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## Interstitial defects in 316L austenitic stainless steel containing "colossal" carbon concentrations: An internal friction study

A.H. Heuer,<sup>a,\*</sup> F. Ernst,<sup>a</sup> H. Kahn,<sup>a</sup> A. Avishai,<sup>a</sup> G.M. Michal,<sup>a</sup> D.J. Pitchure<sup>b</sup> and R.E. Ricker<sup>b</sup>

<sup>a</sup>Case Western Reserve University, Cleveland, OH, USA <sup>b</sup>National Institute of Standards and Technology, Gaithersburg, MD, USA

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Carburization of 316L austenitic stainless steel under paraequilibrium conditions results in extremely hard (~1100 HV) singlephase cases containing surface carbon concentrations of ~15 mol.% and very high residual compressive stresses ( $\ge 2$  GPa). Carburization produced an anelastic relaxation peak at 543 K (1.0 Hz), due to a carbon-containing defect with a highly anisotropic strain field. Interstitial solid-solution strengthening theories can explain the approximate three-fold increase in hardness, using reasonable parameters for the strain ellipsoids of these defects.

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Carburization of austenitic stainless steels under paraequilibrium conditions leads to materials with remarkably improved properties. Paraequilibrium refers to low-temperature (725-775 K) conditions such that substitutional solutes are effectively immobile, whereas interstitial solutes, such as carbon, have considerable mobility. For example, paraequilibrium carburization of a 316L austenitic stainless steel for 24 h at 735 K [1,2] leads to a case  $\sim$ 25 µm deep, with a Vickers surface hardness of ~1100 HV (~70.5 HRC), compared to a core Vickers hardness of ~400 HV (Fig. 1a). There is no evidence of carbide or other second-phase precipitation when samples are examined by X-ray diffraction and electron microscopy [1,2], and the absence of carbide on other precipitates was confirmed by atom probe topographic microanalysis [3]. The carbon concentration  $(X_c)$  at the surface is ~15 mol.% (~3.7 wt.%) (Fig. 1b). This "colossal" interstitial carbon concentration is also evident from the topographic atom probe analysis [3] and was confirmed by microprobe analysis [4] and glow-discharge optical emission spectroscopy (GDOES) [5]. The marked departure from the errorfunction-like depth profile shown in Figure 1b is evidence that the diffusion coefficient of carbon varies strongly with carbon concentration in this alloy [6].

The lattice expansion associated with the colossal supersaturation of interstitial carbon, combined with the carbon depth profile shown in Figure 1b and the constraint provided by the non-carburized core, results in residual compressive stresses at the surface that exceed 2 GPa. As expected, these residual stresses greatly enhance the fatigue resistance [2,7] and their magnitude indicates a yield stress for this interstitially hardened surface layer well above 2 GPa, consistent with the surface hardness data of Figure 1a. Nevertheless, the inherent ductility of austenitic stainless steels is hardly compromised by the very high paraequilibrium carbon concentration [2,7]. Moreover, the high carbon concentration present in the passive oxide film on these alloys considerably enhances the corrosion resistance of the 316L steel [8,9].

The present study was motivated by cross-plotting the hardness data of Figure 1a against the concentration data of Figure 1b (using  $X_c^{2/3}$ ), as shown in Figure 1c. The data in Figure 1c are those of Figure 1b, with each datum assigned a hardness value appropriate to its depth, based on a polynomial fit to the data of Figure 1a. The choice of  $X_c^{2/3}$  for the abscissa (the Labusch model [10]) was motivated by the high carbon concentration in this alloy, and recognition that the Labusch model of solid-solution hardening is more general than the Fleischer dilute-solution model, for which the abscissa would have been  $X_c^{1/2}$  [11]. Figure 1c reveals that the

<sup>\*</sup>Corresponding author. Tel.: +1 216 368 3868; fax: +1 216 368 8932; e-mail: heuer@case.edu



**Figure 1.** (a) Vickers surface hardness as a function of depth from the paraequilibrium carburized surface of 316L stainless steel [1,2]. (b) Carbon concentration as a function of depth from the paraequilibrium carburized surface of 316L stainless steel, as determined by calibrated Auger microanalysis. The dashed line is the error function solution to the carburization diffusion equation for the same surface carbon concentration. (c) Vickers surface hardness as a function of mole fraction of carbon in solution to the 2/3 power as determined from (a) and (b).

hardness at high carbon concentrations is higher than would be expected from linear extrapolation from lower carbon concentrations. This behavior is not consistent with the Labusch model [10], which suggests a linear increase in hardness with  $X_c^{2/3}$ , and cannot be attributed to the precipitation of carbides or other second phases. This suggests that at the very high carbon concentrations in the case, a carbon-containing interstitial defect forms which interacts more strongly with dislocations than do isolated carbon interstitials. We postulate the presence of interstitial defects that consist of a carbon interstitial paired or grouped with (i) other carbon interstitials, (ii) vacancies or (iii) substitutional solutes. We assume that the strain fields produced by these defects will be highly anisotropic and possess lower symmetry than the face-centered cubic matrix (they could have, for example, tetragonal symmetry), and that these defects will attempt to align their strain fields with an applied stress. (We refer henceforth to these defects as tetragonal.) The thermally activated response of the tetragonal defects to a sinusoidally oscillating applied force will result in an anelastic relaxation that should be detectable in an internal friction experiment.

Dynamic modulus analysis (DMA) experiments were conducted on a 316L stainless steel specimen carburized under the paraequilibrium conditions described previously [1,2,12], and a non-carburized control specimen with identical dimensions (approx. 60 mm × 12 mm ×0.87 mm). DMA is a subresonance internal friction technique that measures the complex-valued elastic modulus,  $E^* = E' + iE''$ , by applying a sinusoidally oscillating load and measuring the phase shift between force and displacement [13]. These experiments were conducted in a three-point bending mode, with a 50 mm span, at a strain range of  $6.26 \times 10^{-5}$  at five different frequencies (0.1, 0.3, 1.0, 3.0 and 10 Hz), while the temperature was scanned at 5 K min<sup>-1</sup> from 173 to 873 K. Initially, the samples were run several times at 1.0 Hz to evaluate the reproducibility of the observed peaks and the effects of the annealing inherent in our experiments on the peaks. The specimens were then run at the different frequencies to determine if the observed peaks showed Arrenhius behavior.

The ~25 µm thick carburized layer (Fig. 1) on the upper and lower surfaces of the test specimen constituted ~5.7% of the sample volume. However, as shown in the last paragraph preceding the acknowledgments, because the elastic strain energy per unit volume increases with the square of the distance from the neutral axis in three point bending, 16.6% of the energy associated with each loading cycle was contained within the carburized region. Given the carbon concentration-depth profile shown in Figure 1b, we are convinced that the anelastic behavior found in the carburized sample (Figs. 2 and 3) arises from the hardened case.

Figure 2a shows the 1.0 Hz data for both samples. The non-treated material exhibits low-temperature peaks that are not present after carburization. These peaks, observed near room temperature in the initial scan, are reminiscent of the dislocation relaxation peaks first reported in face-centered cubic metals by Bordoni [14], although Bordoni peaks usually occur at much lower temperatures [15]. Hasiguti et al. [16] reported either two or three low-temperature peaks in cold-worked, pure, face-centered cubic metals, and a small peak near 200 K can be seen in Figure 2a. However, Hasiguti et al. [16] also reported complex annealing behavior for these peaks, including that annealing at room temperature results in their complete disappearance. Igata et al. [17,18] reported similar peaks to those in Figure 2a in



**Figure 2.** (a) Internal friction peaks for 316L and low-temperature carburized 316L stainless steel (LTCSS for "low-temperature colossal supersaturation") as determined from DMA measurements at 1.0 Hz. (b) Internal friction peaks for carburized 316L stainless steel at 1.0 Hz showing changes due to thermal transients during DMA measurements.



**Figure 3.** (a) Internal friction peaks in carburized 316L stainless steel at different frequencies after background subtraction. (b) Analysis of the activation energy of the internal friction peak found in carburized 316L stainless steel from the frequency dependence of the peak temperature.

a cold-worked 304L steel which they attributed to dislocation pinning by interstitial carbon and nitrogen. Talonen and Hanninen [19] also found peaks near room temperature in cold-worked 301 and 304 austenitic steels which they attributed to strain-induced  $\alpha'$  and  $\varepsilon'$  martensite and stacking faults.

At higher temperatures, Lambri et al. [20,21] reported a non-thermally activated cold-worked peak in a commercial 316H alloy at 733 K, and small peaks can be seen near this temperature in Figure 2a. While the exact nature of these peaks remains unclear, it is certain from Figure 2a that carburization does not increase the peak heights. Hence, these peaks cannot originate from the defects causing the increased strength of the carburized material.

The carburized sample shows three peaks, a major peak at 543 K, which is not sensitive to annealing, and two minor peaks at 393 and 703 K, which disappeared after heating the sample to 873 K in the course of these measurements (Fig. 2b). The two minor peaks appear to be related to peaks at corresponding temperatures in the uncarburized material. However, inasmuch as a brief annealing at 873 K does not significantly alter the hardness of the carburized layer, we conclude that the two minor peaks are not related to the enhanced strength levels; they were therefore not studied further. There was no evidence of a peak in the uncarburized material in the range of the major peak found in the carburized material. Therefore, this peak must originate from the anelastic relaxation of defects created by the carburization treatment. These defects are most likely responsible for the progressive non-linear increase of strength with increasing carbon concentration shown in Figure 1c.

The frequency dependence of the major peak is shown in Figure 3a. An Arrhenius plot of the internal friction data (Fig. 3b) indicates an activation energy of  $1.62 \pm 0.10$  eV and an intercept of  $-34.3 \pm 2.1$ , corresponding to a frequency factor of  $10^{14.9 \pm 0.9}$  Hz. Both of these parameters are in the range expected for anelastic relaxations due to thermally activated motion of atomic-scale defects [22]. However, as the octahedral interstices occupied by carbon in austenite have cubic symmetry, Snoek peaks are theoretically impossible. Snoek-like peaks in face-centered cubic lattices due to interstitial solutes have been reported previously, but they are usually attributed to the bonding of interstitial solutes to other defects that create deviations from the ideal interstitial defect symmetry. For example, Gibala et al. [23-25] reported peaks in a variety of austenitic alloys with more conventional carbon contents (up to 4.0 mol.%) and attributed these peaks to the formation of a carbon-interstitial vacancy (i-v) bound pair-defect with a binding energy of 0.36-0.41 eV. These bound pairs would generate strain fields with non-cubic symmetry. The solid solution strengthening and strain aging behavior of their alloys was attributed to these interstitial carbon defects [23–25].

The alloys studied by Gilala et al. would correspond to the concentration range and trend of the lower carbon content materials in Figure 1c. However, the 1 Hz internal friction peak found in the carburized material occurs  $\sim$ 50 K higher than the relaxation found by Gibala et al. [23–25] and the activation energy is  $\sim$ 0.4 eV greater than they report [23,25]. This suggests that this l Hz peak is due to a more complex or more strongly bound defect that arises from the higher carbon concentrations in this material – for example, an interstitial pair (*i*–*i*), a multi-interstitial defect (*i<sub>n</sub>*), or a variety of multi-interstitial vacancy or substitutional defects (*i<sub>n</sub>*–*v*, *i<sub>n</sub>*–*s*). The presence of substitutional alloying elements in these defects could explain why the width of the peak is greater than that expected for a theoretical Debye peak with the observed activation energy [22].

In summary, we assume that isolated interstitials and/or the bound pair reported by Gibala et al. [23-25] control the hardening at low carbon concentrations (the carbon content of the non-carburized 316L steel is very low), but that a carbon-containing composite defect causes hardening in the rapid hardening regime of Figure 1c, and that these defect complexes are responsible for the major internal friction peak of Figure 2. The precise nature of these defects cannot be determined from the present data, and extensive studies on specimens treated to vary vacancy and dislocation concentrations will be required for a complete elucidation. However, the simplest defect with lower symmetry than the matrix, whose concentration would increase with increasing carbon content, would be an interstitial pair defect (*i<sub>n</sub>* with n = 2) with tetragonal symmetry of the type reported by Diamond and Wert [26] for carbon in Ni and subsequently studied extensively for interstitial solutes in pure face-centered cubic metals [22,26-28]. While evaluation of the exact nature of these defects is beyond the scope of the present study, the results are completely consistent with the hypothesis that composite interstitial defects of this type are created during paraequilibrium carburization due to the "colossal" carbon concentrations, and that these defects are responsible for the increased hardness levels.

While these defects may be simple interstitial pairs, we do not believe that this is the only possibility. Unpublished 0 K calculations of Gibala [24] indicate that multicarbon interstitial-vacancy complexes are surprisingly stable in austenitic alloys. For example, complexes of two or three interstitial carbon atoms bound to a single vacancy  $(i_n-v)$  are more stable than the single carbon vacancy (i-v) defect complex considered in Ref. [23]. Our interpretation of a multicarbonvacancy defect complex causing this peak is consistent with the peak temperature being higher than that reported by Gibala et al. [23,25].

Unfortunately, the concentration of the tetragonal defects cannot be estimated from the peak heights of the anelastic relaxation, unless the exact nature of the defects and the anisotropy of their strain fields (or increment of strain per defect) are known. However, by assuming axial (tetragonal) symmetry, a range of possible defect concentrations corresponding to a range of strain ellipsoid asymmetries can be estimated, using the relationship developed by Nowick and Heller [29], as discussed by Nowick and Berry [22]. According to these workers, the compliance peak height ( $\delta J$ ) is related to the concentration of the defects ( $C_0$ ) and the eccentricity of the strain ellipsoid ( $\delta \lambda$ ) as

$$\delta J = \beta \left( \frac{C_0 v_0}{kT} \right) \delta \lambda^2, \tag{1}$$

where  $\beta$  is a constant with a value near unity,  $v_0$  is the molecular volume and kT has its usual meaning. Assuming a difference between the major and minor axes of the defect strain ellipsoid between 0.1 and 0.4, the height of the peaks in Figure 2b indicates a defect concentration between 0.86 and 0.05 mol.%, a range of concentrations and strain fields that could readily explain the rapid hardening shown in Figure 1c. However, Eq. (1) also predicts that the height of the peaks should decrease with increasing temperature, whereas an almost linear trend of peak height increasing with temperature is shown in Figure 3a. Therefore, the product of the variables describing the defect in Eq. (1),  $(C_0 \delta \lambda^2)$ , must be increasing with the square of temperature to produce this trend. This could result from increasing temperature affecting the strain field of the defect.

We plan further work on 316L samples with "colossal" carbon supersaturations, using a torsion pendulum type apparatus with wire specimens with different but constant carbon concentrations, up to the paraequilibrium solubility limit, [12] and given different amounts of cold work. Such studies should also shed light on the nature of two minor peaks in Figure 2 that are eliminated on heating to 873 K.

In conclusion, a major internal friction peak is present in a 316L austenitic stainless steel carburized under paraequilibrium conditions. The peak temperature at a frequency of 1.0 Hz is 543 K. The peak is characterized by an activation energy of  $1.62 \pm 0.10$  eV and a frequency factor of  $10^{14.9\pm0.9}$  Hz. All observations to date are consistent with this peak being due to the anelastic relaxation of a composite cluster consisting of two (or more) point defects bound together and possessing lower symmetry than the cubic matrix. The presence and strength of these defects are consistent with their being responsible for the observed hardness of the carburized case.

Under the usual assumptions of linear-elastic continuum theory, the elastic strain energy volume density u is related to Young's modulus E and the stress  $\sigma$  by

$$U = \frac{\sigma^2}{2E}.$$
 (2)

Though not explicitly expressed in Eq. (2),  $\sigma$  depends on the spatial coordinates x, y, and z. In our specimens with section modulus I, and defining the spatial coordinate z as the distance from the neutral axis, the stress depends on the bending moment M

$$\sigma[z] = \frac{M}{I} z. \tag{3}$$

The total strain energy of the slab between  $z_1$  and  $z_2$  per unit area on the x, y plane is

$$U = 2 \int_{z_1}^{z_2} \frac{M^2}{2EI^2} z^2 dz = \frac{1}{3} \frac{M^2}{EI^2} (z_2^3 - z_1^3).$$
(4)

(The factor 2 originates from the bending geometry.) Accordingly, the ratio of the strain energy  $U_c$  in the carburized layer ( $z_1 = 410 \ \mu\text{m}$ ,  $z_2 = 435 \ \mu\text{m}$ ) and the strain energy  $U_a$  of the non-carburized austenite ( $z_1 = 0 \ \mu\text{m}$ ,  $z_2 = 410 \ \mu\text{m}$ ) is

$$\frac{U_{\rm c}}{U_{\rm a}} = 0.16.$$
 (5)

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