

April 2009

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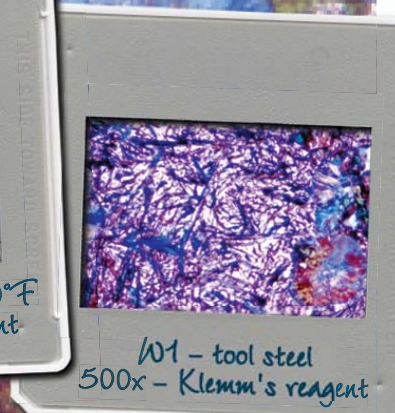
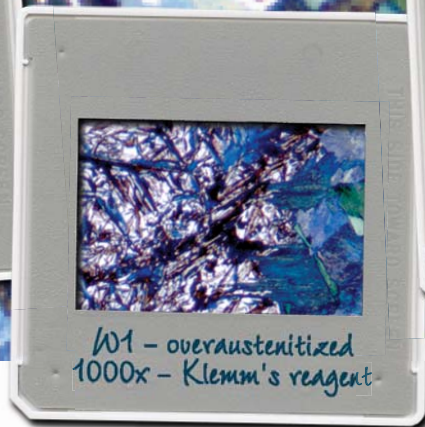
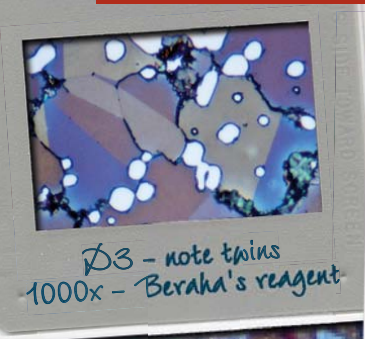
THE INTERNATIONAL JOURNAL OF THERMAL TECHNOLOGY

## Martensite and Retained Austenite

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# Martensite and Retained Austenite

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**Martensite development is critical to many heat-treatment processes. This paper examines the conditions under which austenite is retained and the problems associated with its presence, with detecting it and with measuring it.**

Depending upon the carbon content of the parent austenite phase, either lath (low-carbon) or plate (high-carbon) martensite may form, as well as mixtures of the two. In general, lath martensite is associated with high toughness and ductility but low strength, while plate martensite structures are much higher strength but may be rather brittle and non-ductile.

Increasing the carbon content of the austenite also depresses the martensite start ( $M_s$ ) temperature and the martensite finish ( $M_f$ ) temperature, which leads to difficulties in converting all of the austenite to martensite. When this happens, we have retained austenite, which may be either extremely detrimental or desirable under certain conditions.

## History

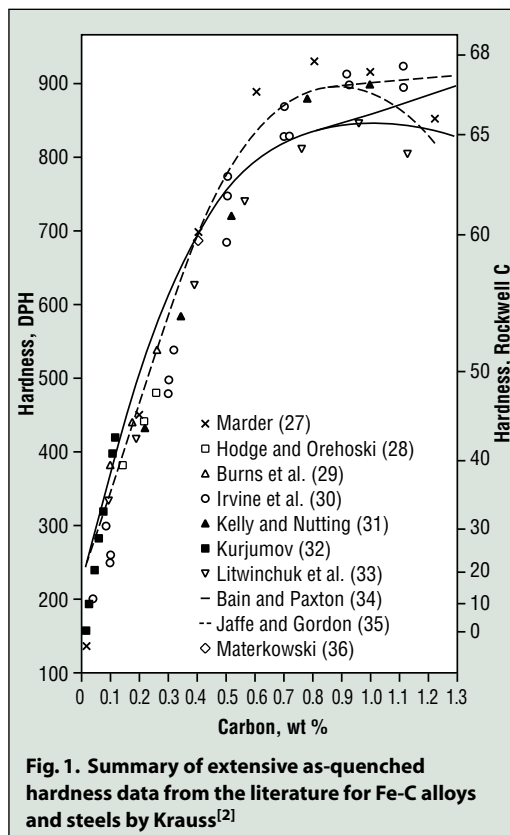
Up to about 100 years ago, the heat treatment of steels was certainly an art as the science behind what was happening was just starting to be understood. The control of grain size in carburizing was just becoming possible by the work of McQuaid and Ehn. They discovered that small additions of aluminum would keep the grain size fine after a long exposure, generally 8-10 hours, at the carburizing tempera-

ture. Prior to that, coarse prior-austenite grain structures would be observed in the carburized case that would initiate brittle intergranular fractures at minor loads.

Next, Grossman and Bain developed the theory of hardenability where the ideal critical diameter ( $D_I$ ) could be calculated from the prior-austenite grain size and the composition. Then, the  $D_I$  could be used to estimate the as-quenched hardness profile of a uniformly shaped bar given a particular strength quench.

About the same time, isothermal transformation (IT) diagrams were developed, and it became easier to identify these lesser-understood microstructures of upper and lower bainite. An IT diagram, while it is helpful in understanding microstructures and in developing annealing cycles, is not particularly useful for understanding heat-treatment structures. This problem was solved by developing continuous cooling transformation (CCT) diagrams. Shortly before the writer joined the Homer Research Laboratories of Bethlehem Steel, they had developed

CCT diagrams using the arrested-Jominy-bar method – a rather painful process indeed. Dilatometer-based CCT diagrams were far easier to develop and in less time, but this equipment came later.



**Fig. 1. Summary of extensive as-quenched hardness data from the literature for Fe-C alloys and steels by Krauss<sup>[2]</sup>**

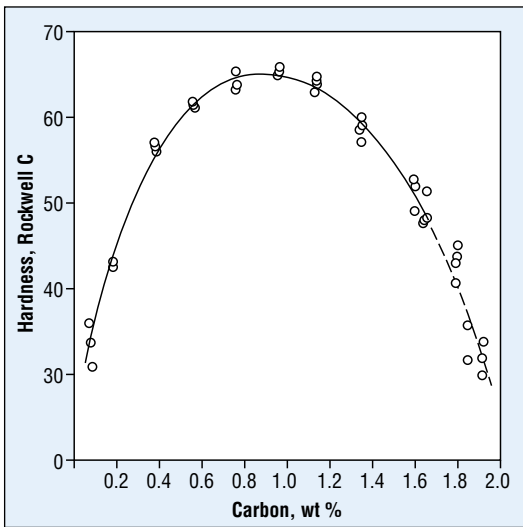


Fig. 2. As-quenched of brine quenched Fe-C alloys up to nearly 2 wt. % by Litwinchuk et al.<sup>[3]</sup>

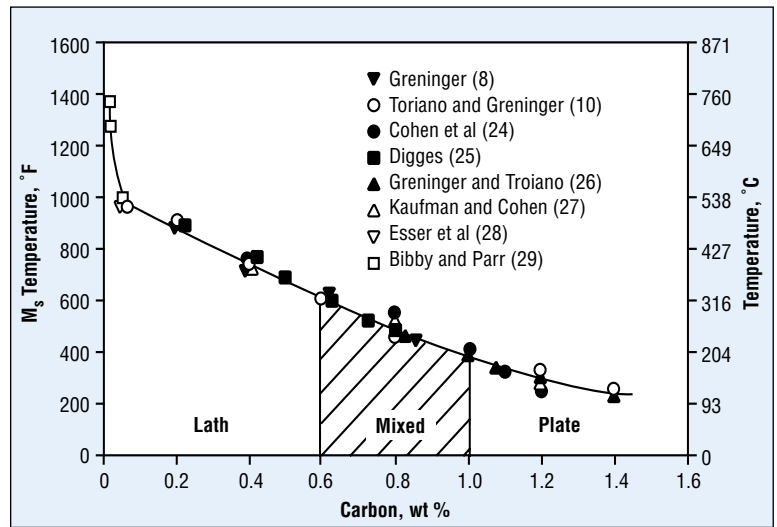


Fig. 3. Relationship between carbon content, martensite type and  $M_s$  temperature<sup>[4]</sup>

### Technological Advantages

Development of thin-foil technology for the transmission electron microscope (TEM) produced a far-deeper understanding of the fine details of steel microstructures because these features were well beyond the resolution of the light optical microscope (LOM). The development of IT and CCT diagrams had shown that martensite began transforming at temperatures relative to the composition of the austenite, with its carbon content being most critical.

Problems due to excessive retained austenite had plagued the tool-steel industry since the late 19<sup>th</sup> century. X-ray diffraction had been the primary tool for the study of retained austenite and certainly for its quantification, but it could not image this microstructure. LOM could not image retained austenite until it was at least present in the 10-15% range. TEM thin foils could detect and image retained austenite even at levels somewhat under 2% with careful use of dark-field illumination. The morphology of the martensite makes it difficult to distinguish small particles of retained austenite within the complex plate-martensite patterns. With low-carbon lath martensite, thin films of retained austenite could be seen with very careful TEM work, but this was very difficult work.

### Tool Steels

In the tool-steel industry, excessive retained austenite is universally considered to be detrimental. Exactly what constitutes "excessive" is difficult to define as not enough data exists, and what is excessive will vary with the grade and application. For example, relatively low-carbon 5%-Cr hot-work die steels such as H11 and H13 have been used for years as gauge blocks. Any dimensional change with time is to be avoided. Consequently, these steels are triple tempered at a relatively high temperature where retained austenite will be converted to either fresh martensite or bainite, and they will be tempered with the next tempering cycle.

In other applications, any observable (by LOM) retained austenite is highly detrimental. Service stresses will convert the retained austenite on the first use. As the carbon content of the retained austenite is high, the martensite that forms is highly tetragonal and the resulting expansion cracks the steel because the matrix is not ductile enough to tolerate the expansion stresses.

With carburized gears, on the other hand, only a very thin layer at the surface is carburized and may contain 20-25% retained austenite. The bulk of the gear is a highly ductile (compared to a tool steel), low-carbon alloy steel. Gears are usually

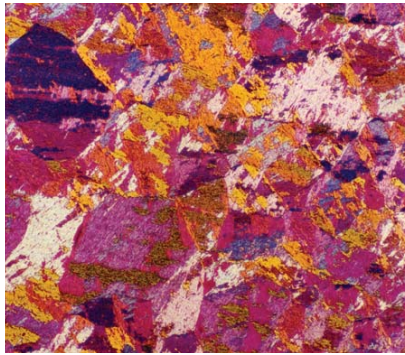
not impact loaded like a tool-steel die, so the stresses are much lower and the retained austenite usually does not transform substantially during service. If the retained austenite did transform, the steel around it and below it is ductile enough to accommodate the strains without fracture. Retained austenite does become stable with time, and some will transform to martensite at room temperature. Samuels<sup>[1]</sup> states that up to 5% of the austenite present after quenching and low-temperature tempering (<200°C) will transform to martensite soon after quenching or over a period of some months.

### Influence of Carbon Content of the Austenite

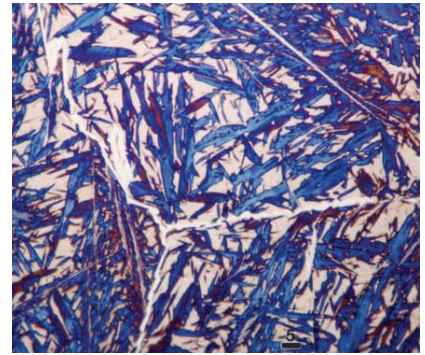
Starting in the 1930s with the development of hardenability concepts, a number of investigators have demonstrated that the hardness of as-quenched martensite increases in a relatively linear fashion from about 0.05 to 0.5 wt. % carbon. Figure 1 shows data from a number of investigators summarized by Krauss.<sup>[2]</sup> Note that when the carbon content of the austenite is >0.8%, the as-quenched hardness drops. This is due to the presence of retained austenite, which is much softer than plate martensite. Litwinchuk et al.<sup>[3]</sup> took this curve to nearly 2% carbon which demonstrates the effect of retaining large



**Fig. 4. Carbon-free martensite in 18Ni250 maraging steel (Fe-<0.03% C-18.5% Ni-7.5% Co-4.85% Mo-0.4% Ti-0.1% Al) etched with Fry's reagent (1000x - marker bar is 10  $\mu$ m long)**



**Fig. 5. Low-carbon martensite in Carpenter Technology's AerMet 100 ultrahigh-strength steel (Fe-0.23% C-13.5% Co-11.1% Ni-3.1% Cr-1.2% Mo) heat treated (1093 °C, AC, age at 675 °C for 6 h, AC) to coarsen the grain size and etched with 10% sodium metabisulfite (100x)**



**Fig. 6. High-carbon plate martensite (blue and brown), retained austenite (white), plus intergranular and intragranular cementite in a carburized specimen of 9310 alloy steel etched with Beraha's reagent (100 mL water, 10 g  $\text{Na}_2\text{S}_2\text{O}_3$  and 3 g  $\text{K}_2\text{S}_2\text{O}_8$ ) at 1000x (marker bar is 5  $\mu$ m long).**

amounts of retained austenite upon the as-quenched hardness.

Figure 3, from the work of Marder and Krauss<sup>[4]</sup>, shows the relationship between the type of martensite observed and the carbon content and martensite-start temperature for Fe-C alloys. Figures 4 and 5 illustrate the appearance by LOM of carbon-free martensite in a maraging steel and lath martensite in an ultrahigh-strength, low-carbon steel (AerMet 100). Figure 6 shows plate martensite, retained austenite and both intergranular and transgranular cementite in carburized 9310 alloy steel. Plate martensite frequently contains microcracks from the impact of one plate into a previously formed plate. These cracks can initiate subsequent failures.

Speich and Leslie<sup>[5]</sup> showed how increasing carbon in the austenite caused the percentage of retained austenite to increase, the  $M_s$  to decrease and the change in martensite type from lath to plate. A number of studies between Payson and Savage in 1944 and Andrews in 1965 have developed empirical formulas to calculate the  $M_s$  based on composition, not simply from the carbon content. Carbon, of course, has the largest effect, but the influence of alloying elements upon lowering the  $M_s$  cannot be ignored. The  $M_f$  temperature falls with the  $M_s$ , so the formulas predict only the  $M_s$  temperature.

### Detecting Retained Austenite

Over the years, the writer has tried many etchants, plus tint etchants, in an effort to try to preferentially color retained austenite. In almost all cases, these efforts have failed. Many years ago, an investigator published a short paper claiming that the addition of 1% zephiran chloride – a wetting agent frequently added to 4% picral to increase the speed of etching<sup>[6]</sup> – would reveal retained austenite by creating a strong contrast between the dark martensite and the unetched austenite. This author claimed to be able to see and measure, by point counting, retained austenite down to ~2% in steels.

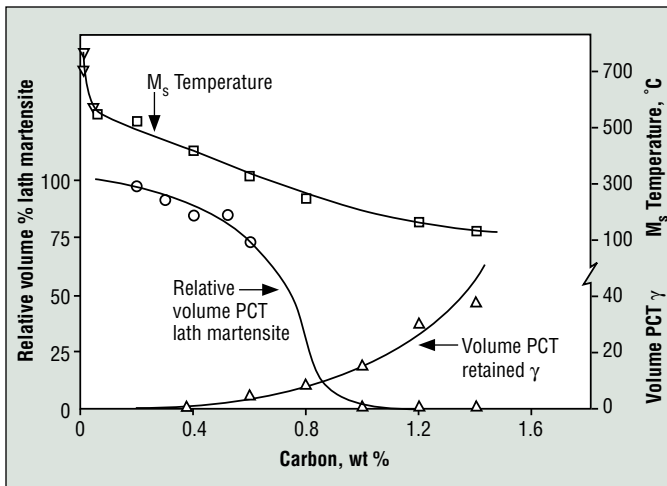
The writer has tried to duplicate this experiment using railroad cone bearings of carburized 8720 alloy steel. Unfortunately, details of how these bearings were processed and then prepared for metallography were unknown. But at some earlier time they were analyzed by X-ray diffraction (XRD). Three pieces claimed to contain 25.4, 19.7 and 16.2% retained austenite were given to the writer, who mounted them in a low-temperature-curing epoxy compound and ground and polished them. Nital plus zephiran chloride did reveal the retained austenite much better than nital without the addition, and higher amounts of retained austenite were recorded when zephiran chloride was added. The image-analysis results, however, were very low compared to the XRD results. Of course, it is possible that some of the retained austenite had iso-

thermally transformed between the time when the XRD work was done and when the image analysis work was done – a time that may have been a few years.

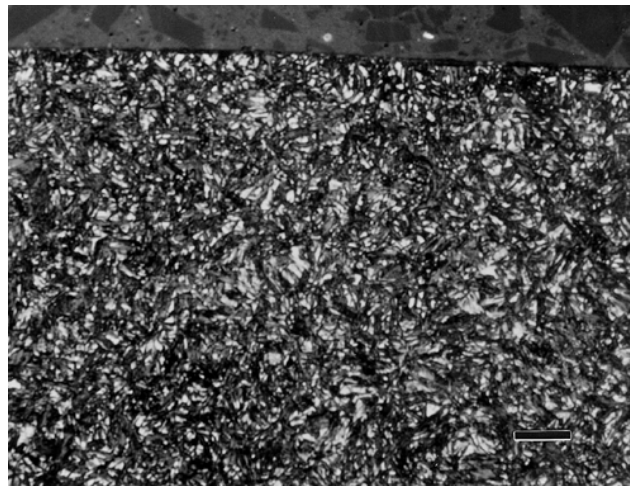
Figure 8 shows the microstructure of the cone bearing that was reported to contain 25.4% retained austenite etched with 4% nital plus 1% zephiran chloride. The image, by eye, does not appear to be one-fourth retained austenite, and image analysis measured only 13.3% with this etch (and less with other etchants). The specimen with 19.7% retained austenite was measured as 8.5% by image analysis with this etch, and the specimen with 16.2% retained austenite was measured as only 1.2% retained austenite by image analysis with this etch. In general, this is the type of difference that the writer has always seen when doing such experiments previously.

A new technique utilizing the scanning electron microscope (SEM) has been developed. Called electron backscatter diffraction (EBSD), it has the ability to map microstructures according to crystal-structure differences. The writer has tried recently (about five years after the image-analysis work was done) to determine the percent retained austenite of the 25.4% specimen by EBSD.

Some authors have claimed that EBSD can detect and measure retained austenite down to ~2% and get data that agrees with XRD data. The specimen with 25.4%



**Fig. 7. Influence of carbon content of the austenite on the percentages of lath (or plate) martensite,  $M_s$  temperature and percentage of retained austenite<sup>[5]</sup>**



**Fig. 8. Surface of a carburized 8720 alloy-steel railroad-cone bearing etched with nital plus 1% zephiran chloride. Image analysis yielded 13.3% retained austenite vs 25.4% by XRD (1000x).**

retained austenite was re-prepared metallographically using the best procedures for EBSD and analyzed by Stefan Zaeferrer of the Max Planck Institute for Steel Research in Düsseldorf, Germany. EBSD showed only about 5% retained austenite in this specimen. Examination of the mapped pixels around the patches of retained austenite revealed that there were many that appeared black on an index of quality map, indicating that they were not producing an indexable diffraction pattern. It is possible that these pixels were from austenite that had transformed to fresh martensite. But even if these pixels were added to the pixels that were from FCC austenite, the percentage would still be much less than 25.4%.

### Future Work

Working with a carburized specimen presents difficulties due to the variation in carbon and microstructure in the case. The writer is planning additional EBSD work

with Dr. Zaeferrer using 1.25-inch-diameter bars (to avoid mounting and conductivity problems) of O1 and 52100 alloy steels, high-carbon steels with enough hardenability to be through-hardened and with enough carbon and alloy content to produce >10% retained austenite. As their alloy content is not high, carbide interference peaks and texture problems by XRD should be minimal. Transverse and longitudinal specimens will be prepared and tested by XRD, then by LOM and EBSD. These tests will be performed quickly, and other labs will participate to evaluate the reproducibility of the data. Some experiments will be run at a later date to access the influence of time since heat treatment upon the data. **IH**

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