Does liquid nitrogen immersion improve wear resistance of steel and cast iron?

Christian B. Thompson and Keith A. Brown

A study of eight iron-based alloys considered the effects of cryogenic treatment on resistance to abrasion.

Can the wear resistance of steel and cast iron be improved by cryogenic treatment? This was the question addressed in a study of the effects of liquid nitrogen immersion on hardness and abrasive wear resistance.

For ferrous alloys in which the austenite-to-martensite solid-state reaction is only completed at subzero temperatures, conventional quenching (e.g., into brine or oil) cannot produce a 100% martensitic microstructure. As a result, some residual austenite remains. Under highly stressed service conditions, there is a danger that this austenite may transform to "white" (or untempered) martensite, giving rise to dimensional instability and embrittlement. To avoid this problem, high-precision components such as gears are often held at cryogenic temperatures to ensure completion of the austenite-martensite reaction. Liquid nitrogen is commonly used for this purpose on account of its ready availability and relatively low boiling point (77°K).

Because of the effect of cryogenic treatment on martensite formation, there has long been interest in use of the technique to increase the wear resistance of steels (*1-7*). Despite this interest, an examination of the literature shows that there is no universal agreement as to either the effectiveness of the method or the mechanism(s) by which cryogenic treatment enhances wear resistance. Canadian pulp and paper mills have shown interest in this use of liquid nitrogen.

The object of this study was to investigate the effects of liquid nitrogen immersion on the abrasive wear resistance of a range of steels and cast irons that are typically used in the pulp and paper industry.

The experiment

Materials

Eight different iron-based alloys were selected for this work. They included two white cast irons, five steels, and a strip steel coater blade from a fine paper machine. The cast-iron alloys (a low alloy Ni-Hard and a high chromium X-alloy) were obtained from used high-consistency chip refiner plates. They were selected because previous work had shown them to contain significant amounts of retained austenite (*8*). The six steels included one cast martensitic E-alloy stainless steel (again taken from a used refiner plate) and five wrought steels. These were AISI 1020 carbon steel, AISI 316L stainless steel sheet, a proprietary "abrasion resistant" (AR) steel designated AR 360, AISI W1-grade tool steel and a high carbon strip steel coater blade. The wrought steels were selected because they are commonly used for either making tools or for fabricating mill equipment. Additionally, the 1020 carbon steel and the 316L stainless steel are not hardenable materials, according to conventional metallurgical practice (*9*). Therefore, it was of special interest to see if their wear resistance could be improved by cryogenic treatment.

Compositions of the eight test alloys are given in **Table I.** The W1 tool steel was fully hardened and tempered to R_c65 for this study by an experienced heat treatment company. All the other alloys were tested in the as-received condition.

Wear testing

Abrasive wear is known to be the most common type of wear in many industries, including pulp and paper (*10, 11*). Therefore, it was decided to investigate the effect of cryogenic treatment on the abrasion resistance of the eight test alloys. Two different abrasion tests were used in order to study the effects of two different abrasion modes.

The first wear test used was a Dry Sand Rubber Wheel apparatus (DSRW), as specified in ASTM Standard Practice G65-85 (*12*). The apparatus is shown in **Fig. 1.** Its operation is described in detail in the standard. Briefly, a specimen is held against a revolving rubber-rimmed wheel at constant load, and dry sand flowing between the wheel and the specimen produces a low-stress scratching type of abrasion.

The second wear test used was a slurry abrasion rig (*13*), as shown in **Fig. 2.** In operation, 16 specimens are held inside a watertight chamber and exposed to a moving slurry composed of 1% sand and distilled water adjusted to a pH of 10 to minimize the effect of corrosion. Wear damage produced by this apparatus is erosive in nature.

Thompson and Brown are research engineer and assistant technical specialist, respectively, with the Pulp and Paper Research Institute of Canada, 570 St. John's Blvd., Pointe Claire, PQ H9R 3J9, Canada.

I. Chemical compositions of the test alloys

Alloy	Element, % by weight							
	C	Cr	Ni	Mn	Si	S	P	Mo
Carbon, low-alloy steels								
1020	0.18	0.03	0.02	0.76	0.01	0.012	0.010	...
AR 360[a]	0.23	0.02	0.02	1.23	0.26	0.001	0.012	...
Coater blade[b]	0.80	0.22	0.04	0.39	0.25	0.008	0.010	0.01
W1	0.99	0.43	0.09	0.34	0.19	0.009	0.013	...
Stainless steels								
316L	0.022	17.30	11.30	1.57	0.49	0.005	00.33	2.18
E[c]	1.00	18.10	1.76	0.50	0.68	0.015	0.011	0.52
Cast irons								
X[d]	2.95	28.19	0.52	0.41	0.60	0.030	0.030	0.14
Ni-Hard[d]	3.17	2.46	3.81	0.79	0.81	0.110	0.020	0.20

[a]Algoma Steel Corporation.
[b]Uddeholm Strip Steel AB.
[c]General Machinery Works Inc.
[d]Sprout-Bauer Inc.

All eight alloys were tested in the Dry Sand Rubber Wheel apparatus, and four alloys were tested in the slurry abrasion rig—the Ni-Hard, 316L, E, and W1.

Specimen preparation and measurement of abrasive wear

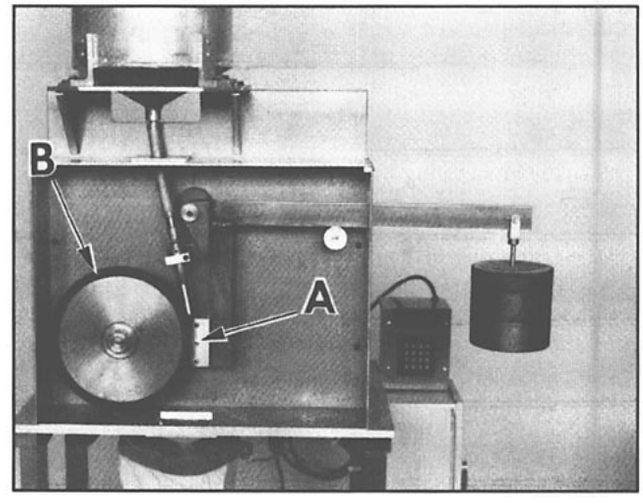
The refiner plate specimens were trepanned from used plates by electrospark machining and then turned down to final size. Specimens of the wrought steels were prepared by conventional machining; the strip steel was prepared using shears. Because of practical restraints on dimensions imposed by the different sources of materials, it was necessary to use different-sized specimens in the tests. The specimen dimensions used are given in **Table II.** The use of variously sized specimens did not affect the validity of the test data because the intent of the program was to measure abrasion resistance of individual alloys before and after cryogenic treatment. The performance of different alloys cannot be directly compared, however, unless identical specimen geometries have been used.

Specimen test surfaces were wet ground to a 240 grit finish and cleaned with ethanol before insertion into the wear tester. All specimens were demagnetized before testing. Abrasive wear losses were measured gravimetrically and converted to a volumetric basis using an average density of 7.8 g/cm^3. Weight losses were measured to ±0.1 mg. Abrasion resistance was calculated as the reciprocal of volume loss.

Cryogenic treatment

Cryogenic treatment was carried out using liquid nitrogen in a 1 L Dewar flask; specimens were completely immersed in the liquid nitrogen for a given time. Hardness was used as a primary indicator of the effect of a given cryogenic treatment. Hardness was evaluated as a function of both cooling rate and immersion time, using an Avery Hardness Tester.

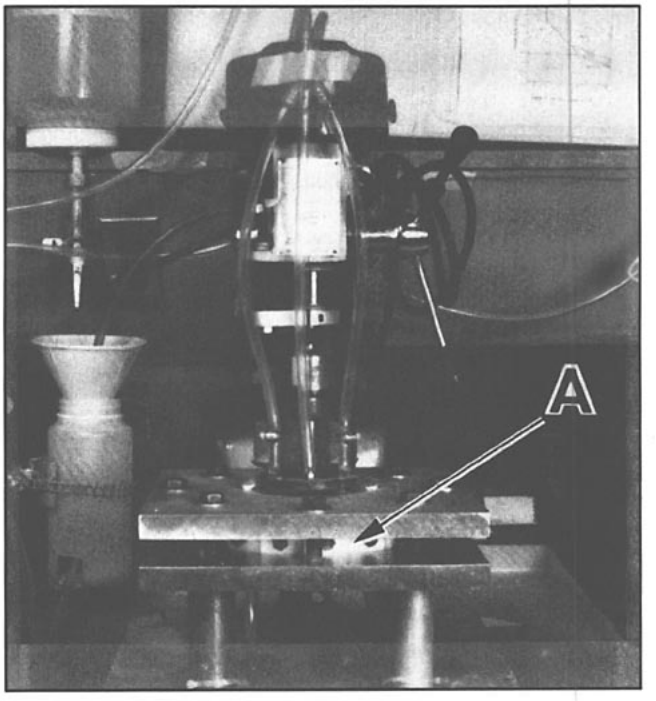
1. A Dry Sand Rubber Wheel tester. The specimen (A) is pressed against a rubber-rimmed wheel (B), and dry sand flows between them, causing abrasion.



To investigate the effect of cooling rate, two immersion methods were used: rapid, by plunging the specimen into the liquid nitrogen; and slow, by placing the specimen in an empty beaker and then slowly pushing the beaker into the liquid nitrogen until the liquid overflowed and immersed the specimen. This latter method gave a cool-down rate of about 6° K/min.

To investigate the effect of immersion time, specimens were cooled rapidly and then removed after known periods of time to remeasure their hardness. For the first 5 min after initial immersion, hardnesses were measured every

2. A slurry abrasion tester. Specimens are held within a water-tight chamber (A) through which a sand-liquid slurry is circulated.



II. Test specimen dimensions

Alloy	Specimen geometry and nominal dimensions: Plug 17 mm dia.	Rectangular 25 mm × 75 mm	Rectangular 10 mm × 22 mm
Carbon, low-alloy steels			
1020	X		
AR 360		X	
Coater blade		X	
W1		X[a]	X[b]
Stainless steels			
316L		X	
E	X		
Cast irons			
X	X		
Ni-Hard	X		

[a]Made from four individual blocks clamped together.
[b]Used for the slurry abrasion testing only.

minute. After 5 min, hardnesses were measured at longer time intervals. Total immersion time was 60 min.

Magnetic measurements

The amount of residual austenite was estimated qualitatively by measuring the force required to pull a magnet off a given specimen. The pull-off force was determined using a Magne-Gage instrument with a No. 1 magnet (*14*); test surfaces were prepared to a 600 grit finish. To avoid errors due to residual magnetization, specimens were demagnetized prior to testing.

Statistical considerations

The precision of the wear tests was monitored using reference coupons. For the Dry Sand Rubber Wheel Test, these were AISI 1020 carbon steel. AISI 316L was used in the slurry abrasion apparatus. Typically, a coefficient of variation of <7% was achieved for the DSRW test and about 7% for the slurry abrasion apparatus. Based on previous experience with these tests (*12, 13*), these values were judged acceptable.

For the DSRW test, each result reported is an average of four to six individual tests. For the slurry abrasion test, each result reported is an average of six individual test specimens. For all alloys, an unpaired t-test (*15*) at the 95% confidence level was used as a test of significance to discriminate between data obtained before and after cryogenic treatment.

Results

Effect of immersion time on hardness

The effect of immersion time on hardness was evaluated by using the Ni-Hard and X-alloy cast irons. Typical results are shown in **Fig. 3**, from which it can be seen that any significant increase in hardness occurred within the first five minutes. Additional tests with other materials showed similar behavior. These increases in hardness are due to an austenite-martensite transformation, which is temperature, rather than time, dependent (*16*).

Effect of cool-down rate on hardness

The effect of cool-down rate was also evaluated using Ni-Hard and X-alloy cast irons. Typical results are shown in **Fig. 4**. For both alloys, maximum final hardness was achieved after slow cooling, although the extra 1-2 points gain in hardness was not very large. The higher hardness indicates that more martensite was formed by slow cooling, i.e., the austenite-martensite reaction was more efficient under these conditions. The crystallographic shear deformations which occur during martensite formation (*17*) are probably more easily accommodated by the crystal lattice during slow cooling than rapid.

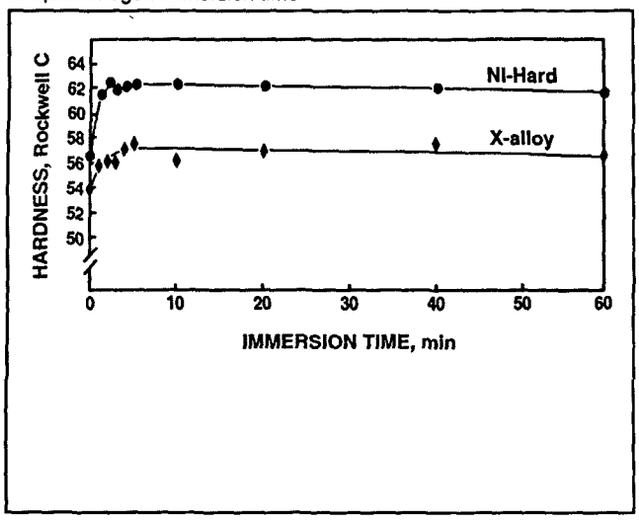
To maximize the possibility of any beneficial effects, a standardized cryogenic treatment of slow cooling plus liquid nitrogen immersion for 48 h was used for the remainder of the test program.

Effect of cryogenic treatment on hardness

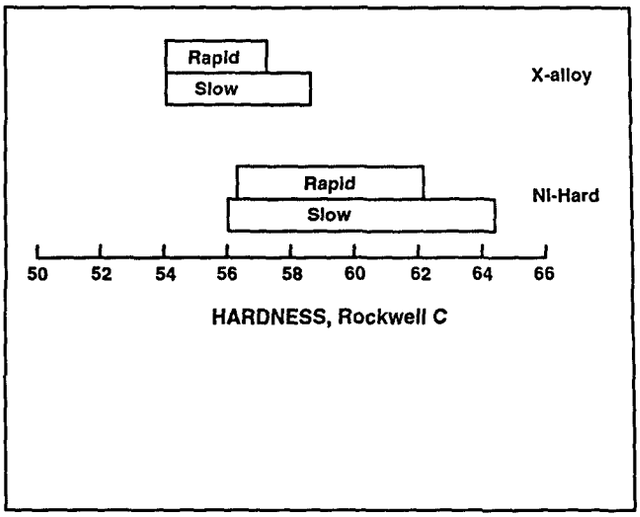
Changes in hardness due to the 48 h cryogenic treatment are shown in **Table III**, which also indicates the statistical significance of these changes. All hardnesses are reported on the Rockwell C scale unless otherwise indicated.

In all cases, cryogenic immersion either had no effect or caused an increase in hardness. The Ni-Hard and X cast irons and the AR 360 steel showed significant increases in hardness; the Ni-Hard had the greatest change of all, by about 8.5 points Rockwell C. Such changes in hardness are due to the transformation of retained austenite to martensite. This was most clearly seen in the

3. Specimen hardnesses for X and Ni-Hard cast irons as a function of liquid nitrogen immersion time



4. Hardness change for X and Ni-Hard cast irons as a function of cool-down rate



III. Effect of cryogenic immersion on hardness

Alloy	*Initial hardness*	*Final hardness*	*Statistically significant change ?*
1020	96.1[a]	95.9[a]	No
Coater blade	73.3[b]	73.9[b]	No
AR 360	37.6	39.1	Yes, increased by 4%
W1	65.0	65.0	No
316L	79.5[a]	80.4[a]	No
Ni-Hard	56.0	64.4	Yes, increased by 15%
X	54.0	58.6	Yes, increased by 8.5%
E	54.3	54.8	No

[a]Rockwell B
[b]Rockwell A

IV. Dry Sand Rubber Wheel test results

Alloy	*Initial abrasion resistance* $(mm^3)^{-1} \times 10^3$	*Final abrasion resistance* $(mm^3)^{-1} \times 10^3$	*Statistically significant change ?*
1020	4.7	5.1	No
Coater blade	25.2	25.5	No
AR 360	4.6	4.3	Yes, decreased by 6.5%
W1	11.4	12.4	Yes, increased by 9%
316L	2.5	2.5	No
Ni-Hard	36.9	34.8	No
X	51.0	47.4	No
E	10.8	10.2	Yes, decreased by 5.5%

case of the Ni-Hard, where Magne-Gage measurements showed a significant increase after cryogenic immersion due to the transformation of the nonmagnetic austenite to the magnetic martensite phase. No distinct Magne-Gage increases were found for the X and AR360 alloys, but there can be little doubt that a similar transformation had occurred with them as well. It is well known that as-cast white irons such as X often contain significant amounts of retained austenite that can be converted by additional heat treatment (*18*).

Abrasion testing

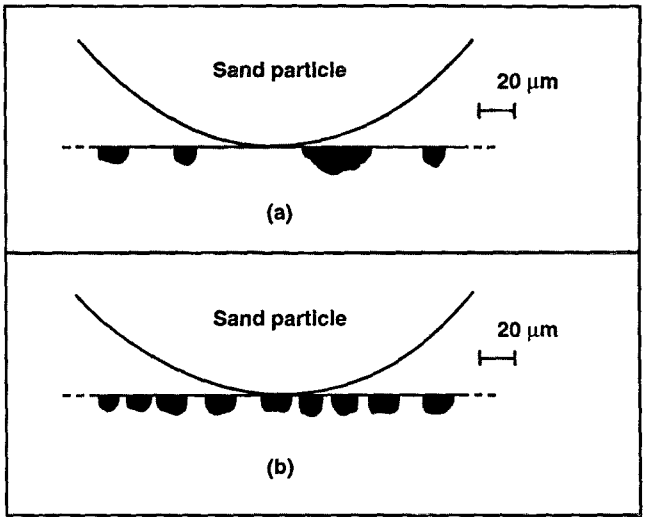
The dry sand rubber wheel test. The abrasion resistance of each alloy before and after cryogenic immersion is shown in **Table IV**, together with the statistical significance of any resultant change. Three alloys (AR360, W1 and E) did show a significant change in abrasion resistance. That of the W1 tool steel increased by about 9%. In contrast, the performance of the AR360 and E alloys decreased by about 6%. The abrasion resistance of the five other test materials was unaffected by the cryogenic treatment.

A comparison of Tables III and IV shows that there was no correlation between increased hardness and abrasion resistance. Specifically, the W1 tool steel showed improved wear resistance with no change in hardness at all. On the other hand, the Ni-Hard and X-alloy cast irons showed significant hardness increases but no change in abrasion resistance. This lack of correlation shows that there is no simple relation between alloy martensite content and abrasion resistance. For the W1 steel, which had been fully hardened by prior heat treatment, the results show that

V. Slurry abrasion test results

Alloy	*Initial abrasion resistance* $(mm^3)^{-1} \times 10^3$	*Final abrasion resistance* $(mm^3)^{-1} \times 10^3$	*Statistically significant change ?*
W1	127.1	136.2	No
316L	18.7	20.3	No
Ni-Hard	200.8	221.7	No
E	68.7	60.4	No

5. Schematic cross-sections of (a) a high steel (e.g., E, AR 360) and (b) a chromium white iron (e.g., Ni-Hard, X)



the improved wear performance was not due to any retained austenite-martensite conversion.

The slurry abrasion test. The abrasion resistance of each alloy before and after cryogenic immersion, as well as the statistical significance of any change, is shown in **Table V.** The data show that the cryogenic treatment had no significant effect on the slurry abrasion resistance of any of the materials tested. The difference in response between the dry sand test and the slurry abrasion test may be related to the different modes of abrasion occurring in the two systems. Any changes in microstructure resulting from the cryogenic immersion are less sensitive to the relatively short-impact, two-body abrasion of the slurry test than they are to the longer-duration, three-body abrasion of the dry sand test.

Discussion

A key question in this study was whether the experimental data obtained could be explained in terms of established metallurgical theory.

Examination of the present results shows, in fact, that they are reasonably consistent with these principles. Some of the data are readily explainable in terms of a retained austenite-martensite conversion. As shown in the previous section, these data include the effect of immersion time and cooling rate on hardness. The lack of any effect due to cryogenic treatment on the performance of either the 1020 carbon steel or the 316L stainless steel is also readily understandable. The carbon steel contains insufficient carbon to make it a hardenable material, and the austenitic structure of the stainless steel is stabilized by its relatively high nickel content.

Interestingly, the explanation of the effects of cryogenic treatment is less obvious for those alloys that did show some change in hardness and/or abrasion resistance. These alloys include Ni-Hard and X, which had no change in abrasion resistance despite a significant increase in hardness; AR 360 and E, which both suffered a reduction in abrasion resistance; and W1, which was the only alloy to show improved abrasion performance.

For the X cast iron, additional tests showed that cryogenic immersion was not as efficient at hardening the alloy as conventional furnace heat treating and quenching. An additional 4 points increase in hardness was obtained after cryogenic treatment by reheating the sample to 1020°C for 4.5 hours and allowing it to air cool. Furthermore, once this cast iron had been furnace hardened, its rubber wheel abrasion resistance did increase significantly (*19*). Other chromium white irons treated in this manner showed the same behavior, and it is probable that Ni-Hard would have a similar response. The inefficiency of the liquid nitrogen treatment may be related to the shear deformations that occur during the formation of martensite. These would be easier to accommodate within the crystal lattice during a high-temperature quench than at cryogenic temperatures. In any case, it is apparent that to get any worthwhile increase in wear performance from these already abrasion-resistant materials, it is necessary that they be fully hardened. The present results show that cryogenic treatment is incapable of doing this.

The behavior of the E and AR 360 steels is especially interesting, as it illustrates the complex relationship that can exist among hardness, microstructure, and wear resistance. As seen in the results section, increased hardness can be related to increases in alloy martensite content. Because of the work-hardening characteristics of austenite, however, abrasion resistance does not necessarily also increase with increasing martensite content (*20*). Small concentrations of residual austenite (e.g., <20% vol) can be beneficial because the austenite can both work harden and form deformation martensite, thus helping absorb the energy of the abrasion process. When the austenite has been replaced in the microstructure by martensite, this absorption capacity is reduced, and wear resistance decreases. Such a mechanism has been discussed by Zum-Gahr in the case of tool steels (*21*) and most probably accounts for the behavior of the E and AR 360 steels in the present study. Unfortunately, it can be difficult to predict how alloys similar to E and AR 360 will behave when cryogenically treated. The determination of residual austenite volume fraction by X-ray

diffraction is time-consuming and is particularly difficult for high-carbon steels such as E, due to interference by the carbide phase (*22*).

An intriguing question is why the presence of residual austenite was beneficial in the case of the E and AR 360 steels but not for Ni-Hard and X cast irons, where fully hardened structures gave the best wear performance. The answer appears to be related to the relative scale of the microstructures involved. **Figure 5** shows representational cross-sections of both a hard steel (e.g., E, AR 360) and a chromium white iron (e.g., Ni-Hard, X). It can be seen that, because the steel has relatively few, widely spaced carbides, an abrasive particle would have easy access to the matrix. The residual austenite content of the matrix is thus important, as it can harden under the influence of the sand. In contrast, the white iron has many closely spaced carbides. As the carbides are much harder than the sand, the abrasive cannot easily penetrate through to the matrix. Hence the effect of any retained austenite is less important than in the case of the steel. The abrasion resistance of the iron increases when fully hardened because the martensite is hard and strong and thus able to give maximum support to its protective carbide network.

The W1 tool steel was the only alloy whose abrasion resistance increased as a result of cryogenic treatment. It is also the only alloy where the effect cannot be explained in terms of the austenite-martensite conversion because, as shown by the absence of any change in hardness after liquid nitrogen immersion, its prior heat treatment had removed all traces of residual austenite. Popandopulo and Zhukova have proposed an alternative mechanism for the cryogenic decomposition of martensite (*23*) that may explain the result obtained for the W1 steel. Also working with tool steels, they used dilatometry to show that martensite decomposition can occur when an alloy is reheated through the temperature range -90°C to + 20°C, causing microdistortion, increased vacancy and dislocation densities, and, possibly, precipitation of coherent (i.e., submicroscopic) carbides. In effect, these reactions would serve to locally strengthen the martensite, and it is reasonable to expect that such a strengthening could increase a steel's abrasion resistance (*24*).

Is this mechanism relevant to the W1 tool steel? There are some indications that it is. First, the W1 is a related type of alloy to those used by Popandopulo. Second, they found that martensite decomposition in the absence of any austenite occurred if the steel had been previously tempered in the range 100°C to 300°C. The W1 steel was tempered at 150°C. Finally, formation of submicroscopic carbides might be expected to increase local matrix hardness. Microhardness measurements of the W1 matrix before and after cryogenic treatment did show a small hardness increase (888 Knoop before, 909 Knoop after). While this evidence is not conclusive, it does give some grounds for attributing the increased abrasion resistance to a martensite decomposition reaction. Any additional proof would require further research.

Implications for mill engineers

Cryogenic treatment is an effective, proven technique used in the heat treatment of ferrous alloys. Its principal use is to convert retained austenite to martensite, thus ensuring microstructural stability in highly stressed components. Cryogenic treatment is also an accepted way to increase the depth of hardening in some low-alloy tool steels, such as W1.

This study has shown that cryogenic immersion had very limited success as a method of increasing the abrasion resistance of steels and cast irons. On this basis, the method cannot be recommended. If for some reason, however, one decides to try the technique, two points are worth emphasizing. First, in some cases a cryogenic treatment can actually cause a reduction in wear resistance. Since such an effect is difficult to predict, the only certain way to be sure is to test.

Second, it is necessary to guard against possible embrittlement. Any use of cryogenics to form additional martensite may require subsequent tempering, especially where significant amounts of retained austenite are being converted.

Conclusions

1. On the basis of this study, cryogenic treatment has only very limited success in increasing the abrasion resistance of ferrous materials. Of the eight alloys tested, only the W1 tool steel showed a significant increase in dry abrasive wear resistance. No improvement was found for any of the alloys when tested under wet abrasive conditions.
2. The abrasion resistance of two steels decreased as a result of cryogenic treatment. Steels appear more susceptible to such a reduction in performance compared to cast irons, because of the smaller volume fraction of carbides in their microstructure. Unless the retained austenite content is known, it is difficult to predict which steels might suffer as a result of cryogenic treatment.
3. The hardnesses of three alloys increased as a result of cryogenic treatment. All changes in hardness occurred within five minutes of immersion. Final hardness was influenced by specimen cool-down rate.
4. There was no correlation between hardness increase and abrasion resistance. The one alloy showing improved resistance because of the treatment had no change in hardness.□

Literature cited

1. Budinski, K. G., Wear Control Handbook (M. B. Peterson and W. O. Winer, Eds.), American Society of Mechanical Engineers, New York, 1980, p. 948.
2. Keen, A. R., Met. Australas., 14(7): 12(Aug. 21, 1982).
3. Metals Handbook, 9th edn., Vol. 4, Heat Treating, American Society for Metals, Materials Park, OH, 1981, p. 117.
4. Tseitlin, L. B., Kolesnichenko, V. D., Karnaushenko, T. V., Umanets, V. V., et al., Met. Sci. Heat Treat. 22(9-10): 706(Sept.-Oct. 1980).
5. Smol'nikov, E. A., and Kossovich, G. A., Met. Sci. Heat Treat. 22(9-10): 704(Sept.-Oct. 1980).
6. Zhmud', E. S., Met. Sci. Heat Treat. 22(9-10): 701(Sept.-Oct. 1980).
7. Barron, R. F., and Mulhern, C. R., Advances in Cryogenic Engineering: Materials, Vol. 26 (A. F. Clark and R. P. Reed, Eds.), Plenum Press, New York, 1980, p. 171.
8. Thompson, C. B., and Garner, A., 1985 Engineering

Conference Proceedings, Book 1, TAPPI PRESS, Atlanta, 1985, p. 223.
9. Budinski, K. G., Wear Control Handbook (M. B. Peterson and W. O. Winer, Eds.), American Society of Mechanical Engineers, New York, 1980, p. 934.
10. Moore, M. A., Fundamentals of Friction and Wear Processes, American Society for Metals, Materials Park, OH, 1980, p. 74.
11. Thompson, C. B., Garner, B. C., and Garner, A., Fifth International Symposium on Corrosion in the Pulp and Paper Industry, Canadian Pulp and Paper Association, Montreal, 1986, p. 261.
12. ASTM Standard Practice G65-85, Annual Book of ASTM Standards, Section 3, Volume 03.02, ASTM, Philadelphia, 1988.
13. Thompson, C. B., and Garner, A., Tappi J. 70(6): 95(1988).
14. Maratray, F., and Poulalion, A., Report M-399E, Climax Molybdenum Co., Ann Arbor, MI, 1984, p. A-6.
15. Statistical Methods Manual, Tech. Sec., Canadian Pulp and Paper Association, Montreal, 1969, p. 17.
16. Hume-Rothery, W., The Structure of Alloys of Iron, Pergamon Press, Oxford, 1966, p. 226.
17. Hume-Rothery, W., The Structure of Alloys of Iron, Pergamon Press, Oxford, 1966, p. 228.
18. Maratray, F., Trans. Amer. Foundryman Soc. 79: 121(1971).
19. Thompson, C. B., Pulp and Paper Report 731, Paprican, March 1989, p. 9.
20. Zum Gahr, K. H., Microstructure and Wear of Materials, Tribology Series, Vol. 10, Elsevier, Amsterdam, 1987, p. 275.
21. Zum Gahr, K. H., Microstructure and Wear of Materials, Tribology Series, vol. 10, Elsevier, Amsterdam, 1987, p. 271.
22. Cousineau, E. J., Metals Technology Laboratories, Energy, Mines and Resources Canada, private communication.
23. Popandopulo, A. N., and Zhukova, L. T., Met. Sci. Heat Treat. 22(9-10): 708(Sept.-Oct. 1980).
24. Zum Gahr, K. H., Microstructure and Wear of Materials, Tribology Series, vol. 10, Elsevier, Amsterdam, 1987, p. 187.

Received for review July 2, 1991.

Accepted Sept. 19, 1991.

Presented at the TAPPI 1991 Engineering Conference.

Keywords: Abrasion resistance, alloys, cast iron, cryogenics, hardness, liquified gas, nitrogen, steel, submersion, test methods, wear tests.