# STRESS CORROSION CRACKING OF COLD-WORKED AUSTENITIC STAINLESS STEELS\*

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Abstract—Stress corrosion cracking (SCC) of AISI 304L and AISI 316L stainless steels, cold-worked under various conditions (i.e. at different degrees of deformation obtained by drawing and rolling at room temperature and at liquid nitrogen temperature) has been carried out in H<sub>2</sub>O containing 1000 ppm Cl<sup>-</sup> at 250°C and in a boiling MgCl<sub>2</sub> solution. The effect of heat treatments at 400 and 900°C on the SCC of previously cold-worked steels has also been studied. Particular attention was directed towards heat treatment at 400°C. In steels deformed at room temperature, it increases the SCC resistance. By contrast, for steels deformed at liquid nitrogen temperature, heat treatment at 400°C reduces the SCC resistance if carried out for short periods of time (1–6 h). Hardness measurements, structural analyses via X-rays, scanning and transmission electron microscopy (SEM and TEM), as well as modified Strauss tests, seem to prove that reduced stress corrosion resistance is not to be related to the chromium-rich carbides precipitation which could have been accelerated by the presence of  $\alpha'$ -martensite. Instead, they tend to suggest that perhaps this phenomenon is connected to an increase in the level of internal micro-stresses which are generated by a reciprocal re-ordering of the  $\alpha'$  and  $\gamma$  structural phases.

## INTRODUCTION

EXTENSIVE study has been done on the stress corrosion cracking (SCC) of ironnickel-chromium alloys in aqueous environment containing Cl<sup>-</sup>: the main factors involved and the mechanism aspects have been reviewed by a number of authors, notably Latanision and Staehle,<sup>1,2</sup> Theus and Staehle,<sup>3</sup> Cowan and Gordon,<sup>4</sup> Thompson and Bernstein,<sup>5,6</sup> Dean,<sup>7</sup> and more recently Hänninen.<sup>8</sup> These reviews should be taken as a guide to the earlier literature.

While most of SCC data refer to the role of applied stresses in order to find the threshold values for SCC occurrence, few efforts have been made until now to clarify the effect that cold plastic deformation can have on the environment-sensitive cracking of these and other types of steels, also in a nuclear context.<sup>9</sup>

In particular, the role played by austenite transformation and internal stresses has yet to be completely defined. As is well known, these stresses are one of the most important factors controlling SCC, together with the substructure of the dislocations, and the  $\varepsilon$  and  $\alpha'$ -martensite caused by cold plastic deformation.<sup>8</sup>

The problem is unquestionably of practical interest since austenitic stainless steels are often used in a totally or locally work-hardened state and immersed in hightemperature aqueous environments containing low concentrations of chlorides.

The aim of this study is to determine the stress corrosion susceptibility of coldworked AISI 304L and AISI 316L austenitic stainless steels, as a function of the type (drawing and rolling), degree (10, 30 and 50%), and temperature (room temperature and -196°C) of the cold-working. We also wanted to identify the role played by subsequent heat treatments at  $400^{\circ}$  and  $900^{\circ}$ C.

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Of the aggressive media usually used for stress corrosion tests on stainless steels, the following were selected: (a) a solution of water containing 1000 ppm Cl<sup>-</sup> heated at  $250^{\circ}$ C, and (b) the classical boiling MgCl<sub>2</sub> solution.

X-ray diffraction and transmission electron microscopy were used to analyze the structural modifications induced by the cold plastic deformation and the subsequent heat treatments. This is one aspect of the problem of correlation between cold plastic deformation and the corrosion behaviour of commercial austenitic stainless steels, which we have been studying systematically for a long time.<sup>10-17</sup>

### EXPERIMENTAL METHOD

The materials subjected to stress corrosion tests were AISI 304L and AISI 316L commercial austenitic stainless steels, i.e. hot-products derived from different heats. Their chemical compositions are given in Table 1. Bars or strips were subsequently cut and properly machined. These were first annealed at 1050°C for 1 h and then water quenched (solution heat treatment) in order to completely dissolve any of the existing carbides and thereby obtain a purely austenitic structure. The austenitic grain size was measured through metallographic etching (standard ASTM E 112).<sup>18</sup> A total absence of carbides was verified at the grain boundaries.

The solubilized bars and strips were cold-worked at room temperature and at  $-196^{\circ}$ C by drawing and rolling, as described in previous papers.<sup>10-17</sup> The  $\alpha'$ -martensite induced by the cold plastic deformation was determined by means of magnetic measurements.<sup>16,17</sup> The structural properties of the materials after cold-working are illustrated in Table 2.

The specimens for corrosion tests were obtained by wheel-cutting the central part of the bars and strips and simultaneously cooling them in a continuous stream of water and oil so as to avoid any overheating or work-hardening. The sizes chosen for the specimens were those which would not excessively modify the internal stress distribution (since this is affected by reductions in specimen size).

The drawn specimens were wet-ground on the two transverse surfaces with emery paper of decreasing granularity, down to 1000 mesh ( $\simeq 25 \,\mu$ m). The rolled specimens were ground on all six surfaces. The specimens were then electropolished in a solution of 80% perchloric acid (at 70%) and 20% ethanol (at 95%) for 45 s at 12 V. Finally, they were ultrasonically rinsed in ethanol and then in distilled water.

A series of specimens was taken from cold-rolled strips with a 50% degree of deformation. Some were heat treated at 400°C for 1, 6, 24, and 1000 h, and others at 900°C for 1 or 6 h; they were then quenched in stirred oil. Vickers micro-hardness tests were conducted on the short-transversal surfaces of these heat-treated specimens.

Corrosion tests were carried out both in hot  $H_2O$  containing 1000 ppm Cl<sup>-</sup> and in a boiling MgCl<sub>2</sub> solution. High purity chemical reagents were used.

The tests in  $H_2O$  containing 1000 ppm Cl<sup>-</sup> were carried out in a pressurized titanium tank at about 250°C. A solution with the required concentration of Cl<sup>-</sup> ions was obtained by adding the corresponding amount of NaCl to naturally aerated distilled water; the resulting pH was  $5.4 \pm 0.05$ . The bottom and walls of the tank were teflon-coated in order to avoid galvanic coupling between the specimens and the tank itself. The tank was then placed in a furnace which was maintained at a constant temperature of 250°C. It took 10 h to reach the selected temperature and the same amount of time to return to room temperature. In these tests, all of the specimens of the two types of steel were simultaneously dipped into the solution and, at each extraction, they were immediately rinsed in distilled water (without removing the corrosion products) and then microscopically examined in order to find any cracks. The crackless specimens were placed in a fresh solution (the previously used solution contained a large amount of corrosion products, resulting mainly from the crevice corrosion of the specimens, caused by the interstice between the specimen itself and the bottom of the tank). The tank was then put back into the furnace and the test was repeated.

It is important to recognize that an appropriate inspection time is extremely difficult to determine. A short period of time would be advisable so as to precisely identify the time of crack initiation. The more frequent the inspection is, however, the more the cracking initiation time increases. Consequently, preliminary tests had to be conducted before determining an appropriate inspection time.

The boiling MgCl<sub>2</sub> solution tests were carried out according to the standard ASTM G 36 at 155°C.<sup>19</sup> Each test consisted of the simultaneous immersion and subsequent extraction of all the specimens which were of the same type of steel and which had been cold-worked at the same temperature. As

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Table

cing	50	50
Cold-worl by	Drawin Rolling	Drawin Rolling
TM micro-grain ( number	6–6.5 4–5	5.5–6 3.5–4.5
S AS	0.021 0.013	0.021 0.011
<u>م</u>	0.035 0.032	0.034 0.008
Cu	0.25 0.24	0.08 0.07
) Mo	0.50 0.32	3.00 2.20
ion (wt % Ni	8.75 10.30	10.90 10.90
Composit Cr	18.60 18.10	16.60 16.10
Mn	1.39 1.40	1.45 1.24
Si	0.47 0.41	0.40 0.41
z	0.037 0.039	0.037 0.034
Ð	0.027 0.020	0.023 0.026
Heat	A B	υq
Stainless steel type	AISI 304L	AISI 316L

Stainless steel type	Heat	Туре	Deformation Temperature (°C)	Degree* (%)	Vickers hardness number†	X-ray diffraction Phases‡
				0	143	γ
				10	200	$\gamma + \alpha'(\mathbf{v}.\mathbf{l}.\mathbf{\dot{b}})$
			25	30	292	$\gamma + \alpha'(m,q)$
				50	366	$\gamma + \alpha'(m.)$
AISI 304L	A	D		10	298	$\gamma + \alpha'(m.) + \epsilon(v.l.)$
			-196	30	406	$\gamma + \alpha'(p)$
				50	494	$\gamma + \alpha'(l.p.)$
				0	136	γ
				10	192	γ
			25	30	272	Ŷ
	_	-		50	331	Ŷ
AISI 316L	С	D		10	246	$\gamma + \alpha'(l_{\star})$
			- 196	30	400	$\gamma + \alpha'(m,q_{\star}) + \epsilon(\mathbf{v},\mathbf{l}_{\star})$
				50	413	$\gamma + \alpha'(\mathbf{p}.)$
				0	135	γ
				10	203	$\gamma + \alpha'(v.l.)$
			25	30	272	$\dot{\gamma} + \alpha'(v.l.)$
	_	-		50	320	$\gamma + \alpha'(l.)$
AISI 304L	В	ĸ		10	272	$\gamma + \alpha'(m.q.) + \epsilon(v.l.)$
5012			- 196	30	417	$\gamma + \alpha'(p_1) + \epsilon(v_1)$
				50	460	$\gamma + \alpha'(l.p.) + \epsilon(v.l.)$
· · · · · · · · · · · · · · · · · · ·				0	142	γ
				10	200	γ̈́
			25	30	280	Ŷ
		P		50	337	Ŷ
AISI 316L	D	R	·	10	260	$\gamma + \alpha'(m.q.)$
2102			- 196	30	421	$\gamma + \alpha'(p.) + \varepsilon(v.l.)$
				50	456	$\gamma + \alpha'(l.p.)$

TABLE 2. STRUCTURAL PROPERTIES OF THE COMMERCIAL

\*Quantified as reduction in the cross-sectional area.

†Values measured on transversal sections (in the case of rolling long-transversal sections) with respect to the deformation direction.

type: to the deformation direction.  $v.l. = very little (\leq 1\%); l. = little (1-10\%); m.q. = medium quantity (10-40\%); m. = much$ (40-50%); v.m. = very much (50-60%); p. = prevailing (60-80%); l.p. = largely prevailing(> 80%); n.o. = not observed; n.d. = not discernible; h.d. = hardly discernible; s.d. = stilldiscernible.

D = Drawing.R = Rolling.

Magnetic	Dislocations	Transmission	, <u>.</u>	
Ferro-magnetic phase (wt%)	density (× 10°cm/cm <sup>3</sup> )	Deformation bands‡	α'-martensite‡	Austenite‡
0.30	0.90	and the second	-	<b>≃100</b> %
0.40	30	ι.	n.o.	<b>≃100%</b>
9.2	—	v.m.	m.q.	l.p.
35.7		p.	v.m.	p
31.6		v.m.	v.m.	р.
78.2		h.d.	р.	Ι.
88.8		h.d.	l.p.	n.d.
0.04	1.0			100%
0.04	20	l.	n.o.	$\simeq 100\%$
0.20		v.m.	v.l.	l.p.
1.70	anderes a	l.p.	i.	l.p.
3.2		v.m.	1.	l.p.
54.8		s.d.	р.	m.q.
75.6	· 1998	h.d.	l.p.	Ι.
0.05	1.0			$\simeq 100\%$
0.14	17	m.q.	n.o.	l.p.
0.60	>20	p.	n.o.	l.p.
2.35	>20	p.	n.o.	l.p.
26.2	139M	m.	m.g.	p.
63.0		р.	v.m.	m.q.
86.5		h.d.	l.p.	n.d.
0.06	1.6			100%
0.06	> 20	m.q.	n.o.	$\simeq 100\%$
0.13		р.	n.o.	l.p.
0.70		p.	n.o,	l.p.
26.6		v.m.	m.g.	p.
57.3		р.	v.m.	m.g.
62.6		s.d.	l.p.	l.

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soon as the specimens were taken out of the solution, they were rinsed in distilled water, microscopically examined and then, if no cracks were found, they were dipped again in the flask.

A series of specimens heat-treated at  $400^{\circ}$ C were subjected to a modified Strauss test (A262E)<sup>20</sup> in order to monitor sensitization. Prior to this test, all specimens received a final ultrasonic cleaning and were weighed. They were then placed in a boiling solution of sulphuric acid and copper sulphate (with Allihn condenser) for 24, 48, 72 and 96 h. During the test, the specimens were in direct contact with copper turnings. Afterwards, they were removed from the solution, ultrasonically cleaned and weighed again.

The steels which had been deformed and then heat treated at 400°C were subjected to structural analysis by taking X-ray diffraction patterns and transmission electron micrographs. A Jeol DX 8S diffractometer was used; the radiation was CuK $\alpha$  filtered with a graphite monochromator. The short-transverse surfaces of the specimens were exposed to radiation, and the diffraction patterns were registered via a rotating goniometer at a speed of 0.5° min<sup>-1</sup>.

After the stress corrosion tests, the fracture surfaces were systematically analyzed under a scanning electron microscope.

## EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1 and 2 show the results of stress corrosion tests in hot naturally aerated distilled water containing 1000 ppm of Cl<sup>-</sup>, for drawn alloys and rolled alloys respectively. The plotted curves correlate (at each one of the two temperatures of deformation) the degree of deformation with the time for the appearance of cracks, the latter being indicated as failure time.

From these results, it is evident that: (a) the susceptibility of the considered alloys to SCC is unrelated to the type of cold deformation, (b) the susceptibility to SCC increases as the degree of deformation increases. When the degree of deformation is kept constant, the susceptibility to SCC increases as the deformation temperature decreases, and (c) the susceptibility to SCC is substantially the same for the two alloys



FIG. 1. Effect of cold-drawing on resistance to SCC of AISI Types 304L and 316L stainless steels in high temperature chloride water. Deformation at room temperature:  $\triangle = \text{no cracking}$ ,  $\blacktriangle = \text{cracking}$ ; deformation at  $-196^{\circ}\text{C}$ :  $\bigcirc = \text{no cracking}$ ,  $\blacklozenge = \text{cracking}$ .



FIG. 2. Effect of cold-rolling on resistance to SCC of AISI Types 304L and 316L stainless steels in high temperature chloride water. Deformation at room temperature:  $\Delta = \text{no cracking}, \blacktriangle = \text{cracking}; \text{deformation at } -196^{\circ}\text{C}: \bigcirc = \text{no cracking}, \blacklozenge = \text{cracking}.$ 

at a deformation temperature of  $-196^{\circ}$ C. The opposite is true for deformation at room temperature, where AISI 316L seems to behave better than AISI 304L. In fact, for AISI 304L, SCC always manifests itself when deformation degree is higher than 10%. For AISI 316L, this is true only for deformation at  $-196^{\circ}$ C; for deformation at room temperature, SCC appears when deformation degree is higher than 30%.

The cracks always initiated from the transverse surface for the drawn specimens, and from the short transverse for the rolled ones, as can be seen from Fig. 3.

Figures 4 and 5 show the results of analogous stress corrosion tests conducted in boiling aqueous  $MgCl_2$ . These results prove that: (a) the susceptibility of the two alloys to SCC is unrelated to the type of cold deformation, (b) the susceptibility to SCC increases as the degree of deformation increases. When the latter is kept constant, susceptibility is little affected by deformation temperature [this is particularly true for drawn specimens (see Fig. 4)], and (c) the susceptibility of the two alloys to SCC is substantially the same if all experimental conditions are kept constant. SCC always appears when deformation degree is greater than 10%.

In the rolled alloys, susceptibility to SCC is greater on the short transverse surface than on the long transverse, as can be seen by comparing Figs 5 and 6. This latter figure illustrates that when the short transverse surface is epoxy-resin coated, cracking time on the long transverse surfaces is longer; it also reveals that for deformation at room temperature, SCC appears in rolled AISI 316L when deformation degree is greater than 30 %.

Finally, if both the long and short transverse surfaces are coated, so that only the longitudinal surfaces are exposed to the aggressive medium, stress corrosion does not occur.



FIG. 4. Effect of cold-drawing on resistance to SCC of AISI Types 304L and 316L stainless steels in boiling magnesium chloride solution. Deformation at room temperature:  $\triangle =$  no cracking;  $\triangle =$  cracking; deformation at - 196°C:  $\bigcirc =$  no cracking,  $\triangle =$  cracking.



FIG. 5. Effect of cold-rolling on resistance to SCC of AISI Types 304L and 316L stainless steels in boiling magnesium chloride solution. Deformation at room temperature:  $\triangle$  = no cracking;  $\triangle$  = cracking; deformation at - 196°C:  $\bigcirc$  = no cracking,  $\bigcirc$  = cracking.



FIG. 3. Typical macroscopic appearance of stress corrosion cracks on specimens of cold-drawn (a) and cold-rolled (b) AISI Types 304L or 316L stainless steels in high temperature aqueous environment containing Cl<sup>-</sup>.



FIG. 7. Scanning electron micrographs of typical stress corrosion fractures on specimens of cold-rolled AISI Types 304L (a) and 316L (b) stainless steels in boiling magnesium chloride solution. Thermo-mechanical conditions: 50% rolling at -196°C and subsequent heat treatment at 400°C for 0, 1 and 1000 h (as indicated).



FIG. 11. Bright and dark fields in transmission electron micrographs of the AISI Type 304L stainless steel 50% rolled at  $-196^{\circ}$ C and heat-treated at 400°C for 1 h (a) and 1000 h (b). The carbides in (b) were indexed as  $M_{23}C_6$ .



FIG. 6. Effect of cold-rolling on resistance to SCC of AISI Types 304L and 316L stainless steels in boiling magnesium chloride solution. Cracking on long-transversal (L-T) surfaces. Deformation at room temperature: △ = no cracking, ▲ = cracking; deformation at - 196°C: ○ = no cracking, ● = cracking.

The cracks initiated from the transverse surface for drawn specimens and from the short-transverse surface for rolled specimens. The cracks revealed a mixed morphology of the trans-intergranular type, as shown in the micrographs in Fig. 7.

A comparison of the tests in the two different aggressive media (compare Figs 1 and 2 with Figs 4 and 5), shows substantially the same behaviour with two quantitative differences: (a) a shorter cracking initiation time in boiling aqueous  $MgCl_2$ ; this was to be expected given the particularly high and specific aggressivity of such a solution, and (b) a minor effect (in some cases, no effect at all) of the deformation temperature on the susceptibility to SCC in boiling aqueous  $MgCl_2$ . This can be a direct consequence of point (a) in the sense that the particularly high aggressivity of boiling aqueous  $MgCl_2$  does not permit a differentiation between a work-hardened prevalently austenitic structure and one which is predominantly martensitic (see Table 2), both of them having the same chemical composition.<sup>21</sup>

Figure 8 shows the effect of heat treatments at 400 and 900°C on the two considered steels which were rolled up to a 50% degree of deformation respectively at room temperature (Fig. 8a) and at -196°C (Fig. 8b). In this case the plotted curves correlate (for each one of the considered steels) the heat treatment duration with the cracking initiation time.

As was to be expected, heat treatment at 900°C eliminates susceptibility to SCC in boiling aqueous MgCl<sub>2</sub> in less than 1 h. The metallographic, magnetic, and X-ray diffraction analyses demonstrate that the initial structure of the cold-worked steels (in particular, the  $\alpha'$ -martensite) (see Table 2) was transformed into austenite of equiaxed re-crystallized grains. Thus, heat-treatment at 900°C cancelled out the



FIG. 8. Effect of heat treatments at 400° and 900°C on resistance to SCC in boiling magnesium chloride solution for AISI 304L ( $\triangle =$  no cracking,  $\blacktriangle =$  cracking) and AISI 316L ( $\bigcirc =$  no cracking,  $\bullet =$  cracking) stainless steels 50% rolled at room temperature (a) and at - 196°C (b).

internal stresses and consequently susceptibility to SCC, as was confirmed in boiling  $MgCl_2$  tests carried out for 30 days.

The phenomena resulting from heat treatment at 400°C are particularly interesting. This treatment diminishes, but does not cancel out, susceptibility to SCC in boiling aqueous MgCl<sub>2</sub> for the two steels with 50% deformation, rolled at room temperature (Fig. 8a). For specimens deformed at  $-196^{\circ}$ C (Fig. 8b), it initially increases (between 1-6 h) and then diminishes susceptibility; moreover AISI 304L is made less resistant than AISI 316L. Along with the appearance of a maximum susceptibility to SCC, the following was also noted: (a) a strong increase in Vickers hardness in the first hour of treatment at 400°C, and a gradual and slight increase for longer periods of time (Fig. 9), (b) the lack of sensitization until approx. 24 h of treatment at 400°C in AISI 304L, and until approx. 6 h in AISI 316L (Fig. 10), (c) a mixed trans-intergranular crack which, in any case, is similar to the cracking noticed in specimens which are coldworked and not heat-treated at 400°C (Fig. 7), and (d) the lack of precipitates after 1 h and the appearance of a very fine precipitate after 1000 h of treatment at 400°C, as



FIG. 9. Effect of heat treatments at 400 and 900°C on Vickers hardness of AISI Types 304L and 316L stainless steels 50% rolled at room temperature and at -196°C.

observed in the TEM analysis on AISI 304L which is used as an example (Fig. 11).

Finally, Fig. 12 shows the results of X-ray diffraction tests from which the following conclusions can be drawn: (a) in the solubilized state, the alloys are only composed of austenite having a preferred orientation; the predominant reflexion seems to correspond to plane (111), (b) alloys rolled at  $-196^{\circ}$ C, up to a 50% deformation, are mainly composed of highly oriented grains of  $\alpha'$ -martensite and of retained austenite [the grains of both are more oriented in AISI 316L than in 304L; the reflexion of the (110) and (111) planes is predominant, though that of the (200) plane can still be seen in AISI 304L], (c) heat treatment for 1 h at 400°C seems to cause a contraction of the reticular parameter of the  $\alpha'$ -martensite [the peaks shift to the right with respect to the situation described in point (b)]. The  $\alpha'$ -martensite maintains its preferred orientation. Furthermore, in AISI 304L, the  $\alpha'$ -martensite platelets, which were finer and of greater reticular parameter, seem to disappear [variation in the shape of the (110) peak]. Austenite seems to maintain its preferred orientation. On the other hand, in AISI 316L, retained austenite seems to lose some of its preferred orientation and to become divided into finer grains [the reflexion of the (111) plane greatly diminishes in intensity, the (111) peak widens, and the reflexion of the (200) plane re-appears], and (d) heat treatment for 1000 h at 400°C seems to produce an expansion in the reticular parameter of the  $\alpha'$ -martensite (the peaks shift back to the left, particularly noticeable in AISI 316L).  $\alpha'$ -martensite tends to become highly disoriented in AISI 304L [increase in the reflexions of the (200) and (211) planes]. This is much less noticeable in AISI 316L [slight increase in the reflexion of the (200) plane]. There seems to be a particular increase in the preferred orientation of retained austenite in AISI 304L [the only reflexion is that of the (111) plane], while in AISI 316L retained austenite seems to re-arrange itself in larger grains.



FIG. 10. Effect of heat treatment at 400°C on corrosion in boiling copper sulphatesulphuric acid solution for AISI Types 304L and 316L stainless steels 50% rolled at -196°C.

In order to give an explanation of the results of stress corrosion tests, the structural effects of cold plastic deformation of austenitic stainless steels should be kept in mind. Cold-plastic deformation induces the following (see Table 2)<sup>15,17</sup>: (a) a distinct increase in the density of dislocations, with a tendency towards cell aggregates, (b) the appearance of deformation bands which can be resolved as deformation twins or  $\epsilon$ -martensite, and (c) the appearance of platelets of  $\alpha'$ -martensite (1  $\mu$ m in length and 0.1  $\mu$ m in width) at the intersection of the deformation bands.

The density of these structural elements obviously increases with the degree of deformation. It should be noted that dislocations and deformation bands are generally predominant in deformations at room temperature, while platelets of  $\alpha'$ -martensite are predominant from deformation at low temperatures. It should be noted that there is always a higher quantity of  $\alpha'$ -martensite in AISI 304L than in AISI 316L, and that  $\alpha'$ -martensite tends in any case to become the predominant structural component during low temperature deformation.



Fig. 12. X-ray diffraction patterns of AISI Types 304L and 316L stainless steels 50% rolled at - 196°C and heat-treated at 400°C for 1 h and 1000 h.

Finally, cold plastic deformation, and perhaps austenite-martensite transformation as well, create internal stresses (of a macro, micro or sub-micro type). The level and distribution of these stresses are difficult to quantify and will depend upon such factors as the type, degree, temperature and rate of deformation. It is reasonable to assume that when the material and rate of deformation are maintained constant, the level of internal stresses will increase as the degree of deformation increases and as the deformation temperature decreases.

The results of stress corrosion tests and the structural state of the cold-worked alloys described above would lead one to conclude that the necessary (and sufficient) condition for the insurgence of SCC in work hardened austenitic stainless steels is not the presence (or lack thereof) of  $\alpha'$ -martensite,<sup>22</sup> but rather the creation of a minimum level of internal stress. On the other hand,  $\alpha'$ -martensite seems to worsen the resistance to SCC, either directly (as a more susceptible structural phase) or indirectly (through an eventual increase in the level of the internal stresses). In any case, the pejorative effect of  $\alpha'$ -martensite seems to appear as the aggressivity of the chosen medium diminishes: consequently, particular attention should be paid to a hot water environment with very low chloride concentration.

Heat treatment at 400°C on steels rolled at -196°C with 50% deformation, reduces the resistance to stress corrosion if conducted for short periods of time (1-6 h), and tends to restore it if conducted for longer periods. This corrosion behaviour, can be attributed to the initial increase in the level of the internal microstresses (generated in the  $\alpha'$  and  $\gamma$  structural phases or at their interface), as is confirmed by the initial hardness values (Fig. 9). This variation of internal stress can in turn be attributed to the complex metallurgical phenomenon connected with the reciprocal re-ordering of the two phases\*, as can be seen from the initial X-ray diffraction tests (Fig. 12). On the other hand, prolonged heat treatments probably involve a decrease in micro-stresses and consequently a re-instated resistance of SCC. Nevertheless hardness is maintained at high levels due to chromium rich carbide precipitates (Fig. 11).

The validity of this hypothesis will eventually be examined more extensively. For the moment, under conditions of our investigation, we can already reject the hypothesis of the intervention of a fine precipitation of carbides (perhaps favoured by the presence of  $\alpha'$ -martensite<sup>23,24</sup>) and of the consequent sensitization of the steels. In fact, the TEM analysis (Fig. 11) and the Strauss corrosion tests (Fig. 10) show that the "real" presence of carbides is found after greatly prolonged periods of heat treatment which are longer than the time interval noted for minimum resistance to SCC. Furthermore, sensitization does not modify behaviour towards SCC in boiling aqueous MgCl<sub>2</sub>.

# CONCLUSIONS

The results of the studies carried out on stress corrosion behaviour of workhardened AISI 304L and AISI 316L stainless steels in hot water with low chloride concentration and in boiling aqueous  $MgCl_2$  are consistent with the following conclusions.

(1) After cold-working, AISI 316L does not have a markedly higher resistance than AISI 304L to stress corrosion cracking.

\*Magnetic measurements show that the quantity of ferro-magnetic phase in deformed steels remains unchanged after greatly prolonged periods (up to 1000 h) of treatment at 400°C.

- (2) The greater the degree of deformation of the material, the shorter the cracking initiation time. The pejorative effect of  $\alpha'$ -martensite induced by austenite transformation is to be found in hot water with low chloride concentration.
- (3) Both types of steel reveal a threshold value for the degree of deformation, below which corrosion cracking does not occur.
- (4) In cold-rolled specimens, cracks initiate on the short-transversal surfaces with respect to the rolling direction. In tests in which these surfaces are epoxy-resin coated, cracking initiation times are longer on the long-transversal surfaces. Finally, if both the long and short-transversal surfaces are coated, so that only the longitudinal surfaces are exposed to the aggressive medium, stress corrosion cracking does not occur.
- (5) Even when carried out for short periods of time, heat-treatment at 900°C removes the stress corrosion cracking susceptibility in both types of deformed steel. The steels lose their magnetic characteristics and there is a complete austenitic grain re-crystallization, which cancels out the internal stresses.
- (6) In steels deformed at room temperature, heat treatment at 400°C causes an increased resistance to stress corrosion cracking. On the contrary, for steels deformed at liquid nitrogen temperature, heat treatment at 400°C reduces the resistance to stress corrosion cracking if carried out for short periods of time (1-6 h), while it improves it in longer periods of time (> 6 h). Hardness measurements, structural analyses via X-rays, SEM and TEM, as well as intergranular corrosion tests seem to prove that reduced stress corrosion resistance is not related to the precipitation of chromium rich carbides which could have been accelerated by the presence of  $\alpha'$ -martensite. Instead, they tend to suggest that perhaps this phenomenon is connected to an increase in the level of internal micro-stresses which are generated by a re-ordering of the  $\alpha'$  and  $\gamma$  structural phases.
- (7) The results of stress corrosion tests and the structural state of the cold-worked alloys seem to suggest that the necessary (and sufficient) condition for the insurgence of stress corrosion cracking in work-hardened austenitic stainless steels is not the presence (or lack thereof) of  $\alpha'$ -martensite, but rather the creation of a minimum level of internal micro-stress.

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