RESEARCH ARTICLE

IMPROVED REPRODUCIBILITY OF D2 TOOL STEEL AFTER CRYO-TREATING AT -78°C (DRY ICE)

G.K. Egert, T. D. Burleigh

Materials & Metallurgical Engineering Department, New Mexico Institute of Mining and Technology, Socorro, NM 87801.
Corresponding Author Email: Thomas.Burleigh@nmt.edu

ARTICLE DETAILS

ABSTRACT

The exposure of steel to very cold temperatures (cryogenics) as a means to improve properties of the metal has had a controversial history. This study employed several tests to determine differences between D2 tool steel cryo-treated in dry ice (-78°C) versus in liquid nitrogen (-196°C), as compared to control D2 steel (not cryo-treated). These tests showed no major changes between the control and the liquid nitrogen treated steel, but the dry ice (-78°C) treated steel showed narrower XRD peaks, more reproducible hardness measurements, less scatter in the corrosion weight loss, and lower corrosion currents in the cyclic polarization tests in saltwater. All these differences were measured even though there was no measurable difference in retained austenite. The authors hypothesize that the -78°C (dry ice) allowed internal stress reductions, while the -196°C (liquid nitrogen) was too cold to allow any transformations.

KEYWORDS

Temperatures, D2, measurements, polarization, transformations.

1. INTRODUCTION

Cryogenic treatment has a controversial history in the engineering community. Some reports claim sweeping improvements to material properties, while others claim insignificant changes, and even a loss of properties such as impact resistance (Baldissera and Delprete, 2008). However, the process has been in regular use since shortly before World War II, with anecdotal evidence citing Swiss watch-makers as pioneers in using shallow cryogenic treatment to obtain parts which could be more accurately honed and more easily machined (History of Cryogenic Processing, 2012).

"Cryogenics" is the study of how materials behave at very low temperatures, while "cryogenic treatment" concerns imparting lasting changes to the material as a result of a low temperature exposure. For this paper, there are two sub-categories of cryogenic treatment, deep versus shallow. In both methods, a gradual cooling and warming process is required to prevent thermal shock and cracking (History of Cryogenic Processing, 2012). In shallow cryogenic treatment, the material is cooled to -78°C (195K), the temperature of dry ice, before being returned to room temperature. In deep cryogenic treatment, the material is cooled to a liquid-nitrogen temperature of -196°C (77K), and then warmed.

This process of cooling a material to its optimal cryogenic temperature can cause several unique effects (Zurecki, 2012):

1. Retained austenite transforms into martensite.
2. Precipitation of eta carbides (reported to increase wear resistance).
3. Residual stresses in the metal are relieved.

The precipitation of eta carbides has been reported during the tempering processes, and Meng also reported eta carbides forming during the cryogenic processing (Hirotsu and Nagakura, 1972; Barron, 1966; Meng et al., 1994). Meng theorized that the expansion and the contraction of the crystal structure resulted in the carbides having space to diffuse and agglomerate (Barron, 1966; Meng et al., 1994). Meng stated, "...cryogenic treatment makes a contribution to wear resistance due to fine eta-carbide precipitation rather than the removal of retained austenite."

An important metallurgical property of steel is hardness, or a material's resistance to deformation. This value can be related to properties such as strain hardening, strength and ductility, and is used to examine the effects of cryogenic treatment. However, hardness testing has extremely varied results, as reported in Baldiserra and Delprete's review of cryogenic treatment (Baldissera and Delprete, 2008). Researchers have reported changes in hardness from an insignificant 0.5% reduction to a 19% increase in Vickers hardness (Baldissera and Delprete, 2008).

The corrosion resistance of cryo-treated steels has shown very limited and contradictory results. Barron reported in 1989 that the corrosion rate of an array of high-carbon (316, 410, 4142, S2, and M1) steel samples was reduced by a factor of 1.10 to 1.786 (Carlson, 1991; Barron and Thompson, 1990). Barron used a hydrogen sulfide gas with water vapor to corrode the steel for 30 days, and then measured the weight loss.

Baldissera and Delprete stated that, "no difference was detected on the corrosion resistance of the cryo-treated material..." (Baldissera and Delprete, 2010). Their paper examined the effect of corrosion on the fatigue life of AISI 302 stainless steel samples. The corrosion test used was ASTM standard, B-117, a salt-spray test, rather than submersion.

Other papers and documents state that corrosion resistance is increased by cryogenic treatment (Calvey, 2010). Sendooran claimed that the cryogenic treatment improved the corrosion resistance by, "...minimization of galvanic couples in the material" (Sendooran and Raja, 2011). These studies illustrate the widely varying conclusions as to

whether corrosion resistance is or is not improved by cryogenic treatment.

2. EXPERIMENTAL PROCEDURE

This current research was undertaken to determine the results of cryogenically treating D2 tool steel either in liquid nitrogen or in dry ice, and the effects of these treatments had on the hardness, the XRD spectra, and the corrosion resistance. The D2 tool steel forms austenite during heat treatment and martensite upon air-cooling. The steel alloy D2 was chosen for this research because its high carbon content should amplify any carbide precipitation and martensite transformations. The measured composition of the D2 steel is given in Table 1. While several authors have studied tool steels [2], only few researchers have studied D2, and none have studied its corrosion resistance (History of Cryogenic Processing, 2012; Collins and Dormer, 1997; Das et al., 2008; Das et al., 2009a; Das et al., 2009b; Das et al., 2009c; Das et al., 2006; Surberg et al., 2008; Das et al., 2009d; Wierszyllowski, 2006).

The heat treatment process for the samples is shown in Figure 1. Tests were conducted on 6 mm thick disk samples that were cut from the same 25 mm diameter D2 steel rod. The samples were wrapped in stainless steel foil (to prevent decarburization), then preheated at 824°C for fifteen minutes, solution heat treated (solutionized) at 990°C for fifteen minutes, and then air-cooled. Samples were not tempered afterward to ensure that only the effect of the cryogenic treatment was examined. The samples were randomly divided into three groups—(a) control, (b) shallow dry ice samples, and (c) deep liquid nitrogen samples. The shallow cryogenic samples were embedded in dry ice for 12 hours, and the deep cryogenic samples were immersed in a dewar flask of liquid nitrogen for 12 hours. In order to isolate only the effect of the cryo-treatment, there was no tempering given to the D2 steel after the cryo-treatment.

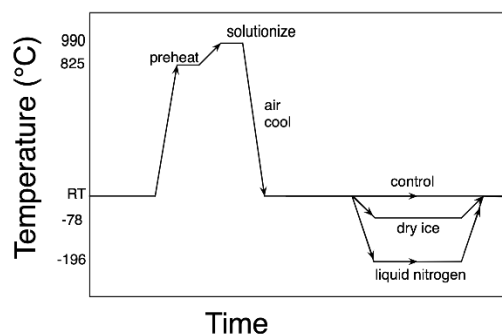| Table 1: Weight percent composition of the D2 tool steel.									
	C	Cr	Co	Mn	Mo	P	Si	S	V	Fe
D2	1.56	11.35	0.01	0.25	0.74	0.02	0.28	0.009	0.77	85.011

Figure 1: The heat treatment process used for the D2 steel samples. Samples were held at the preheat and solutionizing temperatures for 15 minutes each, then cooled down to the cryogenic temperature and held for 12 hours. There was no tempering afterwards.

2.1 Hardness Testing

The samples were sanded and polished from 60 grit SiC, using gradual steps to reach 1200 grit SiC, and the hardness was measured using a Buehler Macromet II Rockwell Hardness C tester. The three disk samples for each condition were tested twice on the top surface and twice on the bottom surface, giving twelve hardness data points per condition. There was no significant difference found in the hardness between the top and the bottom surfaces.

2.2 X-Ray Diffraction

The X-Ray Diffraction was performed using the PANalytical X'Pert[3] Powder X-Ray Diffractometer with a copper X-ray source. The polished D2 steel disks were scanned over a two theta angle from 40° to 46° at a rate of 0.008 degrees per second according to ASTM E-975 (ASTM Standard E975, 2003).

2.3 Metallography

The microstructure was revealed on each sample by polishing then etching the samples in Vilella's reagent (100 mL of ethanol, 5 mL of hydrochloric acid, and 1 gram of picric acid) for 10-15 seconds. Images were taken with the Olympus GX41 inverted microscope.

2.4 Cyclic Voltammetry

Cyclic Voltammetry and Open Circuit Potential (OCP) measurements were made using a PARSTAT 2263 potentiostat running PowerSuite software. The electrolyte was acidified saltwater (10 drops of HCl per liter of 3.5% NaCl with pH = 2.5), and bubbled with nitrogen gas to deaerate the solution. The samples were deaerated for one hour while the open-circuit potential (OCP) was measured, then a cyclic voltammetry test was run for ten cycles from -1000 mV to -400 mV vs. SCE. The exposed surface area was 3.14 cm².

2.5 Weight Loss

A weight loss test was used to compare the corrosion rates of the different samples. The D2 disks were 25 mm in diameter, and 6 mm thick. Each disk was polished, weighed, and placed on edge in a 1L container containing an acidified, oxygenated, saltwater solution. This electrolyte was commercial 3% H_2O_2 plus 35g NaCl, and 10 drops hydrochloric acid to make 1L. The corrosion cell was covered, and allowed to corrode for one week. At the end of seven days, the corroded samples were removed, rinsed, and the corrosion product was dissolved by coating with Naval Jelly for 10 minutes and rinsing with water and acetone prior to re-weighing.

3. RESULTS AND DISCUSSION

3.1 Hardness Testing

The hardness results are shown in Figure 2. The average values of the hardness of the control, dry ice, and liquid nitrogen treated were 60.3, 60.7, and 60.2 respectively. The average hardness showed a slight increase with the shallow cryo-treatment, and a decrease in the scatter in the data. The standard deviation decreased by over 40% between the control and dry ice samples, as shown in Figure 2. A statistic T-Test between the shallow and the deep cryo-treat hardness data gave a value of p=0.0495 (on the cusp of significant difference). The shallow (dry ice) treatment made the steel slightly harder and more homogenous than the control or the deep (liquid nitrogen) treatment.
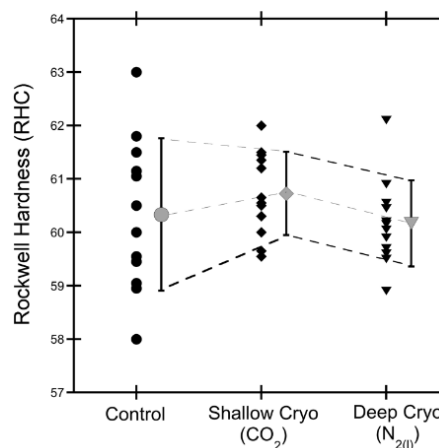

Figure 2: The Rockwell C hardness of the samples. The dry ice samples showed an increase in hardness and a decrease in the standard deviation.

3.2 X-Ray Diffraction

Diffraction measurements were made on both sides of the samples but found no differences between the top and the bottom, nor across the samples. A typical XRD data is shown in Figure 3. There were no eta-carbide peaks found. There were no significant differences in the relative magnitudes of the martensite peak at 44.7° and the austenite peak at 43.0°. Therefore, we conclude that there was no reduction in the amount of retained austenite. The only significant difference in the XRD data was the full width measurement of the austenite peak at half maximum (FWHM), and these measurements are shown in Figure 4. The FWHM dimension is a measure of the fine grain size and/or the residual stresses in a material. Since the grains are not fine, then the decrease in the FWHM is evidence of a decrease in the residual internal stresses. The average FWHM and standard deviation is smallest for the dry ice sample, and largest for liquid nitrogen samples (p=0.015). In summary, there were no carbide XRD peaks seen, and the ratio of the austenite to martensite XRD peaks were unchanged. The only difference observed was that the austenite peaks were narrower after the dry ice exposure, indicating lower residual stresses in the metal and more homogeneity.
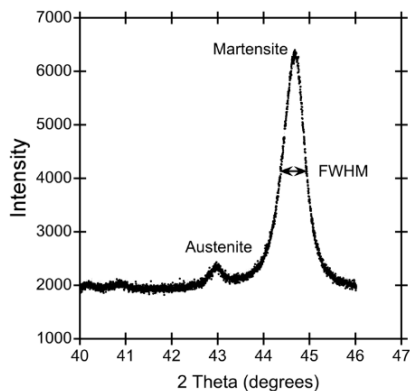
Figure 3: Typical XRD spectra for the D2 steel with illustration of Full Width at Half Maximum (FWHM).
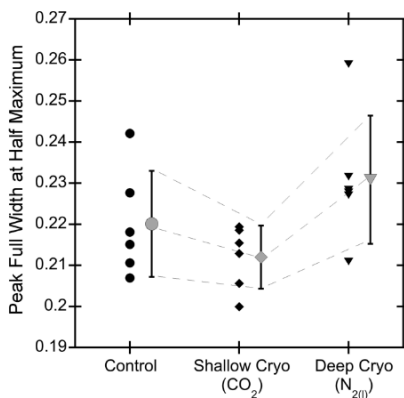

Figure 4: The changes in the FWHM of the secondary (austenite) peak. The austenite phase shows less residual stress in the dry ice treatment, but more for the liquid nitrogen treatment.

3.3 Metallography

Metallography was employed to see differences in the microstructures of the samples, with and without cryo-treatment. Figure 5 shows the retained austenite as the light phase, and the martensite as the dark phase. There were no significant differences in the images between the control, dry ice, and liquid nitrogen samples.
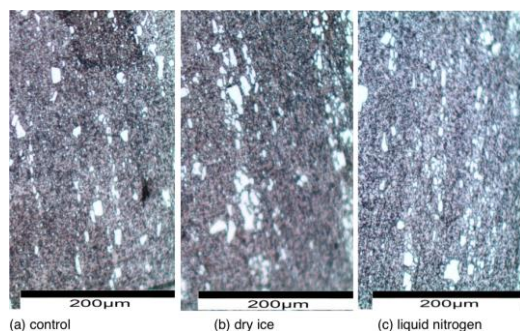

Figure 5: The polished and etched samples are similar, and show retained austenite in white.

3.4 Cyclic Voltammetry

Cyclic voltammetry tests were performed to determine if a significant difference could be seen in the corrosion resistance of the samples. In these tests, each sample was cycled for ten cycles to determine the effect of cycling on the corrosion rate, and a typical single cycle is shown in Figure 6. The maximum current at -400 mV vs. SCE was measured for each cycle, and is plotted in Figure 7. The control and liquid nitrogen samples showed similar results, but the dry ice samples were significantly different (p=0.008 from the control), and the corrosion rate was reduced by an average of 13% per cycle. This reduction in corrosion rate is hypothesized to be due to the reduction in residual stresses (leading to reduced stored energy), which translates into less energy to initiate pitting corrosion. In contrast, in the deep liquid nitrogen cryo-treat samples had similar corrosion rate as the control (no cryo-treat) samples.
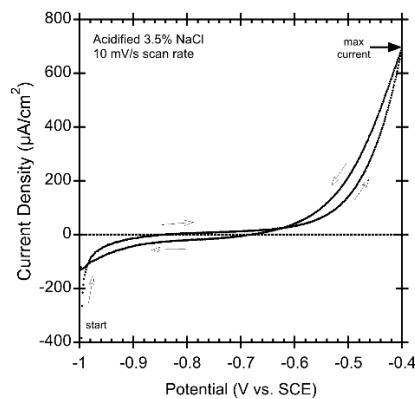

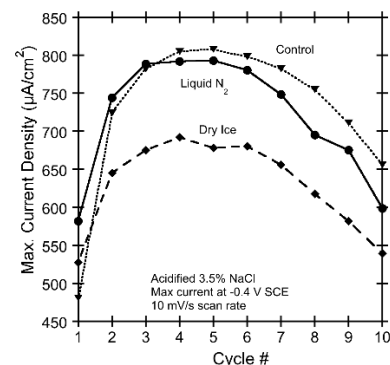**Figure 6:** Typical cyclic voltammetry of the D2 steel in the acidified, deaerated saltwater.

Figure 7: The maximum current density at -400 mV for each of the ten cycles. There is a significant lower current density for the dry ice treated samples.

3.5 Weight Loss

A weight loss test was conducted in an aggressive acidified, oxygenated, saltwater solution of 3% H_2O_2, 3.5% NaCl, and 10 drops of HCl (pH=2.5) per liter with an immersion time of one week. The results of two separate tests, each with triplicate samples, is shown in Figure 8. The difference between the two sets of tests corrosion rates was likely due to the different strength (concentration) of the H_2O_2 solutions, with the Test 2 being a slightly newer solution (higher concentration of H_2O_2). In both of these tests, the dry ice samples show a slight decrease in scatter (greater homogeneity) compared to the control or the liquid nitrogen samples.
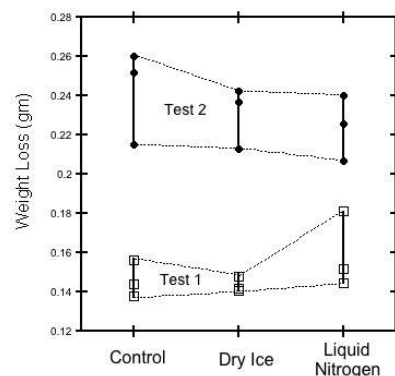

Figure 8: Weight Loss Results. The average values vary only slightly, but the standard deviation decreases for the dry ice samples.

The above results show that the shallow cryo-treat (dry ice) reduced the experimental scatter in all of the tests for the D2 tool steel. It is proposed that cryo-treating the tool steel in dry ice reduced of residual stresses in the steel, which in turn reduced the experimental scatter. In contrast, direct immersion in liquid nitrogen (deep cryo-treat) increased the experimental scatter, and was detrimental to the properties due to stresses caused by thermal shock. This is similar to research being done on other steels (Senthilkumar et al., 2011; Bensely et al., 2008). This study did not vary the rate of cooling, which in addition to the final temperature, can also be an important factor, as proposed by others (Dhokey et al., 2012; Oppenkowski et al., 2010). The effect of tempering was also not studied herein.

4. CONCLUSION

The cryogenic treatment of the D2 steel did not cause large changes in the average measured properties, but there were significant reductions in the standard deviation for the majority of the tests for the D2 samples embedded in dry ice. There was no measurable change in the amount of retained austenite, nor did the XRD show any additional peaks due to carbide formation. However, the Rockwell C hardness, the XRD full width at half maximum, the maximum current density in acidified saltwater, and the weight loss in acidified, oxygenated saltwater, all showed significant reductions in the experimental scatter for the dry ice sample indicative of greater homogeneity and lower residual stresses.

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