

**Part 2**  
**Chairs: C. Fazio and R. Wright**

## **Stress corrosion cracking and oxidation of austenitic stainless steel 316 L and model alloy in supercritical water reactor**

**A. Sáez-Maderuelo, D. Gómez-Briceño, G. Diego**  
CIEMAT, Spain

### **Abstract**

*In this work, an austenitic stainless steel type 316 L was tested in deaerated supercritical water at 400°C and 500°C and 25 MPa to determine how variations in water conditions influence its stress corrosion cracking behaviour and to make progress in the understanding of mechanisms involved in SCC processes in this environment. Moreover, the influence of plastic deformation in the resistance of the material to SCC was also studied at both temperatures. In addition to this, previous oxidation experiments at 400°C and 500°C and at 25 MPa were taken into account to gain some insight in this kind of processes. Furthermore, a cold worked model alloy based on the stainless steel 316 L with some variations in the chemical composition in order to simulate the composition of the grain boundary after irradiation was tested at 400°C and 25 MPa in deaerated supercritical water.*

### **Introduction**

Generation IV nuclear reactors are the future of nuclear energy. Among all proposed designs, the SCWR is one of the more feasible options due to its more simple design, based on LWR, and the use of standardised materials which are well known. The result is a nuclear reactor with higher efficiency, around 45%, and safer than LWR. In spite of this, corrosion of cladding and structural materials in a not well-known coolant such as SCW is still one of the most important issue to be studied. The current design for the SCWR is a direct cycle system operating at 25 MPa with a inlet coolant temperature that moves from 280°C to 620°C and an average temperature around 500°C [1]. In this range, water moves from liquid to the supercritical zone where its behaviour is uncertain although, in general, it is thought to be a mixture between liquid and gas. Specifically, in the range between the critical point (374°C) and around 450°C, the properties of water such as density, ionic product and dielectric constant significantly drop [2]. These properties mainly depend on the pressure and increase when pressure increases. Moreover, since these reactors work at high temperature, this variable accelerates the corrosion processes. In fact, corrosion tests in supercritical water (SCW) are being used as an accelerated method to establish the behaviour of highly resistant materials, such as Alloy 690, to corrosion and SCC under LWR conditions, assuming that the mechanisms of corrosion and SCC are the same under the two sets of conditions [3-4] but this is not yet determined therefore it is not easy to interpret results from SCW tests. Austenitic stainless steels are candidate materials to build the SCWR. In many cases, austenitic stainless steels are cold worked to improve their mechanical properties or as result of manufacturing or welding processes. In any case, it has been shown that plastic

deformation in the material accelerates SCC in liquid water [5-6]. For this reason, it is necessary to study the influence of plastic deformation on these alloys in SCW. In this paper the resistance to SCC of austenitic stainless steel 316 L at 400 and 500°C, 25 MPa in deaerated supercritical water, with and without deformation was studied in order to understand the influence of different variables associated with the process. The SCC tests were performed by means of constant extension rate tensile (CERT) tests. In addition to this, to gain some insight of processes involved, previous oxidation results from a 316 L at 400°C and 500°C were taken into account. Furthermore, as a first step to understand the behaviour of these alloys under irradiation conditions in SCW, a cold worked model alloy, based on an austenitic stainless steel 316 L with some changes in its composition that simulates the composition of the grain boundary after irradiation was tested in deaerated SCW at 400°C and 25 MPa.

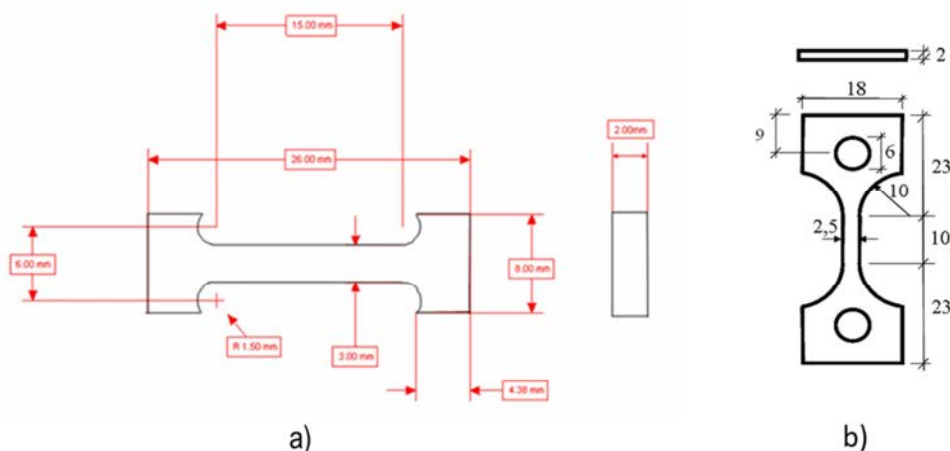
## Experimental

The austenitic steel 316 type L in as-received condition originated from a rolling plate. This plate was annealed at temperatures between 1 040 and 1 100°C. Subsequently, the plate was heated at 1 060°C for 30 minutes and then water quenched (WQ) to avoid carbides precipitation within the grain [7], to homogenise the microstructure and to relax tension from manufacturing process. The microstructure of the material after heat treatment shows an austenitic matrix without carbides in grain boundaries and in the matrix and with a grain size of 45 µm. Moreover, ferrite was observed in the rolling direction. Model alloy was manufactured from a 316 L alloy cast with an alteration in the chemical composition: an increase in Ni and Si content and a reduction in Cr content. After manufacturing process the ingot was heated up to 1 200°C for 2 h, then it was forged at 1 200°C up to 7-8 mm thickness, annealed at 1 050°C for 30 min., cold rolled and eventually it was annealed at 1050°C. The final thickness of the plates was approximately 10 mm. The chemical compositions of austenitic stainless steel 316 L and model alloy are listed in Table 1. Afterward, samples were machined by Electro Discharge Machining (EDM) from the plate with geometries shown in Figure 1.

**Table 1: Chemical composition of the stainless steel 316 L and the model alloy under study (wt%)**

	Al	C	Co	Cr	Cu	Fe	Mn	Mo	N	Ni	P	S	Si
<b>316L</b>	–	0.020	0.14	17.39	–	Bal.	1.28	2.20	0.020	11.49	0.032	0.001	0.45
<b>Model</b>	0.031	0.026	–	11.91	0.19	Bal.	0.96	0.381	0.0176	27.90	0.018	0.004	2.63

**Figure 1: a) Geometry of the samples for the alloy 316 L. b) Geometry of the samples for the model alloy (all measurements are in mm).**



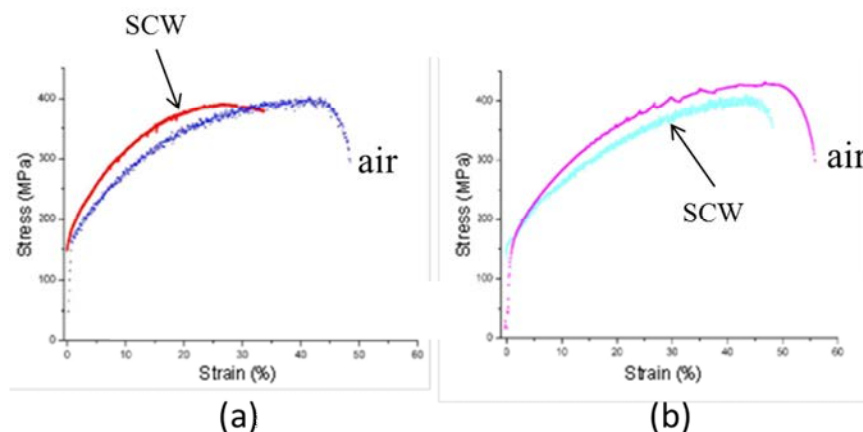
Some samples were strained by tensile at room temperature with a 100 kN MTS servo-hydraulic test machine to a strain rate of  $10^{-4} \text{ s}^{-1}$  to 20% of elongation for the purpose of studying the effect of strain in the behaviour to SCC of the 316 L and model alloy in supercritical water. The same machine was equipped with a furnace to study the mechanical properties of the material at room temperature, 400°C and 500°C. In all cases surfaces of samples were prepared using sandpaper to a grain size of P600. The study of SCC behaviour of 316L steel in supercritical water was carried out by CERT type tests in a circuit designed for this purpose and equipped with an autoclave made of alloy 625 with 4 liter capacity and a charging system that allows testing four samples at a time. Alloy 316 L specimens were tested at 400 and 500°C, at a pressure of 25 MPa in deaerated supercritical water and model alloy specimen was tested at 400°C and 25 MPa in deaerated supercritical water.

## Results and discussion

### Austenitic stainless steel

Austenitic stainless steel 316 L was tested to failure in supercritical water at 400°C and up to three different strain percentages: 3, 16 and 35% (failure) at 500°C. The stress-strain curves to failure at both temperatures are shown in Figure 2. Stress-strain curves at 400 and 500°C in air are included for comparison. At this point, it should be noted that this comparison is possible even though the material was tested in air at a rate faster than the rate of a CERT test ( $10^{-7} \text{ s}^{-1}$ ) because face centered cubic (FCC) metals and alloys are not affected (with some exceptions) by changes in the strain rate [8], moreover air is not very aggressive at 400-500°C. Mechanical parameters and results of surface analysis of 316 L samples after the tests are shown in Table 2.

**Figure 2: Stress-strain curves for alloy 316 L tested in supercritical water at 500°C (a) and 400°C (b) in deaerated water. (Stress-strain curves at 500°C and 400°C in air are included for comparison.)**



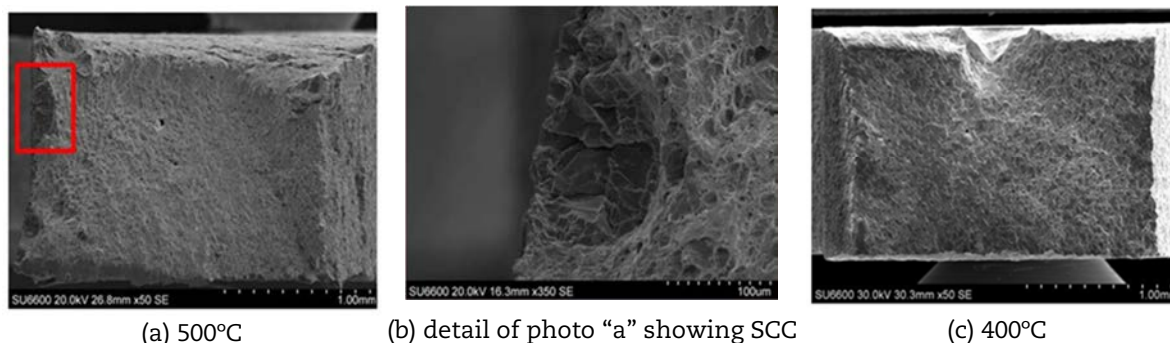
A lower elongation can be observed at both temperatures for samples tested in SCW (Figure 2) due to the effect of the environment. When both elongations are compared it is noticed that the decrease is higher in the sample tested at 500°C where the environment is apparently more aggressive. Moreover, in SCW at 500°C the material shows a higher hardness than in air. However, this effect is not observed in the sample tested in SCW at 400°C. This situation is supported by the crack density since the material has a higher density and a larger size crack at 500 than at 400°C. The higher susceptibility of the material to corrosion processes at 500°C is evidenced again studying the fracture surfaces, Figure 3. The image obtained by SEM of the fracture surface of the sample tested at 500°C shows a predominantly ductile fracture with small areas of granulated cracks [9]. On the other hand, the fracture surface of the sample tested at 400°C shows only a ductile fracture.

Although the rate used to carry out the CERT test ( $10^{-7} \text{ s}^{-1}$ ) is widely used [10,11], considering these results it is possible to ask whether the rate of this order of magnitude is slow enough to demonstrate the susceptibility of the material to SCC or it is too fast and, in cases like the specimen tested at 400°C, masks the possible effect of the environment [12].

**Table 2: Results of constant extension rate experiments performed in deaerated supercritical water for the alloy 316 L (<10 ppb O<sub>2</sub>).**

Material	Test conditions	$\sigma_Y$ (MPa)	$\sigma_{rs}$ (MPa)	$\epsilon$ (%)	Strain rate ( $\text{s}^{-1}$ )	Crack density ( $\text{n}^\circ/\text{mm}^2$ )	Crack size ( $\mu\text{m}$ )	Crack morphology
316 L	500°C/25 MPa/ <10 ppb O <sub>2</sub>	223	-	3	$10^{-7}$	Not observed	-	-
316 L	500°C/25 MPa/ <10 ppb O <sub>2</sub>	220	-	16	$10^{-7}$	Isolated cracks	~ 25	?
316 L	500°C/25 MPa/ <10 ppb O <sub>2</sub>	221	391	35	$10^{-7}$	61	65	?
316 L	400°C/25 MPa/ <10 ppb O <sub>2</sub>	260	410	48	$10^{-7}$	53	36	?

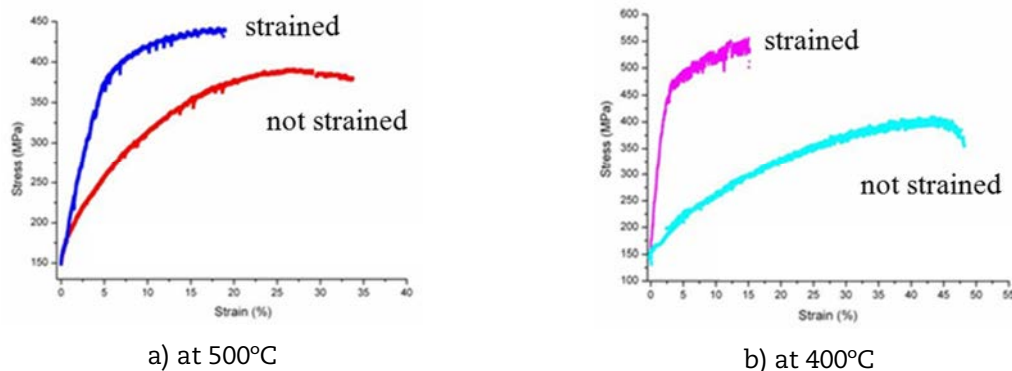
**Figure 3: Fracture surfaces of specimens tested at different temperatures in SCW (All surfaces are cleaned.)**



In addition, study of the SCC by CERT tests is a challenge because of the different trend of the results depending on the criteria used to evaluate them. Teyseyre and Was [10] presented results for several alloys where the material showed different susceptibility to SCC depending on the measurements performed by the authors: density of cracks or crack depth. Stress-strain curves of strained samples tested in SCW at 400 and 500°C are shown in Figure 4. Results of CERT tests for these samples are shown in Table 3.

**Figure 4: Stress-strain curves for alloy 316 L strained samples tested in supercritical water in deaerated water**

(Stress-strain curves in SCW at 400°C and 500°C of samples without strain are included for comparison.)



**Table 3: Results of constant extension rate experiments performed in deaerated supercritical water for 316 L strained samples.**

Material	Test conditions	$\sigma_Y$ (MPa)	$\epsilon$ (%)	Strain rate ( $s^{-1}$ )	HV	Crack density ( $n^\circ/mm^2$ )	Crack size ( $\mu m$ )	Crack morphology
316 L	400°C/25 MPa/ <10 ppb O <sub>2</sub>	473	18	10 <sup>-7</sup>	229	Isolated cracks (+slip bands)	-	?
316 L	500°C/25 MPa/ <10 ppb O <sub>2</sub>	413	17	10 <sup>-7</sup>	220	53	17	?

According to these results, in general, the presence of deformation in the material produces an increase of susceptibility to SCC in SCW of the alloy 316 L, as it happens for the same material under PWR conditions [5]. Again, the sample tested at 500°C is more susceptible of SCC than the one tested at 400°C. Nevertheless, it should be pointed out that the sample tested at 400°C also shows attacked zones where dislocations emerge, like slip bands. It may be caused by the higher oxidation effect of supercritical water in zones with localised deformation. For this reason, evaluating the crack density in this sample is not easy. In PWR conditions it is accepted that alloy 316 L is susceptible of SCC for hardness around 300 HV [13-15]. However, in supercritical water this material shows cracks for lower hardness values. Currently some authors [15] are taking into account other criteria, such as the maximum applied stress, to evaluate the susceptibility of the material. Comparing stress-strain curves for samples tested in SCW with and without deformation it could be seen again the hardening of sample tested at 500°C which is higher than the hardening of sample tested at 400°C. At 500°C the curve of the sample without strain is closer to the curve of the strained sample. At 400°C differences between these two curves are more pronounced. Results obtained in this work along with difficulty to evaluate results from a CERT test [10,16] do not establish a clear trend in the behaviour of the material to SCC in SCW, although apparently it may be more susceptible at higher temperature. Before giving an explanation to this behaviour it is important to consider the drop of properties of water into the supercritical zone. Some authors suggest that between 400°C and 500°C, around 470°C where density of water is 100 kg/m<sup>3</sup>, the mechanism switches from electrochemical oxidation to chemical oxidation. This change could play an important role in the response of the material to SCC and oxidation in SCW. Previous oxidation tests in SCW performed with the alloy 316 L at 400 and 500°C and 8 ppm O<sub>2</sub> [1] shows subtle differences between the composition of oxide layers formed at both temperatures like the presence of Ni in the oxide layer formed at 500°C but not at 400°C. Another important point that must be considered is the behaviour of the Cr in SCW. Recent articles [17] present Pourbaix diagram for Cr from subcritical to supercritical conditions, specifically to 400°C. Despite the limitations of these diagrams, in test conditions at 400°C and neutral pH, Cr<sub>2</sub>O<sub>3</sub> is stable but also depends on the potential of the medium (not known in this study), the oxidation may also be possible. Some authors [18] establish the stability range for Cr<sub>2</sub>O<sub>3</sub> at 350°C for an amount of dissolved oxygen between 0 and 400 ppb. The threshold seems to be above 400 ppb at a temperature of 450°C although more studies are necessary to define it clearly. In any case, it is expected that the potential of the reaction Cr<sup>3+</sup>/Cr<sup>6+</sup> decreases as temperature increases [19].

### Model alloy

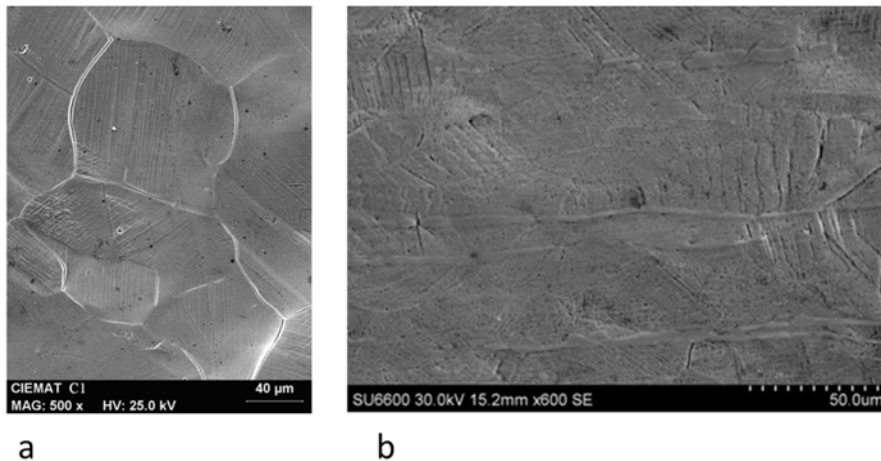
The model alloy was previously strained by tensile until 20% of strain and then it was tested in deaerated SCW at 400°C. Mechanical parameters and results of surface analysis of model alloy sample are shown in Table 4.

**Table 4: Results of constant extension rate experiments performed in deaerated supercritical water from prestrained model alloy sample.**

Material	Test conditions	$\sigma_y$ (MPa)	$\epsilon$ (%)	Strain rate ( $s^{-1}$ )	HV	Crack density ( $n^\circ/mm^2$ )	Crack size ( $\mu m$ )	Crack morphology
Model	400°C/25 MPa/ <10 ppb O <sub>2</sub>	426	8.7	10 <sup>-7</sup>	256	Isolated cracks (+slip bands)	-	?

It is known that the model alloy is susceptible to SCC under Primary Water Reactor (PWR) conditions [20]. Nevertheless, there is no information about its behaviour in SCW. Although it could be expected a higher susceptibility for the model alloy to SCC in SCW than for the alloy 316 L, according to results obtained in this work there are not big differences between the behaviour of these alloys. Moreover, the evaluation of crack density of the model alloy is not easy due to the existence of attacked zones where dislocations emerge as it was reported for the alloy 316 L strained and tested at 400°C in SCW. On the other hand, comparing results obtained for the model alloy in SCW and results from other authors [20] for the same alloy but obtained under PWR conditions, it could be expected a higher crack density at 400°C than in PWR conditions only because of the effect of temperature. Furthermore, the model alloy was previously deformed up to 20% while the sample tested in water was deformed up to 10%. After CERT test, model alloy in SCW was strained up to around 9% while sample tested in PWR conditions was strained up to 5%. In spite of the most unfavourable conditions, sample tested in SCW do not show clear cracks which are observed in samples tested under PWR conditions (Figure 5). For this reason, the behaviour of the environment seems to be different under both conditions. To gain some insight, more studies are necessary in order to clarify these results where the effect of the environment, which is not well known, seems to play an important role.

**Figure 5: Micrographs obtained by scanning electron microscope from model alloy samples previously deformed and tested in liquid water (PWR conditions; a) and in deaerated supercritical water at 400°C (b)**



## Conclusions

- The stainless steel 316 L has a good behaviour at both temperatures showing a better response at 400°C with a lower crack density on the surface and no signs of corrosion in the fracture surface. Nevertheless, there are several doubts about whether the rate test is appropriate to show the real behaviour of this alloy to SCC in supercritical water at 400°C. Furthermore, the study of the SCC by a CERT test is a challenge because of the different trend of the results depending on the criteria used to evaluate them.

- The presence of deformation in the material increases the susceptibility of the alloy to SCC in supercritical water. Again, the sample tested at 400°C shows a better response to SCC than the one tested at 500°C.
- Previous studies of the oxide layers obtained in supercritical water at 8 ppm O<sub>2</sub> show subtle differences between the composition of oxide layers like the presence of Ni only in the oxide layer formed at 500°C.
- There are not big differences neither between the behaviour of the austenitic stainless steel 316 L and the model alloy previously strained in SCW at 400°C, in spite of differences in the composition, nor between results from the model alloy tested in PWR conditions and from SCW. For this reason it is suspected that water behaves in a different way in the liquid region and in the supercritical region.

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