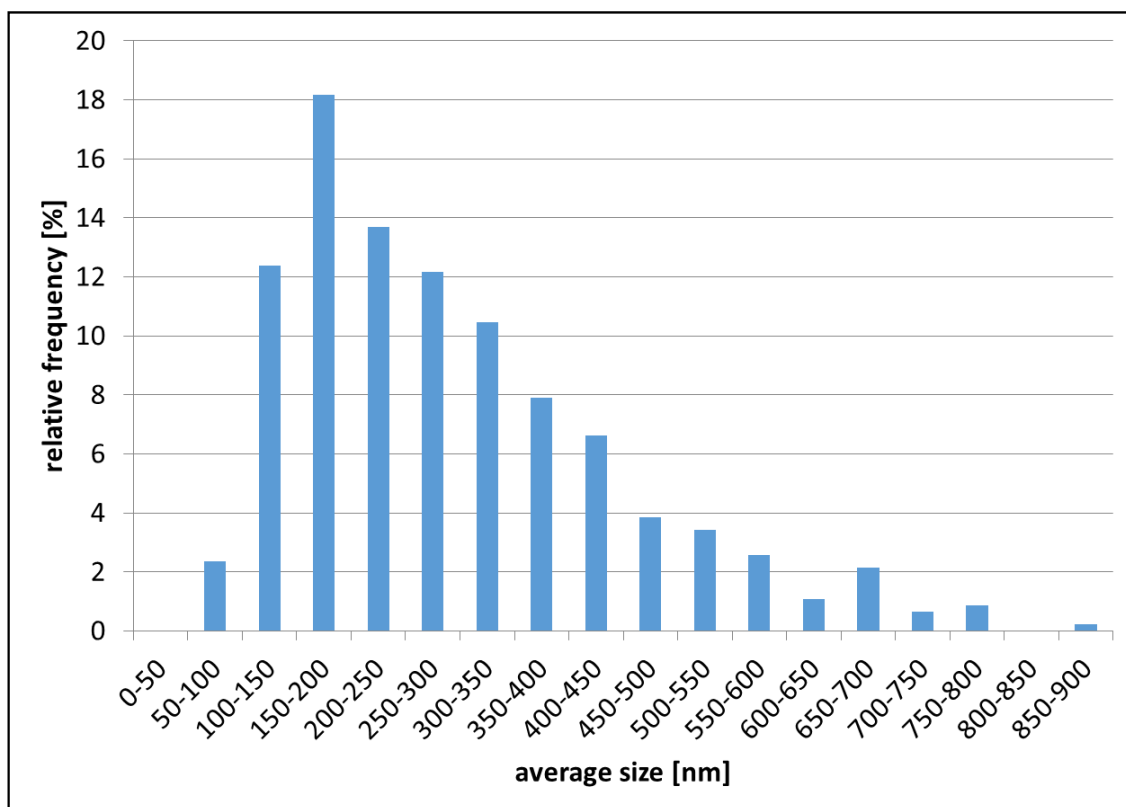


Figure 7. Average size distribution (calculated as average diameter) of Cr-rich carbides $M_{23}C_6$ in specimens from S1.

No creep damage was found, as only few small, isolated, cavities were spotted. For Laves phase, furthermore, the area fraction F_A (calculated as the percent ratio between the area sum of all Laves particles found in the field and the area of the field itself) was measured and the value found was 0.015.

The micrograph of S2 (Figure 8) shows an almost completely recovered martensite matrix, with no traces of the pre-existing needle-shaped structure typical of the as cast material. Several large cavities are easily observable.

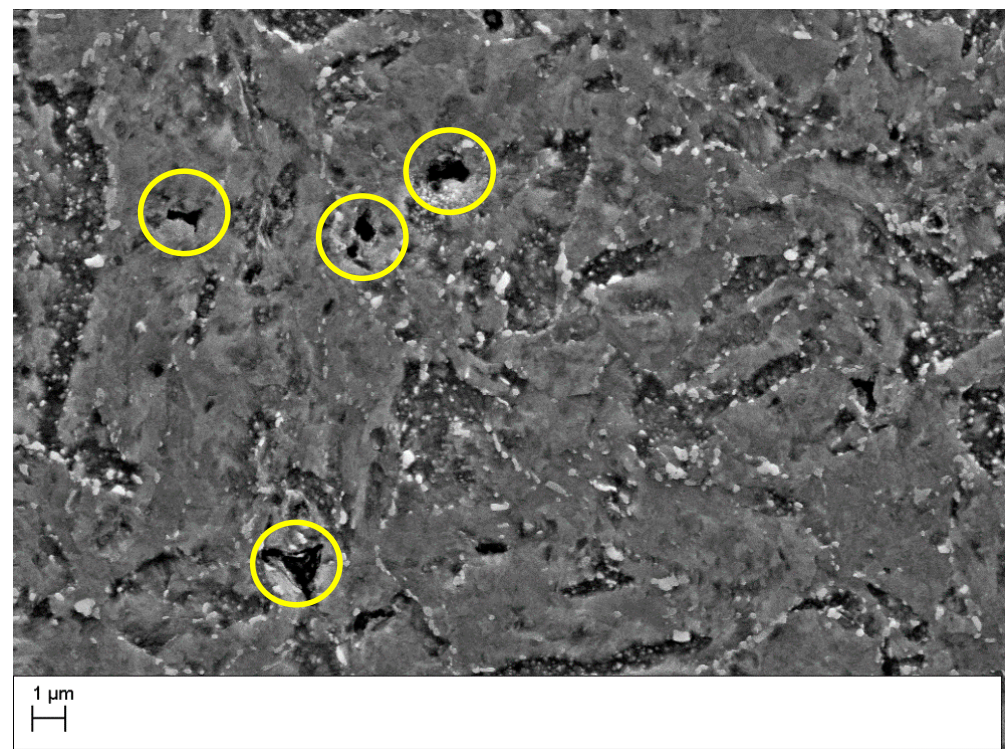


Figure 8. Microstructure of metallographic specimen from S2 tube. FEG-SEM micrograph, cross section. Etching: Vilella 20 s. Some cavities are evidenced by yellow circles. The secondary phases can be spotted as bright particles.

The size distribution of Laves phase is reported in Figure 9. The most frequent value is found in the 200–250 nm interval. This size is appreciably lower than the value (300–350 nm) found in samples aged under the same conditions (600 °C, 45,000 h), as shown in Figure 10; moreover, a comparison between these data pools shows that the number of smaller particles is larger in the ex-service material than in the aged one.

The area fraction F_A (calculated as the percent ratio between the area sum of all Laves particles found in the field and the entire area covered by the field itself) was 0.005: this is almost identical to the value found in the samples aged at the same conditions (600 °C, 45,000 h).

Then, data collected about secondary phases evolution in the ex-service materials suggest that a critical role in precipitation and particle coarsening is played by the applied stress (σ). S1 worked at low σ values, and its microstructure is almost similar to the typical structure of an aged grade 91 steel. S2, on the contrary, was exposed to a higher stress (over 250 bar) and shows appreciable differences with respect to a merely aged material. For the sake of precision, the stress which the tubes S1 and S2 were subjected to was tensile stress.

As also found by Orlova during creep tests performed up to a predetermined fractions of creep life t_F [18], in fact, if the temperature is the only factor acting on the microstructure evolution, there is a continuous monotonic increase in both size and number of Laves particles. If stress is also applied, an increase is observed in both number and size during

early stages of life (up to $0.2 t_F$), followed then, in the latter stages ($0.7 t_F$), by a decrease in size and by an increase in the number of smaller particles.

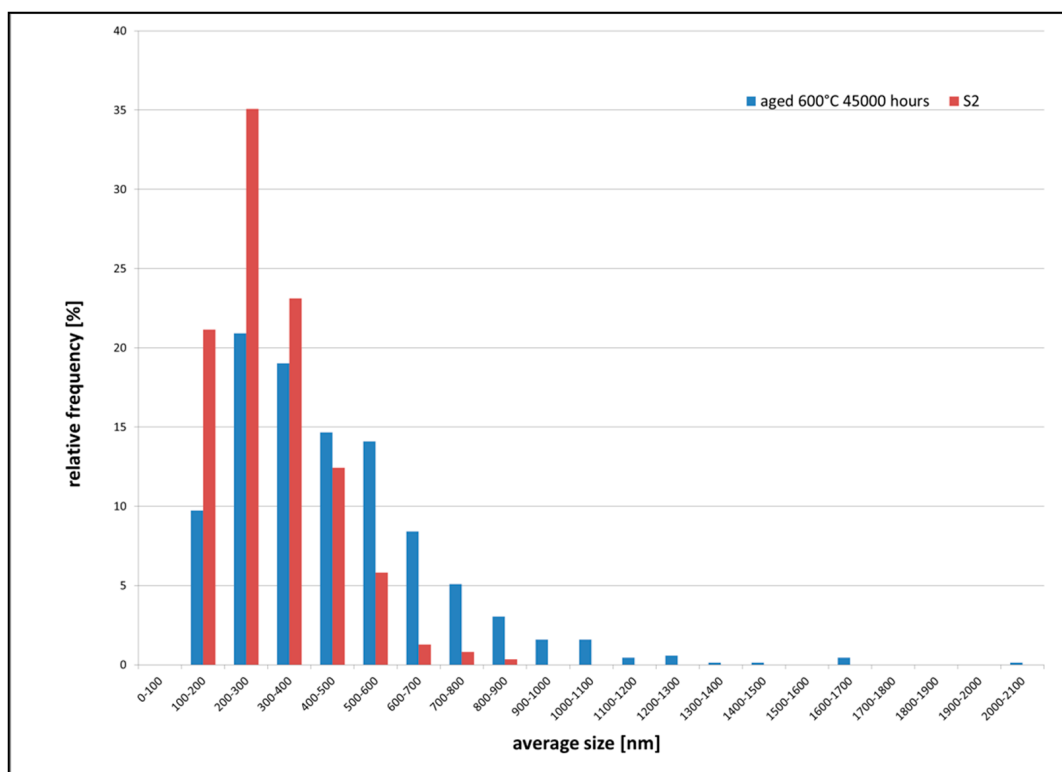


Figure 9. Average size distribution (calculated as average diameter) of Laves phase in steel specimens from S2.

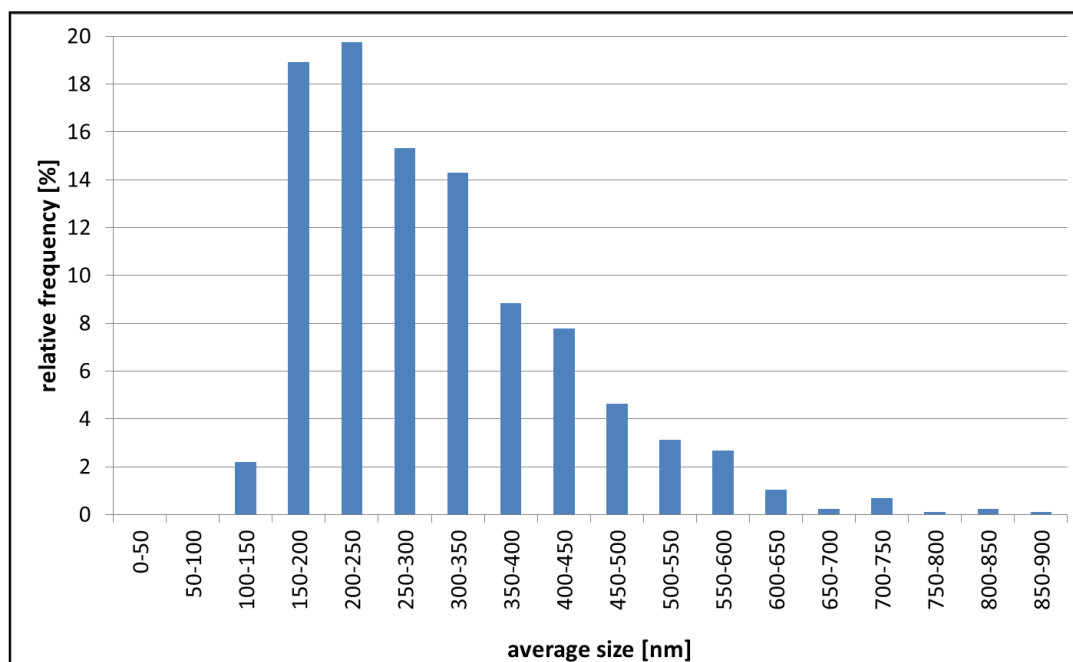


Figure 10. Comparison between Laves particles average size distributions of steel from S2 and a grade 91 sample aged 600 °C 45,000 h.

This trend seems to be influenced by two separate phenomena: the nucleation of new particles and the coarsening of pre-existing ones. Orlova assumes [18] that the increase in strain during the final stages of creep life triggers new precipitation of particles, so that their size distribution changes. The higher the applied stress, the more pronounced is the variation in the size distribution. In order to deepen knowledge on this topic, a Laves phase distribution study was performed on specimens, made by steel from S1, subjected to small punch creep tests, set to 580 °C and 480 N. The load was chosen using the conversion factor reported in the literature [20] in order to simulate a stress value of 210 MPa (i.e., a σ value comparable to the stress applied to S2 during service life). The specimens were named SPTa and SPTb and were tested up to rupture. As reported in Figure 11, in the tested specimens both smaller and larger particles show an appreciable increase in number; the most frequent value of the mean diameter is lower than in non-tested material (S1). The area fraction F_A (calculated as the percent ratio between the sum area of all Laves particles found in the field and the entire area covered by the field itself) shows a mean increase of approximately 11% (data not shown).

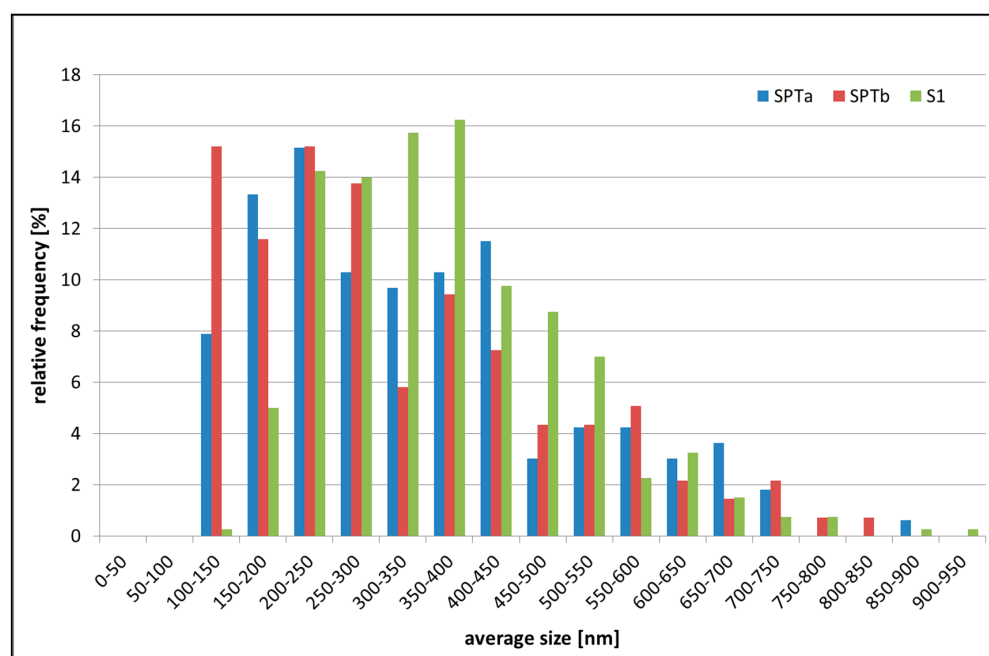


Figure 11. Laves particles average size distributions of specimens from SPTa, SPTb and S1.

Several cavities were spotted at PAGBs (Figure 12). The overall evolution pattern of the material was very similar to that observed on S2 sample. Results of small punch creep tests confirmed that when applied stress is high (over 200 MPa), it plays a remarkable role in Laves particles evolution and creep damage.

According to the experimental evidence, it is clear that temperature is an important factor affecting the microstructure evolution of grade 91 steels, but a more crucial role is played by applied stress. This latter, in fact, enhances precipitation of stress-concentrating Laves particles, promoting cavitation and creep damage. For this reason, it is now essential to concentrate the efforts on the following points:

- To continue material aging until 1×10^5 h;
- To start new creep tests on P91;
- To increase the small punch testing on new specimens from both as cast and ex-service P91;
- To continue ex-service material testing until 1×10^5 h as well as start new testing from ex-service P91.

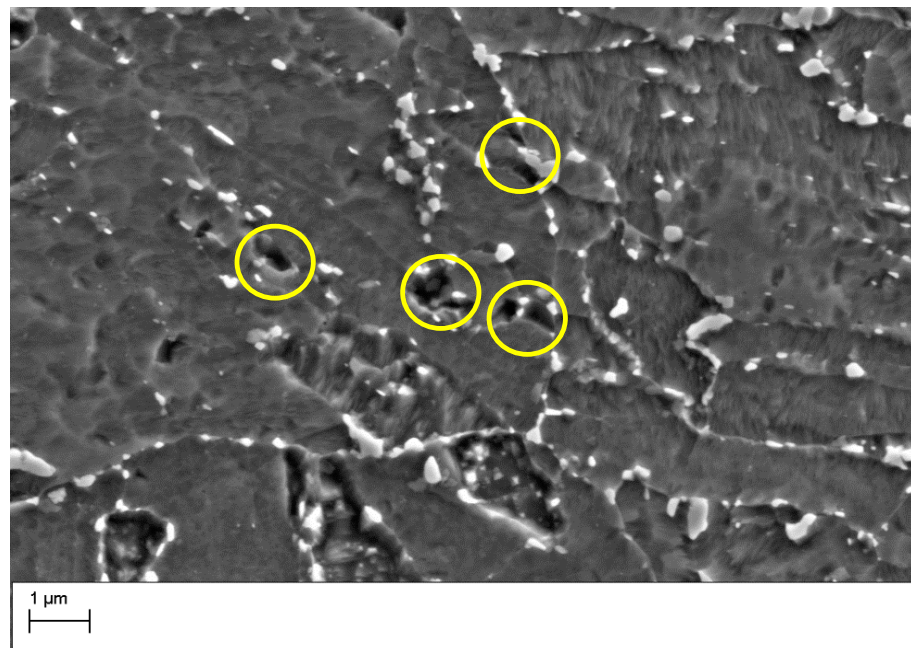


Figure 12. Microstructure of metallographic specimen cut from SPTa. FEG-SEM micrograph, cross section. Etching: Vilella 20 s. Some cavities are evidenced by yellow circles. The secondary phases can be spotted as bright particles.

The creep tests will allow for the evaluation of the effect of the mechanical stress on the evolution of the microstructure.

4. Conclusions

Some interesting trends were evidenced by this study regarding the microstructure evolution on both aged and ex-service materials:

- The martensite recovery is a patent proof of microstructure evolution. This is more evident if the stress is applied on the steel, in addition to temperature;
- The Laves phase precipitation and coarsening is the most evident indication of material aging. It starts to precipitate after 5000–10,000 h, generally at PAGBs. If temperature is the only applied factor, Laves particles show a monotonic increase in both size and number; temperature, however, must not exceed 600 °C, since over this threshold, Laves phase is more soluble into the matrix and particles become rare. If the stress is also applied, an increase is observed in both number and size during early stages of life, followed in the latter stages by a decrease in size and by an increase in the number of smaller particles. Laves phases can be considered preferential sites for stress concentration and are suspected to promote cavitation, especially if they nucleate at PAGBs;
- $M_{23}C_6$ carbides coarsening is minimal since their average diameter does not exceed 200–300 nm. These particles, however, show a typical evolution pattern that starts with a moderate coarsening, followed by a reduction when Laves phase precipitation occurs;
- The amount of MX carbonitrides remains almost unvaried during aging or service. These precipitates nucleate during the tempering and seem to be unaffected neither by aging nor by the applied stress;
- Z-phase was not found in either aged or ex-service materials, so that precipitation and coarsening of such particles cannot be considered a damage factor of grade 91 steels. Nevertheless, several hybrid particles, identified as Z-phase precursors, were spotted in some specimens.

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