Grain-size and heat-treatment effects in hydrogen-assisted cracking of austenitic stainless steels

E. MINKOVITZ, D. ELIEZER
Department of Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel

Hydrogen embrittlement of 304L and 316L types austenitic stainless steels has been studied by charging thin tensile specimens with hydrogen through cathodic polarization. Throughout this study we have compared solution-annealed samples, having various prior austenite grain size, with samples given the additional sensitization treatment. The results of the tensile tests while undergoing cathodic charging show that the additional sensitization treatment and coarse-grained samples together, lower the mechanical properties in both 304L and 316L types, and the sensitized steel is more susceptible to hydrogen-assisted cracking. However, the room-temperature yield and ultimate strengths, and the elongation of type 316L, were much less affected depending on the heat treatment and prior austenitic grain size. The fracture surfaces of the specimens tested while cathodically charged show considerable differences between the annealed and the sensitized specimens. The sensitized coarse-grained specimens were predominantly intergranular in both 304L and 316L types, while the annealed 316L type specimens fracture shows massive regions of microvoid coalescence producing ductile rupture and the annealed 304L type specimens fracture were primarily transgranular and cleavage-like. Sensitization seems both to facilitate the penetration of hydrogen along the grain boundaries into the steel and to introduce susceptibility to fracture along grain boundaries while refined grain size improves resistance regardless of the failure mode.

1. Introduction

The occurrence of hydrogen embrittlement in austenitic stainless steels is substantial with ductility losses, and by the appearance of non-ductile fracture surfaces [1–10]. It has been shown that the ductility of these steels is reduced up to 50% when sensitized type 316L is tested under conditions of high hydrogen fugacities such as cathodic polarization [8] or when type 304L is tested in 69 MPa hydrogen [9]. However, there had been little progress towards an understanding of the fracture mechanisms of these failures. The determining factor which controls the hydrogen-cracking susceptibility of austenitic stainless steels has remained unclear. The deleterious effect on mechanical properties caused by hydrogen charging has been found to depend strongly on metallurgical variables [10–13].

The object of the study was to evaluate the effect of grain size and heat treatment on the hydrogen susceptibility of 304L and 316L types austenitic stainless steels. Throughout this study we have compared solution-annealed samples having various prior austenitic grain size with samples given the additional sensitization treatment. An attempt was made to correlate between the tensile properties of the hydrogen-charged thin specimens and their mode of fracture. The martensite formation was detected in connection with the susceptibility of the steel to hydrogen cracking. The implication of these findings on hydrogen embrittlement is discussed.

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TABLE I Chemical composition of 304L and 316L types stainless steels

	Element (wt %)										
	Cr	Ni	Mn	Si	Co	Mo	Cu	N	P	C	S
304L	18.68	9.02	1.80	0.64	0.16	0.07	0.06	0.035	0.02	0.025	0.004
316L	17.65	11.10	1.80	0.50	0.35	2.08	0.21	0.061	0.03	0.026	0.009

2. Experimental procedure

Thin specimens, tensile tested while undergoing cathodic polarization, were investigated as a function of both grain size and heat treatment. The studies were carried out on 304L and 316L types austenitic stainless steels. The steels were of commercial grade of compositions shown in Table I, and were received in the form of sheets 0.2 mm thick. Tensile specimens were prepared with their long axes parallel to the rolling direction according to [14]. Two austenitic grain sizes, ASTM8 and ASTM6 were obtained following various times at austenitizing temperatures. Some samples of each group were given a further heat treatment at 650° C for 24 h. This additional sensitization heat treatment should allow the precipitation of chromium carbides along grain boundaries. The samples were sealed in a charging cell and were tensile tested at room temperature at an extension rate of 0.005 cm min^{-1} while undergoing cathodic polarization. The hydrogen charging cell contained 1 N H_2SO_4 solution with 0.25 g l^{-1} of $NaAsO_2$, added as an H recombination poison. A platinum counter electrode and a current density of 50 mA cm^{-2} were used. Hydrogen ingress of the austenite matrix is performed by the electrolytic charging cell where hydrogen is liberated at the cathode surfaces and may diffuse into the sample interior. The impressed voltage driving the cell reaction provides a huge hydrogen fugacity and thus large amounts of hydrogen may be driven into the specimen.

For comparison purposes, specimens were tensile tested in air at room temperature. After failure the fracture surfaces were examined with a scanning electron microscope (SEM). Hydrogen effects on the martensitic transformation have been studied using transmission electron microscopy (TEM).

3. Results and discussion

The results given in Fig. 1 and Table II demonstrate the influence of both grain size and heat treatment on the mechanical properties and the fracture mode of 304L and 316L types austenitic stainless steels under conditions of high hydrogen fugacities. A significant feature of the results is that the additional sensitization treatment and coarse-grained samples together, lower the mechanical properties in both 304L and 316L types. However, the room-temperature yield and ultimate strengths and the elongation of 316L type, were much less affected depending on the heat treatment and prior austenitic grain size.

As can be seen from Fig. 1 and Table II, the sensitized coarse-grained 304L type specimens were the most susceptible steel, resulted in 77% reduction of elongation and 44% reduction in ultimate strength at fracture while the sensitized coarse-grained 316L type specimens resulted in 42% reduction of elongation and 12% reduction in ultimate strength at fracture.

Another significance of the results is that the susceptibility of the fine-grained 316L type specimens is not changed by the additional heat treatment of 650° C for 24 h. The results show a slight reduction in ultimate strength and 34%

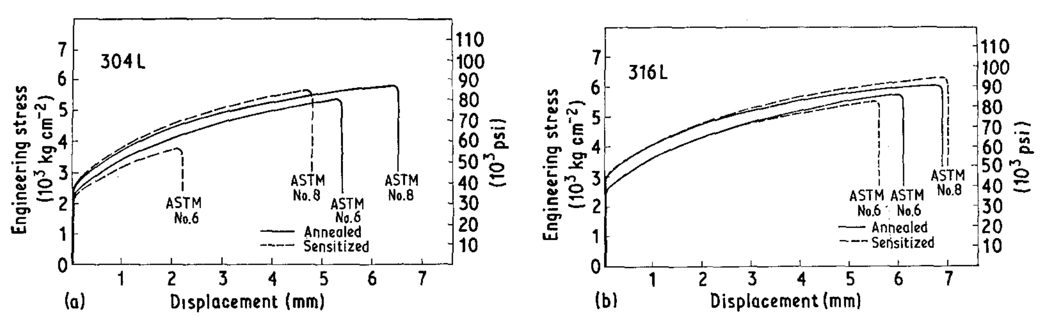

Figure 1 Plot of engineering stress against displacement curves for annealed and sensitized 304L and 316L types austenitic stainless steels tensile tested while undergoing cathodic charging (grain size ASTM8 and ASTM6).

TABLE II Percent reduction in tensile properties of specimens (a) 304L and (b) 316L types stainless steels, tensile tested while undergoing cathodic polarization as compared to those of uncharged specimens

Heat treatment and grain size	Properties		
	Yield strength	Ultimate tensile strength	Elongation
(a) 304L			
Annealed ASTM8	7	16	37
Sensitized ASTM8	6	20	54
Annealed ASTM6	8	21	44
Sensitized ASTM6	7	44	77
(b) 316L			
Annealed ASTM8	None	8	34
Sensitized ASTM8	None	7	34
Annealed ASTM6	None	5	38
Sensitized ASTM6	None	12	42

reduction of elongation at fracture, whether the material was sensitized or not. However, the fine-grained 304L type specimens shows 37% reduction of elongation and 16% reduction in ultimate strength for the annealed specimens and 54% reduction of elongation and 20% reduction in ultimate strength for the sensitized specimens.

Typical fracture and outer surfaces from these samples are shown in Figs. 2 and 3. A significant feature of these results is that the fracture mode is very sensitive to both grain size and heat treatment. Three fracture modes were observed: microvoid coalescence producing ductile rupture; transgranular fracture; and intergranular fracture. Dimpled rupture was the main feature mode in both annealed and sensitized fine-grained 316L type steels (Fig. 2a and 2c) and for the annealed coarse-grained 316L type (Fig. 3a). A common feature of this cracking was two narrow intergranular zones of about 10 μm on both fracture surface sides of the annealed and sensitized fine-grained 316L steel, and two narrow transgranular zones on both fracture surface sides of the annealed coarse-grained 316L steel.

Another typical feature was the existence of the linear separations on the fracture surfaces of the sensitized fine-grained 316L samples. Fig. 2c shows that the separations, which are believed to be fractures around grain-boundary carbides [15], comprise chains of voids, and are therefore ductile in origin. Typical transgranular fracture was the main fracture mode for both annealed fine- and coarse-grained 304L samples (Figs. 2b and 3b) while a narrow zone of about 10 μm, which shows ductile tearing, was observed only in the middle of the annealed fine-grained specimens (Fig. 2b). Fig. 3c shows typical fracture surfaces of the sensitized coarse grained 316L type. Over 50% of the fracture surfaces were associated with ductile rupture fracture surfaces while intergranular fracture surfaces of about 45% of the fracture surfaces can be also observed. However, a predominantly intergranular fracture can be seen in sensitized 316L type steel, by following the same conditions with coarser grain size-ASTM4. A more detailed analysis of hydrogen-induced cracking in sensitized coarse-grained 316L steel is given elsewhere [8]. The initial hydrogen fracture in the sensitized fine-grained 304L type (Fig. 2d) was predominantly intergranular, containing a wide zone of about 50 μm of ductile tearing. The existence of chains of voids, mentioned above, in the ductile zone (Fig. 2d, arrowed) can be seen. However, some regions in these samples, and the coarse-grained samples (Fig. 3d) were completely intergranular.

A summary of these results is given in Table III, where three types of fracture modes in percentage of surface are listed as: microvoid coalescence, intergranular and transgranular fractures. The outer surfaces of both annealed 304L and 316L specimens (Figs. 2a, b and 3a, b) show primary and secondary transgranular cracks mainly perpendicular to the applied stress direction while the predominant separation on the outer surfaces of both sensitized 304L and 316L steels (Figs. 2c, d and 3c, d) was intergranular with secondary transgranular cracks within the separated grains. The greater the time-to-failure, the more secondary transgranular cracks resulted on both outer surfaces of the samples.

Many papers [7, 16–19] in the past years, have strongly advocated that the presence of deformation-induced martensite greatly increases the susceptibility of austenitic stainless steels to hydrogen cracking. In this study, the appearance of the transgranular fracture in both annealed fine- and coarse-grained 304L types, strongly

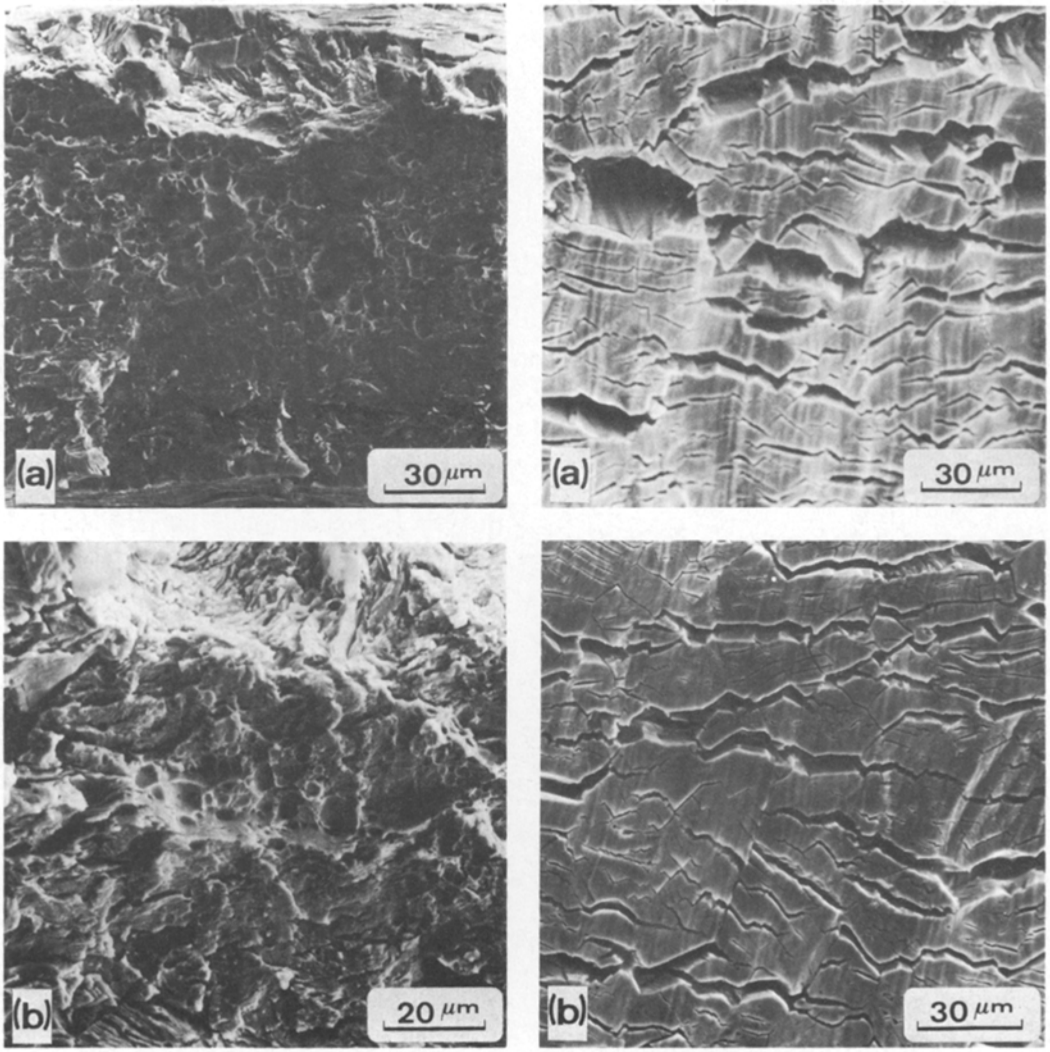

Figure 2 Scanning electron micrographs of the fracture and outer surfaces of the annealed and sensitized stainless steels (grain size ASTM8), tensile tested while undergoing cathodic charging. (a) 316L, annealed; (b) 304L, annealed; (c) 316L, sensitized; (d) 304L, sensitized.

suggest that the hydrogen-induced cracking requires that formation of stress-induced α'-martensite. A recent investigation [20] has revealed the existence of α' b c c martensite in front of the crack tip when cathodic charging was applied for several minutes in the absence of any external forces. Moreover, it has been shown that the propagation of the crack was through the embrittled martensite phase. Thus, stressing 304L type while undergoing cathodic polarization and the existence of stress-induced martensite in the bulk, resulting in transgranular fracture as the main fracture mode in this steel.

The more stable steel exhibits different behaviour, where the main fracture mode was ductile tearing. However, the existence of two narrow intergranular zones on both fracture surface sides of the annealed and sensitized fine-grained 316L types and the two narrow transgranular zones in the annealed coarse-grained 316L type are probably due to interaction of the outer surfaces with high hydrogen fugacities under the applied stresses. No evidence of the appearance of α'-martensite phase after hydrogen-charging 316L thin foil was found within the grains; however, the appearance of α'-martensite along the crack surfaces is probably due to the brittle shallow cracks mentioned above when no α'-martensite is formed in the bulk.

Sensitization seems both to facilitate the

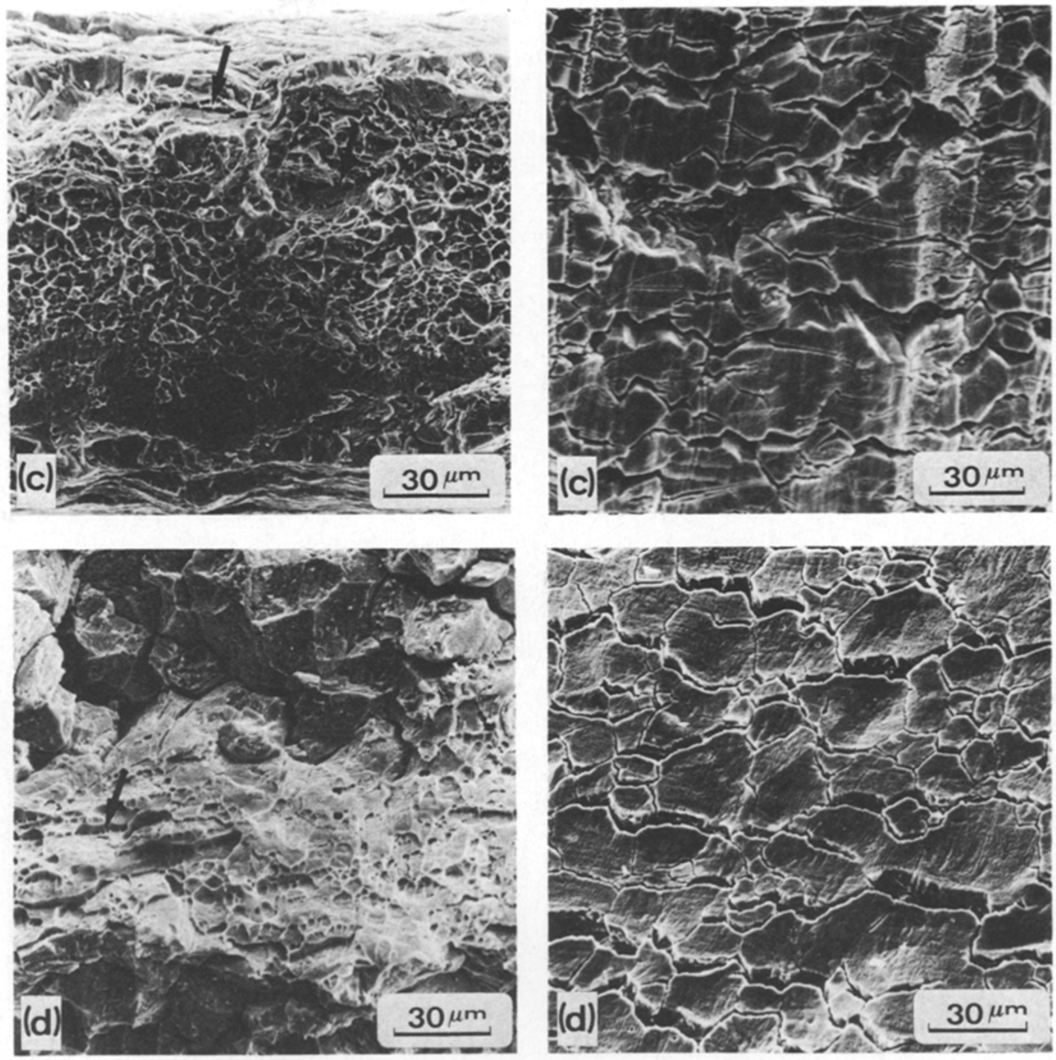

Figure 2 continued.

penetration of hydrogen along grain boundaries into the steel and to introduce susceptibility to fracture along grain boundaries. The intergranular fractures observed in this study, are not due to the continuous grain-boundary carbides as was reported by Fidelle *et al.* [21] for sensitized 304 stainless steel. Briant [10] pointed out that the grain-boundary carbide density was always equivalent in both the aged 304 and 316 alloys. However, our present results show that the grain-boundary carbide density was more massive for the sensitized 304L steel. This behaviour is probably due to the addition of the alloying element, Mo, which acts as a segregation inhibitor in 316L type.

As can be seen from Figs. 1 to 3 and Tables II and III, grain size does play a role in hydrogen embrittlement of austenitic stainless steels. Preliminary results [22–24] also suggest that a refined grain-size improves resistance regardless of the failure mode. The origin of the effect [25] is probably not due to increased strengthening, but rather to an increasing number of trapping sites as the grain-boundary area per unit volume increases.

4. Conclusions

(1) Refined grain-size improves the resistance to hydrogen cracking regardless of the failure mode.

(2) The increased susceptibility of both annealed and sensitized materials increases with increasing grain size.

(3) The sensitized coarse-grained specimens

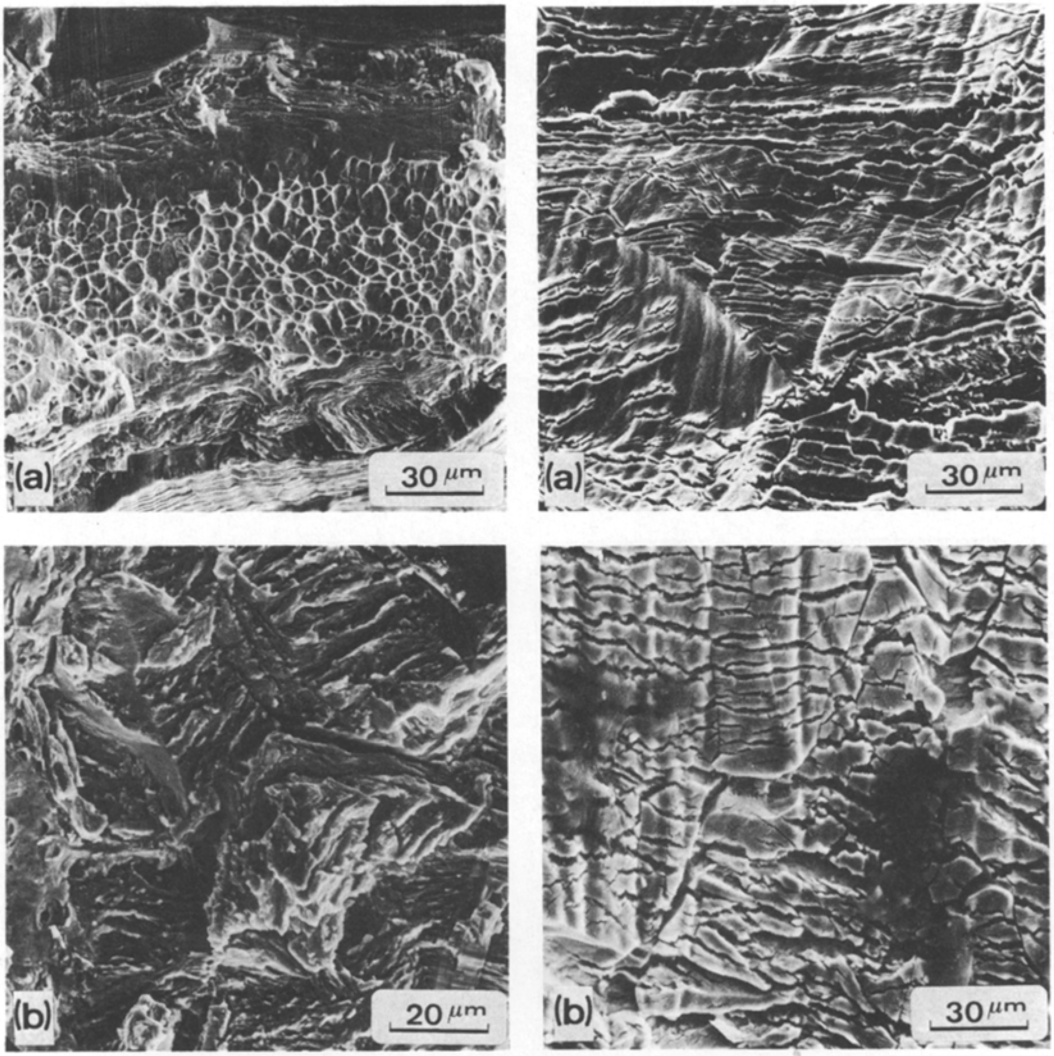

Figure 3 Scanning electron micrographs of the fracture and outer surfaces of the annealed and sensitized stainless steels (grain size ASTM6), tensile tested while undergoing cathodic charging. (a) 316L, annealed; (b) 304L, annealed; (c) 316L, sensitized; (d) 304L, sensitized.

TABLE III Fracture modes in specimens, tensile tested while undergoing cathodic charging

Type of stainless steel	Grain size (ASTM no.)	Heat treatment	Fracture mode (% surface)		
			Microvoid coalescence	Intergranular	Transgranular
316L	8	Annealed	85	15	–
316L	8	Sensitized	85	15	–
304L	8	Annealed	15	–	85
304L	8	Sensitized	30	70	–
316L	6	Annealed	85	–	15
316L	6	Sensitized	50	45	5
304L	6	Annealed	–	–	100
304L	6	Sensitized	–	100	–

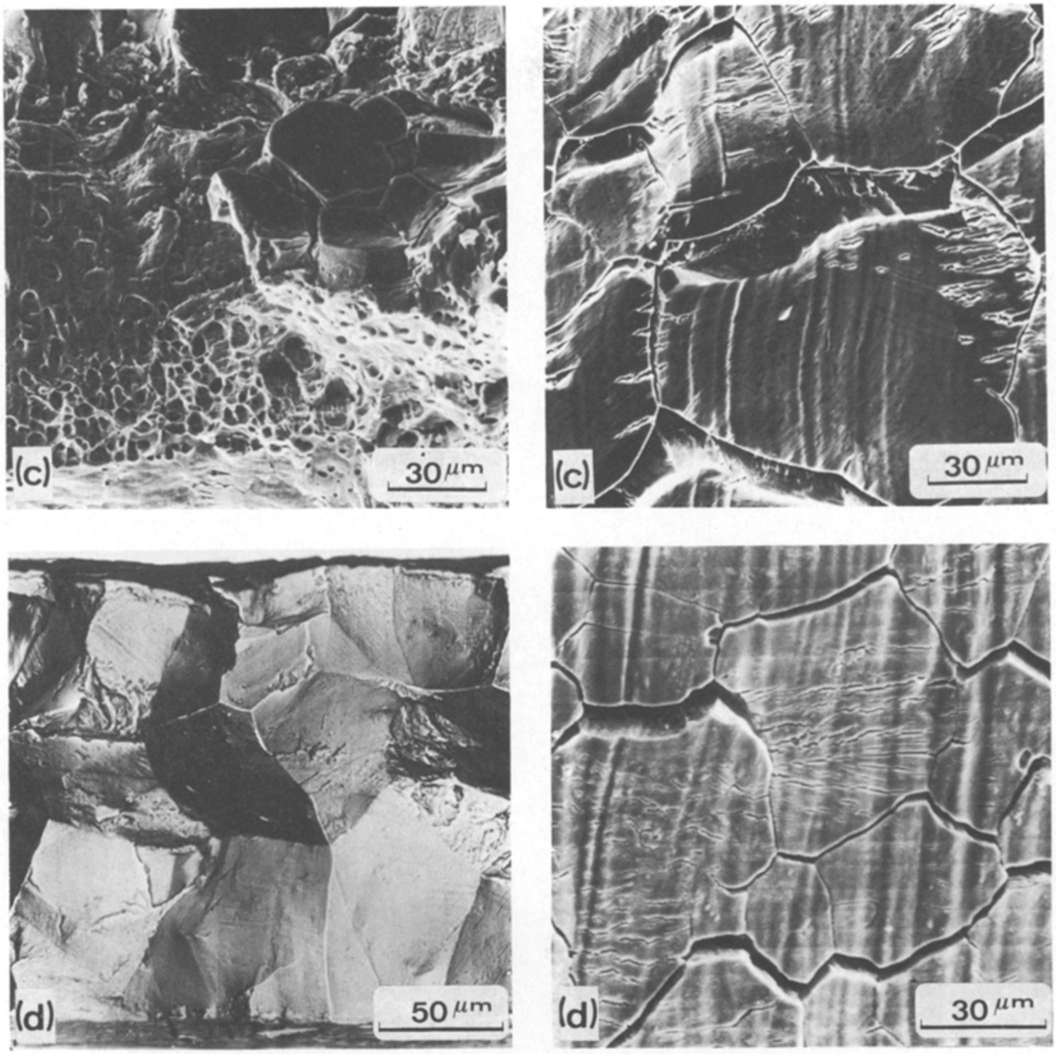

Figure 3 continued.

were predominantly intergranular in both 304L and 316L types. The annealed 316L type specimens fracture shows massive regions of microvoid coalescence producing ductile rupture while the 304L type specimens fracture were predominantly transgranular and cleavage-like.

(4) The reduction in tensile properties of both annealed fine- and coarse-grained 304L type steel is closely related to the deformation-induced martensite.

(5) The intergranular fracture observed in both sensitized 304L and 316L steels is not due to continuous grain-boundary carbides.

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