Middle-East Journal of Scientific Research 27 (7): 554-559, 2019
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2019.554.559

Low Temperature Deep Cold Treatment Alloying Technique to Improve Steel Erosion Resistance

[1]*Juma Yousuf Alaydi and* [2]*Vladimer A. Zabrovitc*

[1]Mechanical Engineering Department, Islamic University of Gaza, Palestine
[2]Material Science, Kharkov Polytechnic State University, Ukraine

Abstract: During the past decade, a new low temperature deep cold treatment alloying technique has been developed to achieve combined improvements in hardness, wear resistance and fatigue properties of austenitic stainless steels, without impairing their corrosion behavior due to the formation of S-phase. This paper reviewscurrent thinking and attempts to explain these differences in terms of theprocessing parameters and to elucidate the implications for the practicalapplication of the technique for optimum properties. An optimized processing route is recommended and a possible further improvement inthe process is suggested. A dense super hard surface layer was produced uniformly across all the samples. The surface hardness, the load bearing capacity and dry wear results, increased with increasing treatment temperature; the samples treated under lower temperatures exhibited the best corrosion and corrosion wear resistance.

Key words: Heat treatment · Deep cold treatment · Tool steels · Erosion resistance

INTRODUCTION

Despite much research over many years, deep cold treatment remainssomething of a mystery. It has been reported to improve the properties ofeverything from tool steels to golf balls and from nuns' habits to copperspot welding electrodes. The greatest improvement reported is in wearproperties. However, many of these miraculous transformations can beascribed to the phenomenon of structure stabilization. It has beensuggested that the deep cold orders the structure, eliminating voids anddislocations so that slip is less likely [1, 2]. This is the reason for deep coldtreating precision engineering parts that are exposed to rapid temperaturechanges but must not deform in service. Typical examples are gun barrelsand parts of racing cars and bikes [3-8]. The magnetic characteristics of the austenitic steelbefore and after nitriding were determined by a vibrating magnetometer. It is known that the values ofparameters of remagnetization of magnetics dependon many factors, including the shape and weight of thesample. Therefore, for magnetic measurements, samples of the same shape and weight were prepared, whilethe employed configuration of measurements minimized the demagnetization factor. In order to investigate tribological characteristics,an automated friction and wear machine was used(high temperature tribometer, for the "ball on disc" testing scheme. It might be supposed that the same argument could be applied to improvements in the pro [8]. A corundum ball with a diameter of 6 mm andmicrohardness of 19 GPa was used as a static frictionpartner. Tests were carried out in air in the mode of dryfriction under a load of 4 N on the counterface holderand the speed of rotation of the sample of 10 cm/s. Inthe process, the sliding distance was 2000 m. In orderto ensure equal conditions of testing of samples, a constant temperature of 30°C was maintained. Tests werein compliance with international standards ASTMG99-959 and DIN50324. The evaluation of wearresistance of samples and the static friction partner wascarried out by the wear factor and tear which wasdetermined after the tests.

The cross section of the wear track of the sample after tribological testing in five areas at three pointseach was measured using a SURTRONIC precision contact profilometer. On the basis of these data, the average value of the cross sectional area was determined. The analysis of the spot of wear on the static partner (the ball) was performed using the Olympus GX 71 optical microscope.

Corresponding Author: Dr. Juma is Associate Professor, Mechanical Engineering Department, Islamic University of Gaza, Palestine. Tel +970567994180.

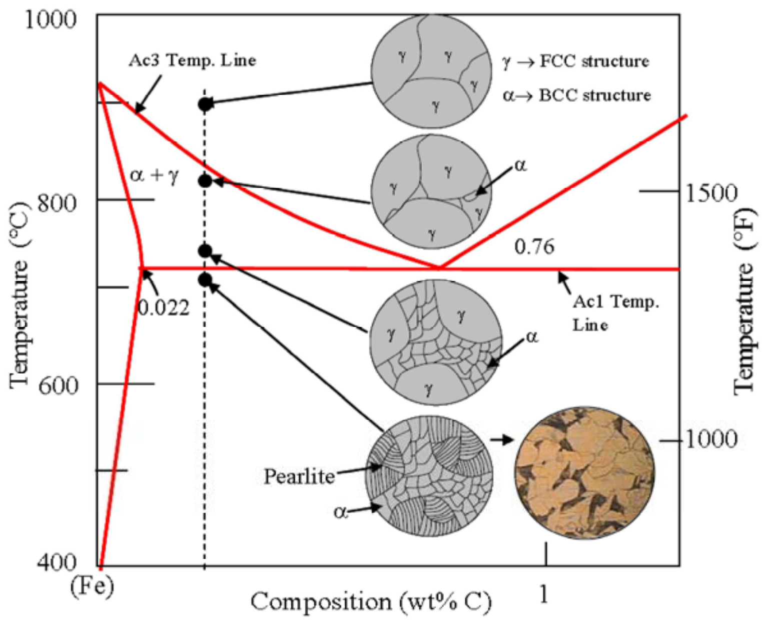

Fig. 1: Phase transformation of hypoeutectoid plain-carbon steel

Tool Treatments: The situation and its explanation in tool steels would, at first sight, appearto be far more clear-cut. The treatment of steels at temperatures in therange -80°C to -120°C is sufficient to fully transform any austenite retained in the quenched micro structure and has been extensively used for this purpose for many years [9]. Examples include case hardening steels such as EN36 (832 H13, 655 H13) and EN 39 (835 H15); hardening tool steels such as M-2 and D-2; and stabilization of components, particularly for the aero space and roll making industries. The stabilization effect can be attributed entirely to removal of the retained austenite as iteliminates the 4% volume change when environmental conditions transform austenite to martensite. Although the transformation of small volumes of well dispersed retainedaustenite increases hardness, it may be counter-productive with regard towear as it is offset by a decrease in toughness and the ability to stopmicro-cracking. It has been reported that deep cold treatment at -196°C (77°K) combined with different austenitising temperatures and hencevarying the volume of initial retained austenite, can optimize the fracture toughness and hardness for a particular application [10-13]. However,these studies used only short duration deep cold treatment that is knownnot to optimize wear resistance [2].

Deep Cold for Wear Resistance: The benefits of deep cold treatment (-196°C) on the wear properties oftools have been known for some years [14, 15], but inconsistencies experienced by its users have limited its acceptance by European industry. Its application has, however, been growing rapidly in the USA where thereare many specialist treatment companies. In recent years some new theories have been developed to explain how deep cold treatment improves wear resistance. These theories can be applied to the processing route to help to eliminate the inconsistencies.

As shown in Figure 1, at high temperatures exceeding the stable austenitetemperature (Ac3), the hypoeutectoid structure is in a stable γ-austenite phase. As thesteel cools below the Ac3 temperature, proeutectoid ferrite will nucleate and grow at the austenite grain boundaries. As the steel continues to cool from the Ac3 temperature to theeutectoid temperature (Ac1), the amount of proeutectoid ferrite formed will continue togrow and the austenite will increase in percent carbon content. At the Ac 1 temperature (approximately 1340°F), the remaining austenite will transform into pearlite with consists of both ferrite and cementite (Fe_3C) layers (Smith 2004). The ferrite that is present with in the pearlite is referred as eutectoid ferrite to distinguish from proeutectoid ferrite. Thus, at ambient temperatures, a Low-Carbon or High-Strength Low-Alloy micro structure consists of proeutectoid ferrite and pearlite.

Most of the treatment routes cool the components in cold nitrogen gasbefore finally immersing them in liquid nitrogen at -196°C, although someprocessors consider it better if the components never touch the liquid, only the cold gas. Since 1965, when commercial

Table 1: The improvement in wear for various tool steels after deep coldtreatment

Steel (AISI No.)	Improvement in wear rate (%)
D-2	817
S-7	503
52100	420
O-1	418
A-10	264
M-1	225
H-13	209
M-2	203
T-1	176
CPM-10V	131
P-20	130
440	121

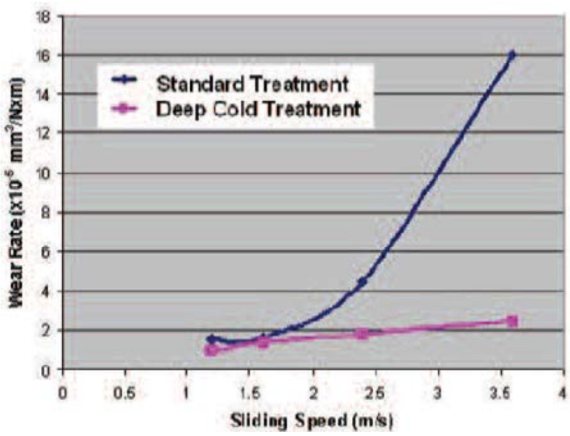

Fig. 2: The effect of sliding speed on the wear rate of tool steel.

deep cryogenictreatments first became available, a number of reports have beenpublished showing the improved performance of some tools steels treatedin this way. The most frequently quoted is that from Barron shown in Table 1 [16]. However, wear is not a simple thing to measure in thelaboratory, where testing parameters significantly affect the result, as Figure 2 shows. The actual wear experienced by a tool may be quitedifferent in practice [17].

It has been reported that some machine elements, such as slitting blades used in paper cutting, have lasted six times longer after deep cryogenic treatment. Results from field trials (Table 2) on punches, stamping dies,and milling cutters, such as those shown in Figure 3, have also shown significant improvement, supporting the experimental data [18, 19]. Deepcryogenic treatment is said to have one important advantage over surface treatments aimed at increasing wear resistance, such as chromium plating, titanium nitride coating or nitriding. This is its ability to change theentire structure of the tool, not just its surface, so that the benefits cannotbe negated by subsequent finishing operations or regrinds [7]. From the start the cold treatment process was dogged by inconsistency.

Table 2: Field trial of wear improvements in deep cold treated tools

Tool Type	Tool Material (AISI No)	Improvement in wear rate (%)
Stamping die	D-2	1000
Punch	M-7	600
End mill	M-42	450
Drills	M-42, M-7, C-2	300
Milling cutters	M-7	250
Drill	M-42	200
Punch	M-2	100

Fig. 3: A selection of deep cold treated tools

It would work on one component, but not on another similar one in thesame material. Today those problems have been solved to some extentthrough an understanding of the mechanisms involved in the wearimprovement.

The Mechanism of Wear Resistance Improvement in Deep Cold Treatment: There have been several studies of the effect of deep cold on wear and the mechanism that may be giving rise to the improvement. Unfortunately some of the papers do not give all the processing parameters and every processing route specified is different. The effectsof deep cryogenic processing are seen as occurring in several stages. Inthe first stage, down to -130°C, retained austenite is transformed inexactly the same way as in conventional sub-zero treatment, increasing the hardness. However, the lattice parameters ofthe martensite formed are different from that formed in conventional treatments, which may well account for its subsequent lack of response to extended exposure to deep cold temperatures [25]. As in the conventional treatment, the transformation is not time-dependent.In the second stage, which occurs at deep cryogenic temperatures (typically -196°C, the temperature of liquid nitrogen), there is a time dependentde composition of the primary martensite. This decomposition causes some initial softening but nucleates numerous coherent nanocarbides [23]. During the subsequent tempering operation the fine-carbides formed and precipitated at these sites are the reason for the increased wear resistance of the treated tools. It has been shown that thelonger the exposure to cryogenic temperatures, the more nano-carbidesare formed [24].

It is suggested, however, that it is only the primary martensite thatdecomposes and not that with the higher c/a ratio produced by thetransformation in the first stage. This mechanism goes some way toexplaining the inconsistency of the results. If a component initially has ahigh retained austenite level then the transformation in the first stage will dramatically increase the hardness, but not necessarily the wearresistance, compared with the original state. If a component has only alow retained austenite level then the carbide formation engendered by thesecond stage would dramatically increase the wear resistance compared toits original state, but without altering the hardness. It is also possible todeep cold treat after high temperature tempering with less, but stillsignificant, fine -carbides precipitation and it has been reported that M 2 that has been deep cryogenically treated twice shows further improvement after the second treatment [25]. The "popular" literature contains many references into the need for low cooling rates and accurate cooling curvecontrol down to liquid nitrogen temperatures [26]. This need appears tobe driven by the desire of the equipment manufactures to sell expensive equipment capable of such control rather than by any evidence in the "technical" literature. It is however, important to cool and reheat slowlyenough to avoid cracking through differential contraction/expansion and the effects of the 4% volume change on transformation of the retainedaustenite to marten site, but it is not critical to -carbide formation. It isoften reported that deep cold treatment should follow immediately afterquenching, but it has also been suggested that a short warm (60°C) ageing after quenching can reduce the tendency to cracking [23]. It has been shown more -carbides are produced by a longer deep coldtreatment at cryogenic temperatures and, as might be expected, the sub sequent wear rate also falls with increasing exposure time [24, 25].

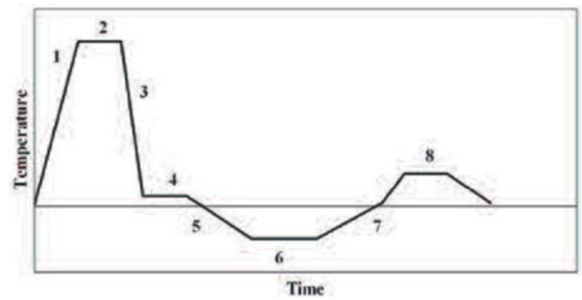

Fig. 4: A schematic of the recommended processing route.

The recommended minimum time at low temperature is 24 hours, however, extended or multiple treatments are known to be beneficial. Toolsteels that normally exhibit secondary hardening do not do so after deepcold treatment so they can be tempered at a lower temperature tomaintain hardness [24, 27]. However, the wear rates are lower when thesteel is tempered at its normal tempering temperature because themorphology of the larger carbides is improved.

Recommended Process Steps: It is not possible to recommend a single process for every tool steel, noreven a single cycle for all tools manufactured from the same steel. Eachtool needs to be separately assessed and an individual process routedevised for it that will depend on the combination of hardness, toughnessand wear resistance required in service. The cryogenic treatment is justone step in that process and must be integrated into the processing route [28]. BOC recommends that tools be treated in specially designed equipment using liquid nitrogen as the refrigerant. The liquid nitrogen issupplied by BOC either via small portable storage containers or static, externally sited, vacuum insulated vessels for larger volumes. The wholeprocess cycle can be automatically controlled for greater consistency and reproducibility. In addition to deep cold capability, some of the units onthe market also incorporate a temper/stress relief facility. This releasesthe heat treatment furnaces for further treatments.

The steps in the processing route for maximum wear resistance in Figure 4 are:

- Heat to an austenitising temperature that will minimise retainedaustenite in the tool steel being treated
- Hold for the recommended time for the steel
- Quench at a rate sufficient to give a fully martensitic structure

- Condition at 60ºC for a maximum of one hour and immediately go tostep 5
- Cool to liquid nitrogen temperature (-196ºC) at a rate slow enough toprevent cracking, preferably in a nitrogen atmosphere to avoidcondensation
- Hold at liquid nitrogen temperature for a minimum of 24 hours,preferably in a nitrogen atmosphere to avoid condensation
- Reheat to room temperature at a rate slow enough to prevent cracking,preferably in a nitrogen atmosphere to avoid condensation
- Temper at the temperature recommended for the steel being treated.

Further Improvements: There is insufficient driving force at liquid nitrogen temperature (-196ºC) to form the nuclei of the -carbides in the martensite formed at low temperature. This limits the useful application of the deep coldprocess to tool steels that have been austenitised at lower temperature to minimise retained austenite formation, but which, however, also minimises hardness. If the driving force were increased by cooling to alower temperature, then it might be possible to form carbides in the martensite formed at low temperatures, thus maximising performance with a combination of high hardness and fine -carbide dispersion. The obvious choice of refrigerant would be liquid helium at -269°C (4°K). However, it is inevitable that treatment times would be very long as thereis little atomic movement at such a low temperature.

CONCLUSIONS

As part of an optimised heat treatment cycle, deep cold treatment candramatically improve measured wear by the precipitation of fine -carbidesin the primary martensite. The transformation of retained austenite to martensite is a minor additional benefit. In many practical uses of tools this increase in measured wear translates into longer tool life.

Cryogenic treatment has enhanced the hardness and wear resistance properties of both cutting discs. This is due to the precipitation of hard carbide particles filling up the voids and vacant spaces and conversion of soft and ductile retained austenite to martensite during the cryotreatment process. Tool disc A has indicated better response to cryotreatment as compared with tool disc B. This is because the hardness values of cutting tool disk B are comparatively higher. This increased hardness could be due to various factors like composition of alloying elements, method of heat treatment post production, etc. Duration of the soak time during cryo treatment process has direct effect on the wear resistance and hardness properties of both the tool discs. Increasing the soak time enhances the wear resistance and hardness properties which in turn improve the useful life of the cutting disk. Soak temperature is also an important factor which can influence the effects of cryotreatment. Hence, the results call for an extended study to optimise the experimental parameters with regard to soak time and temperature during the cryotreatment process.

REFERENCES

1. Paulin, P., 1992. Mechanism and Applicability of Heat Treating at CryogenicTemperatures, Industrial Heating, pp: 22-27.
2. Collins, D.N., 1996. Deep cryogenic treatment of tool steels: a review, Heat Treatment of Metals, 23(2).
3. Semiatin, S. L., Stutz, D. E. & Byrer, T. G. Induction Tempering of Steel: Part I. Development of an Effective Tempering Parameter.
4. Dohacz, R.T., 2003. Rocket Science: adding power and reliability with cryogenics, Journal of Heat Treating, 4: 39-46 (1985)., Drag Racing USA, August 2003, pp: 28-30.
5. Paulin, P., 1995. Cryo-Rifles: Deep Cryogenic Stress Relief, PrecisionShooting, March, pp: 74-76.
6. Race & Rally, 1996. Deep Freeze, Deep Secret?", Heat Treatment of MetalsJanuary, pp: 26-56.
7. Paulin, P., 1992. Cold cuts, Cutting Tool Engineering, 44(5).
8. Schiradelly, R. and F.J. Diekman, 2002. Cryogenics; the racers edge, HeatTreating Progress, pp: 43-49.
9. Moore, C., 1975. Development of the BOC Ellenite process (cold treatmentof metals with liquid nitrogen), Heat Treatment '73, The Metals Society, 1975, Book No 163: 157-161.
10. Mahmudi, R., H.M. Ghasemi and H.R. Faraji, 2000. Effects of cryogenictreatments on the mechanical properties and wear behaviour of highspeedsteel M2, Heat Treatment of Metals, 2000, 27(3): 69-72.
11. Leskovsek, V., B. Lišcic and B. Ule, 2001. Some aspects of sub-zerotempering at vacuum heat treatment of HSS, Proceedings of the 21st Conference 5-8 November 2001, Heat Treating Society.
12. Leskovsek, V. and B. Ule, 2002. Influence of deep cryogen treatment onmicrostructure, mechanical properties and dimensional changes invacuum heat-treated high-speed steel, Heat Treatment of Metals, 29(3): 72-76.

13. AI Wojcieszynski, "Cryogenic treatment: a mystery or misery of heattreatment", Proceedings of the 19th Heat Treating Society conference,pp 237-243, 1999
14. Keen, A.R., 1982. Cryogenic treatment to improve wear resistance of steelby the "Cryotough" process", Metals Australasia, 14(7): 12-12,21.
15. Reasbeck, R.B., 1989. Improved tool life by the Cryotough treatment, Metallurgia, 56(4): 178-179.
16. Barron, R.F., 1982. Cryogenic treatment of metals to improve wear resistance, Cryogenics, 22(8): 409-413.
17. Blau, P.J., 2001. Compositions, functions and testing of friction brake materials and their additives (Oak Ridge National Laboratory, Oak Ridge) pp: 38.
18. Bensely, A., *et al*., 2007. Effect of Cryogenic treatment on tensile behaviour of case carburised steel 815M7 2007 Material Characterization 58 485http://www.diversifiedcryogenics.com/testresults.htm
19. Alexandru, L., G. Coman and V. Bulancea, 1986. The change of the substructure elements and the redistribution of the alloying elements by means of cryotreatments in alloy tool steels, Proceedings of the5th International Congress on Heat Treatment of Materials, 2: 901-908.
20. Alexandru, L., C. Baciu and G. Ailincai, 1990. Contributions on the study of the increase of durability of the high-alloyed tool steels by thermal treatments at cryogenic temperatures, Memoires et Etudes Sci. Rev. Metall., 87(6): 383-339.
21. Dormer, J., 1994. The cryogenic treatment of tool steels, Thesis, National University of Ireland, University College Dublin, August 1994.
22. Meng, F., K. Tagashira, R. Azuma amd H. Sohma, 1994. Role of eta-carbide precipitation's in the wear resistance improvements of Fe-12-Cr-Mo-V-1.4C tool steel by cryogenic treatment, ISIJ International, 34(2): 205-210.
23. Collins, D.N. and J. Dormer, 1997. Deep cryogenic treatment of a D2 cold work tool steel. Heat Treatment of Metals, 24(3): 71-74.
24. Yun, D., L. Xiaoping and X. Hongshen, 1998. Deep cryogenic treatment ofhigh speed steel and its mechanism, Heat Treatment of Metals, 25(3): 55-59.
25. Hallum, D.L., 1996. Cryogenic tempering delivers better cutting tooldurability, American Machinist, pp: 140-141.
26. Collins, D.N. and J. Dormer, 1998. Deep cryogenic treatment of an ASP 23 high speed steel, Proceedings of the 18th Heat Treating Society conference, pp: 255-258.
27. Collins, D.N. and G. O'Rourke, 1998. The response of tool steels to deepcryogenic treatment: effect of alloying elements, Proceedings of the 18th Heat Treating Society conference, pp: 229-247.
28. Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus 2000 ASTM G99.