Over the years, the possibility of enhancing the properties of hardened steels by treating them at temperatures below room temperature has been of interest. Two types of low temperature thermal treatments are subzero, or cold treatment, and cryogenic treatment. Subzero treatment is carried out at -145°C (-230°F), while cryogenic treatment is carried out at -195°C (-320°F), the boiling point of liquid nitrogen. Interest continues based on anecdotal evidence of the benefits of “cryo” treatment not only for steels but also in nonferrous metals like copper, aluminum and titanium. The literature contains many claims about the advantages of cryogenics[1-5]. However, there is little information available in the scientific literature regarding understanding the mechanism behind property improvements[6-8] beyond the obvious conversion of austenite to martensite, which only applies to steels. The objectives of this study were to quantify any property improvements and correlate them with microstructural changes.

**Experimental Procedure**

To understand property and response changes, M2 tool steel (molybdenum high speed tool steel having nominal composition of 0.85-1.00% C, 4.0% Cr, 2.0% V, 6.0% W, 5% Mo) was subjected to five different heat treatment sequences including:

1. Austenitize and quench
2. Austenitize, quench, and temper
3. Austenitize, quench, temper, and cryo treat
4. Austenitize, quench, and cryo treat
5. Austenitize, quench, cryo, and temper

Hardening was carried out by austenitizing in a vacuum furnace at 1200°C (2190°F) followed by gas quenching using 20 bar nitrogen. Tempering was performed in a box type furnace at 565°C (1050°F) for two hours followed by furnace cooling. Cryogenic treatment was performed in a cryoprocessor at -184°C (-300°F) followed by 40 hours of holding. Heating and cooling were carried out at the controlled rate of 21°C/min (40°F/min).

Conventional processing of M2 tool steel includes hardening followed by triple tempering. When cryogenic treatment is used, only a single temper is used, which seems sufficient to convert martensite to tempered martensite. Sequence 3 represents the current industrial practice for cryogenic treatment. Figure 1 shows the various test samples used for compression and hardness testing, x-ray diffraction, internal friction, and dilatometry. Additional testing included metallography, resistivity measurements, and photon induced positron annihilation (PIPA).

**Test Results**

A plot of hardness as a function of...
the different thermal processing sequences is shown in Fig. 2. Quenched and tempered samples have higher hardness (by 0.7 HRC) compared with that for the quenched only sample, which could be due to secondary hardening from tempering at 565°C. Cryo treatment of the tempered sample results in a boost of 1 HRC, possibly due to conversion of retained austenite to martensite. The highest hardness (64.9 HRC) was achieved by cryogenic treatment directly after quenching, which is due to transformation of retained austenite to martensite. The hardness of the quenched, cryotreated, and tempered sample is 1.4 HRC lower due to precipitation of carbides and reduction in tetragonality of martensite during tempering.

Further tempering may produce very small spherical carbide precipitation, which is important with respect to wear resistance, but may not provide an improvement in hardness.

Compression testing was used to determine the yield strength (Fig. 3). Yield strength values are clustered for tempered and untempered samples, respectively. The highest value for the quenched and cryotreated sample can be attributed to the greater dislocation density resulting from cryogenic treatment, which converts almost all retained austenite to martensite.

Internal friction tests were used to quantify dissolved carbon and nitrogen in solution and to detect the presence of mobile dislocations. A plot of internal friction versus frequency is shown in Fig. 4. The complete absence of the carbon peak can be attributed to the quench aging, which allows carbon to form clusters around the dislocations or possibly form small size carbides. Higher level of background for sequences 1 and 4 indicates higher density of dislocations or dislocation-interstitial interaction. Internal friction is lower for sequence 2, 3 and 5, which suggests lower mobile dislocation density. Moreover, the background is higher for sequence 4 compared with sequence 1, which suggests cryogenic treatment results in more dislocations in the sample. These results appear to be logical and consistent with the resistivity measurements, which are used to characterize changes in interstitial contents like carbon, carbide precipitates and dislocations (Fig. 5).

Higher resistivity in sequences 1 and 4 is attributed to clustering of carbon atoms and the high density of dislocations. Resistivity decreases after tempering due to carbide precipitation and reduction or rearrangement in dislocation density. Two competing processes further decreases resistivity after cryogenic treatment. Resistivity must increase due to greater dislocation density. Also, carbon atoms could cluster at dislocations and subsequently precipitate during tempering. Thus, loss of carbon from the matrix may result in lower resistivity. The highest resistivity for sequence 4 suggests higher
dislocations and clustering of carbon atoms. Further tempering reduces carbon in solution due to precipitation, and there is a reduction in dislocation density, thus lowering resistivity. An example of the change in resistivity with material condition is shown in Fig. 6.

Dilation plots for all treated and as-received samples are shown in Fig. 7. The starting microstructure was martensite or tempered martensite. Samples were heated to a temperature of 1000°C (1830°F) with 10°C/min. (18°F/min) heating and cooling. There is no significant difference for all samples in terms of contraction. During heating, there is a clear distinction between tempered and untempered samples. The latter have a lower thermal expansion during heating, which is attributed to the conversion of tetragonal martensite to a lower tetragonality martensite due to clustering and/or carbide precipitation.

Induced strain in martensite and c/a ratio for the martensite were measured using x-ray analysis processed by Rietveld analysis, the general structure analysis system (GSAS) software from LANL (Fig. 8). The value of strain depends on the tetragonality of the martensite and the mismatch between precipitates and the matrix. Sequence 3 has the maximum strain of 1.6, which is attributed to secondary carbide precipitation from tempering and nanoscale carbide precipitation from cryotreatment, in addition to strain from mismatch between primary carbides and matrix from cryotreatment. The minimum strain of 1.06 (sequence 5) is attributed to carbide coarsening resulting from cryogenic treatment during subsequent tempering. Strains for as-quenched and quenched plus cryotreated samples are similar but higher than those for the tempered samples. These results indicate that the dislocation density is higher in as-quenched and quenched plus cryotreated samples. Photon induced positron annihilation is used to identify the defect density in materials[9]. Data in Fig. 9 indicate the relative number of dislocations present in the material. All samples were normalized to the as-received sample (sequence 0). Sequence 4 has the highest dislocation density, the effect of full transformation of retained austenite to martensite and relative thermal contraction of the matrix compared with primary carbides during cryogenic treatment. Conversion to martensite results in a 4% volume expansion; on the other hand, there is thermal contraction from the cryogenic treatment. The two distinct effects produce a greater number of dislocations compared with the as-quenched sample. The negative value of S parameter for sequences 2 and 5 indicates a lower number of dislocations compared with the as-received sample. The lowest S parameter value (sequence 5), could be due to the annihilation of dislocations and recovery processes. The decrease in the S parameter on tempering (sequence 2) is expected due to a combined effect of precipitation and recovery. Cryotreatment on the same sample (sequence 3) produces a higher dislocation density from transformation of retained austenite to martensitic with a corresponding increase in S parameter. Tempering after cryotreatment results in a lower dislocation density than tempering before cryotreatment (sequence 5).

Summary and Conclusions

There is no large difference in terms of hardness and yield strength for processes sequences 2, 3, and 5, which simulate actual practices. Also, hardness, resistivity, and PIPA results indicate that sequence 5 should have higher toughness. Good wear resistance requires a combination of hardness and toughness[6], which can be achieved by cryotreatment followed by tempering.

Cryotreatment produces two ef-
fects: differential contraction between matrix and primary carbides (in the case of tempering before cryotreating) and transformation of retained austenite to martensite; and a 4% volume expansion from austenite transformation to martensite. Both effects can induce more strain in the material, which, in turn, may produce more dislocations. Diffusion of carbon atoms to dislocations reduces the overall energy of the system, and can occur to a limited extent at such a low temperature. However, significant segregation of carbon to dislocations occurs on warming back to room temperature. Dislocations are preferred sites for carbon to segregate (i.e., it has 0.5 eV binding energy compared with 0.4 with the other carbides). Thus, small clusters of carbon can precipitate upon heating. The precipitates produced in this way are homogeneous and very fine. In service, these precipitates can act as crack arresters and can increase the toughness. Cryogenically treated material should have an improved combination of hardness and toughness, but the effect is small and difficult to quantify.

Acknowledgement: Special thanks to C. Rideout, Positron Systems Inc., Boise, Idaho, Fred Otto, Midwest Thermal-Vac, Kenosha, Wis., Rick Diekman for cryotreatment, and Prof. Sheldon Mostovoy for helpful discussions.

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Fig. 9 — S parameter normalized to as-received sample versus processing sequence number.

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