Correlation of Measurements of Retained Austenite in Carburized Steels by X-Ray Diffraction and Quantitative Metallography

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The retained austenite contents in carburized samples of EX24, EX32, and SAE 4820 were measured by both X-ray diffraction and automated quantitative metallography. The carburized samples were tempered 1 h at 200 °C prior to determination of the austenite contents. For the metallographic measurements, the specimens were etched in a nital solution which allowed clear distinction among the three principal microconstituents present: retained austenite, bulk martensite, and surface martensite which forms in retained austenite during specimen preparation. It was found that the usefulness of the metallographic procedure was limited to case carbon contents in excess of about 0.6 wt pct. At lower carbon contents, the morphology of the martensite was predominantly nonlenticular, and detection of the austenite in such a matrix was impossible by metallography. Carbon contents in excess of 0.6 wt pt resulted in a predominantly lenticular martensite matrix, so that retained austenite was readily detectable by metallography and good agreement between the X-ray and metallographic measurements was obtained. At high retained austenite contents, it was found that the X-ray measurements tended to detect less retained austenite than was detected by metallography. This was ascribed to the inability of the X-ray technique to differentiate the surface martensite from the bulk martensite. With quantitative metallography, the surface martensite can be distinguished as a separate microconstituent and properly counted as retained austenite.

INTRODUCTION

Retained austenite in carburized components can have a strong influence on mechanical properties because of its relatively low hardness, its influence on residual stresses and its potential for strain induced transformation. Therefore, any quantitative analysis of the mechanical behavior of carburized material must include a measurement of the amount and distribution of retained austenite in the case.

Two techniques available for measuring the gradient of retained austenite through the case are X-ray diffraction and quantitative metallography. The main advantages of the diffraction method are its accuracy and its ability to measure austenite even when this is distributed in a manner not detectable by optical or scanning electron microscopy, as at lath boundaries in low carbon martensite. The disadvantages include the requirement of a flat specimen surface and the need for multiple repreparation and measurement of the same sample at various case depths to obtain the austenite gradient. In addition, if the specimen has a distinct crystallographic texture, special steps are required to compensate for this. The overall procedure can thus be quite time consuming.

In contrast, the main advantages of the metallographic method are the lack of any restriction on

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exterior specimen geometry (*i.e.*, curvature of the carburized surface) and the potential for determining the entire austenite gradient with a single specimen preparation. Once a cross section through the case is metallographically prepared, the gradient can be directly measured along a line perpendicular to the carburized surface. The principal disadvantage is that the accuracy of the metallographic method is limited to austenite that can be resolved in the microscope. For high carbon materials having a lenticular martensite matrix, detection of austenite is relatively easy and agreement between X-ray and metallographic measurements has been demonstrated with austenite volume fractions as low as 3 pct.[1] However, for lower carbon material exhibiting a lath martensite matrix, considerable austenite may be present as revealed by diffraction methods,[2,3] and yet be undetectable by metallography. Another disadvantage of the metallographic method is that if traditional manual point counting is used, the procedure is time consuming and tedious.

In carburized materials, the outer or "effective" case (hardness >50 HRC) is generally the region of greatest interest. Here, the carbon content is sufficiently high that a lenticular martensite matrix is present. The metallographic method of austenite measurement is thus potentially of use, at least through the effective case. This potential is further enhanced by the relatively recent introduction of image analyzing computers which eliminate the tedium and time consumption of manual point counting. The purpose of this investigation was to compare the results of retained austenite measured in carburized samples by both X-ray diffraction and computer-assisted quantitative metallography.

EXPERIMENTAL PROCEDURES

Materials

Three carburizing steel grades were selected for this study, SAE 4820, EX32, and EX24. These were chosen because they span a range of nickel contents (0 to 3.5 pct) typically found in carburizing steels. Since nickel can have a strong effect on martensite morphology,[4] it was desirable to include nickel content as a variable in this study. The materials were prepared as 57 kg laboratory heats, induction melted in air. The ingots were hot-forged to 30 mm diam bar stock and normalized from 925 °C. Table I gives their compositions.

Table I. Steel Compositions

Steel	Alloy Content, Wt Pct C	Mn	Si	Ni	Cr	Mo
EX24	0.20	0.88	0.28	—	0.52	0.25
EX32	0.19	0.82	0.27	0.80	0.53	0.52
4820	0.19	0.60	0.28	3.48	—	0.27

Development of Suitable Martensite/Austenite Etching Contrast

A necessary condition for automated metallographic measurement of retained austenite is that the samples be prepared in such a way that both the operator and the machine can distinguish the austenite from other microconstituents present. Preliminary studies were undertaken to establish the most suitable preparation technique. The goal was to develop a method that was fast, yielded reproducible results, and required only ordinary metallographic skills. In addition, the technique should result in easy distinction among the three principal microconstituents, austenite, martensite, and surface martensite. The latter forms on the specimen surface in the retained austenite during specimen preparation and generally cannot be avoided, even by electropolishing techniques.[5,6] Its presence can mask the true amount of retained austenite in the sample.

For this preliminary work, 13 mm diam cylinders of each of the three steels were gas carburized as described below and oil quenched. The cylinders were cut into discs approximately 13 mm thick and tempered for 1 h at 100, 150, 200 or 250 °C. The tempered discs, as well as those that had received no tempering, were mounted in epoxy resin and prepared for metallography by standard mechanical polishing techniques. A vibratory polisher using 0.05 μm alumina was used for the final step. Electropolishing techniques were also tried but abandoned because of the great difficulty of retaining flatness at the specimen edge, the area of greatest interest.

The polished samples were etched in various media as outlined in Table II. A nital + zephiran chloride etch (No. 4 in Table II) was found to meet all the requirements of ease of use, reproducibility of results, and good delineation of microconstituents, when applied to a specimen tempered at 200 °C. Therefore this etchant/heat treatment combination was used in all subsequent work.

Figure 1 shows the microstructure as developed by this procedure. In the optical micrograph, the bulk martensite has etched dark-gray to black, the retained austenite remains white, and the surface martensite is readily detected as a light gray constituent. The electron micrograph in Fig. 1(*b*) reveals the reason for the

Table II. Etchants Used in Preliminary Studies

No.	Name	Composition	Procedure
1	Modified picral	5 ml HCl + 1 g picric acid + 100 ml ethanol	Immersion
2	Picral-nital	4 g picric acid + 1 ml HNO_3 + 100 ml ethanol	Immersion
3	2 pct nital	2 ml HNO_3 + 100 ml ethanol	Immersion
4	2 pct nital + zephiran chloride	2 ml HNO_3 + 100 ml ethanol + 1 drop zephiran chloride	Immersion
5	—	$CuSO_4$ solution; followed by Na_2S solution	See Reference 7
6	—	50 ml saturated sodium thiosulfate solution + 1 g calcium metabisulfite; followed by 30 ml 5 pct NaOH + 10 ml 3 pct H_2O_2	See Reference 8

different etching behavior of the surface martensite. This microconstituent formed after tempering, during specimen preparation, and hence is untempered relative to the bulk martensite.

Fabrication and Heat Treatment of Specimens

Two cylindrical samples 25 mm diam were machined from hot-forged and normalized bar stock of each of the three steels. One of each pair, to be used for X-ray and metallography, was made to 30 mm length. The second sample was machined to an overall length of approximately 100 mm and was used for carbon gradient determination as described below.

The shorter specimens, hereinafter referred to as X-ray specimens, were surface ground so that the end faces were parallel and then copper plated leaving only one end face exposed. This was done to ensure carburization through only the one exposed flat face and hence a homogeneous carbon content on subsequent planar sections parallel to this face. All specimens were gas carburized for 20 h at 925 °C in a Leeds and Northrup Homocarb furnace with an atmosphere carbon potential setting of 1.15 pct relative to plain carbon steel. The specimens were oil-quenched after carburizing. Carbon gradient bars were tempered 1 h at 620 °C to soften for machining and then turned on a lathe. The chips from each pass were analyzed for carbon content to establish the carbon gradient. The X-ray specimens were tempered 1 h at 200 °C.

Metallographic Preparation and Retained Austenite Measurements

The carburized surface of each X-ray specimen was surface ground to an initial depth of 0.25 mm. During all grinding operations, care was taken to use freshly dressed wheels, ample water cooling and low feed rates. The ground surfaces were then mechanically polished and etched as described above. A 6 mm square area was marked on the center of each polished and etched face, and X-ray and metallographic retained austenite measurements were made on this designated area. After measurement as described below, the preparation pro-

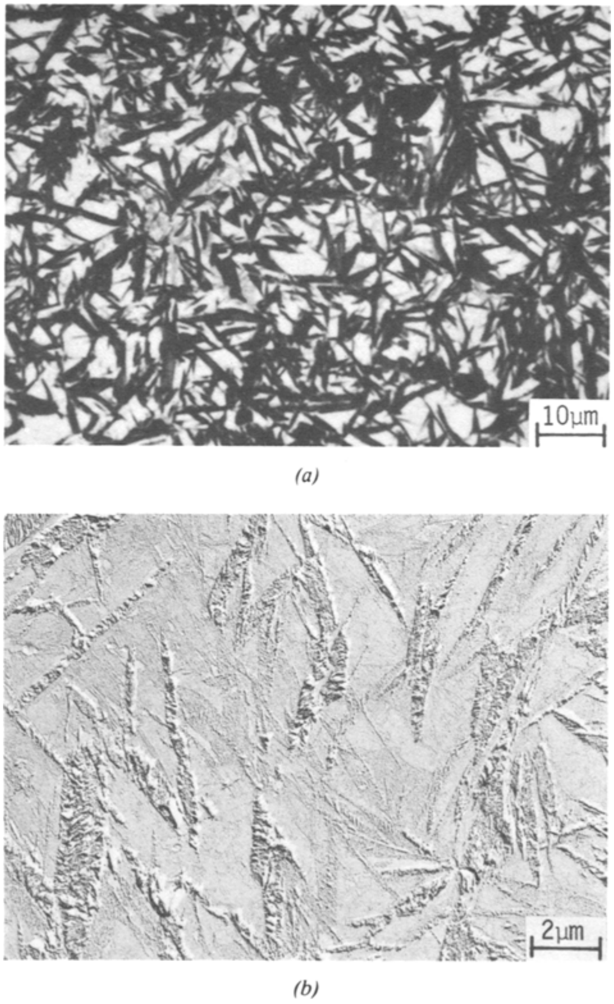

Fig. 1—Carburized X-ray specimen of EX32, 0.100 mm case depth. 2 pct nital + zephiran chloride. (*a*) Optical micrograph. (*b*) Electron micrograph (carbon replica). Surface martensite is the light-etching lenticular microconstituent in (*a*) and the untempered, carbide-free lenticular microconstituent in (*b*).

cedure (grinding, polishing, etching) was repeated to expose a new surface approximately 0.1 mm below that just examined. Preparation and measurement were repeated until the martensite matrix became so nonlenticular that the retained austenite could no longer be clearly detected metallographically.

On each prepared surface, retained austenite was first measured metallographically and then by X-ray. For metallography, a Quantimet image analyzing computer was employed. The specimen was observed under a 63X objective /8X ocular combination, resulting in the display of a 0.09 × 0.11 mm^2 area of the specimen at approximately 2000X on the video screen. Unfiltered tungsten lamp illumination was used, and the sensitivity of the instrument was set at approximately midrange. The instrument was set to detect microconstituents whiter than a certain threshold level. That is, of the 500,000 points making up the video picture, only those having a given minimum level of brightness were counted. The threshold was set so that, in the author's judgment, all of the observable austenite and surface martensite were detected as a single microconstituent. Approximately 200 areas were examined on each specimen, and the point count from each was recorded. The mean and variance of the data were then calculated.

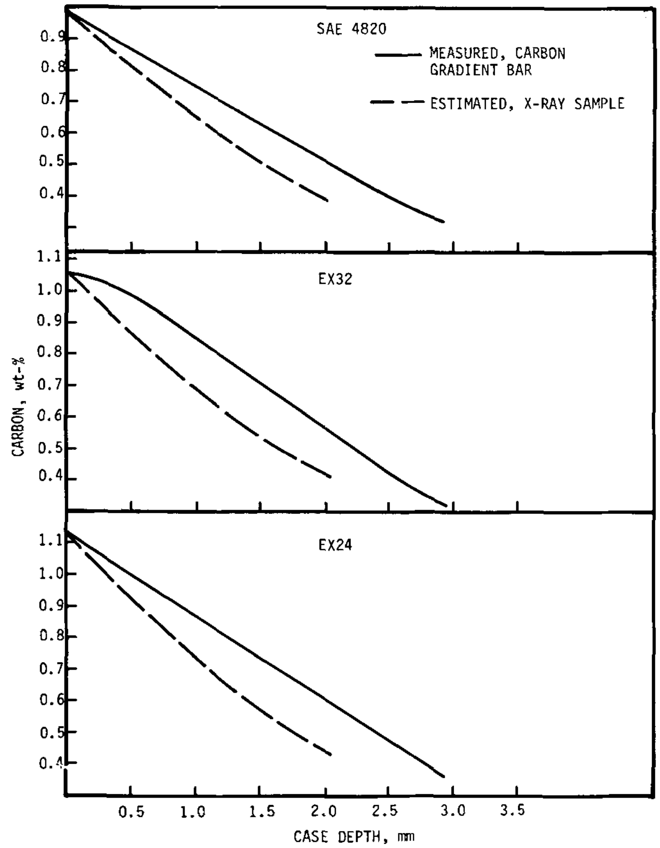

Fig. 2— Carbon gradients resulting from carburizing 20 h at 925 °C, 1.15 pct atm.

The X-ray procedure for determining retained austenite content has been detailed elsewhere.[9] In this study, molybdenum $K\alpha$ radiation was used. The specimens were held stationary, since it was determined they did not have sufficient texture to significantly influence the retained austenite measurement: An initial examination of several successive austenite and martensite peaks revealed their relative intensities to be within a few percent of that expected for a completely random texture. The X-ray beam impinged on the same specimen area which was measured by quantitative metallography. Retained austenite content was determined from the 200_α, 211_α, 220_γ, and 311_γ peaks according to the equation

$$\text{Pct}\ \gamma = \frac{100}{1 + \dfrac{I_{200_\alpha} + I_{211_\alpha}}{I_{200_\gamma} + I_{311_\gamma}}} \cdot K \qquad [1]$$

where the α and γ refer to the body-centered and face-centered phases, respectively, I represents the integrated intensity of each respective peak, and K is a constant which involves terms for structure factor, Lorenz polarization factor, multiplicity absorption and temperature factor.

RESULTS AND DISCUSSION

The carbon gradients resulting from carburizing the three steels for 20 h are shown in Fig. 2. The solid curves are the result of chemical analysis of the respective carbon gradient bars. The dashed curves represent estimated carbon gradients for the X-ray samples, which were carburized through one flat face only. To obtain these estimates, the empirical carbon gradients (solid curves) were compared with graphical solutions to the diffusion equation in cylindrical coordinates[10] to estimate an effective carbon diffusion coefficient, D_{eff}. The result was the same for all three steels, namely $D_{\text{eff}} = 2.2 \times 10^{-7}$ cm^2/s. This value was then used to calculate the concentration gradient in the X-ray sample using the solution to the one dimensional diffusion equation

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{X}{2\sqrt{D_{\text{eff}}t}}\right) \qquad [2]$$

where C = carbon content, X = distance from surface (case depth), t = time, and the subscripts s, o and x denote the surface, core, and position x, respectively.

Figure 3 shows the individual X-ray and metallographic measurements of retained austenite as a function of case depth for all three steels. These X-ray results have not been corrected for the volume fraction

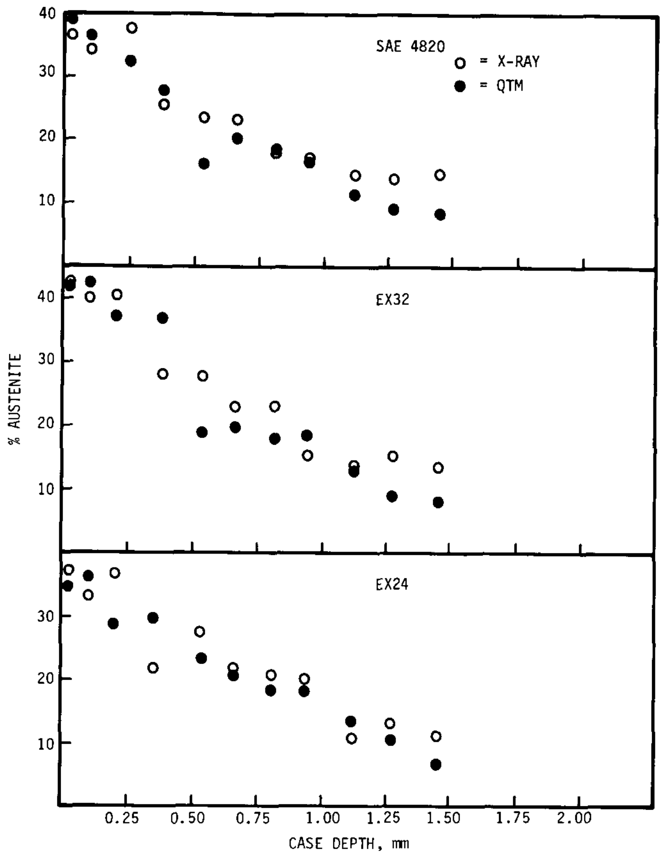

Fig. 3—X-ray and metallographic measurements of retained austenite at various depths in case. X-ray results not corrected for carbides in tempered martensite.

of carbides resulting from tempering. That correction is discussed below.

Neither of the two experimental techniques revealed a monotonic decrease in austenite content with case depth (carbon content). Although experimental errors are affecting both sets of measurements, as discussed below, the nonmonotonic retained austenite gradients are probably attributable in part to the normal heterogeneity of substitutional alloy distribution present in all steels. The austenite measurements were terminated at a case depth of approximately 1.4 mm which, as shown in Fig. 2, corresponds to a carbon content of about 0.6 pct or less in the X-ray specimens. At greater depths, the martensite morphology was sufficiently nonlenticular to prevent accurate metallographic detection of the austenite. Figure 4 is an optical micrograph of such an area which clearly illustrates the difficulty when compared with Fig. 1.

Basically the same austenite gradient is revealed by both techniques. Assuming the X-ray values are absolutely correct, then automated quantitative metallography appears to be quite useful down to retained austenite contents on the order of 10 pct, in materials with carbon contents as low as 0.6 pct. This would cover

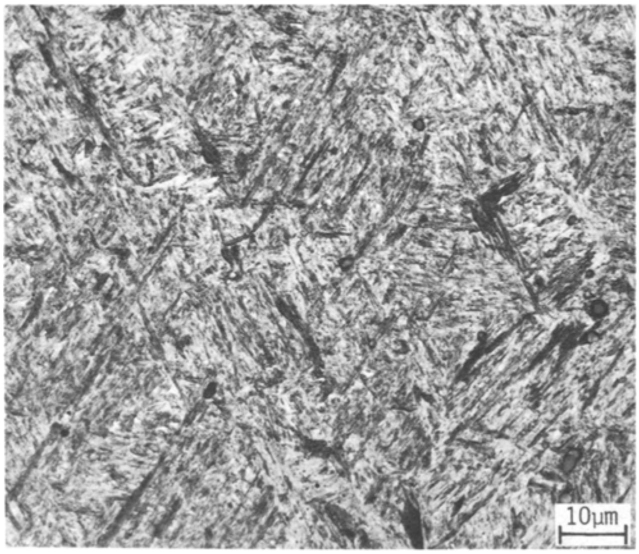

Fig. 4—Carburized X-ray specimen of EX32, 1.55 mm depth. 2 pct nital + zephiran chloride. Approximately 4 pct austenite detected by X-ray diffraction.

the region of greatest interest in most carburized materials.

Equation [1] assumes the specimens consist only of martensite plus austenite. However, the 200 °C temper treatment given to all specimens precipitates carbides in the martensite, and this carbide volume must be taken into account to correct the X-ray results and obtain the true volume fraction of austenite. This correction is effected by changing the numerator in Eq. [1] from 100 to $100 - V_c$, where V_c is the volume percent carbide in the entire specimen.

The carbides are so fine that they can be resolved only by transmission electron microscopy, so an exact correction for V_c cannot be made here. However, a reasonable estimate of V_c can be made as follows.

Table III. Change in Retained Austenite Values after Correcting for Assumed 10 Volume Percent Carbides in Tempered Martensite. 4820 Steel

	Retained Austenite by X-Ray,	
Case Depth, mm	Uncorrected	Corrected
0.025	36.6	34.3
0.100	34.2	32.0
0.255	37.6	35.3
0.380	25.5	23.6
0.535	23.5	21.7
0.660	23.2	21.4
0.815	17.9	16.4
0.940	17.2	15.8
1.120	14.6	13.4
1.270	13.9	12.7
1.450	14.7	13.4

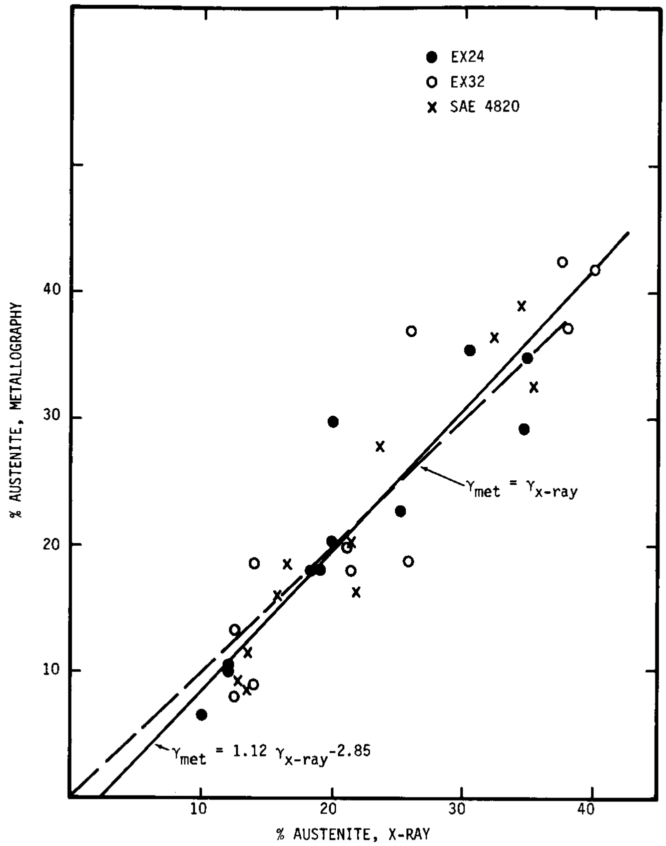

Fig. 5—Measurements of retained austenite, metallography *vs* X-ray. X-ray data corrected for presence of 10 vol pct carbides in martensite.

Assuming that simple iron carbides have formed, their carbon content is on the order of 7 wt pct. A reasonable estimate for the carbon remaining in solution in the tempered martensite is 0.2 pct.[12] The overall carbon content in the carburized cases studied here ranges from about 0.6 pct to 1.1 pct. Using these figures, a simple lever rule calculation yields that the volume fraction of carbides in the martensite ranges from 6 pct to 13 pct. If we assume an average value of 10 pct for all the data recorded here, then the numerator of Eq. [1] becomes

$$100 - V_c = 100 - (0.10 \times V_m) \qquad [3]$$

where V_m is the volume percent martensite present.

Table III presents the results of applying this correction to the X-ray data. The correction is not large, ranging from 1 to 2.5 vol pct.

Figure 5 shows the individual austenite measurements, plotted as the results of the X-ray technique (corrected for carbides) *vs* the metallographic method. The dashed line has a slope of one and represents the locus of data points if the results of the two experimental techniques were in perfect agreement. The solid line is the least-squares line through all the data. Linear regression was tried for the data of each steel individually, but there was no statistically significant difference among the slopes and intercepts. The data shown in Fig. 5 fit the equation

$$\text{Pct}\gamma_{\text{Met}} = 1.12 \times \text{Pct}\gamma_{\text{X-ray}} - 2.85 \qquad [4]$$

where γ signifies austenite and the subscripts refer to the metallographic and X-ray techniques, respectively. The equation shows the general trend that at low austenite contents metallography reveals less austenite than X-ray diffraction, while at high austenite contents metallography detects more austenite than X-ray diffraction.

This trend can be readily explained, and it points out an inherent inaccuracy in the X-ray method at high austenite contents, resulting from difficulties in specimen preparation. At low austenite contents, which in this investigation are synonymous with low carbon contents and a tendency toward nonlenticular martensite, the austenite becomes distributed in such a manner that it is not detectable by optical microscopy, as discussed previously. Hence, only the X-ray technique can resolve any austenite that may be present. At high austenite contents (here, higher carbon contents and lenticular martensite), a considerable amount of surface martensite is present, as shown in Fig. 1. The X-ray technique cannot distinguish between this microconstituent and the bulk martensite, while the metallographic technique can, if the specimen has been tempered as in this study. The X-ray results will thus err on the low side, that is, will register less austenite and more martensite than is actually present in the as-carburized and heat treated specimen. The magnitude of this error will be quite variable for two reasons. First, the amount of surface martensite present will vary with the care exercised in specimen preparation. Second, the X-ray technique samples a small volume of the specimen. That is, the beam penetrates the specimen to a certain depth below the surface. With Mo K_α radiation as used here, this penetration will be about 15 μ.[11] But the thickness of the surface martensite is variable, ranging from 0.3 to 30 μ.[6] Hence, for a given area fraction of surface martensite as measured metallographically, the X-ray results would vary, depending on surface preparation.

The data of Fig. 5 and Eq. [4] which describes them indicate that this surface martensite effect becomes significant when the retained austenite content is on the order of 20 to 25 pct and above. That is, the X-ray results will tend to yield erroneously low austenite contents, depending on surface preparation, at retained austenite contents in excess of about 20 vol pct. Eq. [4] also indicates that when austenite can no longer be detected metallographically ($\text{Pct}\gamma_{\text{Met}} = 0$), there will be, on average, about 2 to 3 vol pct austenite still present and detectable by X-ray diffraction. This is also indicated in Fig. 4, where no austenite can be seen but approximately 4 pct is detected by X-ray.

SUMMARY

Comparison of measurements of retained austenite contents in carburized steels, as determined by X-ray diffraction and automated quantitative metallography, indicates that the metallographic technique is suitable for such measurements. Over a range of case carbon contents of 1.1 to 0.6 pct, coincident with a range of 40 to 10 pct retained austenite, both techniques indicated similar retained austenite gradients. This range of carbon and retained austenite is sufficient to cover the range of greatest interest in carburized materials, namely, the effective case depth.

Comparison of individual retained austenite measurements reveals two interesting features. At low retained austenite contents, quantitative metallography tends to yield lower austenite contents than X-ray diffraction. At higher austenite contents, the reverse is true. The disagreement at low retained austenite contents can be ascribed to the concurrent decrease in carbon content and change of the martensite morphology from lenticular to lath. The distribution of austenite in such a matrix cannot be detected by the optical microscope, and this creates the principal limitation for quantitative metallography. The disagreement at high retained austenite contents can be ascribed to the presence of surface martensite. This microconstituent forms during metallographic preparation of the specimens. Although quantitative metallography can detect this microconstituent by its etching behavior and properly count it as retained austenite, the X-ray technique cannot distinguish the surface martensite, resulting in too low a retained austenite measurement when this microconstituent is present.

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REFERENCES

1. B. L. Averbach and M. Cohen: *Trans. AIME*, 1948, vol. 176, pp. 401–15.
2. B. L. Averbach, L. S. Castleman, and M. Cohen: *Trans. ASM*, 1950, vol. 42, pp. 112–20.
3. G. Y. Lai, W. E. Wood, R. A. Clark, V. F. Zackay, and E. R. Parker: *Met. Trans.*, 1974, vol. 5, pp. 1663–70.
4. G. R. Speich and P. R. Swann: *J. Iron Steel Inst.*, 1965, vol. 203, pp. 480–86.
5. J. A. Klosterman and W. G. Burgers: *Acta Metall.*, 1964, vol. 12, pp. 355–62.
6. I. H. Schwartz and K. J. Kim: *Met. Trans.*, 1976, vol. 7A, pp. 1567–70.
7. E. J. Klimek: *Met. Eng. Q.*, February 1975, pp. 55–61.
8. W. Uhlig, W. Schröter, and G. Schmidt: *Neue Hütte*, 1970, vol. 15, pp. 22–26.
9. C Kim: *J. Heat Treat.*, 1979, vol. 1, pp. 43–51.
10. J. Crank: *The Mathematics of Diffusion*, 2nd edition, Clarendon Press, Oxford, 1975.
11. B. D. Cullity: *Elements of X-Ray Diffraction*, Addison-Wesley, Reading, MA, 1956.
12. G. R. Speich: *Trans. AIME*, 1969, vol. 245, pp. 2553–63.