Comparison of Effects of Cryogenic Treatment on Different Types of Steels: A Review

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ABSTRACT
Cryogenic treatment (CT) is the supplementary process to conventional heat treatment process in steels, by deep–freezing materials at cryogenic temperatures to enhance the mechanical and physical properties of materials being treated. Cryogenic treatment (CT) of materials has shown significant improvement in their properties .Various advantages like increase in hardness, increase in wear resistance, reduced residual stresses, fatigue Resistance, increased dimensional stability, increased thermal conductivity, toughness, by transformation of retained austenite to martensite, the metallurgical aspects of eta-carbide formation, precipitation of ultra fine carbides, and homogeneous crystal structure. Different approaches have been applied for CT to study the effect on different types of steels and other materials. This paper aims at the comprehensive analysis of strategies followed in CTs and their effects on properties of different types of steels by application of appropriate types of CTs from cryogenic conditioning of the process. The conclusion of the paper discusses the development and outlines the trends for the research in this field.

Keywords
Austenite, Cryogenic Treatment, Carbide formation, Cooling rate, Dimensional stability, Deep-freezing, Martensite, Soaking, temperature, Wear resistance.

INTRODUCTION
The word, "Cryogenics" is taken from two Greek words – "kryos" which means 'frost' or freezing, and "genic" meaning to 'produce' or generated. Technologically, it means the study and use of materials (or other requirements) at very low temperatures. Deep Sub-zero treatment of metals and alloys is a deep stress relieving technology. Whenever material is subjected to any manufacturing operation, it is subjected to stresses. The stress manifests itself in the nature of defects in the crystal structure of materials. The most commonly observed defects are in the form of vacancies, dislocations, stacking faults etc. As the level of stress increases, the density of these defects increases, leading to increase in inter atomic spacing. When the distance between the atoms exceeds a certain critical distance, cracks develop and failure takes place.

The third law of thermodynamics states that entropy is zero at absolute zero temperature. Deep subzero treatment uses this principle to relieve stresses in the material. The materials are subjected to extremely low temperatures for a prolonged period of time leading to development of equilibrium conditions. This leads to ironing out of the defects in the material and also attainment of the minimum entropy state. Grain shape and size gets refined and is made uniform. Defect elimination takes place
and inter atomic distance is reduced. When the material is brought back to room temperature, the defect level reflects an equilibrium concentration. Compaction of the crystal structure leads to much superior abrasive, adhesive and erosive wear resistance and enhances corrosion resistance as well as fatigue strength and resilience [1].

Brief History

Cryogenics in [2] is the science of production and effects of very low temperatures. It is clear from the above definition that, in the studies of cryogenics lowest temperatures below the freezing of water (0^{o} C) to be considered. However, Prof. Kamerlingh Onnes of the University of Leiden in the Netherlands first used the word in 1894 to describe the art and science of producing much lower temperatures. He used the word in reference to the liquefaction of permanent gases such as oxygen, nitrogen, hydrogen, and helium. Oxygen had been liquefied at –183^{o}C. Over the years the term cryogenics has generally been used to refer to temperatures below approximately –150^{o}C.

According to the laws of thermodynamics, there exists a limit to the lowest temperature that can be achieved, which is known as absolute zero. Molecules are in their lowest, but finite, energy state at absolute zero. Absolute zero is the zero of the absolute or thermodynamic temperature scale. It is equal to – 273.15 ^{o}C or –459.67 ^{o}F. In terms of the Kelvin scale the cryogenic region is often considered to be that below approximately 120 K (-153^{o}C). The common permanent gases referred to earlier change from gas to liquid at atmospheric pressure at the temperatures shown in Table 1, called the normal boiling point (NBP). Such liquids are known as cryogenic liquids or cryogens [2].

Table 1. Normal boiling points of common cryogenic fluids

The most notable and persistent pioneer of cryogenics was Dr..

Cryogen	(K)	(^oC)	(^oR)	(^oF)
Methane	111.7	-161.5	201.1	-258.6
Oxygen	90.2	-183.0	162.4	-297.3
Nitrogen	77.4	-195.8	139.3	-320.4
Hydrogen	20.3	-252.9	36.5	-423.2
Helium	4.2	-269.0	7.6	-452.1
Absolute zero	0	-273.15	0	-459.67

Papers by Randall Barron of Lauisiana Technical University are widely cited in the cryogenics research and industry [3-5].

Untill the end of 1960s, attempts made to perform CT with the results of cracking components. The cryogenic treatment system developed by Ed Busch in the late 1960s and latter improved by Peter Paulin with a temperature feedback control on cooling and heating rates allows to perform effective and crackles. CT until very low temperatures subsequently, the research about CT has been validated during the 1980s by the first request in machine tools [6,7]. Latter with research and development, computerized temperature control systems have been developed to get crackless cryogenic treated components to achieve maximum benefits [8-11].
NASA engineers were the first to notice the effects of cold temperatures on materials. They noticed that many of the metal parts in the aircraft that had returned back from the cold vacuum of space came back stronger than they were before flight.

2. PROCESS OF CRYO-HEAT-TREATMENT

The complete treatment process of the steels consists of hardening that is Austenitizing and quenching, cryo-treatment or deep cryogenic treatment (DCT), and Tempering. To achieve better microstructure of the steel to get most desired properties, it is recommended by the most researchers to execute DCT after completion of quenching and before tempering in conventional heat-treatment cycle as shown in Fig-1. The complete process sequentially consists of the steps austenitizing, quenching, cryoprocessing and tempering

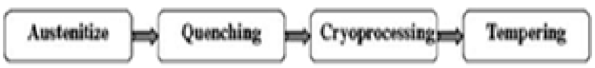


Fig- 1 Heat treatment sequence for maximizing martensite transformations

To harden steels, the heat treatment process in [12] includes heating to austenitizing temperatures. The microstructure is composed of the metallurgical phase austenite plus the primary carbides. Austenitizing is followed by quenching, or rapid cooling, which transforms some or all of the austenite into the higher strength martensitic structure, supersaturated

with carbon. Tempering allows the supersaturated carbon to form carbides, called transition carbides, that relieve micro-stresses in the martensite matrix and prevent cracking of the part.
D. Das et.al. [13] Studied Influence of varied cryo treatment on the wear behavior of AISI D2 steel and has been demonstrated that, deep cryogenic processing (C) was incorporated intermediate between hardening (Q) and tempering (T) in cryo treatment (QCT), the details of each step being illustrated in Fig.-2. The cryogenic processing was done by uniform cooling of the samples to 77 K, and holding the samples at this temperature for different time durations (0, 12, 36, 60 and 84 h), followed by uniform heating to room temperature. A typical deep cryogenic processing cycle is illustrated in Fig. 2(b).

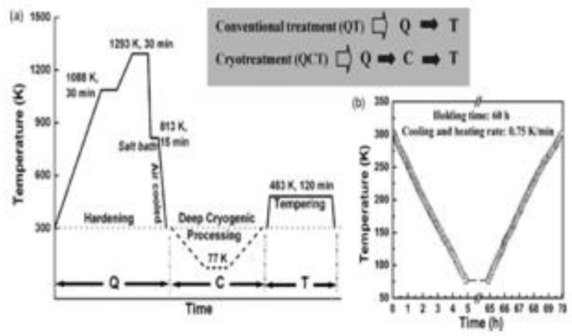


Fig.2. (a) Schematic representation of the heat treatment schedule consisting of hardening (Q), deep cryogenic processing (C) and tempering (T) cycles, and (b) typical time-temperature profile of a deep cryogenic processing cycle

2.1 Austenitizing

Austenite steel is an alloy of iron and carbon with other elements in the solution, by the diffusion process it begins to dissolve and homogenize in the austenitic solution. When steel is heated the iron crystal changes to face centered cubic (FCC).

The transformation from austenite to martensite begins at a well-defined temperature called the martensite start temperature or M_S. For most practical steels, the transformation is isothermal and progresses smoothly as the temperature falls to the martensite finish temperature, or M_F. Some austenite, designated retained austenite, is always present after hardening. Higher martensite contents and carbon percentages increases the hardness of steel. The amount of carbon also affects the temperatures where the martensite transformation begins (M_S) and is completed (M_F). The M_f and M_s temperatures can be lower than room temperature. The steel might only partially transform to martensite with the remaining structure being retained austenite. M_s and M_f temperatures are also depressed with increase in grain size.

Moore and colline [14] have concluded that optimum austenitization temperature varies from metal to metal. However, for D2 steel it lies between 1075^0C (1348K) and 1100^0C (1373K).Collin and Dormer [15] observed the influence of change in austenitization temperature as in (Fig -3), which indicates more number of carbides present as the austenitization temperature lowers from 1070^0C (1343K) to 970^0C (1243K) in D2 steel. Furthermore they have studied the influence of austenitizing temperature on the microstructure and hardness of D2 steel specimens subjected to sub-zero treatment & conventional heat treatment (CHT). They observed that increase of austenitizing temperature enhances the bulk hardness for CHT and sub-zero treated D2 steel this has been attributed to increase in amount of retained austenite γ_R with increasing austenitizing temperature. This is agreement with Surberg et. al. [121], they have also reported that amount of γ_R increases with increasing austenitizing temperature. Increase in amount of γ_R with increasing austenitizing temperature for steels is well known [16-21].

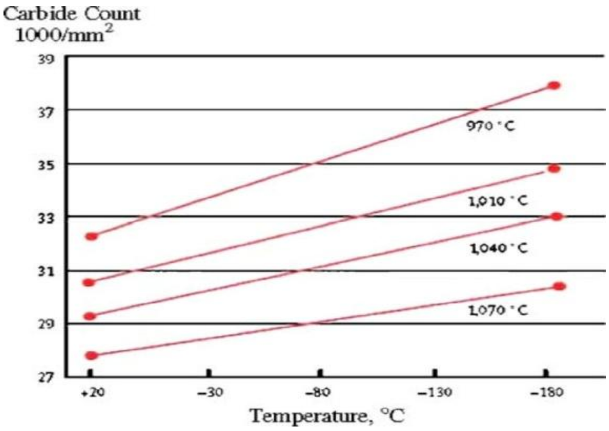


Fig.-3. Effect of cooling to subzero temperature on Carbide number for D2 steel. Austenitizing temperatures 970, 1010, 1040, and 1070^0 C were used before hardening [15].

2.2 Quenching

After attending the austenitizing temperature in the CHT. Further it is cooled down to ambient temperature rapidly in a suitable quenching media fluid like oil, water or air. Once the austenite is cooled below its critical temperature it becomes unstable and it starts to transform in to martensite. Properties of such steels depend upon rate of cooling. Steel is quenched to increase its hardness, strength and wear resistance.Quenching process consists of heating and holding the steel at its upper critical temperatures (above 1200^{0}C) to disperse the carbon and alloying elements in the austenite phase. Quenched steel crystal structure is now a body centered trevagonal (BCT) called martensite.Reheating these crystallographic and microstructural changes results in to the precipitation of finer carbides in the tempered microstructure, with increase in toughness and wear resistance [22-25]. After CHT there would always be some retained austenite in the steel which is up to 20-30%.

3 PROCESS OF CRYOTREATMENT

Cryotreatment is add-on process to conventional heat treatment by deep-freezing steels at cryogenic temperatures to enhance mechanical properties of steels being treated. Various advantages like increase in wear resistance, reduced residual stress, increase in hardness, dimensional stability, fatigue resistance, toughness by transformation of retained austenite to martensite and precipitation of ultra fine carbides. Cryotreatment technology is inexpensive an eco-friendly, non-toxic and non-explosive.Deep cryogenic treatment (DCT) commonly refered to as cryotreatment, is an add- on process to conventional heat treatment (CHT) of steel.

The sub – zero treatment can be classified into three different temperature regimes:
Cold treatment (223-193K), shallow cryogenic treatment (SCT,193-113K) and deep cryogenic treatment (DCT,113-77) [26]. Research since last two decades indicated that enhancement of mechanical properties, particularly wear resistance, can be achieved substantially by further lowering the temperature of sub – zero treatment by using liquid nitrogen (LN_2) as cryogen or as cooling agent [19,21,7,26-31].

Any changes in property are attributed to the micro-structural changes. Thus in tool steels, the following are the possible processes changes that need to be considered for the property change [41]
The effectiveness of the cryotreatment at liquid nitrogen depends on;

- Elimination of retained austenite.
- Transformation of retained austenite to more stable as tempered martensite matrix.
- Formation of Eta – carbides
- Precipitation, nucleation and growth of ultra fine small secondary carbides (SSCs) with high population density.
- Homogeneous and well distributed Microstructure

As reported DCT has many benefits. It not only gives dimensional stability to the material, but also improves abrasive [7,32-34] and fatigue, wear reistance [35] and increase strength and hardness of the material [33,14,36]. The main reason for this improvements in properties are the complete transformation of retained austenite in to martensite and the precipitation of ultra fine eta- carbides dispersed into the tempered martensitic matrix [7,37]. Numerous practical successes of cryogenic treatment and research projects have been reported worldwide [7,14,26,33-40]. However, the treatment parameters including cooling rate, soaking temperature, soaking time, heating rate, tempering temperature and time need to be optimized with respect to the material and application [42].

3.1 Rate of cooling

Das et.al. [13] also observed the slow cooling rate of ~0.75 K min^{-1} in case of AISI D2 steel.[17]Zhirafar et.al.[22] set the cooling and heating rate at 1.8^0 C/min. in case of 4340steel.M. Arockia Jaswin et.al.[43] have determined the cooling rate at 1^0 C/min. and 1.5^0 C/min. for EN52 and 21-4N valve steel respectively. It has been identified by Darwin et al. [42,44] that cooling rate has about 10% contribution in the process to increase wear resistance and the optimum value is 1K/min, in case of 18% martensite stainless steel. Preciado et al. [45] also recommended slow cooling rate of approximately 1K/min. Bensely et al. [46] processed the case-carburized steel 815M17 samples by slow cooling from room temperature to 77 K (−196°C) at 1.24 K/min, soaking at 77 K (−196°C) for 24 h, and finally heating back to room temperature at 0.64 K/min. Molinari et al. [33] has observed the slow cooling rate, the cooling rate about 0.3–0.5K/min to avoid any thermal microcracking. Fast cooling rate reported to creation of non stationary defects in the crystal structure [49]. Dobbins [47] has also mentioned that change in cooling rate significantly affects the material properties. He also proposed slow cooling rate of 1.5K/min. On the contrary, Kamody [48] concluded that the rate of cooling has negligible effect in the process. Also several studies suggested that the damage that can occur by rapid cooling in the form of thermal shock cracks [21, 36, 45].

However, Kalsi et.al. [50] suggested that slow rate of lowering down to the lowest most temperature would be helpful to achieve maximum improvement in wear properties and to avoid any microcracking, the value may be to 1K/min. Still further investigations would be needed to optimize the impact of this parameter on various types of materials. They also observed that commonly applied values for cooling rate vary from 0.35 to 3.0K/min. Generally, it is preferred to take cooling rate as low as possible to avoid any type of risk of microcracking in the material. Still, it is very difficult to conclude any optimal value for a particular material. Barron et. al.[3] studied on AISI T8 and C 1045 steels shows that cooling rate does affect wear resistance of the final product and that with increase in cooling rate, wear resistance of the steel decreases [3]. His analysis is also shown in Fig.- 4.

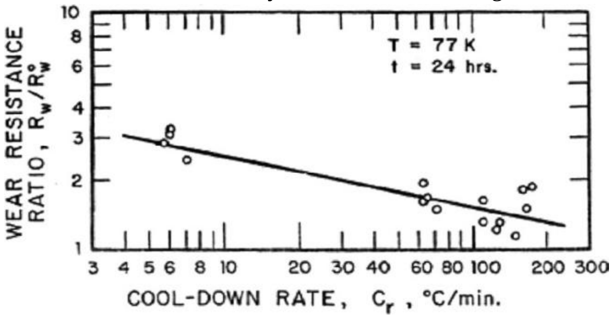


Fig.- 4 Variation of the wear resistance ratio for AISI-T8 steel with cool-down rate during CT [3].

3.2 Soaking Period

Gogte et al. [51] reported that the period for which the samples are held at low temperature is known as soaking period. It may vary from 8h to 40h. The long "soaking period" is necessary to allow transformation of retained austenite to martensite, and to precipitated to fine carbides and the crystal lattice to achieve the lowest energy state possible throughout the material, whereas evidence have also shown that this change begins within the first 8h. Das et al. [13] studied the wear behavior of AISI D2 steel and kept the soaking temperature 77 K constant with the different soaking periods at 0, 12, 36, 60 and 84 h. They found that at 77 K with holding time 36 h obtained the best combination for desired microstructure and increased wear properties of AISI D2 steel beyond which it shows monotonic decrease with further increase in holding time. Das et al. [20] in his another study, the effect of soaking period on the tribological behavior and carbide precipitation of D2 steel and suggested that soaking period does not affect the hardness, but the wear resistance increases by increasing the soaking period.

Darwin et al. [42] in their experimental study concluded that the soaking period may have about 24% contribution to enhance wear resistance properties of the steel. Several researchers reported the increase in wear resistance by Mohan Lal et al. [26], Collins and Dormer [15], and Yun et al. [52]. Collins et. al. [15]proved experimentally the metallurgical effects of cryoprocessing on tool steels. They concluded that, cryogenic temperature significantly affects the amount of carbide precipitated, which increases with increased soaking period at cryogenic temperature as shown in Fig.-5. The influence of soaking period on hardness as shown in Fig.-6 illustrates that processing time in excess of 24 h yields a higher hardness.

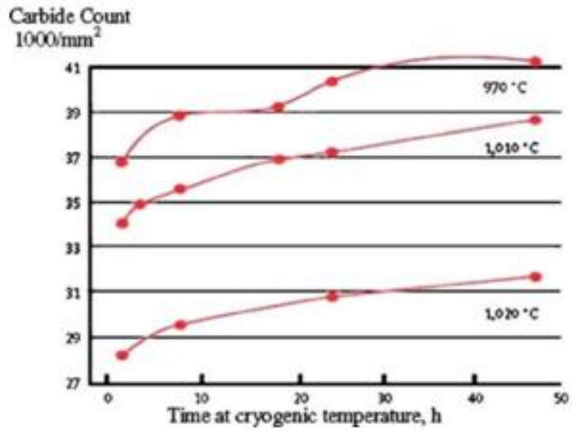


Fig.-5 Effect of soaking period at −196°C (−320°F) on carbide number for D2 steel. Carbides were measured using optical techniques. Austenitizing temperatures of 970°C, 1,010°C, 1,040°C, and 1,070°C were used before hardening [

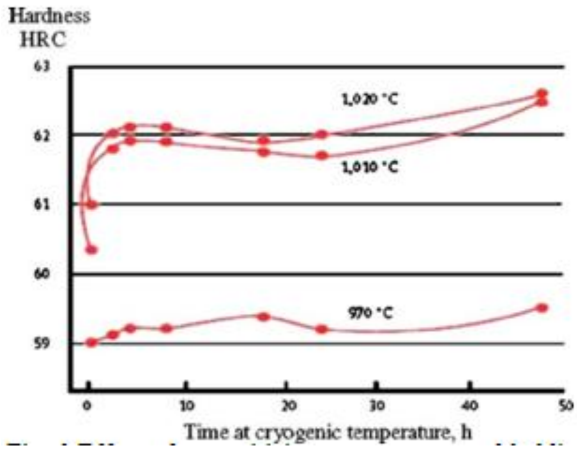


Fig.-6 Effect of austenitizing temperature and holding time at cryogenic temperature on hardness of D2 cold-work tool steel

The increase in wear resistance of tool steels by cryotreatment with increasing holding time has been reported earlier by Mohan Lal et al. [26], Collins and Dormer [15] and Yun et al. [52]. However, the results reveal, for the first time, that there exists a critical holding time in the cryotreatment of D2 steel for obtaining the best combination of desired microstructure and wear property of die/tool steels. Further they observed that the larger number of SCs and their finer sizes are the key factors for the improvement in wear resistance in cryotreated specimens and in delineating the critical time of holding.

Barron and Mulharn [3] have studied the effect of soaking time on wear resistance of AISI-T8 steel. They observed a drastic change during first few hours and then gradual small increase.

Jinyong et al. [53] treated the Mo–Cr HSS by cryoprocessing for 2 and 16 h as soaking period and showed that wear resistance is more in case of steel treated for 16 h. Barron et.al. [54] and Dobbins et.al. [47] in their two different studies they proved that the soaking period is important to the final properties of the tool steels and soaking period of 20 h is enough as the atoms in the material require time to diffuse to new locations.

On the contrary, Kamody [55] in his patent, asserts that the soaking period has no role in deciding the final condition of the material being processed and a soaking period of 10 min was recommended to allow the material to achieve thermal equilibrium before it is removed and reheated. Work by Moore [14] describes the effect of soaking time on three different steel samples. The hardness of two metals, Vanadis 4 and D2 tool steels, were found to be unaffected by the soaking time. A third steel however, H13 tool steel, showed a higher hardness after soaking for 400 min. Fig.-7 shows the effects of varying soaking time on the hardness of H13 tool steel. After 400 min, H13 showed little improvement in hardness. They also asserts that an optimum soaking time may therefore exist for each type of material, though as one can see from Fig.-7, the difference in properties between different soaking times may be quite small.

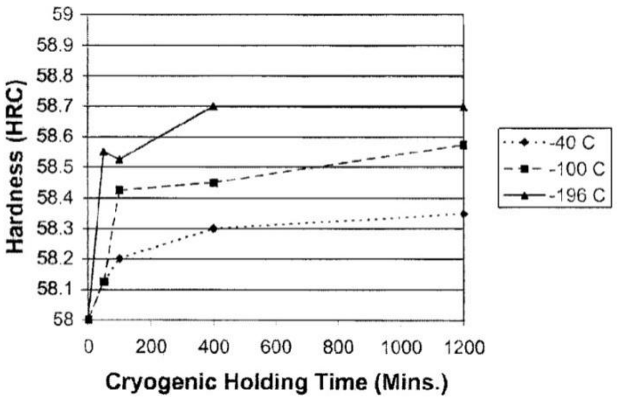


Fig.-7 Changes in hardness of H13 tool steel with soaking time.

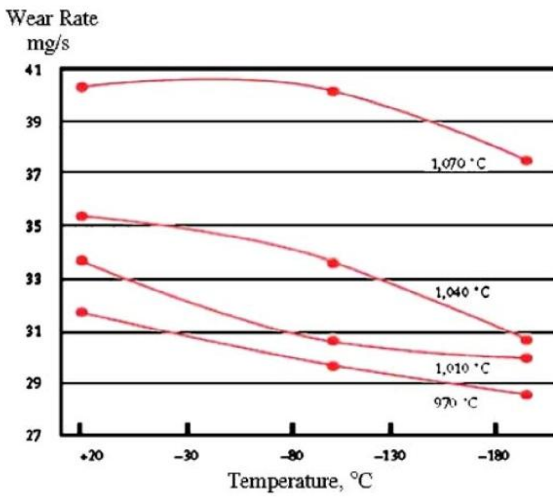
3.3 Soaking Temperature:

Soaking temperature is the temperature at which the samples are held to be cryogenically treated by using liquid nitrogen. Samples can be soaked to a minimum of −196^{0}C (77K), the boiling temperature of nitrogen. Many researchers believe that depending upon the material, complete transformation takes place at the lowest temperature [50]. Darwin et al. [44] concluded in their study that the soaking temperature is the most significant factor and the maximum percentage contribution of soaking temperature on the wear resistance of the SR34 piston ring material was 72%. An optimum lowering temperature of steel to be around 89K (-300^{0}F), should take several hours. The reason is that, the internal temperature at core and surface temperature of the specimen being treated significantly should not differ, to avoid any possibility of cracking. The more recent application, known as deep cryogenic processing, subjects to the material to be controlled lowering of the temperature to −196°C [21]. Babu et. al. [56] conducted experiments at various temperatures from 0^{0}C (273K) to -190^{0}C (83K) on M1, H13, and EN 19 Steel and analyzed its effect on wear resistance of the steel. They concluded that with lowering down of cryogenic soaking temperature wear properties of the steel improved. They found overall improvement of about 3.2 to 3.8 times.

Reddy et. al. [57] have also concluded that the life of P-30 tool insert increases by 9.58% when treated at −96^{0}C (177K) and 21% when treated at −175^{0}C (98K). Bensely et.al. [23] in their study on EN 353 found that improvement in wear resistance by 85% more in case of samples treated at 193 K (SCT), than the conventionally treated. They also found the significantly increase in wear resistance by 3.2 times in case of samples treated at 77 K (DCT). Collins and Dormer et. al. [15] they studied the influence of low temperature treatment and concluded that wear rate decreases with lowering the cryotreatment soaking temperature as shown in Fig.-8
Further they also proved that the amount of carbides precipitated increases with lowering down the cryogenic soaking temperature for D2 cold-work tool steel as shown in Fig.-3. Barron [7] in another study on various materials (Table 2) concluded that the wear resistance was better in case of cryotreatment at 77K as compared to 189K. It indicates that lower temperature in cryotreatment is important for improvement of wear resistance in most of the materials.

Table 2.—Wear resistance ratio for the two CTs

	Wear resistance ratio, R_w/R^0_w	
Material	**189K soak**	**77K soak**
	Group I	
D-2	**3.164**	**8.177**
S-7	**2.417**	**5.031**
O-1	**2.216**	**2.721**
A-10	**2.305**	**2.645**
M-1	**1.455**	**2.253**
H-13	**1.646**	**2.094**
T-1	**1.418**	**1.763**
	Group II	
440 SS	**1.280**	**1.218**
M-2	**1.125**	**1.204**
430 SS	**1.162**	**1.199**
8620	**1.037**	**1.116**
303 SS	**1.053**	**1.108**
	Group III	
CPM-10V	**0.939**	**1.313**
A-2	**0.982**	**1.116**
	Group IV	
P-20	**1.231**	**0.972**
	Group V	
C1020	**0.982**	**0.972**
AQS	**0.966**	**0.964**



The work of Mohanlal et al. [26] concluded that tempered samples when cryotreated at 133 K for 24 h yielded negative results but when cryotreated at 93 K for 24 h the results were favorable. In contrary to all the above-cited studies, Seah et al. [58] observed no significant gain in wear resistance of tungsten carbide inserts by cryoprocessing at −80°C or −196°C.

3.4 Tempering

Tempering is the process of reheating the steel at predetermined temperatures which is lower than the transformational temperature to obtain different combinations of mechanical properties in steel. Tempering as-quenched martensite precipitates fine carbides, which are named as transition carbides. Nucleation of these carbides relieves micro-stresses in the brittle primary martensite and prevents micro cracking on surface of the steel. Tempering reduces residual stresses, increases ductility, toughness and ensures dimensional stability.

During tempering, martensite rejects carbon in the form of finely divided carbide phases. The end result of tempering is a fine dispersion of carbides in the α-iron matrix, which bears little structural stability to the original as-quenched martensite. Hence, the microstresses and hardness of all the samples are reduced after tempering.

Avner [59]and Vanvlack [60] have explained that the tempering reduces hardness and residual stress but it increases ductility and toughness and also it provides dimensional stability. They observed that a progressive reduction in compressive stresses from CHT (+245 MPa), to SCT (+145 MPa) and DCT (+115 MPa), respectively. The influence of cryogenic treatment on the martensitic microstructure seems to be the sole factor affecting present value of residual stress after temper-ing. Darwin et al. [42, 44] concluded in their study that the contribution of tempering temperature on the wear resistance of the SR34 piston ring material was 2%, and effect of Tempering Period is insignificant. The cryogenically treated steels are harder and brittle as compared to untreated one due to difference in martensite contents. Generally, low-temperature tempering at 150–200^{0}C (423–473K) after DCT is performed to relieve any residual brittleness/thermal stresses of the treatment [24, 26, 61]. Zhirafar et.al. [22] as shown in Fig. 9; cryogenically treated samples which show a slightly higher level of hardness over the tempering temperature range compared to the conventional heat treatment, this is due to formation of new martensite from retained austenite, and it is well supported by Thelning et al. [17].

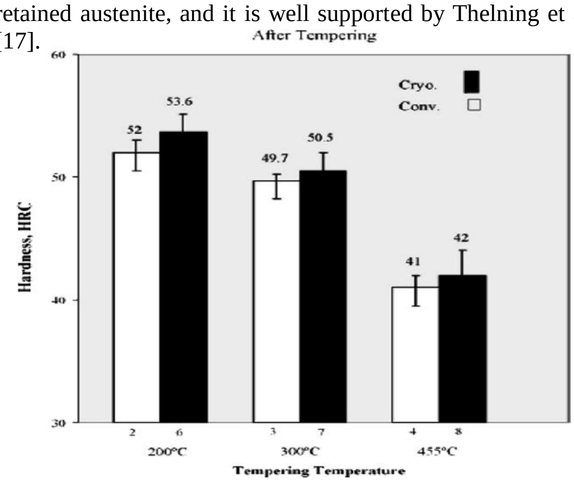


Fig. 9- Hardness for different tempering temperatures after cryogenic and conventional treatments

The overall hardness decreases with increase in tempering temperature when the tempering is carried after DCT. This has been observed by Leskovsek et al. [62] on AISI M2 high-speed steel under DCT. They reported that the wear rate of DCT material with one tempering cycle strongly depends upon its tempering temperature. The wear volume decreased by approximately 62% with increase of tempering temperature from 500^{0}C (773K) to 600^{0}C (873K). Seah et al. [58] have considered Tungsten Carbide cutting tool inserts to find effects of SCT and DCT followed by tempering in three cycles on mechanical and metallurgical properties of Tungsten Carbide.

Another cycle, as shown in Fig.-10, with two and three tempering cycles has also been studied. It has been observed that only one tempering cycles may attribute to excessive brittleness of the material, whereas more than one number of cycles will make the tool tougher and release the stresses at the cost of small reduction of brittleness to increase the life of the tool [33, 63].

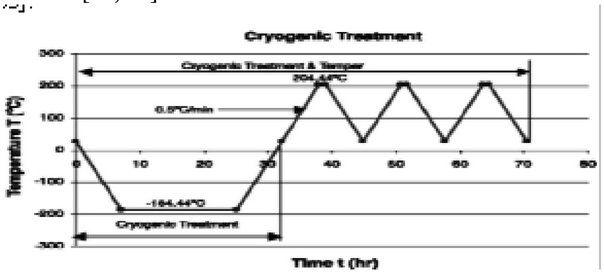
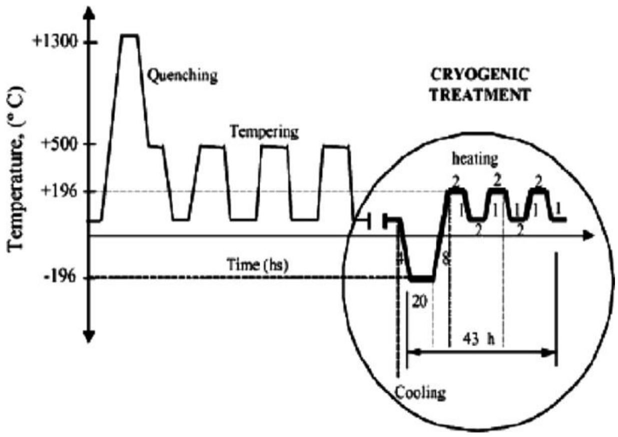


Fig.-10-CT cycle

In a study on AISI-M2 steel high-speed steel, Silva et al. [25] have followed three tempering cycles along with CT cycle with holding time of 2h during each tempering cycle as shown in Fig.-11 for better distribution of the heat and to achieve homogeneous metallurgical properties throughout the material [25].



Pen-Li Yen et.al. [64] reported that, the content of eta-carbide increases with tempering time at both 477K (204 C or 400 F) and 811K (538°C or 1000°F). They pointed out that eta-carbides precipitate during the tempering process only and that the longer the tempering time, the more eta-carbides precipitate. The result also shows that higher content of eta-carbide s are found for groups tempered at 811K (538 C or 1000°F) than for those groups tempered at 477K (204°C or 400°F. It is also concluded that tempering after CT on W18Cr4V and WOMoSCr4v2 steel can increase their impact toughness by 58% and 43%, respectively [6]. Yun et al. [52] have also stated that the post-tempering DCT gives a remarkable increase of the ultimate tensile strength by 11%.

Each material is to be assessed separately and the treatment parameters to be decided; that will depend upon the combination of wear resistance, hardness, and toughness required to be achieved. Many researchers have worked by changing various parameters to find the standard method and sequence to optimize the process with different materials.

4. METALLURGICAL ASPECTS

In the cryogenic treatment, to optimize the metallurgical aspects by material to be treated under very cold low temperature for a predetermined period of time to obtain the metallurgical crystalline structure of the material to improve the hardness, strength, ductility, toughness, were resistance etc. and to reduction in residual stresses, which improves the stability during the machining.

There are four main metallurgical aspects that claim to explain the changes in properties of cryoprocessed materials: Transformation of Retained Austenite to Martensite, Formation of Eta (η)–Carbides, Precipitation of ultrafine Carbides, Homogeneuous Microstructure. These three processes are described below.

4.1 Transformation of Retained Austenite to Martensite

Akhbarizadeh et.al. [66] studied on wear behavior of D6 tool steels they observed that, in tool steels, a low percentage of austenite is retained after the conventional heat-treatment named “retained austenite”. The retained austenite as a soft phase in steels could reduce the product life and, in working conditions, it can be transformed into martensite [26]. This new martensite could cause several problems for working tools. This new martensite is very brittle and differs from the tempered one, which is used in tools. Furthermore, this martensite causes micro cracks and reduces the product life. Moreover, the retained austenite-to-martensite transformation provides dimensional instability [26].

Das et.al. [67] in their experimental study on AISI D2 steel observed that the presence of high carbon and high alloying elements in tool/die steels lower their characteristic temperatures of martensite start and martensite finish; the latter lies well below the ambient temperature for commercial tool/die steels [16]. Therefore, conventional hardening treatment of these steels fails to convert considerable amount of austenite into martensite often leading to unacceptable level of retained austenite (γ_R) in the as-quenched structure of these steels. The γ_R is soft and thus adversely affects the desirable properties such as hardness and wear resistance (WR) [16,17]. Moreover, γ_R is unstable and transforms into martensite at the service conditions of tool/die steels. The freshly formed martensite being untempered is very brittle and hence undesirable. Pen-Li Yen et. al. [64] studied on the alloy steels they concluded that, the content of austenite before cryogenic treatment is 17.7% and decreases to 7.8% after cryogenic treatment. This indicates that cryogenic treatment causes the transformation of significant amounts of retained austenite to martensite. Bensely et. al. [36] in their experimental study on case carburised En353 steel, found that the amount of retained austenite in CHT, SCT and DCT samples was found to be 28%, 22% and 14% respectively. Furthermore they claimed that DCT steel when subjected to tempering has undergone a reduction in compressive residual stress. Such stress reliving behaviour was mainly due to the increased precipitation of fine carbides in specimens subjected to DCT with tempering.

However, Jun Wang et. al. [68] studied on micro-structure and abrasion resistance of high chromium they concluded that, cryogenic treatment can effectively reduce the retained austenite content after the destabilization heat treatment, but cryogenic treatment cannot make retained austenite transform to martensite completely.

Fig.-12 shows the transformation of the lattice structure and occupied atomic sites.

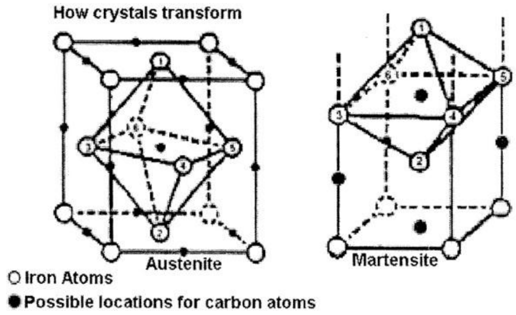


Fig.-12 Transformation of retained austenite to martensite

4.2 Precipitation of Fine η- Carbides

Philip Nash et.al. [71] in their study on M2 tool steel claimed that the advantage of using deep cryogenics is due to an enhancement of the precipitation of fine eta-carbides during the subsequent temper. The strain energy in the martensite lattice increases at a lower temperature. As a consequence Carbon atoms migrate and form a clusters. During the subsequent heating back to the room temperature or even a tempering, these clusters act as nuclei for the formation of the ultra fine eta-carbides. The eta-carbides that form are uniformly distributed throughout a highly decomposed microstructure.

Das et.al. [70] Observed in their study on AISI D2 steel that the sub-zero treatments do not alter the nature of primary and/or secondary carbides. The improvement in population density of small secondary carbides is 193% by deep cryogenic treatment against 80% by cold treatment and 109% by shallow cryogenic treatment, when these are compared with respect to the conventional heat treatment. Results related to the micro-structural analyses, thus, assist to infer that sub-zero treatments not only alter the amount of retained austenite content but also considerably modify the precipitation behavior of secondary carbides which is observed to be increasingly pronounced in the order of cold treatment, shallow cryogenic treatment and deep cryogenic treatment. Das et. al. [67] in their another study on sub-zero treatments of AISID2 steel they inferred that, the degree of precipitation of secondary carbides during tempering of martensite not only depends on the amount of martensite in as-quenched structure but is also controlled by the state of tempering of martensite. Further they also concluded that, sub-zero treatments accelerate the decomposition of martensite and modify the precipitation behavior of secondary carbides on AISI D2 steel. Das et.al. [31] further they concluded that, correlation of the examined microstructures with their wear behaviour unambiguously establishes that substantial modification in the precipitation behaviour of SCs and reduction in γ_R content are the governing mechanisms for the improved of WR of tool/die steels by DCT.

Paulin [72] also verified the presence of fine precipitated carbide particles and their importance to the material properties. The precipitated carbides reduce internal tension of the martensite and minimize microcracks susceptibility, while the uniform distribution of fine carbides of high hardness enhances the wear resistance. Collins and Dormer [15] later reiterated the same view using extended experimental investigations. Low-temperature conditioning of martensitic structure implies crystallographic and microstructural changes which, on reheating, result in the precipitation of a finer distribution of carbides in the tempered microstructure with consequent increase in toughness as well as in wear resistance. Meng et al. [73,37] it was envisaged by these authors that cryogenic treatment improves preferential precipitation of fine η-carbides during the primary stage of tempering in a high-carbon alloy steel. These carbides might enhance the strength and toughness of the martensite matrix and thus improve the wear resistance.

4.3 Formation of Eta (□)-Carbides

Senthilkumar et.al [74] observed that the mechanism of this process responsible for stabilization of the structure has considerable impact. This stress is caused by the spatial variation in composition and microstructure which leads to different thermal contraction and also by the transformation of retained austenite to martensite. The martensite wants to be cooled below a certain temperature to develop internal stress sufficient to generate crystal defects. The required long holding time suggests a localized carbon distribution occurring by clustering of carbon atoms to lattice defects (dislocations). The martensite becomes more super-saturated with decreasing temperature. This increases the lattice distortion and thermodynamic instability of the martensite, both of which compel carbon and alloying atoms to segregate nearby defects. These clusters act as or grownup into nuclei for the formation of carbides when tempered subsequently. Above observations are agreement with Das et.al. [75] on their experimental study on the wear resistance of tools steels.

Zhirafar et.al. [22] studied the effect of cryogenic treatment on mechanical properties of 4340 steel they observed that, in general, hardness and fatigue strength of the cryogenically treated specimens were a little higher whereas the toughness of the cryogenically treated specimens was lower when compared to that of the conventionally treated steel. Neutron diffraction showed that the transformation of retained austenite to martensite occurred which, along with possible carbide formation during tempering, is a key factor in improving hardness and fatigue resistance of the cryogenically treated specimens.

By reviewing the literature survey, it is observed by Bensely et.al. [46] in their study on case carburised steel-815M17 that, micro-structural analysis of the specimen after cryogenic treatment, showed the presence of ultra fine Eta (η) carbides precipitates of size in the range of 10 nm these were characterized as η-carbide. Alexandru et.al [76] also observed that cryogenic cooling induced the occurrence of very fine carbides with dimension less than 1 μm, which occupy microvoids and contribute to an increase of the density. Meng et. al. [37] proposed that greater wear resistance can be obtained with longer soaking periods (~24h) because of the formation of η−carbides which improves the wear resistance to the maximum possible extent.

Transformation of austenite to martensite at cryogenic temperature followed by prolonged holding induces micro-internal stresses which results in the formation of crystal defects such as dislocations and twins [52,72,77,78]. While, lattice distortion and thermodynamic instability of martensite at 77 K drive carbon and alloying atoms to segregate at the nearby crystal defects. These segregated regions have been hypothesized as the newer sites for nucleation of SSCs [20].

4.4 Homogeneuous Microstructure

Pete Paulin et.al.[72] studied on Frozen Gears they observed that ,deep cryogenically treated metals also develop a more uniform, refined microstructure with greater density. Microfine carbide “fillers” are formed, which take up the remaining space in the micro – voids, resulting in a much denser, coherent structure of the tool steel. The end result is increased wear resistance. Huang et al. [78] confirmed that cryogenic treatment not only facilitate the carbide formation but can also make the carbide distribution more homogeneous. Alexandru Ailincai and Baciu et. al. [76] mentioned that the structure of cryogenically cooled metallic materials has a more uniform and dense microstructure than non-cryogenically treated samples. Das et. al. [67] studied on sub-zero treatment of AISI D2 steel they concluded that, in general, sub-zero treatments refine the size of the secondary carbides, increase their amount and population density, and lead to their more uniform distribution in the microstructures. These favorable modifications of secondary carbides are found to be significantly higher in deep cryogenically treated specimens than that in cold treated or shallow cryogenically treated specimens.

Recent investigations [15,24,36,39,52], however, have established that sub-zero treatments not only substantially lower the retained austenite content but also significantly modify the precipitation behavior of carbide, resulting into considerable change in the characteristics of secondary carbide particles in the microstructure of tool/die steels. The extents of these alterations are reported to be dependent on the types of sub-zero treatments [31]. Microstructural modifications imparted by sub-zero treatments are expected to have considerable influence on the mechanical properties of tool/die steels.

However, the mechanism of microstructure changes in alloys under various treatments, are not yet fully understood [79]. Change in microstructure effects on tool life under certain treatments [63].

5. IMPROVED MECHANICAL PROPERTIES OF STEELS

Any property changes are attributed to the microstructural changes.Here we discuss the improved properties of steels like Abrasion Resistance, Ductility**,** Fatigue Resistance, Hardness, Residual Stresses, Tensile Strength, Toughness and Wear Resistance.

5.1 Abrasion Resistance

Hao-huai Liu et al. [80] investigated the effects of cryogenic treatment on the microstructure and abrasion resistance of CrMnB high-chromium cast iron they found that after cryogenic treatment, the hardness and abrasion resistance of CrMnB high-chromium cast iron can be improved due to the precipitation of carbides, the martensite transformation, and a refined microstructure resulting from cryogenic treatment. Hao-huai Liu et al. [81] in their study on the effects of deep cryogenic treatment on the microstructure, hardening behavior, and abrasion resistance of 3Cr13Mo1V1.5 high chromium cast iron. The results showed that deep cryogenically treated specimens after sub-critical treatment had an increase in hardness and abrasion resistance. This was due to abundant retained austenite transforming into martensite and secondary carbides precipitation.

Pete Paulin et. al. [72] studied the Frozen Gears they inferred that, the Barron study looked at how the changes brought about by cryogenic treatment affected steel's ability to resist abrasive wear. It found that the martensite and fine carbide formed by deep cryogenic treatment work together to reduce abrasive wear. The fine carbide particles support the martensite matrix, making it less likely that jumps will be dug out of the cutting tool material during a cutting operation and cause abrasion.

5.2 Ductility

Das et.al.[70] studied on fracture toughness of AISI D2 steel that the ductility of tempered martensite matrix is controlled by the amounts of dissolved carbon and alloying elements. Enhancement of fracture toughness by refinement of carbides and the improvement of the matrix characteristics by controlling the alloying elements and heat treatment conditions has recently been reported by Kim et al. [82] for AISI M2 steels. Formation of higher amount of secondary carbides increases the ductility of the matrix by reducing the amounts of dissolved carbon and alloying elements [83]. Ductility of the matrix of deep cryogenically treated specimen should be higher which is evident from the presence of numerous small but well defined voids in its fracture surface.

5.3 Fatigue Resistance

Kalsi et. al.[50]observed that fatigue behavior of tool steel is one of the most important properties due to fluctuating stresses and thermal loads on the tool during in service. Life of the tool is affected a lot with fatigue behavior. CT restricts the dislocation of martensite and fine carbide for higher fatigue loads, resulting in longer tool life. Despite this, little work has been done in studying fatigue behavior of material under DCT.

Zhirafar et al. [22] in their experimental study on the mechanical properties of 4340 steel they concluded that, the fatigue limit of the steel was improved after cryogenic treatment and tempering. In another study by Singh et al. [35,84], fatigue life of cryogenic treated AISI 304L weldment was presented. The fatigue life of CT specimen was improved up to 100%. The effect of retained austenite on the properties of steel includes decrease in tensile strength, fatigue resistance, yield strength, and compressive residual stresses. DCT improves the same by transformation of retained austenite to martensite, thereby improving the fatigue resistance [85]. Baldissera [86] has illustrated improvement in fatigue behavior of the carburized 18NiCrMo5 steel. This is attributed to both fine carbides precipitation and residual stress changes.

However, Bensely et. al [87] studied and show that the overall fatigue life has been reported to be increased (71%) by cold treatment but decreased (26%) by deep cryogenic treatment.

5.4 Hardness

Harish et al. [88]have reported improvement in hardness (14%) and reduction in impact toughness (5%) for En31 bearing steel due to deep cryogenic treatment when compared to that obtained by conventional heat treatment. Rhyim et al. [89] and Wierszyłłowski et al. [90] have reported that deep cryogenic treatment improves hardness but reduces impact toughness of AISI D2 steel as compared to conventional heat treatment. Akhbarizadeh et. al. [66] studied on wear behavior of D6 tool steel they observed that, the cryogenic treatment increases hardness. The samples which were cryogenically treated for a longer time (SCT40) or deep cryogenically treated (DCT) showed further increase in hardness. Baldissera et. al. [6] studied on static mechanical properties of 18NiCrMo5 carburized steel, the results they pointed out substantial hardness increases (from +0.6 HRC to +2.4 HRC) for all the cryotreated groups and a remarkable enhancement of the tensile strength (+11%) in one case, indicating that different sequences and DCT parameters must be considered depending on the application requirements. Further they concluded that, the pre-tempering DCT allows to obtain substantial increases of the superficial hardness, up to +2.4 HRC points (M_{24} group), without significant effects on the UTS values.

R. Mahmudi and co-workers [91] studied the effect of cryogenic treatment on the mechanical properties and wear behavior of high-speed steel M2. They concluded that deep cryogenic treatment improves hardness and wear resistance due to advanced state of the transformation of retained austenite and also some precipitation of eta-carbide particles. Their results are shown below.

Shaohong Li et. al. [92] studied on cold work die steel Cr8Mo2SiV they concluded that, the effects of DCT on static mechanical properties show an increase of hardness and decrease of toughness. Mohan Lal et al. [93] studied the effect of cryogenic treatment on T1 type-high speed material and found that soaking at 203 K can attain the maximum hardness of 67 HRC. Even if the deep cryogenic treatment does not influence the hardness, it increases both toughness and wear resistance [33].

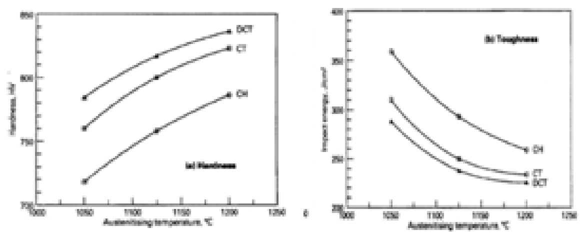


Fig.-13 Eeffect of austentizing Temperature and Cold Treatment on a) Hardness and b) Toughness Where, CH– conventional heat treatment CT–Cold treatment DCT-Deep cryogenic treatment

Jun Wang et. al. [68] studied on high chromium cast iron 16Cr1Mo1Cu cast iron they observed that, the hardening behavior of the alloy subjected to destabilization with air cooling and cryogenic are illustrate in Fig.-14. In destabilization treatment with air cooling, the hardness of the alloy increases until the temperature reaches 1000 °C, and then the hardness falls.

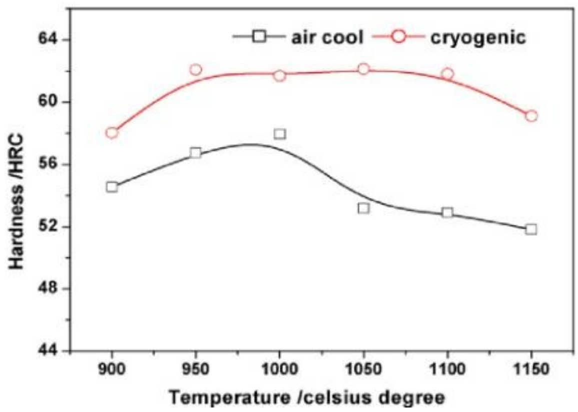


Fig.- 14 The hardening curves of high chromium cast irons after air cool and cryogenic [68].

5.5 Residual Stresses

In recent years metallurgists and engineers tried their efforts in improving the fatigue and impact properties of metals by deliberately producing compressive residual stresses in to the surface of engineering materials. Residual stresses are the stresses that remain within a part after the original cause of the stresses (external forces, heat gradient) has been removed. Kalpakjian et.al [94] pointed out that the residual stresses remain along a cross-section of the component, even without the external cause. Samant and Dahotre et. al. [95] described that these internal stresses become evenly balanced by themselves. They existed in a free body that had no external forces or constraints acting on its boundary.

Senthilkumar et. al. [74] studied on the residual state of stress of 4140 steel, they observed that, residual stresses are caused by means of load or thermal gradients or both. These stresses are developed during different processes like non uniform plastic deformation during cold working, shot peening, surface hammering, grinding, welding, phase transformations, and high thermal gradients. Further they concluded that in 4140 steel maximum compressive stresses develop after DCT, before tempering. This was highlighted to positively influence the state of stress after stress relieving. Compared to tensile stresses observed in CHT and SCT samples, residual compressive stresses were found after DCT. Bensely et. al.[36] stated that Scientists and engineers have been successful in improving the impact and fatigue properties of metals by intentionally introducing residual stresses into the surface of these materials. Residual stress exists in an elastic solid body in the absence of, or in addition to, the stresses caused by virtue of load or temperature or both. Such stresses can arise from deformation during cold working, in welding from weld metal shrinkage, and in changes in volume due to thermal expansion. In recent years, there has been a considerable interest in the properties and development of compressive residual stress. Knowledge of the nature of residual stresses is of paramount importance since they can lead to creep failure, fatigue and stress corrosion cracking in sensitive materials. Mack Alder and Olsson [96] have observed that after case hardening, the gear tooth would experience compressive residual stresses, which are beneficial in maintaining an appreciable endurance limit.

Lower the temperature of cryogenic treatment, greater will be the transformation of austenite to martensite and hence, greater will be the compressive residual stress induced. This compressive residual stress is beneficial with respect to wear and fatigue [85]. This was evident in the earlier research on wear resistance of cryogenically treated En 353 steel [23]. Furthermore Bensely et. al. [36] in their experimental study on case carburized En 353 steel they pointed out that, a comparative study of the three treatments revealed that there was an increase in the compressive residual stress in steel that was subjected to cryogenic treatment prior to tempering. The experimental investigation revealed that deep cryogenically treated steel when subjected to tempering has undergone a reduction in compressive residual stress. Such stress relieving behavior was mainly due to the increased precipitation of fine carbides in specimens subjected to DCT with tempering.

Huang et al.[24]pointed out that the substantial relief of compressive residual stress occurred in the SCT and DCT samples after stress relieving or tempering. The reason is due to the occurrence of finer carbide precipitates throughout the matrix and the loss of tetragonality of martensite. However, the stress relief is higher for the CHT sample, which was not subjected to sub zero treatment.

5.6 Tensile Strength

Xiong et al. [97] reported that the ultimate tensile strength, yield strength and elongation of the cryogenic treated magnesium alloy added with zirconium have improved to 38%, 57% and 280% respectively, as compared to those of the same alloy without cryogenic treatment.

Arockia et. al. [43] studied on the tensile behavior of En 52 and 21-4N valve steels post DCT they observed that the results show a 7.84% improvement in the tensile strength for the En 52 valve steel and 11.87% improvement for the 21-4N valve steel when compared to that of the samples without the cryogenic treatment. Further they also concluded that the deep cryogenic treatment enhances the tensile strength of the valve steels with a marginal reduction in the elongation. The enhancement in the ultimate tensile and yield strength are attributed to the transformation of the retained austenite into martensite and the precipitation of fine carbides. Similarly, Baldissera and Delprete [6] reported that the tensile test results of 18NiCrMo5 carburized steel shows a significant increase of about 11% in the ultimate tensile strength by performing the DCT after the tempering.

However, studies related to the influence of sub-zero treatments on the mechanical properties other than hardness are few and contradictory in nature. For instance, Bensely et al. [46] have shown that deep cryogenic treatment reduce tensile strength by 9% with respect to conventional heat treatment, in contrast, Baldissera et al. [86] have shown that tensile strength improves by 11% due to deep cryogenic treatment over conventional heat treatment; both these studies are related to case carburized bearing steel with near identical chemical compositions.

5.7 Toughness

It is commonly accepted that the reduction of retained austenite content decreases fracture toughness of ferrous materials [122]..

Das et. al. [70] studied on Influence of sub-zero treatments on fracture toughness of AISI D2 steel they concluded that, In general, sub-zero treatments reduce fracture toughness of the selected steel as compared to that of the conventionally heat treated ones. However, the degree of reduction in fracture toughness varies with the types of sub-zero treatments; it is lowest for deep cryogenically treated specimens but highest for shallow cryogenically treated ones..

Similar observations related to reduction of toughness by deep cryogenic treatment over conventional heat treatment has been reported for 4340 steel by Zhirafar et al. [22], En31 steel by Harish et al. [88] and for D2 steel by Collins and Dormer [15], Wier-szyllowski et al. [90] and Rhyim et al. [89]. Only Cajner et al. [98] and Molinari et al. [33] have reported the effect of deep cryogenic treatment on the variation of fracture toughness, though estimated by non standard approaches. Cajner et al. [98]have reported marginal reduction of fracture toughness of PM S390 MC high speed steel, whereas in sharp contrast Molinari et al. [33]have reported considerable improvement in fracture toughness of AISI H13 steel by deep cryogenic treatment over conventional heat treatment.. Zhirafar et. al. [22] studied on the mechanical properties of 4340 steel they concluded that, by employing the cryogenic treatment showed slightly detrimental effects (14.3% decrease) on the impact energy toughness prior to tempering. The fracture features of steel subjected to the cryogenic treatment showed less shear lips compared to the conventionally treated ones, indicating less energy absorption.

However, Senthilkumar et. al. [74] studied on 4140 steel and they concluded that, the toughness of the 4140 steel is not significantly influenced by SCT and DCT samples with respect to CHT samples. These results are agreement with the result obtained by Kollmer [99] also could not find any significant improvement in toughness while DCT on 4140 cold-rolled steel.

5.8 Wear Resistance

The benefit of cryotreatment for the enhancement of wear resistance of tool steels has been cited by several researchers [7,15,20,23,26,33,37,41,45,61,62]. However, the mechanisms responsible for enhancing the wear resistance by cryotreatment are yet to be clearly established. Some investigators [7,61] contend that the enhancement of wear resistance occurs only due to transformation of γ_R to martensite. But, this phenomenon is a common feature to both the cold treatment and the cryotreatment, and thus the significant enhancement of wear resistance of tool steels by cryotreatment vis-à-vis cold treatment cannot be solely attributed to the minimization of γ_R [15,20,37,41,52,77].Several investigators[20,21,23,24,26,77,79] indicate that the refinement of secondary carbides is the major cause for the improvement in wear resistance by cryotreatment; but this opinion lacks appropriate experimental evidences [20,23,26,77].

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Babu et al. [56] (01) have reported that abrasive WR of M1, H13 and EN19 can be improved from 193% to 289% by cold treatment and from 315% to 335% by deep cryogenic treatment in comparison to conventional heat treatment depending on the type of material. Result analysis is summarized as shown in fig.-15. Mohan Lal et al. [26] have studied the effect of sub-zero treatment on the WR of T1, M2 and D3 steels and concluded that WR increases in the order of conventional heat treatment, cold treatment and deep cryogenic treatment. One of the main aims of sub-zero treatment is to enhance the WR of steels. For example, the improvement in WR of AISI D2 steel by deep cryogenic treatment over conventional heat treatment varies from 108% as reported by Collins and Dormer [15] to 817% as reported by Barron [7].

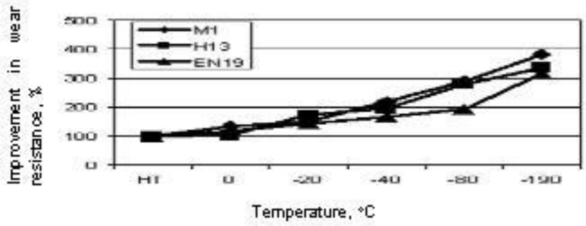

Fig.-15 Wear resistance analysis

Wilson [100] concluded that cryogenically treating slitter knives in paper mills increases the lifetime by more than 500%. The improvement in wear life is due to complete transformation of the retained austenite to martensite at cryogenic temperatures; the amount of retained austenite in typical steel is reduced by a factor of three by the cryogenic treatment. This leads to a small increase in the size of the component, and enhanced stability of the component. Bensely et al. [23] studied the wear resistance of case carburized EN 353 steel after shallow and deep cryogenic treatment and concluded that the improvement over conventional heat treatment was 85% and 372% for SCT and DCT, respectively. Arockia et. al. [101] studied on wear resistance of En 52 and 21-4N valve steels they observed that, the wear resistance of En 52 and 21-4N has improved by 81.15% & 13.49% respectively, due to shallow cryogenic treatment, 86.54% & 22.08% respectively, due to deep cryogenic treatment, when compared to the conventional heat treatment. The microstructural study suggests that the improvement in wear resistance and hardness is attributed to the conversion of retained austenite into martensite, along with precipitation and distribution of the carbides brought in by the cryogenic treatment.

Mohan Lal et. Al. [26] conducted a study on the improvement in wear resistance and the significance of the treatment parameters in D3, M2 and T1 tool & die steel in various treatment conditions. It was found that the cryogenic treatment imparts nearly 110% improvement in tool life.. The improvement in wear resistance and hardness was attributed to the conversion of retained austenite into martensite brought in by the cryogenic treatment. The high wear resistance obtained for the DCT sample was due to precipitation and finer distribution of carbides. J. Y. Huang et al [24] conducted the cryogenic treatment by soaking the samples in liquid nitrogen for 1 week and studied the microstructure changes of M2 tool steel before and after the cryogenic treatment. The results concluded that the cryogenic treatment facilitates the formation of carbon clusters and increases the carbide density in the subsequent heat treatment, thus improving the wear resistance of steels.

A. Joseph Vimal et. al. [102] studied the effect of the cryogenic treatment on En 31 steels at different stages of heat treatment and observed that through the cryogenic treatment the wear can be decreased by a maximum of 75%. Scanning electron microscopy study infers that the improvement in wear resistance and hardness is due to the complete transformation of austenite into martensite, coupled with the precipitation of a higher amount of fine carbides of the size less than 0.5 microns during the cryogenic treatment and subsequent tempering. P Stratton et. al. [103] experimental study on wear of case hardened components of 20 MnCr5 carburised steel they concluded that, The dry wear rate of optimally carburised 20MnCr5 was reduced by approximately 20% by deep cold treatment at -196 °C for 24 h. Fanju Meng et al.[37] have studied the effect of cryogenic treatment on the wear behaviour of Fe–12Cr–Mo–V–1.4C tool steel. The results have shown a dramatic increase in wear resistance especially at high sliding speeds. Microstructural analysis of the sample after cryogenic treatment has shown fine carbide precipitates of size in the range of 10 nm, which are characterized as η-carbide. This formation of η-carbides helps to improve the wear resistance. P. Paulin et. al. [104] has shown the differences in wear life, shown in **Table 2,** between parts cold treated at about –80°C (–110 °F), and parts cryogenically treated at –190°C (–310 °F) using liquid nitrogen.

Table 2: Percentage Increase in Wear Resistance after Cold Treatment and Cryotreatment

US steel designation and corresponding German standards		**Description**	**At –79 °C (–110 °F)**	**At –190 °C (–310 °F)**
AISI(USA)	**DIN**(BRD)	**Materials that showed improvement**	**In percent**	**In percent**
D2	1.2379	High carbon/chromium steel	316	817
S7		Silicon tool steel	241	503
52100	1.3505	Bearing steel	195	420
O1	1.2510	Oil hardening cold work die steel	221	418
A10		Graphite tool steel	230	264
M1	1.3346	Molybdenum high speed steel	145	225
H13	1.2344	Hot work tool steel	164	209
M2	1.3341	Tungsten/molybdenum high speed steel	117	203
T1	1.3355	Tungsten high speed steel	141	176
CPM 10V		Alloy steel	94	131
P20	1.2330	Mold steel	123	130
440		Martensitic stainless steel	128	121
		Materials without significant improvement		
430		Ferritic stainless steel	116	119
303	1.4305	Austenitic stainless steel	105	110
8620	1.6523	Case hardening steel	112	104
C1020	1.0402	0.20 % carbon steel	97	98
AQS		Grey cast iron	96	97
T2		Tungsten high speed steel	72	92

Dhokey et. al. [105] studied on Dry sliding wear of cryotreated multiple tempered D-3 tool steel and they concluded that, It was seen that wear rate was lowest in single tempered D-3 steel, that is 93% reduction in wear rate than that of HT. Das et. al. [31] studied on AISID2 steel and they observed that the correlation of wear properties (Fig. 10) with the results of microstructural analyses reveals that the improvement in WR is dependent on the microstructures generated by different heat treatments apart from its dependence on the test conditions. It can be reiterated at this stage that the reduction of □γ_R content and modifications in the size and distribution of SCs are the primary factors responsible for the improvement in WR by DCT over that obtained by the CHT and cold treatment (CT).

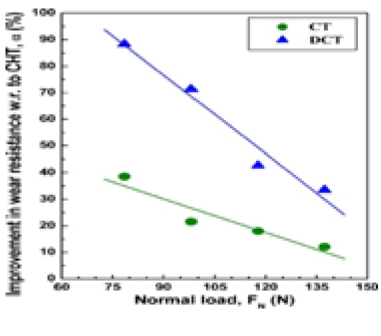

Fig. 10. Variation of estimated degree of improvement in wear resistance of CT and DCT specimens with respect to CHT specimens as a function of applied normal load in wear tests

6 EFFECT OF CRYO-TREATMENT ON DIFFERENT TYPES OF STEEL & THEIR APPLICATIONS

6.1 Steels

AISI 4340 steel

Zhirafar et. al. [22] investigated the effects of cryogenic treatment on the mechanical properties and microstructures of AISI 4340 steel. Mechanical tests, including rotating fatigue, impact, and hardness were carried out. Fracture features of specimens were compared. It was shown that in general, hardness and fatigue strength of the cryogenically treated specimens were a little higher whereas the toughness of the cryogenically treated specimens was lower when compared to that of the conventionally treated steel. Neutron diffraction showed that the transformation of retained austenite to martensite and possible carbide formation occurs simultaneously during tempering. This was the key factor in improving hardness and fatigue resistance of the cryogenically treated specimens

6.2 Carburized Steels

Baldissera et. al. [6] studied deep cryogenic treatment (DCT) on materials, its effects on the static mechanical properties of a commercial gear carburized steel (18NiCrMo5) are investigated through hardness and tensile tests followed by optical fractographic observations. The results point out substantial hardness increases (from +0.6 HRC to +2.4 HRC) for all the cryotreated groups and a remarkable enhancement of the tensile strength (+11%) in one case, indicating that different sequences and DCT parameters must be considered depending on the application requirements.

Bensely et.al. [46] in their another study on tensile behavior of case carburized steel-815M17 they concluded that, a reduction in tensile strength for SCT and DCT samples over CHT by a factor of 1.5% and 9.34%, respectively. However, considering the improvement achieved in earlier studies for wear resistance, where improvements of 85% for SCT and 372% for DCT were reported, the marginal reduction in tensile strength suggests the reduced tensile strength is an acceptable tradeoff in the optimization efforts. Preciado et al. [45] studied the effect of deep cryogenic treatment on the hardness and WR of carburized steels used in gears. The performance of the deep cryogenic treatment on quenched and tempered (first stage of tempering) steels, increased the WR but the hardness was only increased in steels tempered at 473K. It was suggested that the possibility of creation of nuclei sites during the 473K tempering, where new segregations of carbon and alloying elements could cluster during the cryogenic treatment producing an increase in the hardness.

Surberg et.al.[106] investigated the effect of various deep cold treatments on the properties of two common carburizing steels (16MnCr5 and 21NiCrMo2, or UNS G51170 and UNS G86200, respectively), both with and without tempering after the cryogenic treatment and also determining effects of such deep cold treatments at temperatures down to -150ºC (-238ºF) for up to 24 hours,they concluded that, for both carburized 16MnCr5 and 21NiCrMo2, the longer and colder the deep cold treatment, the more of the retained austenite in the case was converted to martensite. In both steels, the case appeared more refined and homogeneous after deep cold treatment. For 16MnCr5, the deep cold treatments only marginally reduced the compressive stresses in the case, but for 21NiCrMo2, the maximum compressive stresses were produced by treatment at -120ºC. Deep cold treatment had a negligible effect on the core properties of either steel.

6.3 Tool Steels:

D2 tool steel

Collins [15] conducted experiments to study the effect of deep cryogenic treatment of D2 tool steel on its hardness, toughness, WR, and microstructure. The study was conducted with respect to various heat treatment parameters like austenitizing temperatures, tempering temperatures, and cryogenic treatment temperatures (viz. 143K and 77K). The results showed that samples with austenitizing temperature between 1283K and 1373K, followed by deep cryogenic treatment (DCT) at 77K and single tempering at 473K had the maximum hardness. It is also noted that the improvement in toughness is greatest for samples austenitized at lower temperatures. The wear rate was lowest with the sample austenitized at 1243K and cryogenically treated at 77K followed by tempering at 473K. The study concludes that those samples treated at the lower austenitizing temperatures, with more martensite in the initial as-quenched condition, undergo more conditioning at the deep cryogenic temperature with consequent increase in both toughness and WR. Akhbarizadeh et.al.[66] on wear behavior of D6 tool steel, it was observed that the cryogenically treated samples have higher wear resistance. Com-pared with the conventionally heat-treated samples (CHT), this improvement was 5–11% in SCT20 and 39–68% in the deep cryo-genically treated samples.

Huang et. al. [78] studied the microstructure changes of M2 tool steel before and after cryogenic treatment. It was found that cryogenic treatment can facilitate the formation of carbon clustering and increase the carbide density in the subsequent heat treatment, thus improving the WR of steels. Mohan Lal et al. [107] carried out experiments in T1 type tool specimens to study the hardness improvement, induced residual stresses and microstructural variations after cryogenic treatment. The study concluded that quenching tool specimen at 203K attained a maximum hardness of 67 HRC. Also it is concluded that the transformation of austenite to martensite is an isothermal process but holding at 203K beyond 3hrs did not result in further transformation. The microstructural observations revealed that larger alloy carbides are broken into finely dispersed carbides in 2hrs and more soaking time.

T1, M2, and D3 steel

Mohan Lal et al. [26] studied the improvement in WR and the significance of treatment parameters in T1, M2, and D3 steel. It was found that cryogenic treatment imparts nearly 110% improvement in tool life. Untempered samples when cryogenically treated yield 3%, 10%, and 10.6% extra life over tempered and cryogenically treated T1, M2, and D3 samples, respectively. Tempered samples when cryogenically treated at 133K for 24hrs yielded negative results, but when cryogenically treated at 93K for 24hrs, the results were favorable. It is also concluded that the stabilization of phases that would take place during tempering requires sufficient degree of under cooling and time to get transformed to stable harder/tougher phases that offer better WR. Cryogenic treatment done at 93K as per prescribed cycle yields 20% extra life as compared to the maximum life achieved through cold treatment. It was reported that the maximum improvement in WR could be attained by cryogenically treating the tool steels at 93K for 24hrs.

M1, EN19 and H13 tool steels

Babu et. al.[108] have studied the improvement in wear resistance of M1, EN19 and H13 tool steels after cryogenic treatment. The materials were tested for improvement in abrasive wear resistance after cryogenic treatment at different temperatures below 0°C. All the samples were first heat treated as per standard norms and re tempered after cryogenic treatment. The samples were treated at 0° C, -20° C, - 40° C, -80° C and -190° C. It was observed that the wear resistance improved for all the samples from 315% to 382% depending on the material.

6.4 High-Speed Steels:

It has been reported that cryogenic treatment can double the service life of HSS tools, and also increase hardness and toughness simultaneously [109. Results in the literature show tool life improvements from 92% to 817% when using the cryogenically treated HSS tools after they have being treated at −196° C are found [72]. Dong Yun et. al. [109] studied the effect of DCT with respect to the microstructure of high-speed steels T1 and M2. The results reported were DCT not only transforms austenite into martensite, but it influences the carbide precipitation as well. These additional changes brought about during the DCT, after the normal heat treatment by quenching and tempering have fundamentally changed the conventional view of cold treatment. The red hardness of the high-speed steels was evaluated by additionally heating the samples for 4hrs at temperatures of 873K, 888K, and 903K. The impact toughness and bending strength were also measured. The hardness increased by 0.6 HRC, while the red hardness was increased by 0.5 HRC. Impact toughness was increased by 17.6% and 11%, respectively, in T1 and M2 tool steels, whereas bending strength increased by 25% and 20% in T1 and M2 tool steels, respectively. Further they studied on the effects of varying the deep freezing and tempering cycles on high speed steel. In tool steels, this treatment affects the material in two ways. Firstly, it eliminates retained austenite, and hence increases the hardness of the material. Secondly, this treatment initiates nucleation sites for precipitation of large numbers of very fine carbide particles, resulting in an increase in wear resistance [15].

Rick Frey [110] conducted experiments on high-speed steel drill bits and cobalt drill bits and a comparative study was done among samples, which are conventionally treated and cryogenically treated. The cryogenically treated high speed drill bits averaged 2.83 times performance increase while the cryogenically treated cobalt drill bits averaged 3.42 times. It was mentioned that the smaller bits have to be tempered after cryogenic treatment to prevent breaking while the larger bits were best when left untempered after cryogenic treatment. Also it was reported that the percentage of retained austenite was reduced from 12% to 6.3% in high-speed steels and from 11.3% to 6.8% in cobalt drills for the cryogenically treated samples while comparing with conventionally treated sample. The soaking time was approximately 20hrs at 77K.

Mohanlal et al.[107] studied the effect of cryogenic treatment on T1 type-high speed steel and found that the conversion of retained austenite to martensite is an isothermal process. The maximum hardness was attained by soaking at 203 K, which led to a hardness of 67 HRc. Mohan Lal et al.[26] in their another study they analyzed the influence of cryogenic treatment on T1 type-high speed steel and concluded that the cryogenic treatment at 93 K, soaking for 24 h, imparts 110% improvement in tool life of T1 type high speed steel.

According to Paulin [72] the cryogenic treatment can be applied to coated tools satisfactorily. The same is cited by Cohen and Kamody [111] who found 42% increase in tool life of cryogenically treated TiCN coated M4 tools when comparing to untreated coated tools in a broaching operation.

P/M High-Speed Steel

Podgornik et. al. [65] studied on Tribological Properties of P/M High-Speed Steel and they concluded that, deep-cryogenic treatment improves microstructure of P/M high-speed steel by producing finer needlelike martensitic structure. Finer microstructure results in higher surface hardness and better wear properties, both abrasive wear resistance and galling resistance against stainless steel. Longer cryogenic treatment times will result in finer microstructure and higher surface hardness; however, this has a limited effect on tribological properties.

6.5 Tungsten Carbide

Vadivel et. al. [112] studied performance analysis of cryogenically treated coated carbide inserts they concluded that, in this research work, the machining operation on nodular cast iron is carried out using cryogenically treated and untreated coated carbide inserts. On the whole, the cryogenically treated coated carbide inserts exhibit better performance than that of the untreated coated carbide inserts. The SEM analysis also concludes that the wear resistance of cryogenically treated coated carbide inserts is higher than that of the untreated ones. This is due to the presence of fine η-phase carbide distribution in the cryogenically treated inserts, learned from microstructural analysis. They observed that tungsten carbide inserts consist of tungsten carbide particles with cobalt as binder. More recently, carbide inserts are provided with coatings to enhance their performances. A very few studies have been carried out on cryogenic treatment of tungsten carbide.Yong et al. [113] addressed that the cryogenic treatments can increase the tool life of tungsten carbide tools in turning. In their another study in [8] they found that cryogenic treatment of tungsten carbide inserts improves tool life performance in milling operations to a certain extent.

Seah et al. [58] did some study on the effect of cryogenic treatment on tungsten carbide and found that such treatment increases its wear resistance, they managed to show that cryogenically treated tungsten carbide tools had a much greater resistance to chipping compared to the untreated ones. In addition, the cryogenically treated tools also performed better than the untreated tools at higher cutting speeds.

Ceramic Cutting Tool Inserts

Quek [114] conducted a research on ceramic cutting tool inserts and concluded that cryogenically treated tool inserts exhibited better wear characteristics than the untreated ones at low turning speeds and feeds.

6.6 Castings:

Hao-huai Liu and co-workers [34,81] have investigated the effects of deep cryogenic treatment on the microstructure and abrasion WR of high-chromium cast irons subjected to sub-critical treatment. These authors have shown that deep cryogenic treatment improves hardness and abrasion WR due to reduction of γ_R content and precipitation of higher amount of finer secondary carbides. In their another study [81] they analyzed the effects of deep cryogenic treatment on property of 3Cr13Mo1V1.5 high chromium cast iron. The results showed that the hardness and abrasion resistance of the deep high chromium cast iron were boosted obviously due to abundant retained austenite transforming into martensite and secondary carbides precipitation. Various researchers reported that the mechanism behind the cryogenic treatment is, the removal of the retained austenite combined with the fine carbide precipitation [22,33,42,81,105].

High chromium cast irons are commonly used for wear-resistance applications in the mining and minerals industry due to their excellent abrasion resistance [115]. In the as-cast condition, the hard alloy eutectic carbides [$(Fe,Cr)_7C_3$] embedded in a predominant martensite matrix that always contains retained austenite resulting from heat treatment [117]. For many applications, the castings are heat-treated prior to service. The destabilization heat treatment is the technique in common use [116].

Jun Wang et.al.[68] studied on the microstructure and abrasion resistance of a high chromium cast iron 16Cr1Mo1Cu they analyzed that, the cryogenic treatment can effectively reduce the retained austenite after destabilization heat treatment, but cannot make retained austenite transform completely. Cryogenic treatment can markedly improve bulk hardness and abrasion resistance of the high chromium cast iron. In the course of destabilization treatment and then cryogenic treatment, the amount of precipitated secondary carbide, $M_{23}C_6$, was more than that in air cooling. The additional fine secondary carbide precipitated during the cryogenics treat after destabilization heat treatment comparing with air cooling, is the main reason for the increase of the bulk hardness and wear resistance.

7. AMBIGUITIES IN CRYOTREATMENT

A. Joseph Vimal et.al.[102] have mentioned that, research in cryotreatment has improved in developed countries, but it is still in the dormant level in many other countries. Researchers are still skeptical about the benefits of the cryogenic treatment. All over the world, there are many controversies prevailing on the reported mechanisms and because of such issues in cryotreatment only limited research has been done on selected alloys.

Dhokey et.al.[105] studied and observed that, literature of cryotreatment does not adequately clarify the selection of tempering, cryogenic temperature and soaking time. There is a need to standardize the process for cryotreatment in particular tool steels and understand the underlying mechanism responsible for improvement of mechanical properties like wear, hardness, toughness etc.

In general cryogenic treatment is still in the dormant level as far as to understand the metallurgical mechanisms are concerned.

Cryotreatment technology has not been widely adopted by the industries due to lack of understanding of the fundamental metallurgical mechanisms and due to the wide variation in reported research findings.[12]. Many researchers demonstrated the effect of cryotreatment and the underlying phenomenon, but to understand why this phenomenon occurs, requires sophisticated and analytical equipment and extensive metallurgical knowledge. [12].

It has been claimed by several researchers that cryotreatment enhances wear resistance of certain steel [15,23,26,33,37,38,41,45,52]. But the reported magnitudes of the enhancement in wear resistance and the governing mechanisms for such enhancement do not provide any unified picture. There are number of treatment processes used for different metals which cause them to behave differently under different conditions [118]. However, the mechanisms of microstructure changes in alloys under various treatments are not yet fully understood [79].

Wayne Reitz et.al. [119] have indicated that, the details for successfully conducting each the step in DCT have yet to be determined. Three main factors of the cooling process that are currently being debated are cooling rate, soaking time, and optimal quenching temperature. However, D. Das et.al.[31] have concluded that, the underlying mechanisms behind the enhancement of wear resistance of tool/die steels by DCT are still debated and yet to get crystallized.

One of the major uncertainties associated with the earlier investigations related to cryotreatment of tool steels is the duration of cryotreatment at the selected temperatures [21,77,119]. The existing literature does not provide any guideline related to the selection of time duration for cryotreatment [20,21] In [31] the state-of-art of cryotreatment of tool/die steels does not present any coherent information either to accept or to reject any of the propositions due to the absence of systematic investigation on the correlation of microstructure with wear behavior of these steels by DCT.

S.S. Gill et. al. [79] indicated that, it is very much comprehensible that the rate of cooling still requires to be debated upon to achieve the desired results. Further they observed that available results in the literature pertaining to structure property relations of tool steels and carbides subjected to cryoprocessing are not coherent and the underlying postulated mechanisms for achieving improved mechanical properties like wear resistance are not well crystallized. Most researchers believe that deep cryogenic process promotes complete transformation of retained austenite into martensite, and this can be attributed to the enhanced wear resistance of the tool steels [7,33,41,52,72]; however, some researchers suggested there was always the retained austenite after cryoprocessing [61,120], whereas another school claims that the cause of increased wear resistance is the formation of fine carbides in martensite matrix and their uniform distribution [15,24,33,52]. The extent of benefits of these emerging processing routes can only be suitably exploited if the underlying mechanisms of these processes are carefully unfolded in an organized manner.

The holding time in cryogenic processing has been varied widely by earlier investigators. For example, holding time employed in the cryotreat-ment for AISI M2 steel is 1 h by Leskovsek et al. [62], 20 h by de Silva et al. [25], 35 h by Molinari et al. [33] and 168 h by Huang et al. [24]. Such wide variation in the selected holding time even for the same material is due to the lack of systematic investigation related to the influence of holding time on the wear resistance of tool/die steels by cryotreatment.

It can be summarized from the above review that lowering down the soaking temperature to the minimum is very important to improve the wear resistance in steel. Lowest temperature CT would enhance wear property to the most. It is believed to be due to complete transformation of the retained austenite to martensite during CT [15,23,102] and this transformation is responsible for improvement in various properties of steel; however, this transformation is claimed to be complete at SCT at around -84^0C (189K) [33,40]. So the exact mechanism is still unpredictable due to which improvement in material properties takes place. Further investigation would be needed.

8. CONCLUSIONS:

The Conclusions of this review study are as follows:

1 The complete process of Cryo-Heat-Treatment must be as follows :
austenitizing, quenching, DCT and tempering; preferably immediate one-by-one sequentially in a cycle.

2 Prior to DCT austenitizing temperatures plays vital role for improving the properties of the steel like wear resistance, hardness, toughness etc. Each material to be assessed separately for selecting the optimum austenitizing temperature and should be co-relate to the required desired properties after DCT.

3 More useful work has been reported by several researchers, but there are many ambiguities in parameters like austenitizing temperature, quenching temperature, rate of cooling soaking temperature, soaking period, rate of warming-up, tempering temperatures and tempering period needs further investigations and optimize all the parameters of DCT process for various materials. Determination of appropriate level of the above parameters results in to enhance the product quality, productivity and wider acceptance in the industries.

4 With a better understanding of this process a wider acceptance of DCT is possible. Researchers must focus their efforts for complete understanding of the mechanisms behind the formation of the ultra-fine carbides precipitation. By understanding the impact of balancing the properties of particular steel to its applications.

5 Information specific to the effect of DCT on steels and specifically what effects these percentage of retained austenite, hardness, wear and service life must gathered. Engineers and metallurgists must work to standardizing processing cycles including cooling and heating rates, hold times and temperature cycles to optimize the properties of the material. International experts must draft the standards and conduct trials to validate the processes for the more promising alloys. Each material needs to be separately assessed and an individual process route devised for it that will depend on the combination of hardness, toughness, and wear resistance required in service.

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