Cryogenic Quenching of Steel Revisited

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Abstract

Subject to a continuing debate, cryogenic treatments of alloy steels have been claimed to significantly increase wear resistance and toughness through the interplay of three effects: completing martensitic transformation, promoting uniform precipitation of fine carbides and imparting residual stresses. This study reexamines effects of various heat-treatment schedules including liquid nitrogen (-196^{o}C) and liquid helium (-269^{o}C) quenching on microstructure and selected properties of A2-grade tool steel. Examination methods include SEM, EDS, microhardness, Charpy impact and wear resistance measured using the standard pin-on-disk as well as a diamond stylus micro-scratching technique adopted from the field of thin-film technologies. Results confirm the cryo-treatment enhanced precipitation in the subsequent tempering step of what turns out to be 100-250 nm alloy-depleted carbides, and moderate improvements in wear resistance and hardness, both scaling with the cryogenic treatment time and at the cost of reduced impact resistance. Reported results and correlations provide a basis for optimizing cryo-quench heat-treatment cycle of tool steels and indicate directions for future work.

Introduction

Cryogenic quenching treatments have been accepted and adopted in commercial practice as an effective method for completing martensitic transformation in alloyed and case-hardened steels as illustrated in [1]. Noted for improving wear resistance, the cryogenic treatments, usually involving cooling within the temperature range of from -120^{o}C to -195^{o}C, replace popular dry ice and mechanical refrigeration treatments applied before a single or multiple tempering steps. However, reported wear resistance improvements vary between a few and a few hundred percent, and conflicting results are presented for the change in impact resistance of treated steels [2]. The inconsistencies in reported data may be, at least partly, explained by a new effect of cryogenic aging observed to take place in the background of retained austenite transformation. Meng observed precipitation of fine □-carbides instead of the usual □-carbides following -180^{o}C cryogenic treatments and noted improvements in both wear resistance and toughness [3]. Lal concluded that cryogenic treatments are most effective if applied soon after quenching, and that the length of cryogenic soaking is more important than the temperature of cryogenic medium [4]. Huang identified highly dispersed, nanosized Fe_2C □-carbides in HSS cutting tools treated and, in contrast to the earlier work, found a linear proportionality between the cryogenic quenching temperature and wear rates [5]. However, a cryogenic treatment study on M2 tool steel, which involved a week-long soaking, found only carbon clustering effect that resulted in increasing carbide density in the subsequent heat treatment [6]. Clustering of interstitial carbon at cryogenic temperature, as opposed to a more complete aging process at room temperature was confirmed by Barbe studying metastable austenite in low-alloyed TRIP steels [7]. Presented scatter in the published results on cryogenic treatments indicates that still more experimental data is needed in order to assist engineers in optimizing conditions for the industrial practice. The objective of this work is to reexamine various heat-treatment schedules involving cryogenic quenching step using an air-hardenable AISI/UNS A2 tool steel, the grade reported to be the best responder to the cryogenic treatment from the wear resistance standpoint [8].

Experimental

Two types of A2 steel samples (nominally 1.0%C – 5.0%Cr – 1.0%Mn –1.0%Mo -- 0.15-0.50%V) were machined: 10 mm dia. x 4 mm thick disks and simple, unnotched Charpy fracture bars (per ASTM E23). Test matrix, figure 1, comprised seven different heat treatment conditions, and there were five sets of A2 samples of each type treated within each condition in order to produce statistically valid averages. The same austenitizing and oil quenching procedure was used in all seven conditions as detailed in figure 1. Cryogenic quenching and holding was realized in liquid nitrogen bath, LIN, (-196^{o}C) for conditions N1-N5 and N7. The procedure involved plunging of room-temperature samples into the liquid which, due to the small size and simple geometry of samples, was expected to produce insignificant stress gradients and eliminate the skin stress issue form this study. Condition N5 included an additional step of quenching in liquid helium, LHe, (-269^{o}C), where cryo-cold samples N5 were transferred inside a specially designed, 2-chamber vessel, directly from LIN to LHe bath, without an intermediate warming. This LHe experiment was included in the matrix to check potential effects of cryogenic temperature, following reported softening and twinning of austenitic phases at the temperatures below the normal boiling point of LIN [9]. The LIN quenching/holding operation used in condition N7 was combined with the simultaneous exposure of metal samples to an alternating magnetic field (615 Gauss, 60 Hz AC, 0.5 kW power dissipation), produced by a commercial demagnetizing unit. This experiment was included in the matrix to explore potential, combined effects of alternating

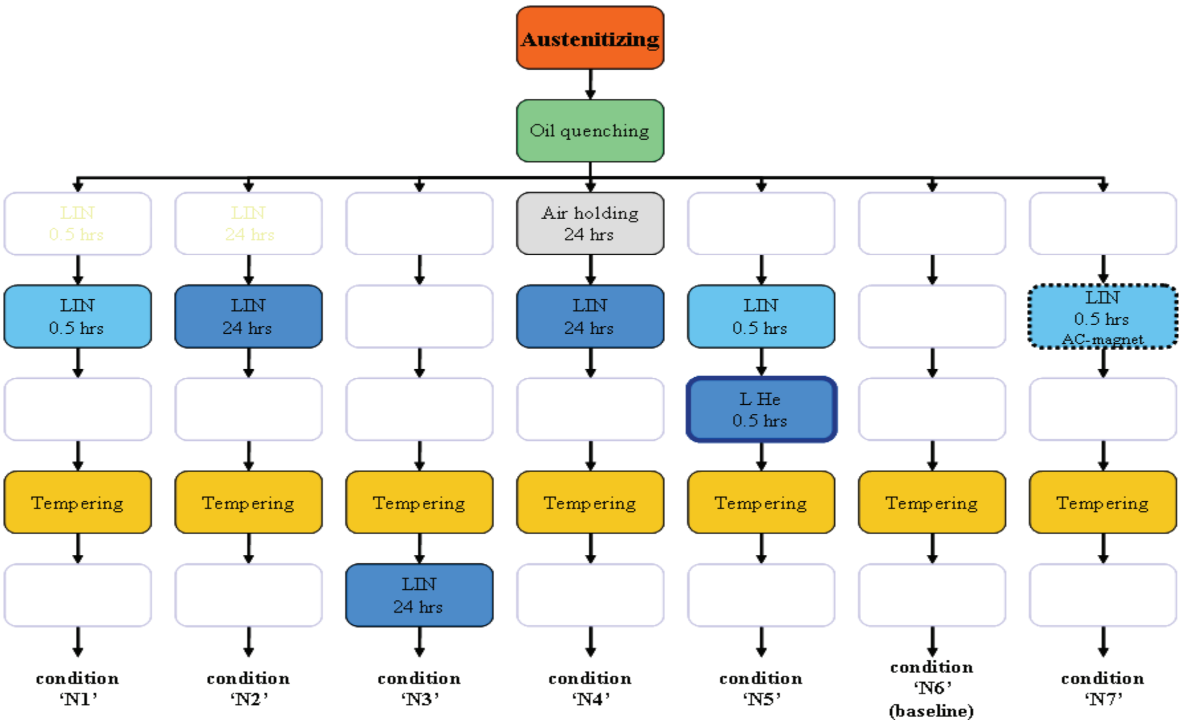

Figure 1: Heat treating test matrix: in all cases, the austenitizing was carried out at 980^{o}C for 0.5 hrs in dry nitrogen gas atmosphere, cryogenic quenching involved direct dipping of samples in liquid nitrogen bath, and tempering was run at 250^{o}C for 2 hrs in dry nitrogen atmosphere and completed with water quench.

magnetic field and cryogenic cooling, following reported enhancement of the martensitic transformation by magnetic/magnetostrictive stressing [10]. Condition N6 was the baseline or the only condition within the entire test matrix that did not involve cryogenic treatment steps. Results of outlined treatments were evaluated using two methods of wear testing, micro- and superficial hardness measurements, Charpy impact resistance, scanning electron microscopy, SEM, and elemental analysis of carbides, EDS.

Results and Discussion

Figure 2 shows raw data and optical images (x 500) of wear grooves acquired during micro-scratch test in which a 20 μm diamond stylus scratches steel surface over a distance of 4.2 mm under a linearly increasing load. This test method was adopted from the field of thin-film technologies. The discontinuities in the depth of wear grooves observed are believed to indicate clusters of carbides in material matrix. It may be easily observed that the wear profile of the sample in baseline condition N6 is the largest in the series, and the wear profile of the sample N2 (held for 24 hours in LIN bath after oil quenching and before tempering) is the most shallow and discontinuous, indicating a large number of wear-resistant carbides in the latter. Figure 3 details the second wear test method used, pin-on-disk, where a 58HRC, fixed 440C steel ball was used as the pin, and all samples, approximately as hard as the ball were used as the spinning disk. Like before, the baseline samples in N6 condition were wearing the most, as evidenced by the wear track revealing an intense material transfer and the largest size (diameter) of wear cap produced on the 440C ball during the test. Figure 4 shows the averages for both wear test methods described above. The results of the micro-scratch tests are represented as the area integrated under the wear depth profile along the distance of the scratch line, and the pin-on-disk results are the diameters of the wear cap, a fairly useful wear rate indicator for the tribological couples in sliding contact, illustrated also in [11]. The highest wear rates are noted for the baseline N6 and the condition N3, where a 24 hr LIN quench was used after tempering, while the best wear resistance characterizes all treatment conditions where the cryogenic quenching was used right after the oil quenching. Interestingly, a fairly close correlation is found between the diamond scratching resistance and the steel sliding wear resistance; the smaller wear caps indicate reduced interfacial sticking, i.e. more of fine, hard precipitates in the A2 matrix. Not surprisingly, the hardness of all cryo-treated samples is higher, and the fracture toughness lower than for the baseline condition, N6, figure 5. Hardening of material on a micro- and macroscale typically reduces ductility but improves wear resistance. The loss of impact resistance with cryo-treatments, as observed here, contradicts conclusions reached by Meng [3] and the others.

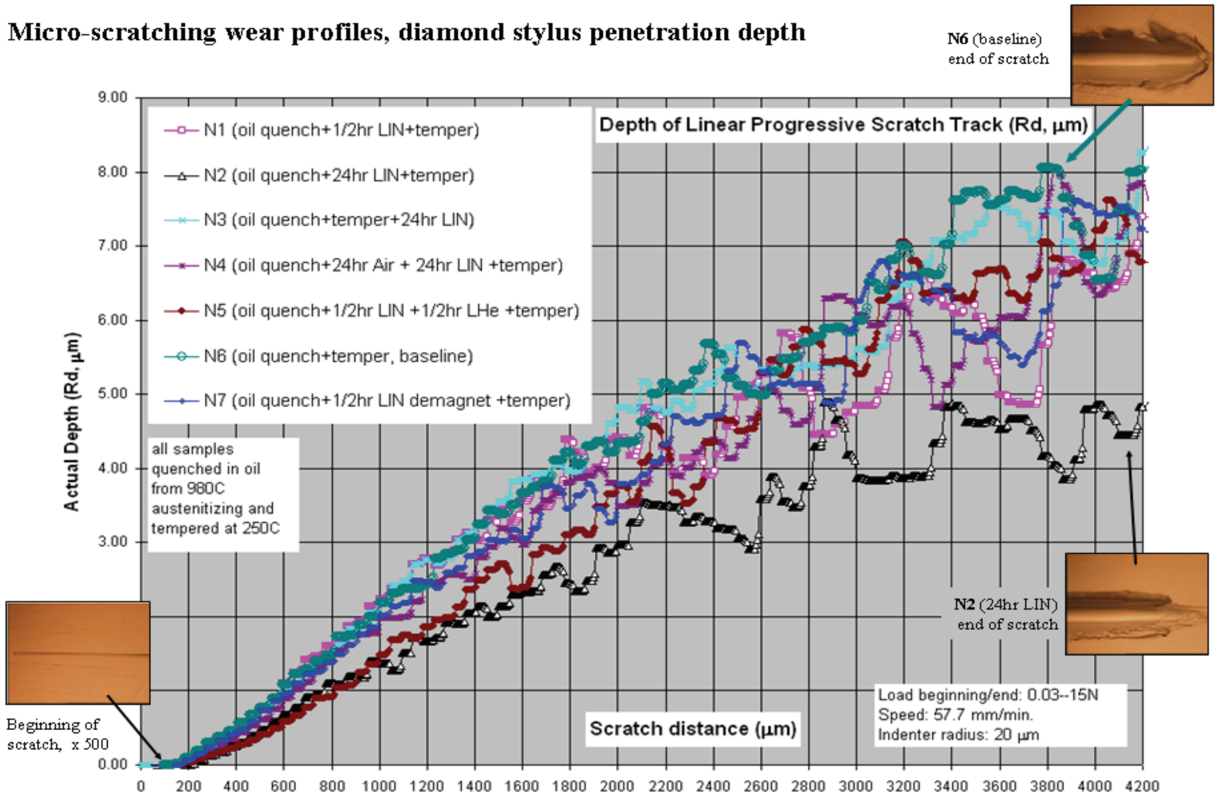

Figure 2: Wear profiles and scratch groove images recorded during micro-scratching test on specimens N1-N7.

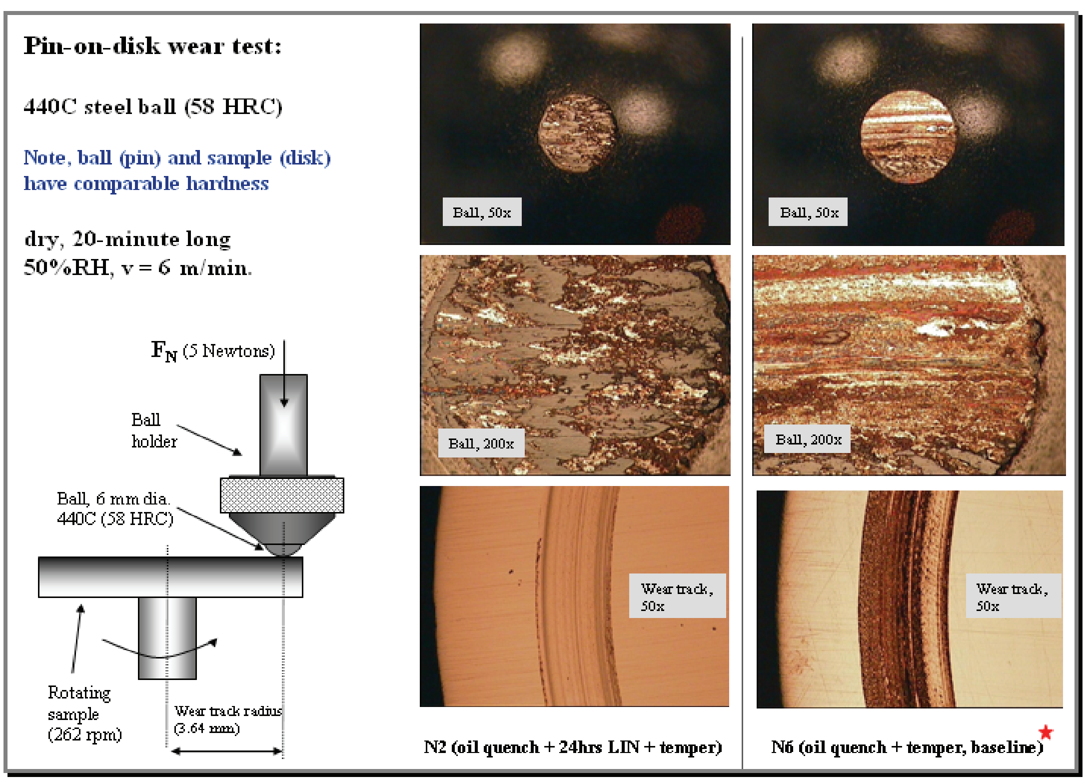

Figure 3: Wear of 440C steel ball (pin) and wear track on A2 steel sample surface (disk) recorded during pin-on-disk wear testing

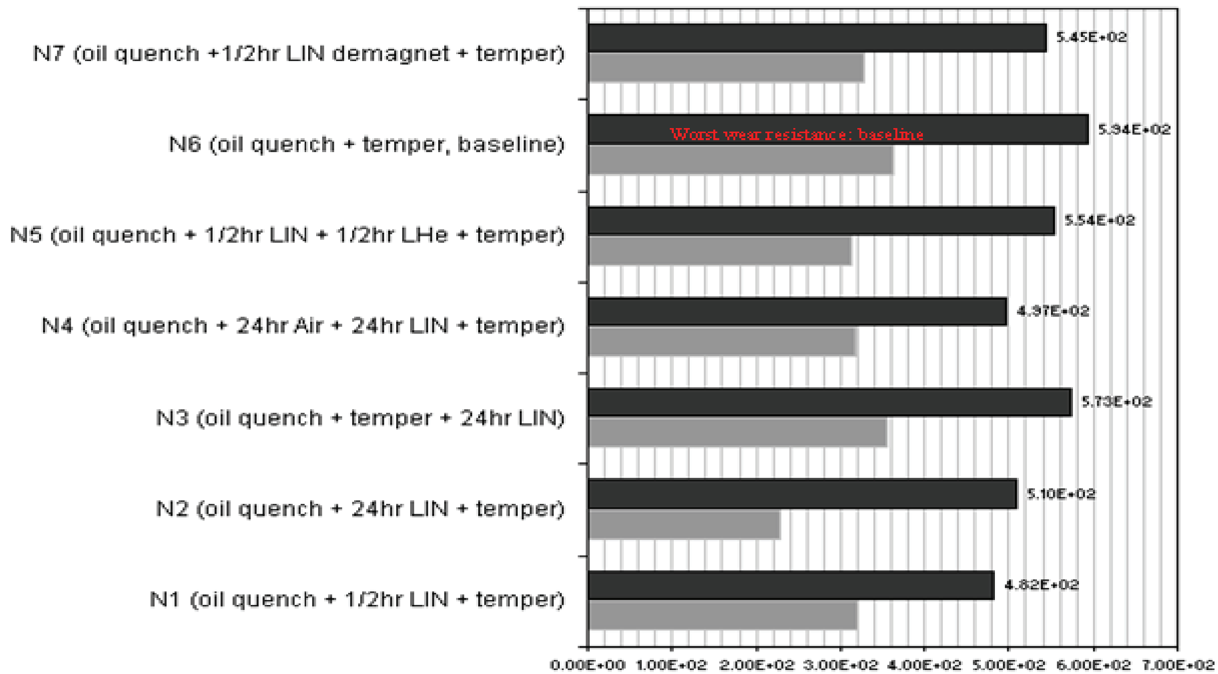

Figure 4: Results of pin-on-disk (black bars) and micro-scratch (grey bars) wear tests combined. The average pin-on-disk wear rate is estimated from the diameter of the wear cap formed on the 440C steel ball during test [plotted in μm], and the average microscratch wear rate is estimated from the area of track depth-profile formed by the diamond indenter [plotted in 0.02 x μm^2].

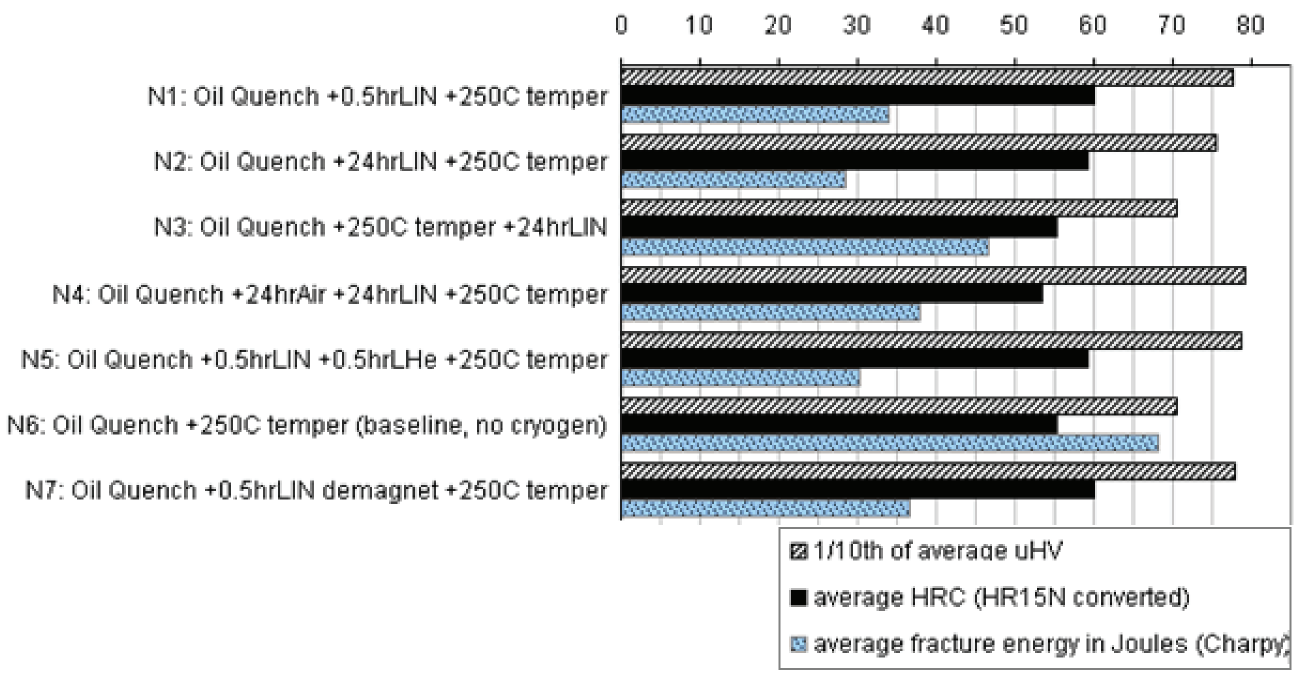

Figure 5: Average values of hardness and impact energy measured for conditions N1-N7. Microhardness Vickers (μHV) was measured using 100G load, superficial hardness HR15N was measured under 15 kG load and converted to HRC scale, Charpy impact fracture energy was measured by fracturing unnotched, 1 cm^2 beams (ASTM E23) and plotted in Joules.

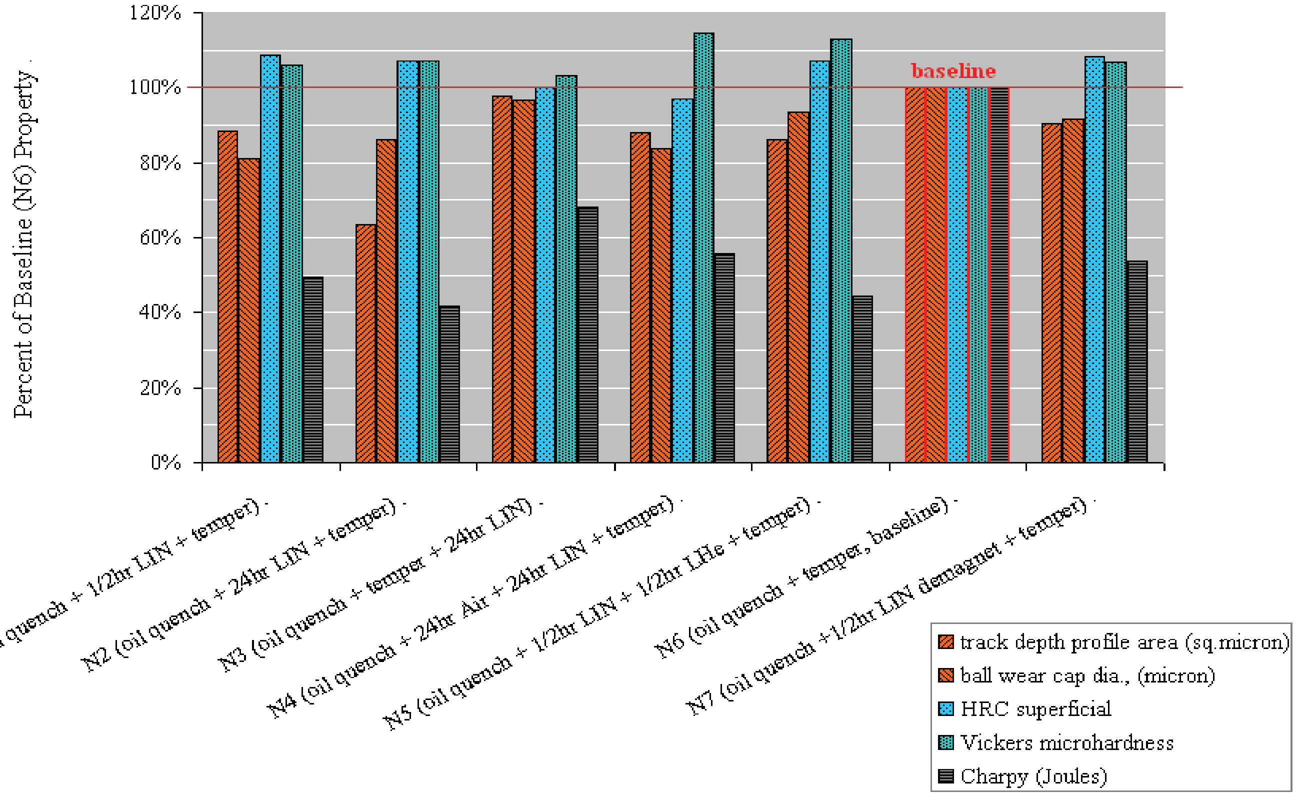

Figure 6: Combined, average results of wear rate, impact energy and hardness measurements, normalized with respect to the baseline condition N6.

Results of the wear rate, hardness, and impact fracture energy measurements were normalized with respect to the baseline N6 (assumed to be 100%) in order to differentiate between particular treatment conditions, figure 6. As already reported by Lal [4], cryo-treatments are, clearly, the most effective in improving wear resistance if applied right after quenching rather than after tempering, the schedule used in N3. Also, wear resistance and hardness improve but fracture resistance deteriorates with increasing the length of holding at cryogenic bath from ½ hr (N1 and N7), to 1 hr (N5), and 24 hrs (N2 and N4). This unequivocally shows that at least some early stages of aging initiate at cryogenic temperatures, and the marginal diffusion rates in LIN may promote formation of finer than normal dispersions of carbide precipitates in the subsequent tempering step. The 24-hr delay between oil quenching and LIN-treatment (condition N4) limits the effect of the subsequent cryo-treatments by room-temperature aging, but the relative contributions of austenite stabilization and solute depletion to that limitation cannot be quantified in the present study. The data shows no additional benefits of LHe quenching and alternating magnetic field beyond what can be expected for the comparatively run LIN cryo-treatments.

Typical microstructures of the baseline (N6) and LIN-treated materials (N1 and N2) show that cryo-treatment, short or long, effectively eliminates residual austenite without affecting the distribution of easily observed, bright carbides, typically ranging in size from 0.5 to 1.2 μm, figure 7. Only high SEM magnifications reveal the presence of additional, dark carbides, sized in most cases from 0.1 to about 0.25 μm. Inspection of figures 8 and 9 clearly shows that the number frequency of the dark carbides is much lower in the case of the baseline condition N6 than for the 24-hr-LIN treated condition N2. With the increasing frequency, some of the dark carbides appear to align into grain boundary-like patterns. This may explain the reduction of both wear rate and impact resistance with cryo-holding time, as observed before. Elemental analysis of the bright and dark carbides of the comparable size was carried out on the surface of SEM samples, figure 10. Bright carbides contained more alloying additions (identified as Cr and V) than the dark ones suggesting that they were first to form. No attempt was made within the scope of this study to identify the phases of the carbides observed, but it is quite likely that the dark ones are ε-carbides (Fe_2C or M_2C) while the bright ones are alloyed □ and/or M_3C carbides.

Conclusions

1. Experimental heat-treatment schedules applied to A2 steel confirmed that cryogenic quenching results in a moderate improvement of wear resistance and hardness, at the cost of impact resistance. Cryo-treated material was more resistant to diamond stylus scratching as well as interfacial sticking during sliding against a steel ball of comparable hardness.

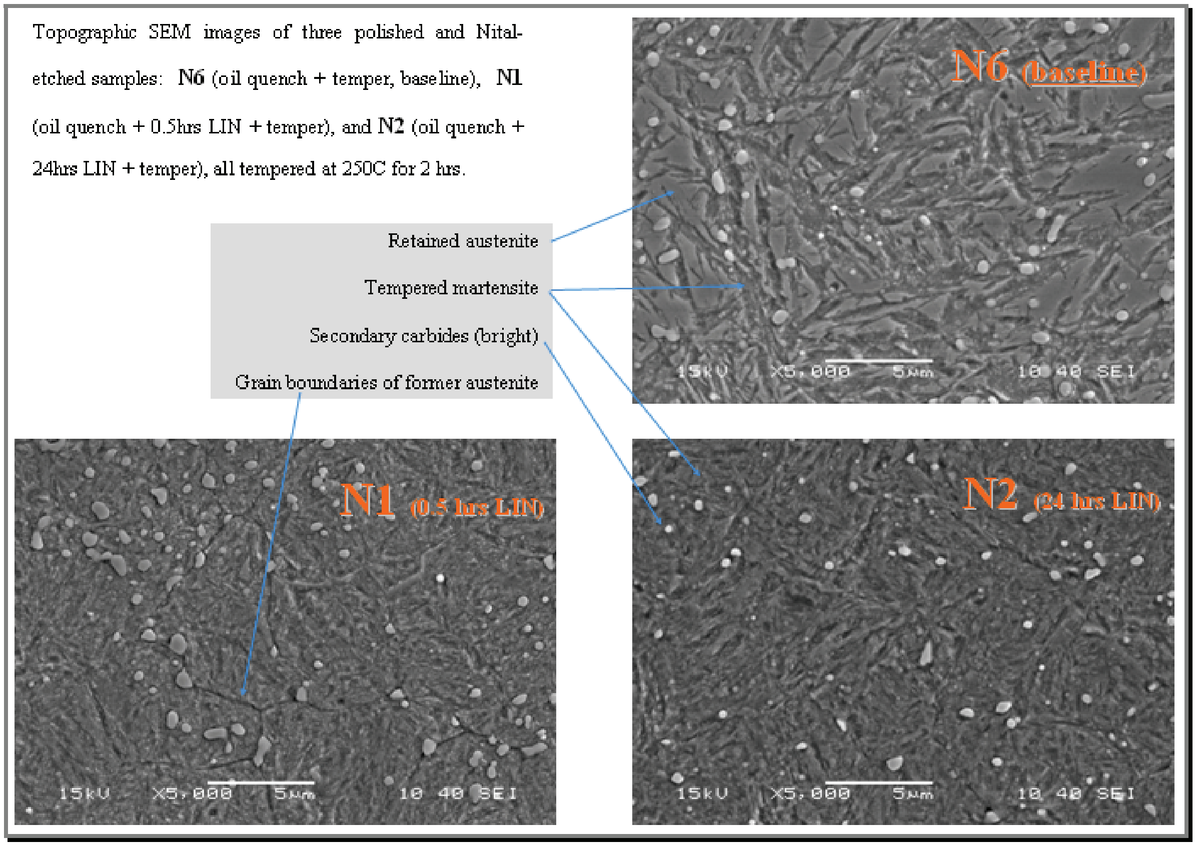

Figure 7: Typical microstructures of the baseline (N6) and LIN-treated materials (N1 and N2) show that cryo-treatment, short or long, eliminates residual austenite without affecting the distribution of easily observed, bright carbides, typically ranging in size from 0.5 to 1.2 μm.

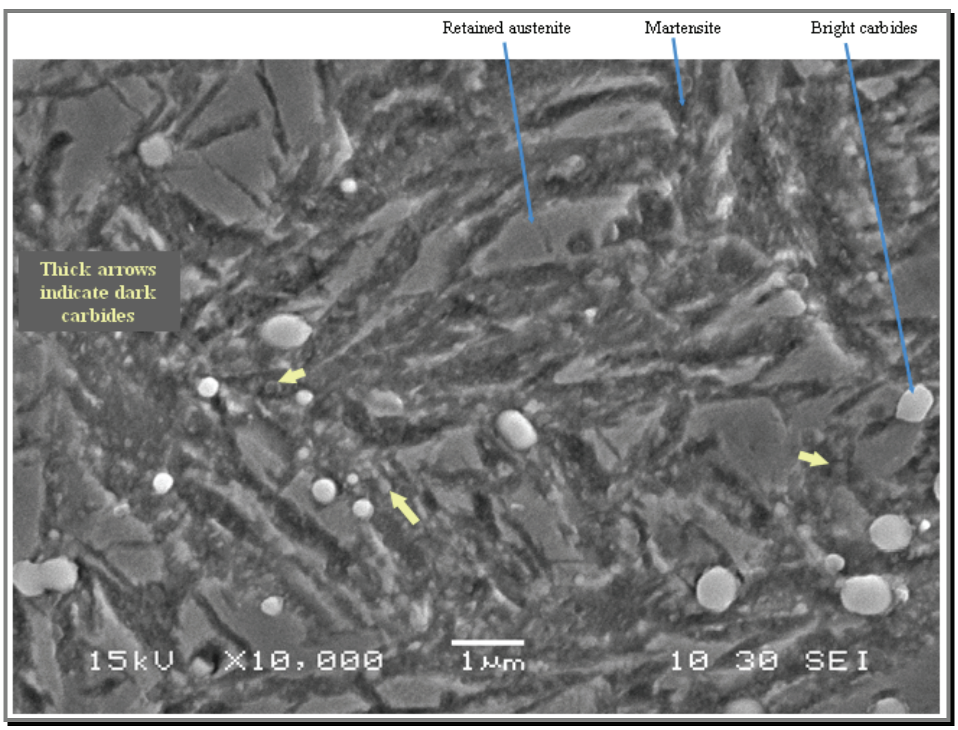

Figure 8: SEM topography of sample N6 (baseline: oil quench + temper), light Nital etch.

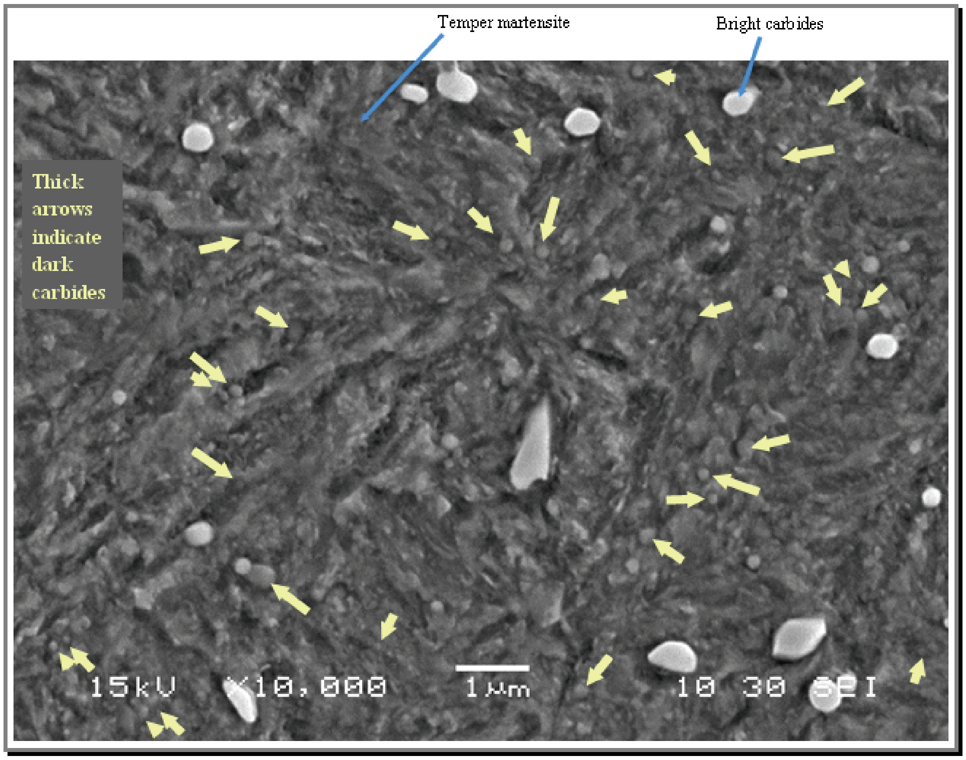

Figure 9: SEM topography of sample N2 (oil quench + 24 hrs LIN + temper), light Nital etch.

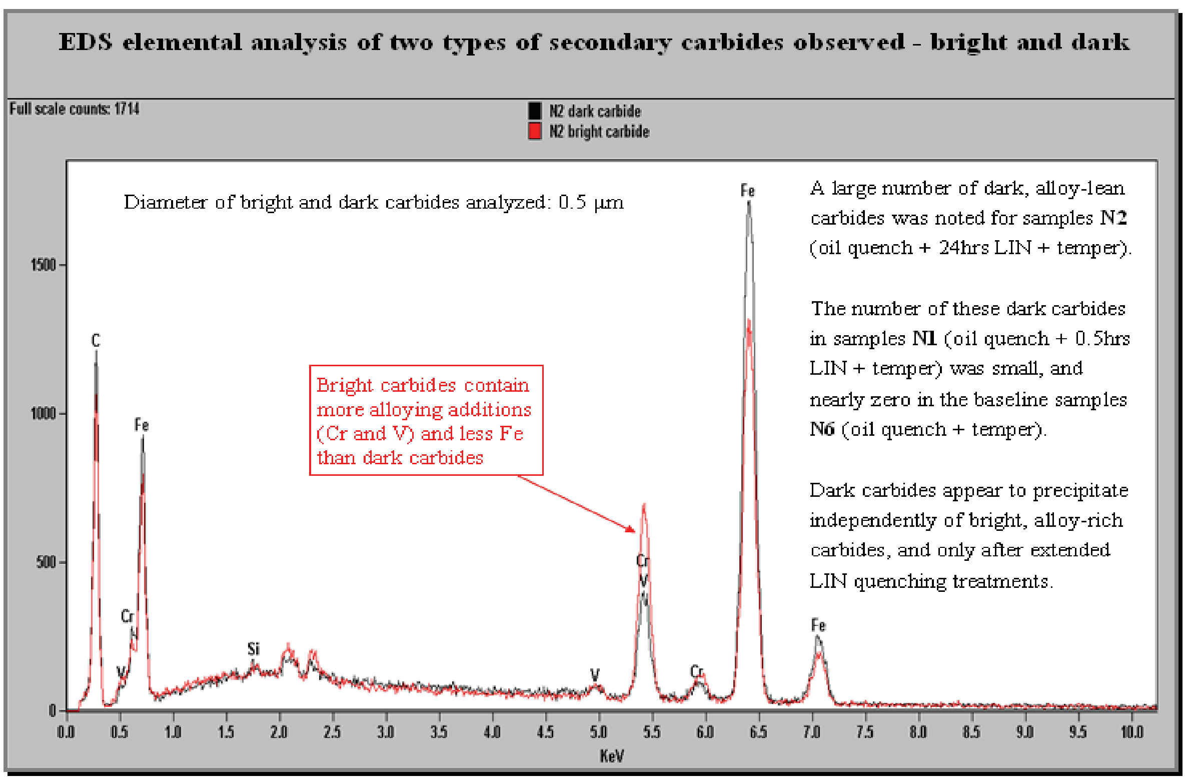

Figure 10: EDS spectrum of 500 nm, bright and dark carbides acquired from the Nital-etched surface of sample N2.

2. A large number of finely dispersed, Cr-V-depleted, dark carbides with the typical size of 100-250 nm dia. was found in cryogen-treated samples which coexisted with a set of more conventional, typically micron sized, alloy-rich, bright carbides. Dark carbide number frequency, material wear resistance, hardness, and the loss of impact resistance were proportional to the length of cryogenic holding time indicating that, apart from the residual austenite transformation, cryogenic treatments effect early stages of aging.
3. Results confirm that, in order to be effective, cryogenic treatments need to be carried out soon after martensitic quenching from austenitic temperatures and before tempering. No additional benefits are observed of LHe-quenching and LIN-quenching in alternating magnetic field, beyond what may be expected for the comparatively run, conventional, LIN-based cryogenic treatments.
4. Future work should focus on a technologically important effect of room-temperature aging before cryo-quenching, phase identification of dark carbides, fractography of cryo-aged and embrittled steels, the role of interstitial gas atoms, and exploration of cryo-treatments of ferrous alloys known for strong aging effects, e.g. structural powder metallurgy steels and iron castings.

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