X-RAY LINE BROADENING ANALYSIS OF COHERENT M₂C PRECIPITATION IN Ni-Co SECONDARY HARDENING STEELS

Y. Nagataki¹, J.B. Cohen², and G.B. Olson²

¹NKK Corporation, Japan
²Northwestern University, Dept. Mat. Sci. & Eng., 2225 N. Campus Dr., Evanston, IL 60208 USA

Abstract

In support of multiscale modeling of microstructural evolution for computational materials design, X-ray line broadening measurements of dislocation cell size and matrix coherency strain are integrated with small-angle neutron scattering measurements of M₂C precipitate size during secondary hardening of ultrahigh-strength Ni-Co martensitic steels. In addition to the retarding effect of Co in solution, M₂C precipitation further retards dislocation recovery, and the effect is greater with the finer-scale precipitation associated with higher thermodynamic driving force. An increase in microstrain amplitude during early precipitation is attributed to carbide coherency strain. A subsequent decrease occurring at or before peak hardness is interpreted as the onset of coherency loss. This supports similar critical particle sizes of ~30Å diameter for coherency loss and the shear-to-bypass transition in strengthening behavior.
Introduction

As a new millennium dawns, the materials profession stands at the threshold of a materials design revolution enabled by a confluence of new computational capabilities and advanced instrumentation(1,2). Heralding this revolution, multiscale microstructural design models developed by the Steel Research Group (SRG) program(3,4) have yielded alloy steels with 50% higher strength for a given carbon content, allowing design of a new class of high performance carburizing steels currently undergoing testing in racecar gearboxes(5,6). The generation and validation of quantitative nanoscale precipitation strengthening models has been based principally on precise Small Angle Neutron Scattering (SANS) measurements by Julia Weertman and coworkers(7,8) integrated with advanced electron microscopy(9) and atom-probe microanalysis(10). This information has allowed calibration of coherent carbide thermodynamics(11,12) and dislocation-based heterogeneous nucleation behavior(13), as well as calibration of the strengthening contributions of both shearable and nonshearable (Orowan) particles(14,15).

The most thorough studies have centered on Ni-Co secondary hardening martensitic steels which exploit heterogeneous M_2C carbide nucleation on dislocations enabled through retardation of dislocation recovery by Co(3), and maximization of coherent M_2C precipitation driving force for particle size refinement for efficient strengthening(5,15). The studies have included both commercial alloys and a series of model 16Co-5Ni-.24C steels designed to avoid austenite precipitation during M_2C precipitation strengthening(5). The latter series verifies the predicted correlation between precipitation driving force and strengthening efficiency, but thorough evaluation of precipitation behavior is so far limited to lower driving force compositions.

The current study was undertaken to extend quantitative precipitation measurements to higher driving force compositions in the 16Co-5Ni-.24C alloy series and to exploit the capabilities of X-ray line broadening analysis to quantify both the dislocation recovery behavior and the state of coherency of the nanoscale M_2C precipitates.

Materials and Experimental Procedures

Alloy compositions of the two model alloys are given in wt. pct. in Table 1. The numbers 4 and 6 in the alloy designations represent the ratio of M_2C carbide forming elements to carbon content, while the B and D correspond to relative Mo/Cr ratios. The higher Mo alloy 6D corresponds to the highest driving force composition in the full 16Co-5Ni-.24C alloy series, previously shown to achieve the highest hardness level during M_2C precipitation strengthening(5). The alloys were vacuum melted, cast as 50kg ingots, homogenized at 1200°C, hot rolled to 2cm thickness plates with a 900°C finishing temperature, and surface ground. Optimal 1hr solution temperatures were found by measuring hardness after 210°C -1hr tempering vs. solution temperature in 25°C intervals. Maximum hardness typically corresponded to 20°C above predicted equilibrium solvus temperatures. Solution treated blanks (2.5cm square by 1.3cm thick) were oil quenched, cooled 1hr in liquid nitrogen to minimize retained austenite, and then cut in half. The sectioned samples were then tempered at 510°C for times ranging from 5sec to 234hrs, using a salt bath for treatment times of 30min or less and a nitrogen atmosphere furnace for longer times, followed by a water quench. Hardness and X-ray diffraction measurements were taken from the center of the sectioned samples. Vickers hardness measurement employed a Micro Vickers test machine at 1kg load.
Table 1. Alloy Steel Compositions (wt. pct.)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Co</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4B</td>
<td>15.81</td>
<td>4.88</td>
<td>3.52</td>
<td>1.50</td>
<td>0.246</td>
</tr>
<tr>
<td>6D</td>
<td>16.11</td>
<td>4.88</td>
<td>4.25</td>
<td>4.01</td>
<td>0.241</td>
</tr>
</tbody>
</table>

Fourier analysis of X-ray diffraction profiles was employed to examine the microstrains due to dislocations, carbide coherency strains, and dislocation spacing or "cell size." The well-known two-peak analysis proposed by Warren and Averbach (16) was employed. In this treatment, the Fourier cosine coefficients of two orders of a reflection are employed to obtain this information. The results are a cell size (D) and rms microstrain \(\varepsilon^2 \) (the microstrain variance) averaged over various length (L) of the diffracting columns normal to the diffracting planes. The 110 and 220 peaks of the martensite matrix were employed and corrected for instrumental affects following Stokes (17) with an annealed ultra-low carbon steel plate standard (15 ppm of C) from NKK Corp., Japan.

The surface of each tempered specimen was polished mechanically and then electropolished with a glacial acetic acid-glycerol solution at 17V, 0.67A/m², and ~15mm were removed. Filtered CuKα radiation (40kV, 20mA) was employed with a Scintag diffractometer equipped with a Si(Li) solid state detector to minimize the fluorescent background. A step scan from 40-49° 2θ was employed for the 110 peak, with steps of 0.04° for 60 seconds, 93-104.5° for the 220 with 250 second 0.12° steps.

The analysis was carried out on a P.C. using programs evolved from that developed by DeAngelis (18) and typical errors were ~0.5 pct. for D and 10 pct. for \(\varepsilon^2 \).

Results and Discussion

The measured evolution of hardness for the two steels is shown in Figure 1. An initial softening associated with cementite precipitation and coarsening reaches a hardness minimum at about 20 sec tempering, corresponding to the onset of \(M_2C\) precipitation strengthening. The higher driving force 6D alloy reaches a peak hardness of 700 Hv which is remarkable for an 0.24C steel. The removal of Cr and Mo from the matrix solution by \(M_2C\) precipitation causes a shift in the matrix lattice parameter which is used to estimate the relative \(M_2C\) phase fraction (normalized to the final equilibrium fraction) as shown in Figure 2. The overall precipitation kinetics is quite similar in the two steels, despite the difference in hardness evolution. Previous SANS measurements (7,8) show that the peak hardness is associated with a 30Å average \(M_2C\) particle diameter, interpreted as the critical particle size for the shear/bypass transition in dislocation interaction, and recent SANS data (8) has also demonstrated this for alloy 6D as shown in Figure 3. As noted by the arrows in Figure 2, the higher peak hardness of alloy 6D is associated with reaching this critical size at a higher relative \(M_2C\) phase fraction, in association with its smaller initial \(M_2C\) critical nucleus size governed by its higher precipitation driving force.

Separation of the size contribution of X-ray line broadening gives the evolution of dislocation cell size depicted in Figure 4. Also plotted as dotted and dashed curves are the evolution of dislocation subgrain size directly measured by electron microscopy in our previous study (3,19) of dislocation recovery in cold-worked Fe and Fe14Co ferrites employed to model martensitic substructures, demonstrating the retarding influence of Co alloying. The 16Co secondary
Figure 1. Evolution of hardness of alloys 4B and 6D with tempering at 510°C. Corresponding coherent $M_2C$ precipitation driving forces (5) indicated.

Figure 2. Evolution of relative $M_2C$ phase fraction (normalized to final equilibrium) in alloys 4B and 6D determined from matrix lattice parameters.
Figure 3. Evolution of $M_2C$ mean particle diameter in alloy 6D from parallel SANS measurements(8). Dotted curve represents corresponding hardness evolution.

Figure 4. Evolution of dislocation cell size determined from line broadening analysis in alloys 4B and 6D. Dotted and dashed curves are calculated from TEM measurements(19) of subgrain coarsening in cold-worked Fe and Fe14Co ferritic steels.
hardening martensitic steels show further retardation attributed to the role of carbide precipitation. We attribute the greater dislocation recovery retardation in the higher driving force 6D alloy to the finer scale of M₂C precipitation underlying its higher peak hardness.

The microstrain contribution to line broadening is found to show a nonmonotonic evolution similar to the hardness behavior of Figure 1. However, these strains include contributions from both the dislocation strain fields and the matrix coherency strains due to carbide formation. The rms microstrains from dislocations have the form:

\[
\langle \varepsilon^2 \rangle^{1/2} = \frac{G^2}{L}
\]  

This has been established both experimentally and theoretically(20), and the value of G for the <110> direction has been measured for pure iron filings as G=0.022Å⁻¹. Equation 1 is plotted in Figure 5 along with the measured rms microstrains for various stages of tempering. The calculated values from Equation 1 and these measurements agree for the later stages of tempering, but the experimental values are considerably larger for short times than the values calculated for dislocations. At large L values in Figure 5, the predicted dislocation values are too large, and the sequence of values follows the hardness evolution closely, as summarized in Figures 6 and 7. It is likely then that the values at large L are due predominantly to the coherency strains. In averaging over large values of L, positive and negative values of the dislocation strain fields cancel, whereas the coherency strains are largely dilatational and less likely to cancel.

The initial increase in matrix microstrain in Figures 6 and 7 is consistent with an increasing phase fraction of coherent carbide. We interpret the subsequent decrease as the onset of carbide coherency loss. Comparison with the hardness curves superimposed in Figures 6 and 7 indicates that coherency loss occurs at, or just before, peak hardness. We conclude that the critical particle size for the M₂C carbide coherency loss is equal or slightly smaller than the 30Å critical size for the shear/bypass transition associated with peak hardness. We believe that the microstrain results in Figures 6 and 7 are the first such demonstration of X-ray line broadening detection of the matrix coherency strains associated with coherent precipitation. This may be associated with the unusually large principal coherency strains arising from coherent M₂C precipitation in steels(11).

**Conclusions**

An X-ray diffraction study of M₂C carbide precipitation strengthening behavior in model 16Co-5Ni-.24C secondary hardening steels confirms that higher M₂C precipitation driving force is associated with reaching a peak hardness condition at a higher relative M₂C phase fraction. Parallel SANS measurements show that peak hardness corresponds to an M₂C particle size of 30Å, interpreted as the critical size for shear/bypass transition in dislocation interaction. Reaching this size at a higher phase fraction provides a higher peak hardness through a higher number density of Orowan obstacles. Separating X-ray line broadening into size and microstrain contributions reveals that dislocation recovery, quantified by the evolution of dislocation cell size, is retarded by finer scale M₂C precipitation. The data provide quantitative input for modeling evolution of the dislocation substructure contribution to strengthening. Microstrain measurements at larger column lengths reveal the increasing matrix coherency strains associated with coherent M₂C precipitation, and indicate a critical particle size for
Figure 5. Dependence of root-mean-square microstrain on Fourier column length in alloy 6D at varying stages of tempering. Solid curve is theoretical form of dislocation contribution from Equation 1.

Figure 6. Evolution of matrix microstrain (L=144Å) in alloy 6D compared with hardness evolution.
coherency loss at, or just below, the 30Å critical shear/bypass transition size. Taken together these results provide valuable quantitative information for refinement of microstructural evolution models for nanoscale precipitation strengthening behavior, to be integrated in further computational design of efficiently strengthened high performance alloy steels.

Acknowledgments

The Steel Research Group research on precipitation strengthening is supported by the Army Research Office under Grant DAAH04-96-1-0266. Visiting Scientist Y. Nagataki was supported by the NKK Corporation of Japan. We are grateful for inspiring discussions and valuable research collaborations with Professor Julia Weertman, whose SANS studies were crucial in initiating and continuing this fruitful line of research.

References


