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Cryogenic Treatment of Uddeholm Orvar 2M tool steel

Diploma Thesis

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Preface

This thesis is written in order to examine the effects of the cryogenic treatment on the mechanical properties and microstructure of Uddeholm Orvar 2M tool steel. It has been written to fulfill the graduation requirements of the Naval Architecture and Marine Engineering studies at the National Technical University of Athens (NTUA). I was engaged in researching and writing this diploma thesis from March 2017 to June 2018.

I would like to thank my professor, Dr. Dimitrios I. Pantelis, for the assignment of this project, for his supervision on the subject as well as his valuable advises during the process. Moreover, I would like to thank Dr. Chara Sarafoglou and Mr Dimitrios Papageorgiou for their guidance and their assistance during the experimental procedure. Additionally, I would like to thank Thodoris Langos and the staff of the laboratory of the Mechanical Engineers field for their assistance during experimental procedure. Many thanks to Prof. Nikolaos G. Tsouvalis and Prof. Dimitrios E. Manolakos for their participation as the examination committee. Last but not least, many thanks to my family and my friends Antonia, Vasiliki, Dimitrios, Elena, Polina, Simos, Dimitrios, Christina for their support and their patience through this study.

Abstract

The purpose of this study procedure is to examine the effect of Cryogenic Treatment on the microstructure and mechanical properties, especially microhardness, of hot work H13 tool steel. The thesis is divided in two parts – theoretical and experimental. During the first chapter of the study, reference regarding the steels is made, focusing on tool steels category, especially H13 hot work tool steel. The second chapter contains an overview of the heat treatment procedures, which are carried out on steels, paying attention on the processes applied on tool steels. The last theoretical part refers to Cryogenic treatment with a presentation of the parameters and factors affecting the treatment and a study of the results on microstructure and mechanical properties of tool steels through years of experiments.

The experimental part concerns a research regarding the effect of cryogenic treatment as an addition to conventional treatment on Uddeholm Orvar 2M tool steel microstructure and microhardness. In case of our study, Uddeholm Orvar 2M tool steel is going to be subjected to cryogenic treatment with subsequent tempering. The experimental procedure consists of two heat treatment cycles, focusing on the impact of cryogenic temperature and soaking time on the material. The tool steel specimens are going to be under austenitization quenching, cryogenic treatment and tempering at different temperatures (TT). All the processes are going to be carried out in the above sequence. Regarding subzero procedure, the first cycle consists of the conventional treatment with an addition of deep cryogenic process at $-195\text{ }^{\circ}\text{C}$ for 24 hrs. The second cycle differs on the conditions, including a cryogenic treatment at $-130\text{ }^{\circ}\text{C}$ for 20 minutes.

By using a microscope and a scanning electron microscope (SEM), the grain boundaries, the retained austenite, as well as the primary and secondary carbides are going to be observed. Moreover, the measurement of the microhardness for every TT will form a distribution, from which, conclusions about the conditions of primary and secondary hardness will be extracted. The experiment of the study showed that the subzero treatment contributes to increase of hardness, decrease of retained austenite and homogenous distribution of finer carbides.

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Chapter I: Tool Steels

Section 1: Introduction

1.1 General Information - Steels

Steels can be manufactured relatively inexpensively in large quantities to very precise specifications. That is the reason they are the most widely used category of metallic material. They are characterized by a wide range of mechanical properties, from moderate yield strength levels (200 to 300 MPa, or 30 to 40 ksi) with great ductility to yield strengths exceeding 1400 MPa (200 ksi) with fracture toughness levels as high as 110 MPa (100 ksi).^[1]

Steel's base metal is iron is able to take on two crystalline forms (allotropic forms), body centered cubic (BCC) and face centered cubic (FCC), depending on its temperature. The interaction of those allotropes with the alloying elements, primarily carbon gives steel and cast iron their range of unique properties. In the body-centered cubic arrangement, there is an iron atom in the center of each cube, and in the face-centered cubic, there is one at the center of each of the six faces of the cube.^[20]

1.2 Classification of Steels^[1]

Steels can be classified by a variety of different systems depending on:

- The composition, such as carbon, low-alloy, or stainless steels
- The manufacturing methods, such as open hearth, basic oxygen process, or electric furnace methods
- The finishing method, such as hot rolling or cold rolling
- The product form, such as bar, plate, sheet, strip, tubing, or structural shape
- The deoxidation practice, such as killed, semi killed, capped, or rimmed steel
- The microstructure, such as ferritic, pearlitic, and martensitic (Fig. 1)
- The required strength level, as specified in ASTM standards
- The heat treatment, such as annealing, quenching and tempering, and thermo-mechanical processing
- Quality descriptors, such as forging quality and commercial quality

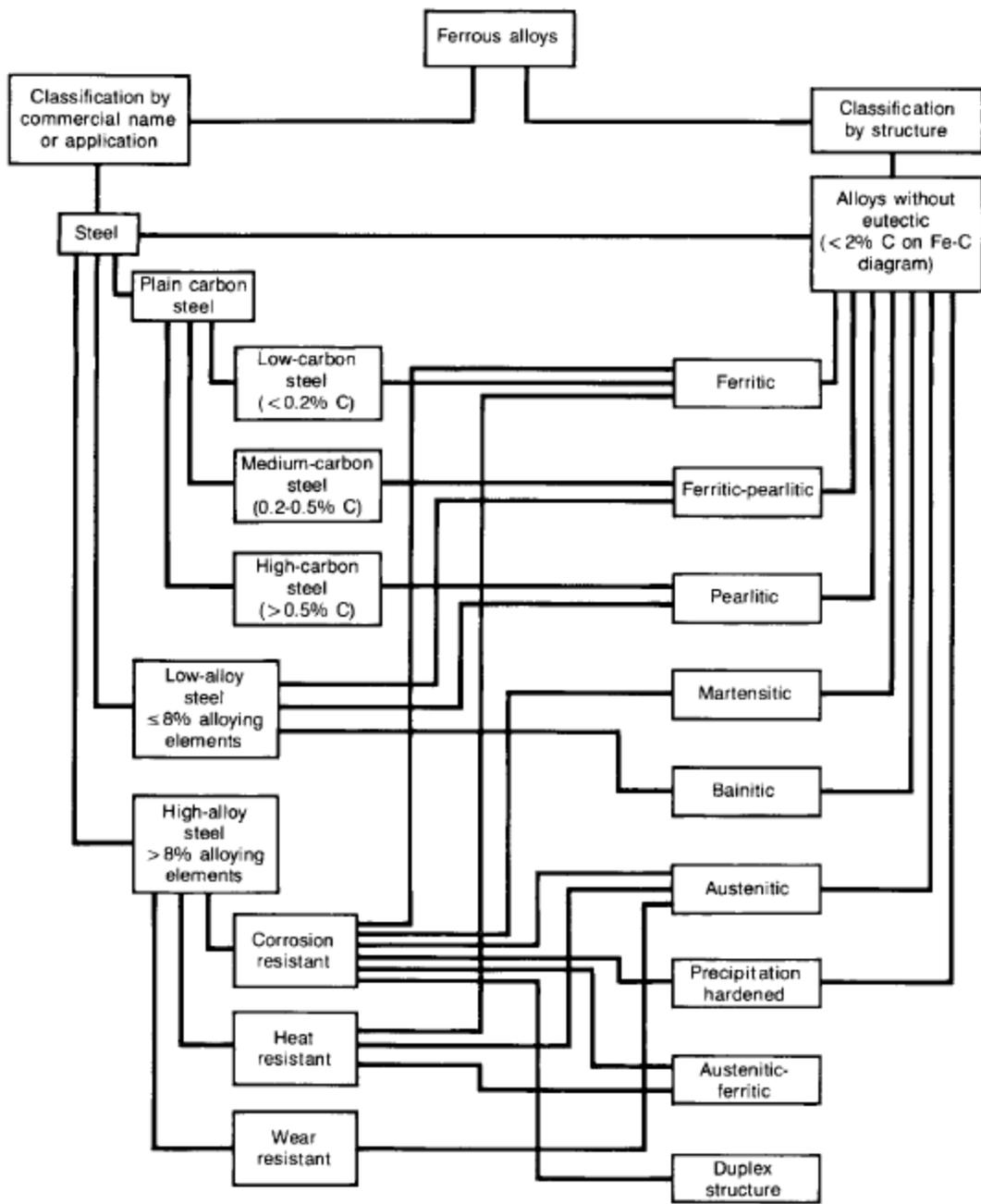


Fig.1 Classification based on microstructure for steels

Section 2: Tool steels

2.1 General Information

Tool steels are used to make tools for cutting, forming, or shaping a material into a part or component adapted to a definite use. Before 1868, tool steels were simple, plain carbon steels, but in the early 20th century, many complex, highly alloyed tool steels were developed. These alloy tool steels, which contain relatively large amounts of tungsten, molybdenum, vanadium, manganese, and chromium, were able to meet increasingly severe service demands and provide much better dimensional control and freedom from cracking during heat treatment. Many alloy tool steels are also widely used for machinery components and structural applications in which particularly stringent demands are to be faced, such as high-temperature springs, ultrahigh strength fasteners, special-purpose valves, and bearings of various types for elevated-temperature service. ^[2]

2.2 Applications

It is essential to notice that most tools are subjected to extremely high loads that are applied rapidly. The tools should be able to withstand these loads a great number of times without breaking and without undergoing excessive wear or deformation. In many applications, tool steels must be capable of resisting any conditions and factors that cause high temperatures in the tool. No single tool material combines maximum wear resistance, toughness, and resistance to softening at elevated temperatures. As a result, the need to achieve the optimum combination of properties requires a proper selection of the tool material for a given application. Most tool steels are wrought products, but precision castings can be used to advantage in some applications. The powder metallurgy (P/M) process is widely used in making tool steels. This method provides a more uniform carbide size and distribution in large sections and special compositions that are difficult or impossible to produce by melting and casting. ^[1, Error! Reference source not found.]

2.3 Classification and Characteristics

The very large number of tool steels is effectively classified by the widely used system developed by the American Iron and Steel Institute (AISI). This system is the starting point for the selection of the proper steel for a given function from the large number of steels available.

The AISI classification system arranges tool steels into groups that are based on prominent characteristics such as: [Error! Reference source not found.]

- Alloying (for example, tungsten or molybdenum high-speed steels),
- Application (for example, cold-work or hot-work tool steels),
- Heat treatment (for example, water-hardening or oil hardening tool steels).

Table 1 lists nine main groups of tool steels and their identifying letter symbols

Table 1 Main groups of tool steels and AISI letter symbols

Group	Identifying Symbol
Water-hardening tool steels	W
Shock-resisting tool steels	S
Oil-hardening cold-work tool steels	O
Air-hardening, medium-alloy cold-work tool steels	A
High-carbon, high-chromium cold-work tool steels	D
Mold steels	P
Hot-work tool steels, chromium, tungsten, and molybdenum	H
Tungsten high-speed tool steels	T
Molybdenum high-speed tool steels	M

Several very general alloying and heat treatment principles are introduced at this point to provide a base for comparing the various groups of tool steels:

- The hardened microstructure of a typical tool steel consists of a matrix of tempered martensite containing various dispersions of iron and alloy carbides.
- High carbon and high alloy content promote hardenability or the ability to form martensite on cooling.
- The higher the carbon and alloy content in supersaturation in the martensite, as inherited from the parent austenite, the higher the density of carbides that can be formed on tempering.
- The higher the content of strong carbide-forming elements, the higher the density of stable carbides in austenite during hot work and austenitizing. These carbides are retained as components of the microstructure in addition to those formed in martensite during tempering.

- The higher the carbon content of the martensite and the higher the density of carbides, the higher the hardness and wear resistance but the lower the toughness of a tool steel microstructure.

2.4 Hot Work steels

Manufacturing operations which involve punching, shearing, or forming of metals at high temperatures require the use of hot work steels. Hot-work steels (group H) have been developed to withstand the combinations of heat, pressure, and abrasion which can be met in these operations.

2.4.1 Chromium hot-work steels (types H10 to H19) ^[1]

These types of tool steels have good resistance to heat softening due to their medium chromium content and the addition of carbide-forming elements such as molybdenum, tungsten, and vanadium. The low carbon and low total alloy contents increase toughness at the normal working hardnesses of 40 to 55 HRC. In the case of higher tungsten and molybdenum contents, the scientists observe increased hot strength but slightly reduced toughness. Vanadium is added to increase resistance to washing (erosive wear) at high temperatures. Tool steels with increased silicon content are characterized by improved oxidation resistance at temperatures up to 800 °C (1475 °F). The most widely used types in this group are H11, H12, H13, and, to a lesser extent, H19. All of the chromium hot-work steels are deep hardening.

Essential advantages of H11, H12, and H13 steels in case of structural and hot-work applications include ease of forming and working, good welding ability, relatively low coefficient of thermal expansion, acceptable thermal conductivity, and above-average resistance to oxidation and corrosion.

2.4.2 Tool Steel H13 ^[1]

AISI H13 is a 5% Cr ultrahigh-strength steel similar to H11 mod in composition, heat treatment, and many properties (Table 2). This results in a greater dispersion of hard vanadium carbides, which contributes to higher wear resistance. Depending on the producer, the carbon content of H13 may be near the high or low side of the accepted range, with a corresponding variation in strength and ductility for a given heat treatment. H13 is a secondary hardening steel. It has good temper resistance and maintains high hardness and strength at elevated temperatures (Fig. 2). H13 steel can be heat treated to strengths exceeding 2070 MPa (300 ksi); it has good ductility and impact strength. The material H13 has good resistance to thermal fatigue. Hot-work tooling made of H13 can be safely water cooled between hot-working operations. Its resistance to thermal fatigue, erosion, and wear has made it a preferred die material for aluminum and magnesium die casting, as well as for many other hot-work applications.

However, H13 is subject to hydrogen embrittlement. It can be nitride for additional wear resistance. Although H13 has not been used as widely as H11 mod as an ultrahigh-strength constructional steel, the similarities in properties make H13 equally attractive for such applications. This is particularly true in noncritical service in which slightly higher wear resistance is an advantage.

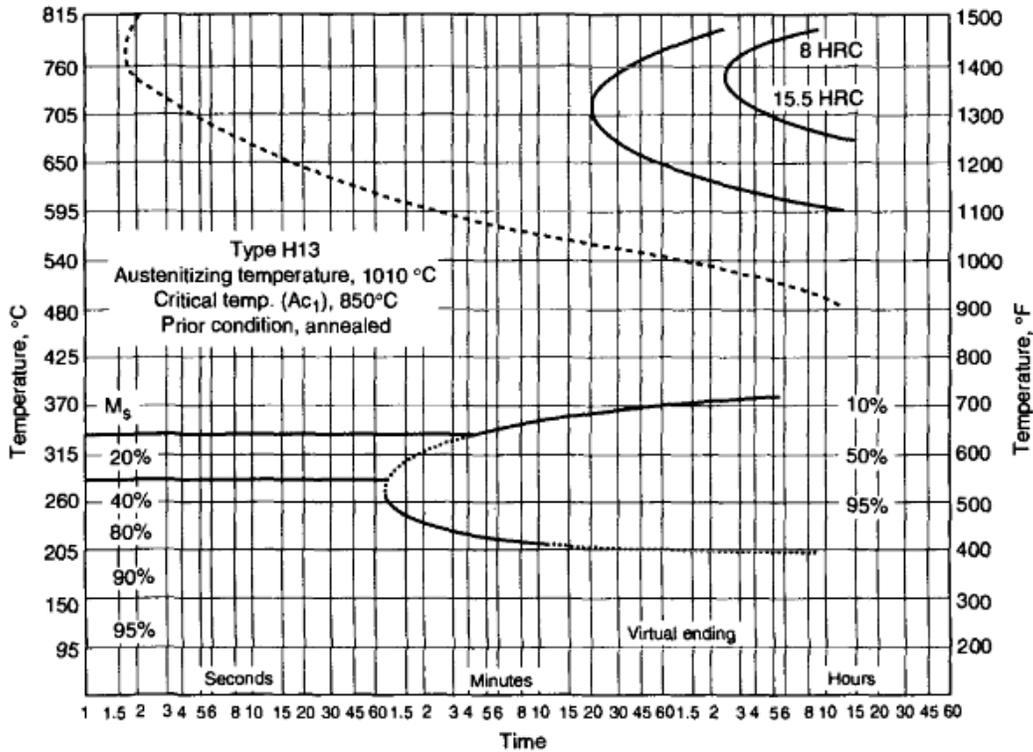


Fig. 2 IT diagram for H13 steel containing 0.40% C, 1.05% Si, 5.00% Cr, 1.35% Mo, and 1.10% V. Courtesy of Crucible Steel Co.

Properties

Table 2 Compositions of H13 steel

Medium-alloy air-hardening steels H13	Composition, wt %					
	C	Mn	Si	Cr	Mo	V
	0.32–0.45	0.20–0.50	0.80–1.20	4.75–5.50	1.10–1.75	0.80–1.20

Somewhat different properties should be expected when the carbon content is near either the high end or the low end of the range.

H13 tool steel is one of the most widely used of all hot-work tool steels. Although the steel is well known, costly tool failures, which happen, can be lead to the insufficient knowledge of heat treatment. The hardening temperature lies between 1000°C and 1050°C. The temperature for the hardening operation is chosen in order for the material to obtain the properties that are regarded as the most important ones. The strength at elevated temperatures increases as the hardening temperature is raised but this increase in strength takes place at the expense of the toughness. The higher the hardening temperature the more susceptible is the steel to grain growth. Coarse-grained steel is less tough than a fine-grained one.

Due to high vanadium content, grade H13 is not unduly susceptible to grain growth. It is essential to notice that the grain size number after hardening should be at least 7 ASTM. In the case of a neutral salt bath heating treatment the holding time is easily kept under control. If the tool is pack-heated, it is difficult to confirm the actual holding time and therefore when this method of heating is used the lower temperature of the hardening range is recommended.

As the hardening temperature increases, the greater the number of carbides go into solution. For grade H 13 this leads to the fact that the higher the hardening temperature the sooner is the start of the carbide precipitation that precedes the pearlite and bainite formation when quenching the steel. [25]

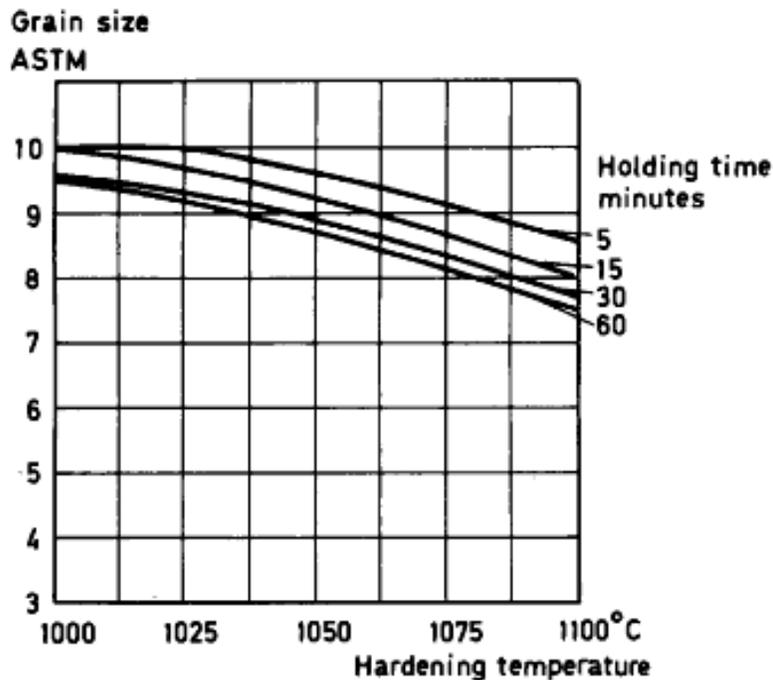


Fig. 3 Influence of hardening temperature and holding time on grain size of steel H 13

Impact strength determinations carried out on specimens of steel H13, after having been hardened from various temperatures, show that toughness decreases with increasing hardening temperature (Fig.3). In this case, grain growth cannot have been the only factor that must be in concern since the steel is relatively insensitive to grain growth. Tests involving different rates of cooling have shown that the lowest cooling rate resulted in the lowest impact strength. It has also been demonstrated that there is a connection between low impact values and the presence of precipitated grain-boundary carbides in the steel. Hence, if the highest possible impact strength is to be imparted to grade H13, a moderately high hardening temperature combined with a high cooling rate should be used. ^[25]

Applications ^[16]

Typical applications for the specific grade H13 include casting dies for aluminium, magnesium and zinc, extrusion dies for aluminium and brass, liners, mandrels, pressure pads, followers, bolsters, die cases, die holders and adaptor rings for copper and brass extrusion. H13 can be used in production of hot stamping and press forge dies, split hot heading dies, gripper dies, hot punching, piercing and trimming tools. Other applications consist of plastic moulds, shear blades for hot work and hot swaging dies and also tooling and structural applications including punches, shafts, beams, torsion bars, shrouds, and ratchets.

Chapter II: Heat Treatment in Tool Steels

Section 1: Introduction

1.1 Heat Treatment Processes for steels^[41]

As it has been discussed, most of the steels, in order to be used in production and industry, should be subjected to heat treatment in order to have their mechanical and physical properties improved. Heat treatments processes are used to provide the demanded properties for the last stage of the steels before production.

Heat treatment processes include two categories, a) heat treatment inside the matrix and b) treatment on the surface of steels.

Heat treatment of steel

- Annealing
- Austenitization
- Quenching
- Tempering

Heat treatment processes are designed with the purpose of increasing steel hardness, decreasing or total elimination of mechanical stresses and regulating the grain size and the properties.

1.2 Annealing^[2]

Steels are submitted to a wide range of annealing processes for improvement of their mechanical and other properties. Annealing is a generic term denoting a treatment that consists of heating and holding at a suitable temperature followed by cooling at an appropriate rate, primarily for the softening of metallic materials. In plain carbon steels, annealing produces a ferrite-pearlite microstructure. Steels can be annealed in order to facilitate cold working or machining, to improve mechanical and electrical properties, or in the case of achieving dimensional stability.

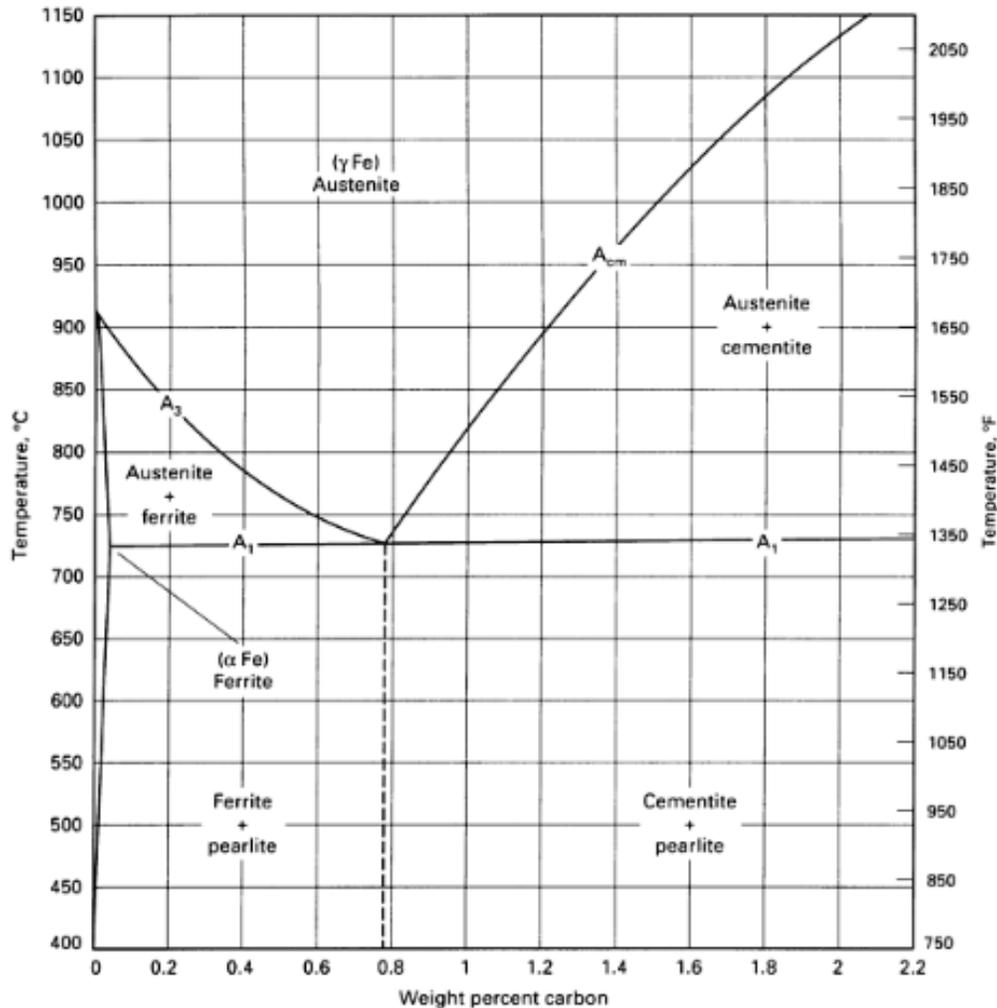


Fig.4 Iron-carbon binary phase diagram

The critical temperatures that must be considered in the annealing process of steel are those that define the onset and completion of the transformation to or from austenite (Fig 4). The critical temperatures depend on whether the steel is being heated or cooled. Critical temperatures for the start and completion of the transformation to austenite during heating are denoted, respectively, by Ac1 and Ac3 for hypoeutectoid steels and by Ac1 and Accm for hypereutectoid steels. These temperatures are higher than the corresponding critical temperatures for the start and completion of the transformation from austenite during cooling, which are denoted, respectively, by Ar3 and Ar1 for hypoeutectoid steels and by Arcm and Ar1 for hypereutectoid steels. (The "c" and "r" in the symbols are derived from the French words *chauffage* for heating and *refroidissement* for cooling.) These critical temperatures converge to the equilibrium values Ae1, Ae3, and Aecm as the rates of heating or cooling become infinitely slow. Various alloying elements markedly affect these critical temperatures. For example, chromium raises the eutectoid temperature, A1, and manganese lowers it.

1.3 Austenitization^[41]

Austenitization includes heating steel on a temperature almost 50 °C above upper critical temperature (Ac3). In order to achieve complete austenitization, steel remains in these temperature conditions for a certain amount of time, to obtain homogeneous austenite without undissolved carbides. The time of austenitization is important since too much extending of duration may cause overheating and eventually unwanted increased grain size.

During heating, a difference in temperature between the surface and inner mass of the alloy is observed. As a result, plastic deformation of the crystalline mesh in the austenitic area is caused. Therefore, it is essential for the process to be carried out on a relatively slow rate. As temperature increases until austenitization, steel is oxidized, causing material loss from the surface and decreasing its content in carbon. The above problems can easily be treated by heating in furnaces of controlled atmosphere conditions.

1.4 Quenching^[2]

Quenching is the process of rapidly cooling metal parts from the austenitizing or solution treating temperature, typically from within the range of 815 to 870 °C (1500 to 1600 °F) for steel. Stainless and high-alloy steels usually are submitted to quenching to minimize the presence of grain boundary carbides or to improve the ferrite distribution. However, most steels including carbon, low-alloy, and tool steels, are quenched in order to produce controlled amounts of martensite in the microstructure. Successful hardening means achieving the required microstructure, hardness, strength, or toughness while minimizing residual stress, distortion, and the possibility of cracking.

The selection of a quenchant medium depends on the hardenability of the particular alloy, the section thickness and shape involved, and the cooling rates needed to achieve the desired microstructure. The most common quenchant media are either liquids or gases. The liquid quenchants commonly used include:

- Oil that may contain a variety of additives
- Water
- Aqueous polymer solutions
- Water that may contain salt or caustic additives

The most widely used gaseous quenchants are inert gases including helium, argon, and nitrogen. These quenchants are sometimes used after austenitizing in a vacuum. The ability of a quenchant to harden steel depends on the cooling characteristics of the quenching medium. Quenching effectiveness is dependent on the steel composition, type of quenchant, or the quenchant use conditions. The success of the procedure is also based on the design of the quenching system and the thoroughness with which the system is maintained.

In conclusion, the objective of the quenching process is cooling steel from the austenitizing temperature sufficiently quickly to form the desired microstructural phases, sometimes bainite but more often martensite. The basic quenchant function is to control the rate of heat transfer from the surface of the part being quenched.

Quenching Process

The rate of heat extraction by a quenching medium and the way it is used substantially affects quenchant performance (Fig. 5). Variations in quenching practices have resulted in the assignment of specific names to some quenching techniques:

- Direct quenching
- Time quenching
- Selective quenching
- Spray quenching
- Fog quenching
- Interrupted quenching

Direct quenching refers to quenching directly from the austenitizing temperature and is by far the most widely used practice. The term direct quenching is used to differentiate this type of cycle from more indirect practices which might involve carburizing, slow cooling, reheating, followed by quenching.

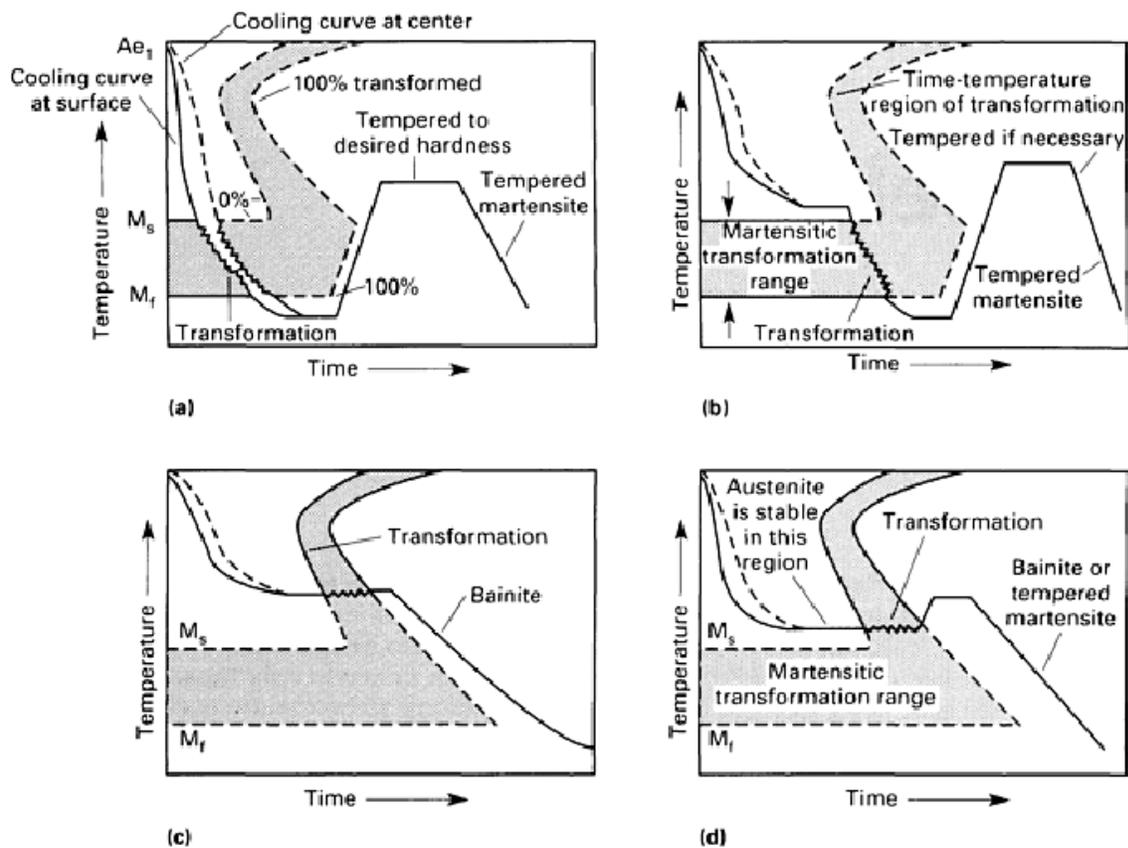


Fig. 5 Comparison of cooling rates and temperature gradients as work pieces pass into and through martensite transformation range for a conventional quenching and tempering process and for interrupted quenching processes. (a) Conventional quenching and tempering processes that use oil, water, or polymer quenchants. (b) Marquenching, which uses either salt or hot oil as a quenchant. (c) Austempering, which uses a salt as a quenchant. (d) Isothermal quenching, which uses either salt or hot oil as a quenchant.

1.5 Tempering ^[2]

Tempering of steel refers to the process in which previously hardened or normalized steel is usually heated to a temperature below the lower critical temperature and cooled at a suitable rate, primarily to increase ductility and toughness, but also to increase the grain size of the matrix. Steels are tempered by reheating after hardening to obtain specific values of mechanical properties and also to relieve quenching stresses and to ensure dimensional stability. Tempering usually follows quenching from above the upper critical temperature. However, tempering is also used to relieve the stresses and reduce the hardness developed during welding and to relieve stresses induced by forming and machining.

Principal Variables

Variables associated with tempering that affect the microstructure and the mechanical properties of tempered steel include:

- Tempering temperature
- Time at temperature
- Cooling rate from the tempering temperature
- Composition of the steel, including carbon content, alloy content, and residual elements

In the case of quenched steel which is characterized by a microstructure consisting essentially of martensite, the iron lattice is strained by the carbon atoms, producing high hardness. Upon heating, the carbon atoms diffuse and react in a series of distinct steps that eventually form Fe₃C or alloy carbide in a ferrite matrix of gradually decreasing stress level. The properties of the tempered steel are primarily determined by the size, shape, composition, and distribution of the carbides that form, with a relatively minor contribution from solid-solution hardening of the ferrite. These changes in microstructure usually decrease hardness, tensile strength, and yield strength but increase ductility and toughness.

Under certain conditions, hardness may remain unaffected by tempering or may even be increased as a result of it. For instance, tempered steel at very low tempering temperatures may cause no change in hardness but may produce a desired increase in yield strength. Moreover, those alloy steels that contain one or more of the carbide-forming elements (chromium, molybdenum, vanadium, and tungsten) can achieve secondary hardening and increase hardness after tempering.

Temperature and time are interdependent variables in the tempering process. Lowering temperature, within limits, and increasing time can usually produce the same effect as raising temperature and decreasing time. However, minor temperature changes have a far greater effect than minor time changes in typical tempering operations. With few exceptions, tempering is carried out at temperatures between 175 and 705 °C (350 and 1300 °F) and for times from 30 min to 4 h.

Section 2: Structural transformation methods ^[41]

The study of structural transformations for metals and alloys depends on the knowledge of the balance curves. In order to learn about metallurgical characteristics of alloys, it is essential to study two types of curves.

- Solidification Curves
- Solid State Transformation Curves

For this section, we study the second category of curves mentioned, in which heat treatment processes are based on. Two basic structural transformation methods that are observed, during heat treatment, are *diffusion* and *martensite transformation*.

2.1 Diffusion ^[41]

Diffusion is the process of migration of individual atoms within materials and takes place in gases, liquids and solids, and consequently occurs in steels and other metallic systems. Diffusion is of immense importance to most heat treatment processes and therefore some appreciation of the mechanisms and laws of diffusion will facilitate the understanding of many heat treatments including carburizing and decarburizing, nitriding and annealing. ^[25]

The atoms move due to the phenomenon of diffusion, which is caused from the temperature difference between neighboring positions. Their transposition is great (of magnitude $1-10^6$ of interatomic distance) and they jump in random positions. Transformation rate depends abruptly on heating temperature. For example, diffusion happens in lower rate for temperature $525\text{ }^\circ\text{C}$ than in $700\text{ }^\circ\text{C}$. It is extremely important to mention that the phenomenon of diffusion cannot be carried out at temperatures below $0.3-0.4T_m$. The total volume of the transformed material also depends on heating temperature and time. In conclusion, diffusion allows the change in chemical composition of different phases in alloys. Furthermore, there is a chance that crystallographic relationship between initial and final structure may occur in the process.

2.2 Martensite Transformation ^[41]

Martensite transformation is happening during quenching, below the temperature M_s (start of martensite transformation), creating instantaneously a new phase called martensite. The martensite phase is formed as soon as the temperature is reached and the phenomenon does not continue in isothermal conditions. Therefore, in order to keep creating the new phase, the temperature must decrease and as a result martensite keeps forming in new areas instead of continuing from the already formed positions. For steels, martensite is formed, since cooling rate is fast enough to prevent pearlitic phase from being generated through mechanism of diffusion. The atoms move in small distances (magnitude of interatomic distance) creating and breaking interatomic bonds and they transpose consecutively in exact sequence.

Transformation rate equals to the rate of the mesh vibrations in the crystal. On the contrary, it is not related to temperature and the transformation is able to happen even on temperature near 4K. The total volume of the transformed material is related only to temperature. The temperature regarding the start of martensite transformation M_s as well as the temperature related to the end of formation M_f decreases as content in carbon increases. The critical quenching rate (V_c) changes according to content in carbon and depends on grain size and clarity of steel.

Chemical composition remains unchanged and the atoms, as they do not have the necessary time to move, they stay at their positions. Moreover, there is always crystallographic relationship between the generated martensite phase and the initial mesh.

Heat treatment of steel, especially martensitic hardening is usually accompanied by the evolution of large residual stresses, which exist without any external load on the part considered. Causes for such stresses include:

- Thermal expansion or contraction of a homogeneous material in a temperature gradient field
- Different thermal expansion coefficients of the various phases in a multiphase material
- Density changes due to phase transformations in the metal
- Growth stresses of reaction products formed on the surface or as precipitates, for example, external and internal oxidation

2.3 Stages of Hardening

It is essential to know that complete transformation from austenite to martensite is generally preferable prior to tempering. However, conditions vary widely, and 100% transformation rarely, occurs. During hardening, martensite develops as a continuous process from start (M_s) to finish (M_f) through the martensite formation range. Except in a few highly alloyed steels, martensite starts to form at well above room temperature. In many cases, transformation is essentially complete at room temperature. Retained austenite tends to be present in varying amounts. However, for some applications, this retained austenite must be transformed to martensite and then tempered.

The below stages describe the procedure of hardening steels.

- a) Austenitization
- b) Quenching
- c) Tempering

Section 3: Tool steels

With few exceptions, all tool steels must be heat treated to develop specific combinations of wear resistance, resistance to deformation or breaking under high loads, and resistance to softening at elevated temperatures. A few simple shapes may be obtained directly from tool steel producers in correctly heat-treated condition. However, most tool steels first are formed or machined to produce the required shape and then heat treated as required.

Improper finishing after heat treatment and most important grinding can damage tool steels through the development of surface residual stresses and cracks. Some tools are heat treated in a blank or semi-finished state and subsequently ground, turned, or electrical discharge machined to create the final tool. Even though the above manufacturing techniques have progressed in recent years, metallurgical damage and surface stresses are still a major worryment.

Annealing ^[2]

Tool steels are usually received from the supplier in the annealed condition in order to be easily machined and heat treated. However, if they are subjected to hot or cold forming, often they must be fully annealed again before subsequent operations. Whether a tool is to be submitted to rehardening, it should first be thoroughly annealed. This procedure is important with the steels of higher alloy content to avoid irregular grain growth occurs and a mixed grain size (sometimes called fish scale or duplex grains). All of the chromium hot-work steels have high hardenability.

3.1 Austenitization ^[2]

Austenitizing is the most critical of all heating operations performed on tool steels. Tools that are subjected to excessively high austenitizing temperatures or abnormally long holding times may produce excessive distortion, abnormal grain growth, loss of ductility, and low strength. This problem can be faced in the case of high-speed steels, which are frequently austenitized at a temperature close to that at which melting begins. Moreover, underheating may result in low hardness and low wear resistance. During the process of quenching, if the center of a tool is cooler than the exterior, spalling or fracturing of the corners may result, particularly with water-hardening steels. Prior to heat treatment, all tool surfaces must be free of decarburization.

During austenitization the final alloy element partitioning between the austenitic matrix (that will transform to martensite) and the retained carbides occurs. This partitioning fixes the chemistry, volume fraction, and dispersion of the retained carbides. The retained alloy carbides contribute to wear resistance, and control austenitic grain size. The finer the carbides and the larger the volume fraction of carbides, the more effectively austenitic grain growth is controlled. Thus if austenitizing is performed at too high a temperature, undesirable grain growth may occur inside the material as the alloy carbides increasingly coarsen or dissolve into the austenite.

3.2 Quenching ^[2]

Quenching from the austenitizing temperature may be carried out in water, brine, oil, salt, inert gas, or air, depending on composition and section thickness. The quenching medium must cool the work piece rapidly enough to obtain full hardness. The selection of the cooling medium is important since mediums which exceed the requirements may cause cracking or excessive distortion may occur.

Tool steels that will harden during air cooling are frequently hot quenched to the range 540 to 650 °C (1000 to 1200 °F) after austenitizing. Quenching time is long enough for decomposition of austenite to begin. After hot quenching, the steels are air cooled or oil quenched to ambient temperature. Hot quenching minimizes distortion without adversely affecting hardness since it prevents the hard scale from forming on most air-hardening steels during air cooling.

3.3 Tempering ^[2]

Tempering produces a more desirable combination of strength, hardness, and toughness than obtained in the quenched steel. The quenched structure of tool steel is a heterogeneous mixture of retained austenite, untempered martensite, and carbides. The changes that take place in the microstructure during tempering of hardened tool steels are time-temperature dependent. Time at tempering temperature should not be less than 1 h for any given cycle.

Most manufacturers of high-speed steels recommend multiple tempers of 2 h or more each to attain the desired microstructure and properties. Carrying out the procedure with recommended tempering times, temperatures, and number of tempers (a minimum of two) ensures attainment of consistent tempered martensitic structures and overcomes uncertainties caused by variations in the amount of retained austenite in the quenched condition. These variances are based on differences in heat chemistry, prior thermal history, hardening temperatures, and quenching conditions. Other factors that influence the tempering requirements of high-speed steels are:

- Increasing the free (matrix) carbon content increases the amount of retained austenite in the as-quenched condition
- The amount of retained austenite significantly affects the rate of transformation, particularly for short tempering cycles. Multiple tempering is more important to attain an acceptable structure if short tempering times are used
- Cobalt in alloys such as M42 reduces the amount of retained austenite in the as-quenched condition and accelerates the transformation of the retained austenite during tempering

3.4 Cryogenic treatment of Steels^[4]

Cryogenics is usually defined as the science and technology dealing with temperatures less than about 120 K. The techniques which are used to produce cryogenic temperatures are significantly different from those dealing with conventional refrigeration. One major point of difference is the need to precool the compressed gas before it is expanded in order to reach cryogenic temperatures when starting from 0 °C or higher. Precooling can be accomplished with a cascade of refrigerant baths or with a heat exchanger. The value of cryogenic treatment of steel and other materials has been debated for many years; even today many metallurgical professionals have serious reservations about its value.

Several theories exist in order to understand the reasons behind the use and evolvement of cryogenic treatment. One theory involves the more nearly complete transformation of retained austenite into martensite. This theory has been verified by x-ray diffraction measurements. Another theory is based on the strengthening of the material caused by precipitation of submicroscopic carbides as a result of the cryogenic treatment. Allied with this is the reduction in internal stresses in the martensite that happens when the submicroscopic carbide precipitation occurs. A reduction in micro cracking tendencies resulting from reduced internal stresses is also suggested as a reason for improved properties.

Cryogenic Treatment Cycles^[2]

Typical cryogenic treatment consists of a slow cool-down (~2.5 °C/min, or 4.5 °F/min) from ambient temperature to liquid nitrogen temperature. When the material reaches approximately 80 K (-315 °F), it is soaked for an appropriate time (generally 24 h). At the end of the soak period, the material is removed from the liquid nitrogen and allowed to warm to room temperature in ambient air. The temperature-time plot for this cryogenic treatment is shown in Fig.6. By conducting the cool-down cycle in gaseous nitrogen, temperature can be controlled accurately and thermal shock to the material is avoided. Single-cycle tempering is usually performed after cryogenic treatment to improve impact resistance, although double or triple tempering cycles are sometimes used.

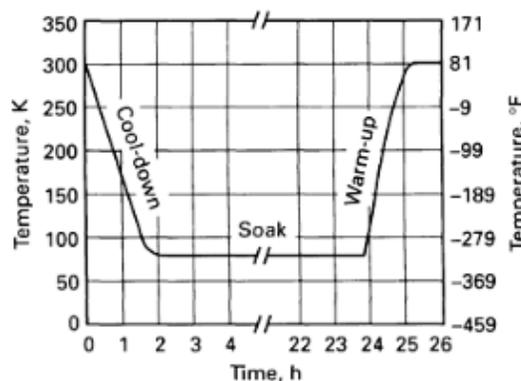


Fig. 6 Plot of temperature versus time for the cryogenic treatment process

Equipment for Cryogenic Treatment ^[2]

Liquid nitrogen systems have become the customary method for achieving cryogenic temperatures. The two types of systems are described below.

- ***The heat-exchanger system*** passes liquid nitrogen through a heat exchanger, and the exhaust gas from the unit is piped into the main gaseous-nitrogen header line. The chamber atmosphere is drawn over the heat-exchanger coils by a fan. In some versions of the system, the cooling is boosted by spraying liquid nitrogen directly into the chamber.
- ***The direct spray system*** sprays liquid nitrogen directly into the chamber, while a fan circulates the gases over the work. In this system, the spent gas cannot be recovered for use as a furnace atmosphere. The equipment design does not permit the liquid nitrogen to come into direct contact with the work, thereby reducing the probability of thermal shock.

In both systems, temperature controllers are used to control the flow of liquid nitrogen (through a solenoid valve) and to monitor the work temperature. Temperature charts of the cycle provide a record of the processing.

3.5 Cryogenic Treatment on Tool Steels

The complete treatment process in case of steels consists of Hardening (Austenitization + Quenching), CT, and Tempering. CT is an expanded process to conventional heat-treatment process (Hardening and Tempering). It has experimentally discovered that the CT, when carried out after quenching and prior to tempering, contributes to activation of the tempering transformations of the virgin martensite because of its high oversaturation attained at $-196\text{ }^{\circ}\text{C}$ (77 K). Due to this, the carbide precipitation occurs with higher activation energy, thus leading to a higher nucleation rate and, in turn, to finer dimensions and a more homogeneous distribution.

Depending upon the application of the temperature it may be classified as

- Cold treatment, which is also recognized as Shallow Cryogenic Treatment (SCT), is to gradually cool the work piece in the range $-84\text{ }^{\circ}\text{C}$ (189 K)
- CT or Cryogenic Treatment may also be explored as Deep Cryogenic Treatment (DCT) is carried out at about $-195\text{ }^{\circ}\text{C}$ (78 K).

Chapter III: Cryogenic Treatment

Section 1: Introduction

During the World War II, scientists found that, when metals were subjected to low temperatures, wear resistance increased. This fact led to the development of cryogenic treatment. The term “Cryogenic Processing” was first introduced by CryoTech Company (Detroit, MI, USA), in 1996. The main reason was the fact that they observed an increase in metal tool life of magnitude 200-400%, after practicing cryogenic and tempering.

Cryogenic treatment is a supplementary process to conventional heat treatment procedure in steels. It is an inexpensive one-time permanent treatment influencing the core properties of the treated material of the component unlike surface treatments, such as coatings. The sub-zero treatment is a well-known and an effective method to improve dimensional stability, fatigue behavior, toughness and wear resistance, which is commercially used to improve the performance of many metallic materials for decades.

In fine blanking, stamping and punching applications tools are exposed to very demanding contact conditions, including high loads, high contact pressures, elevated contact temperatures and wear. However, the type of tool failure mode and its progression depend on the tool material and heat treatment, tool shape, design and manufacturing, forming process parameters and work material. The biggest impact comes from the tool material and its microstructure. Apart from the conventional heat treatment, cryogenic treatment has been used for enhancing hardness and toughness and improving tool life. In the below paragraphs, the effects of cryogenic treatment on tool steel microstructure and mechanical properties will be examined.

Section 2: Microstructure

2.1 Retained Austenite

After conventional heat treatments, a small percentage of austenite remains in the material. This is a result of ambient temperature cooling conditions or temperature M_f of eutectoid martensite. This retained austenite is soft and unstable at lower temperatures. Consequently, this structure will be transformed into martensite in case of reheating or being submitted to a stress field, causing distortion on its body. This retained austenite transformed in non-tempered martensite may cause cracks, particularly in complex shape tools made of highly alloyed steels. However, in case of cryogenic treatment, the retained austenite will be transformed before tempering, providing dimensional stability in the tool steel.

According to the study of the effect of deep cryogenic treatments on the mechanical properties of an AISI H13^[28], the samples which were subjected to cryogenic treatment, reduced the retained austenite content, enhancing the dimensional stability of the dies, and leading to increased service lifetimes. Two specimens (samples 1 and 2) were likewise subjected to the heat treatments, in order the effect of quench severity to be studied, comparing oil and air as quenching media. The samples were heat treated following the bellow procedure (Table 3).

Table 3 Different heat treatment cycles on the samples

Heat Treatments and samples	Processing sequences		
HT1	Austenitizing at 1020 °C for 30 min. followed by gas quench	-	Triple tempering at 590 °C for 2 h
HT2	Austenitizing at 1020 °C for 30 min. followed by gas quench	Cryogenic treatment at -196 °C for 12 h	Triple tempering at 590 °C for 2 h
HT3	Austenitizing at 1020 °C for 30 min. followed by oil quench	-	Triple tempering at 590 °C for 2 h
HT4	Austenitizing at 1020 °C for 30 min. followed by oil quench	Cryogenic treatment at -196 °C for 12 h	Triple tempering at 590 °C for 2 h
Sample 1	Austenitizing at 1020 °C for 30 min. followed by air quench (Q)	Cryogenic treatment at -196 °C for 12 h (C)	Triple tempering at 590 °C for 2 h (3T)
Sample 2	Austenitizing at 1020 °C for 30 min. followed by oil quench (Q)	Cryogenic treatment at -196 °C for 12 h (C)	Triple tempering at 590 °C for 2 h (3T)

Table 4 Retained austenite content as a function of the heat treatment (HT) and the carbide correction, Volume fraction % (error %)

Heat Treatment	HT1	HT2	HT3	HT4
Retained austenite content without carbide correction ^a	3.7 (±1.3)	2.3 (±1.2)	2.9 (±1.1)	2.5 (±1.0)
Retained austenite content after carbide correction ^b	3.3 (±1.1)	2.0 (±1.0)	2.5 (±1.0)	2.2 (±1.0)
^a $V_a + V_\gamma = 1$				
^b $V_a + V_\gamma + V_c = 1$				

As it is observed (Table 4), despite the carbide correction, the samples treated by cryogenic treatment retain a smaller percentage of austenite in their microstructure. In some cases, the retained austenite is minimized. Nevertheless, there is a low austenite content that could not be transformed even after the application of cryogenic treatment. It is hence considered not to have any negative effect during the forging process, as it will not be susceptible to transformation during the service life of the die. Thus, cryogenic treatment contributes to the mechanical stabilization of the retained austenite, avoiding the formation of martensite during the normal service life of tool steels. It is essential to examine the effect of the quenching medium on the retained austenite content (Fig. 7). Oil quenching resulted in lower austenite content than air quenching, due to the former's higher cooling rate. In fact, the higher retained austenite content after air quenching is a consequence of the stabilization of the austenite owing to the lower cooling rate. Thus, the cryogenic stage modifies the residual austenite content, especially for air quenching.

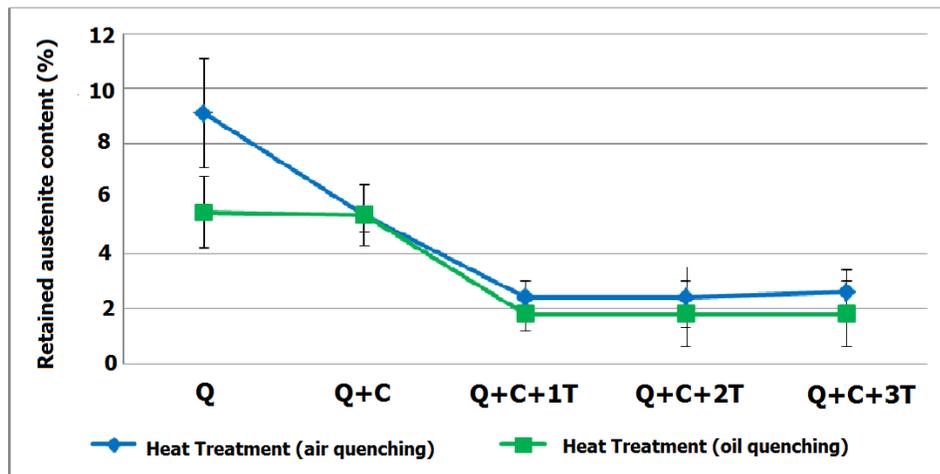


Fig. 7 Evolution of the retained austenite (%) throughout the overall heat treatment (without carbide correction); Quenching (Q), Cryogenic (C), Tempering (T)

It is relevant to note that martensitic transformation never goes to completion, and the retained austenite always exists in the structure of high-carbon martensites. Another study [23] suggested that the reduction of retained austenite, as a transformation into martensite, may improve the wear resistance of the material. In the particular experiment, samples of HSS tool steel, especially M2, are subjected to the heat treatment cycles presented in Table 5.

Table 5 Different cycles applied to M2 high speed steel

Different cycles applied to M2 high speed steel	
A	Quenching from 1250 °C + triple tempering at 560 °C
B	Quenching from 1250 °C + 1 cycle 24 h sub-zero at -196 °C+ triple tempering at 560 °C
C	Quenching from 1250 °C + 1 cycle 48 h sub-zero at -196 °C+ triple tempering at 560 °C
D	Quenching from 1250 °C + 3 cycles 48 h sub-zero at -196 °C+ triple tempering at 560 °C
E	Quenching from 1250 °C + triple tempering at 560 °C+ 1 cycle 48 h sub-zero at -196 °C

Using X-ray diffractometer, Seyed Ebrahim Vahdat et a.l. observed that there is a significant difference in retained austenite between the treated and non-treated samples. The cryogenically treated material showed nearly 0% of retained austenite into microstructure, in comparison with the untreated tool steels which retain austenite in a percentage of 25%. However, the transformation of the retained austenite into martensite did not result in a significant improvement of wear resistance, at the conditions the sliding abrasion test was carried out. Literature results showed that, depending on the test parameters such as normal load, average grain size and type of the abrasive, quantity and shape of the carbides, among others, the increasing of the amount of retained austenite can lead to an increase or to a decrease in the wear rate of ferrous alloys. This behavior is regarded with the ability of austenite to harden during plastic deformation either by workhardening or by martensite transformation.

It is essential to notice that the results depend on the conditions on which the heat treatment has been carried out. The above statement can be confirmed by the next study. J.y. Huang et a.l studied the microstructure of cryogenic treated M2 tool steel [20]. The samples were subjected to austenitization at 1100 °C in a nitrogen atmosphere at 20 Pa, holding for 1 h, followed by quenching to an ambient temperature in a cool nitrogen gas. Cryogenic treatment was performed by soaking the samples in liquid nitrogen at -196 °C for 1 week and both treated and non-treated specimens were tempered at 200 °C in nitrogen atmosphere for 24 h. X-ray diffraction showed no detection of retained austenite in treated samples, due to small percentage. Although, the volume fraction of retained austenite was measured to be almost the same in both treated and non-treated samples, wear resistance was improved in case of cryogenic treatment. Thus, transformation of retained austenite is not a main factor of influence for wear resistance, for the particular tool steel.

Soaking time can be a significant factor influencing the amount of retained austenite. In a study of deep cryogenic treatment in tool steel X220CrVMo 13-4 (DIN 1.2380)^[19], which is a high-carbon, high-chromium air-hardening tool steel, A.I. Tyshchenkoa et al subjected the samples to different cycles of heat treatment, including cryogenic treatment. These specimens were held for austenitization at 1080 °C for 20 min under protective pure argon atmosphere and cooled using the flow of the cold argon. After quenching, some of the specimens were cooled to -196 or -150 °C with holding at these temperatures for 24, 36 or 48 h.

Table 6 Retained austenite after different treatment cycles

Cooling after solution treatment	Martensite	RA	Carbide	F _{e0}	F _{e1}
Quenching at RT	81.7	7.7	10.6	27.2	34.0
RT → -196 °C (24h)	86.6	4.1	9.3	24.3	37.3
RT → -196 °C (36h)	87.0	3.9	9.1	22.8	38.8
RT → -196 °C (48h)	87.3	3.7	9.0	19.9	43.3
RT → -196 °C (24h)	89.1	3.5	7.4	15.2	46.3
RT (1 week) → -196 °C (24h)	85.6	5.8	8.6	21.2	36.5

From Table 6, it can be observed that the samples which were subjected at -196 °C for 48h, showed the smallest percentage of retained austenite into microstructure, among the other groups subjected at the same temperature. However, it is essential to notice that the cryogenic cycle at -150 °C was more effective than the one in liquid nitrogen. Moreover, in case of the preliminary ageing at RT before cryogenic treatment, A.I. Tyshchenkoa et al observed that, in comparison with cryogenic treatment at -196 °C for 24h, the stabilization of the retained austenite decreased the amount of the low-temperature martensite. This behavior is justified by the fact that after quenching, the austenite-to-martensite transformation does not stop sharply and the transformation rate decreases for a number of months.

A. Akhbarizadeh et al^[11] confirmed the above results, after studying the effect of cryogenic treatment on D6 tool steel. The samples were subjected to different cycles of cryogenic treatment and were examined for comparison with the conventional heat treatment (Table 7). As far as deep cryogenic treatment is concerned, retained austenite could not be detected due to its very small percentage. For the other types of treatment, retained austenite was observed in small amount (Table 8).

Table 7 Heat treatment cycles on tool steel D6

Name	Heat Treatment	Sample No
CHT	Conventional heat treatment	1
SCT20	Shallow cryogenically treated at -63 °C for 20h	2
SSCT20	Stabilized for 1 week in room temperature and shallow cryogenically treated at -63 °C for 20h	3
SCT40	Shallow cryogenically treated at -63 °C for 40h	4
SSCT40	Stabilized for 1 week in room temperature and shallow cryogenically treated at -63 °C for 40h	5
DCT	Cryogenically treated at -63 °C for 40h and deep cryogenically treated with quench in liquid nitrogen for 10h	6
SDCT	Stabilized for 1 week in room temperature and shallow cryogenically treated at -63 °C for 40h and deep cryogenically treated with quench in liquid nitrogen for 10h	7

Table 8 Retained austenite percentage

Sample	Retained austenite percent (%)
CHT	12.4
SCT20	8
SSCT20	53
SCT40	65
SSCT40	4.7
DCT	Was not seen
SDCT	Was not seen

The results showed that more retained austenite is transformed by increasing soaking time. Moreover, decrease in soaking temperature achieves the transformation of more retained austenite. As far as the last cycle is concerned, the treated samples, which were stabilized for 1 week, showed lower retained austenite as compared with the non-stabilized samples, which was expected.

Soaking temperature affects the volume fraction of the retained austenite. The lower the temperature, the bigger percentage of austenite transforms into martensite. This is shown by the study of shallow and deep cryogenic treatment on tool steel H13^[10]. The samples were held at 1040°C, achieving austenitization, and then being subjected to air quenching before the cryogenic treatment. Specimens were treated at either cryogenic temperature at -72 °C or deep cryogenic temperature at -196 °C for 8 h. In the end, the tempering procedure was held at 560 °C on some of the samples, in order to compare the results on the properties. The heat treatment procedures are presented in Table 9.

Table 9 Heat treatment sequences of tool steel H13

Samples	Processing Sequences			
1	Heat treated at 1040 °C for 30 min followed by air quench	Tempered at 560 °C for 2 h	-	-
2	Heat treated at 1040 °C for 30 min followed by air quench	Tempered at 560 °C for 2 h	Cryogenic treatment at -72 °C for 8 h	-
3	Heat treated at 1040 °C for 30 min followed by air quench	Tempered at 560 °C for 2 h	Deep Cryogenic treatment at -196 °C for 8 h	-
4	Heat treated at 1040 °C for 30 min followed by air quench	Tempered at 560 °C for 2 h	Cryogenic treatment at -72 °C for 8 h	Tempered at 560 °C for 2 h

The samples, which were subjected to conventional heat treatment, showed a significant percentage of retained austenite, resulting in negative effect on mechanical properties of tool steels, such as machinability, wear resistance, hardness and most important dimensional stability. In Table 10, the percentages of retained austenite for every heat treatment are presented.

Table 10 Retained austenite volume content after different treatment cycles

Sample	Retained austenite percent (%)
1	8.1
2	7.4
3	4.5
4	3.8

In contrast, the application of cryogenic treatment was very effective on the microstructure of the alloy, resulting in transformation of the retained austenite into martensite. Since, two different cryogenic temperatures were applied, Mahdi Koneshlou et al.^[10] observed that as the temperature is lowered, the amount of transformed austenite increases. Moreover, the transformation of austenite into martensite increased the volume, causing tensile stress on austenite. According to Fig. 8, the martensite laths were smaller and distributed more uniformly in the microstructure after holding the samples for a long time at the deep cryogenic temperatures. The microstructure modification can be very important in terms of mechanical properties of and dimensional stability of the tool steel.

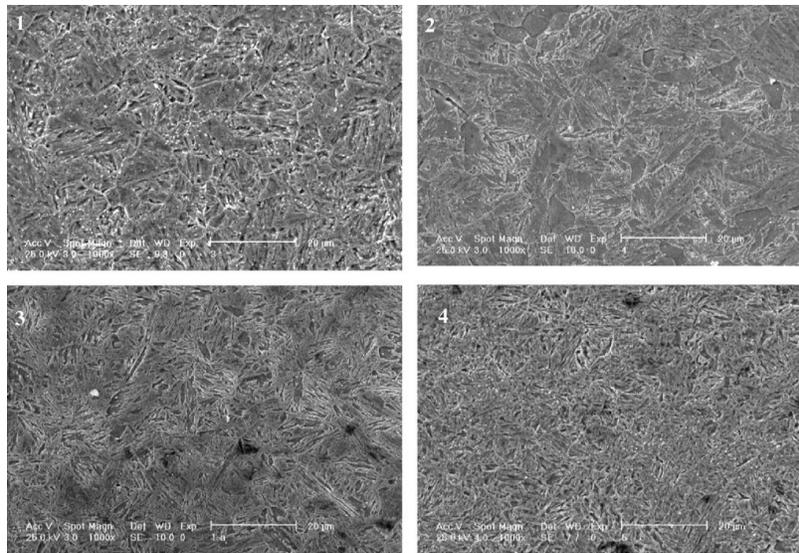


Fig. 8 Scanning electron microscopy images of the samples 1–4 after different heat treatment cycle

After the hardening process by cryogenic treatment, material expansion is observed. This expansion is caused by the phenomenon of transformation of the retained austenite. The tempering procedure is carried out in order to achieve stabilization and releasing the stress of the martensitic structure. Thus, most studies carry out mostly three tempering procedures.

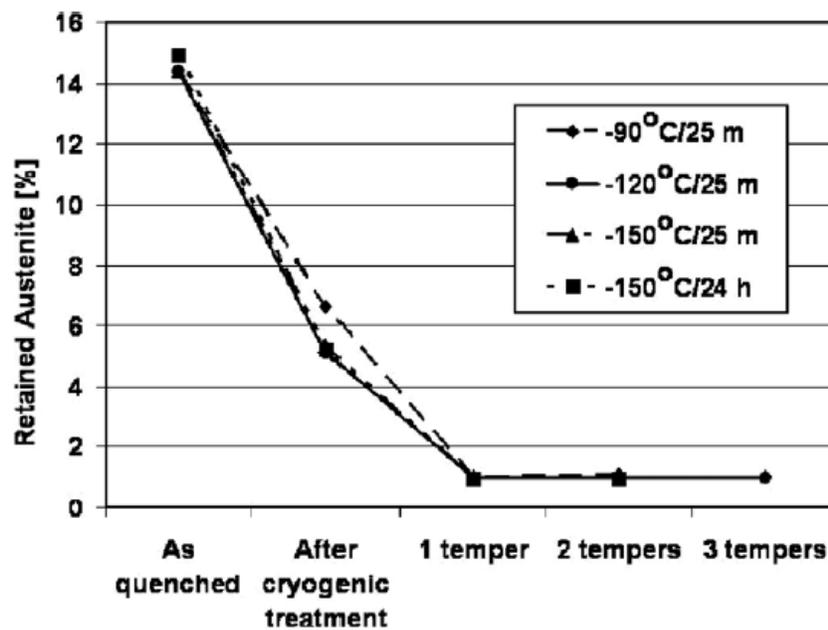


Fig. 9 The effect of deep cold treatment on retained austenite for an austenitising temperature of 1070 °C for tool steel D2.

The first tempering manages to release the stress of the martensite and as a result the material shrinks. During the second tempering, the carbides begin to grow and stabilization is achieved. Finally, the third tempering has usually no noticeable effect. Such procedure is carried out on the study of cryogenic treatment on AISI D2 tool steel [30]. According to Cord Henrik Surberg et al., after third tempering, dimensions do not face significant changes (Fig. 10). Moreover, it can be seen that after the first tempering, the retained austenite remains below 2% with no further change after the second and third tempering procedure (Fig. 9).

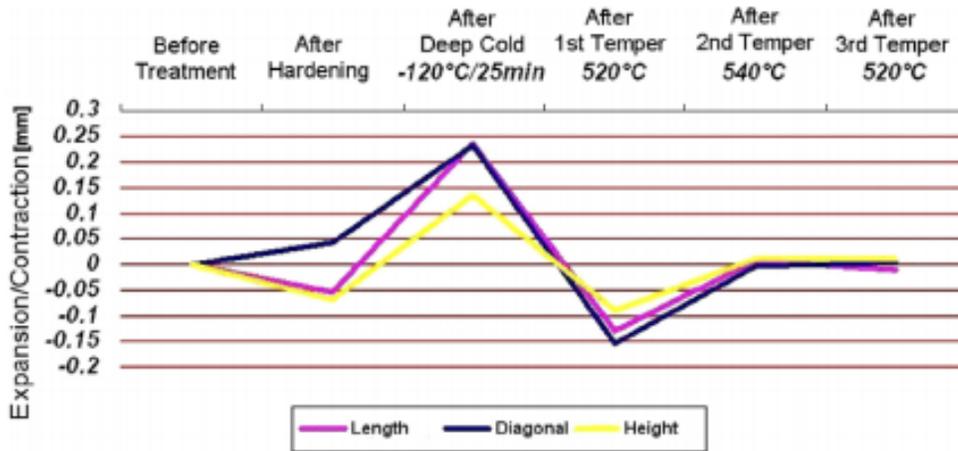


Fig. 10 The effect of a deep cold treatment on dimensional stability

According to the experiment, the samples were subjected to different soaking temperatures and time. Thus, in regard with the previous studies, it is confirmed that the lower the temperature, the greater the expansion during deep cryogenic treatment because more retained austenite is transformed. Dimensional stability is independent of the soaking time during deep cryogenic treatment (Fig. 11).

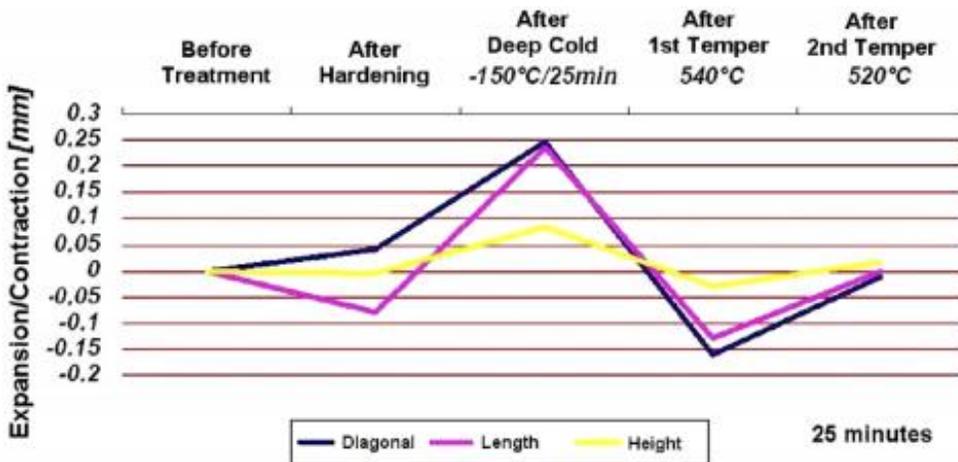


Fig. 11 Comparison of dimensional stability after treatment at various deep cold temperatures for 25 min

This retained austenite is soft and unstable at lower temperatures that it is likely to transform into martensite under certain conducive conditions. Thus retained austenite should be alleviated to the maximum possible before any component or tool is put into service. The degree of undercooling decides the potential to transform retained austenite to martensite completely.

The transformation of the austenite to martensite in combination with thermal contraction caused surface tensile residual stress to all the specimens. According to Marcos Pérez and Francisco Javier Belzunce ^[28], a slight relaxation in stress was observed, during cryogenic procedure, due to fine carbides precipitation (Fig. 12). Specifically, during heating up to room temperature after cryogenic stage, small carbides are formed by clusters. These clusters were made when the carbon atoms inside the martensitic matrix, segregated to nearby structural defects, during cryogenic process. Significant improvement on relaxation of stress is observed during first tempering procedure, as a result of carbide precipitation and decrease in carbon content of martensite. However, the second and third tempering had no effect on the stress state. The second tempering is used as a procedure to transform the martensite, which is formed during cooling of the first tempering. Although, the samples are subjected to third tempering, the new fresh martensite form cooling of the second tempering can be detected.

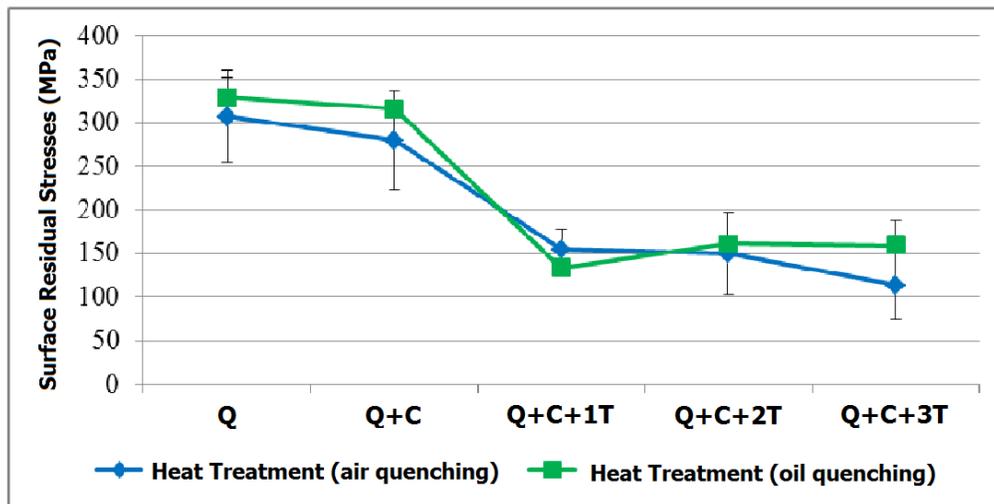


Fig. 12 Evolution of the surface stress versus the quenching medium for each stage of the overall heat treatment (Q-Quenching, C-Cryogenic, T-Tempering)

2.2 Carbide precipitation

Apart from the transformation of the retained austenite into martensite, deep cryogenic treatment contributes to the formation of finer martensite laths in the microstructure and initiates nucleation sites for precipitation of fine carbide particles. The precipitation of finer carbides results in the enhancement of mechanical properties of the alloy. The subzero procedure results in facilitating the formation of carbon clustering and increases the carbide density in the microstructure.

Inside the matrix of tool steel subjected to heat treatment, two types of carbides are observed:

- Primary Carbides (PCs), which form on the grain boundaries during quenching. Although the formation of the primary carbides has no significant impact on hardness, may lower tool steel fracture resistance. This leads to quench cracking intergranular fracture of overheated tool steels, or reduced performance of hot work die steels such as H13.^[24]
- Secondary Carbides (SCs), known as transition carbides. These carbides are formed during the first stage of tempering and are identified as ϵ -carbides (epsilon-carbides) and η -carbides (eta-carbides). The transition carbide has an orthorhombic structure isomorphous with transition metal carbides of the M_2C type. The transition carbide is characterized by carbon contents substantially higher than that of the cementite, Fe_3C , which forms at higher temperatures. Throughout the range of η -carbides formation, a percentage of carbon in the martensite is retained and randomly dissolved in the retained austenite with the martensite, during tempering.^[24]

J.Y. Huang et al.^[20] observed that the carbides, demonstrated in the microstructure, were uniformly dispersed. They were localized in certain regions, and their size varied from region to region. As a result of the precipitation of the fine carbides, wear resistance of material increased and there was reduction in micro cracking tendency from reduced internal stress.

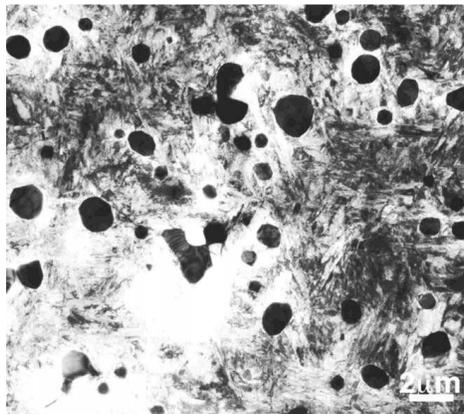


Fig. 13 TEM micrographs of M2 tool steel after cryogenic treatment and tempering.

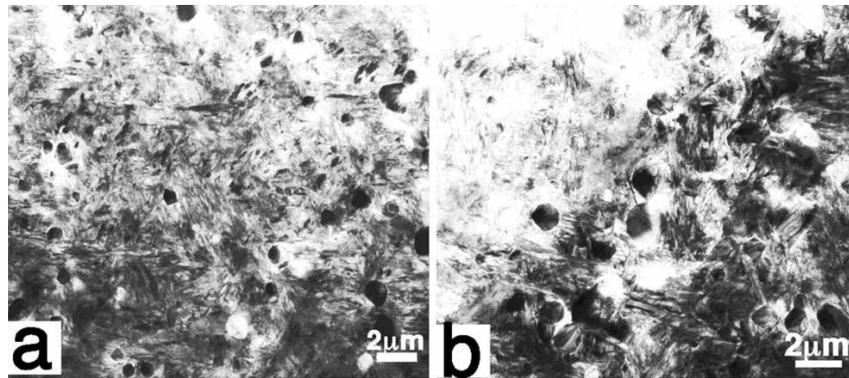


Fig. 14 TEM micrographs of M2 tool steel after non-cryogenic treatment and tempering. Note that the carbides in (a) are small, while those in (b) are large.

It is essential to mention that the volume fraction of carbides in the cryogenically treated sample was higher (11%) than that in the non-cryogenically treated ones (5%) (Fig. 13, 14). The precipitation of more hard carbides in the cryogenically treated samples resulted in reduction of carbon and alloy contents in the matrix, which improved the toughness of the matrix. J.Y. Huang et al.^[20] mentions the fact that the combination of higher carbide content and tougher matrix enhanced the wear resistance.

A study of cryogenic treatment on W9Mo3Cr4V high speed steel^[13], showed the different types of carbides that are precipitated in the microstructure. Fig. 16 exhibits a non-uniform distribution of primary carbides and a fairly uniform distribution of secondary carbides in the tempered martensite matrix. Every SEM picture shows the microstructure for samples cryogenically treated at 193 K (b), 153K (d), 113 K (f), 77 K (h) respectively. The first picture shows the microstructure of the samples that are subjected to conventional heat treatment (a). In the microstructure, X.G. Yan and D.Y.Li observed resolved prior austenite grain boundaries. As it can be seen, the large, irregular white regions represent the primary carbides (PCs – Primary Carbides). The amount, size and distribution of them appear identical irrespective of the type of heat treatment. This behavior is justified because time and temperature of austenitization are responsible for the characteristics of the primary carbides. Moreover, there are two types of the secondary carbides. The SEM pictures show some tiny white patches (SSCs – Small Secondary Carbides) and some small white regions (LSCs – Large Secondary Carbides). The volume fraction of the secondary carbides, especially the SSCs, is affected by the heat treatment condition. Apparently, fraction volume of the secondary carbides increases with the decrease of the cryogenic temperature.

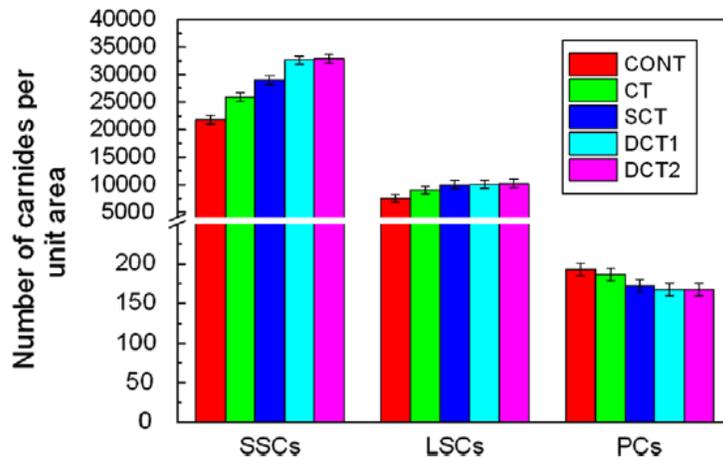


Fig. 15 Quantitative information on the volume fractions of carbides in samples experienced different sub-zero treatments of W9Mo3Cr4V high speed steel. The volume fraction of carbides is represented by the number of carbides per unit area

Fig. 15 presents that the samples, which were subjected to cryogenic treatment, showed increase for all the types of carbides, in comparison with the conventional heat treatment. The deep cryogenic treatment provided increase in secondary carbides, in contrast with the shallow cryogenic treatment.

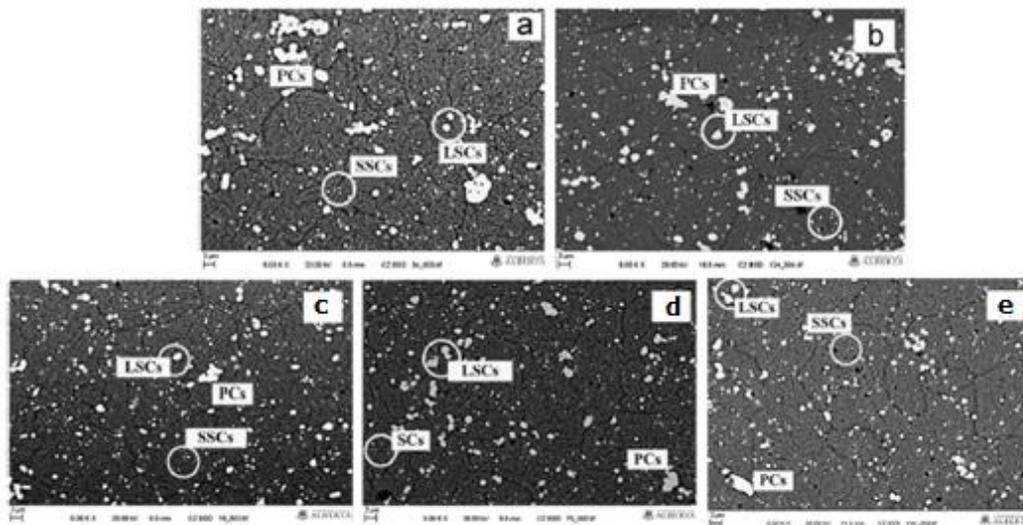


Fig. 16 SEM micrographs of samples experienced different heat treatment processes. The microstructure of the W9HSS samples generally consists of a matrix of tempered martensite and carbides, including primary carbides (PCs: size 45 μm) and secondary carbides (SCs: size 5 μm), which are further sub-classified as large secondary carbides (LSCs: 1 μm < size < 5 μm) and small secondary carbides (SSCs: size < 1 μm): (a) SEM micrograph of CONT; (b) SEM micrograph of CT; (c) SEM micrograph of SCT; (d) SEM micrograph of DCT1; (e) SEM micrograph of DCT2;

Seyed Ebrahim Vahdat et al. examined microstructure of 45WCrV7 tool steel after deep cryogenic treatment [22]. The specimens were subjected to austenitization at 900 °C for 1h, then deep cryogenic treatment at -195 °C for 24h, 36h, 48h and finally they are tempered at 200 °C for 1h, 2h, 3h. (Fig. 17).

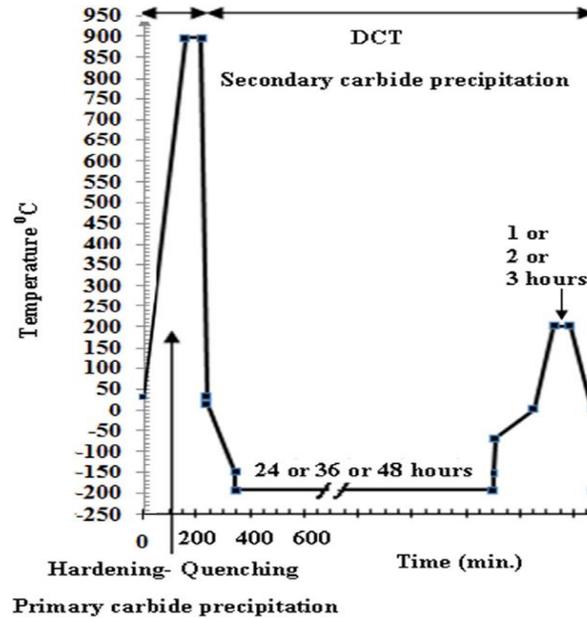


Fig. 17 DCT cycle

According to researchers, the first mechanism of precipitation of secondary carbide (SCs) is the result by the expansion from the transformation of retained austenite into martensite. The second mechanism is caused by the difference in thermal contraction of the phases. The below SEM picture (Fig. 18) shows the different types of carbides inside the matrix of the samples.

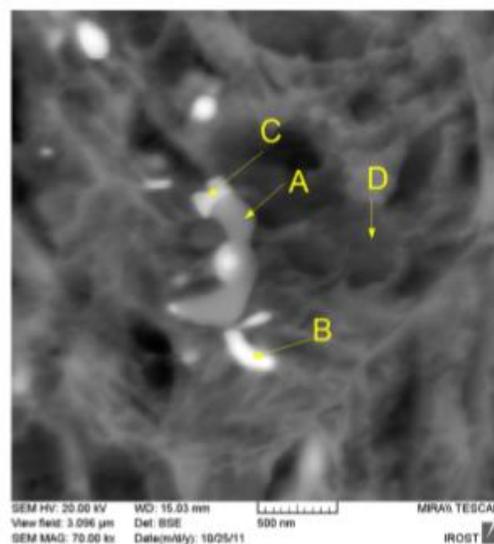


Fig. 18 SEM image, 20 kV, in which letters A, B and C show different carbides and D is the matrix of 45WCrV7

Letters A and C represent the primary carbides (M_7C_3) and letter B represent the secondary carbides ($M_{23}C_6$). Letter D is the matrix of the material. The primary carbides are characterized by grey color, since they have higher carbon content than the secondary carbides. Thus, region B is presented by a white spherical phase. Letter M represents either W, or Cr, Si, Fe.

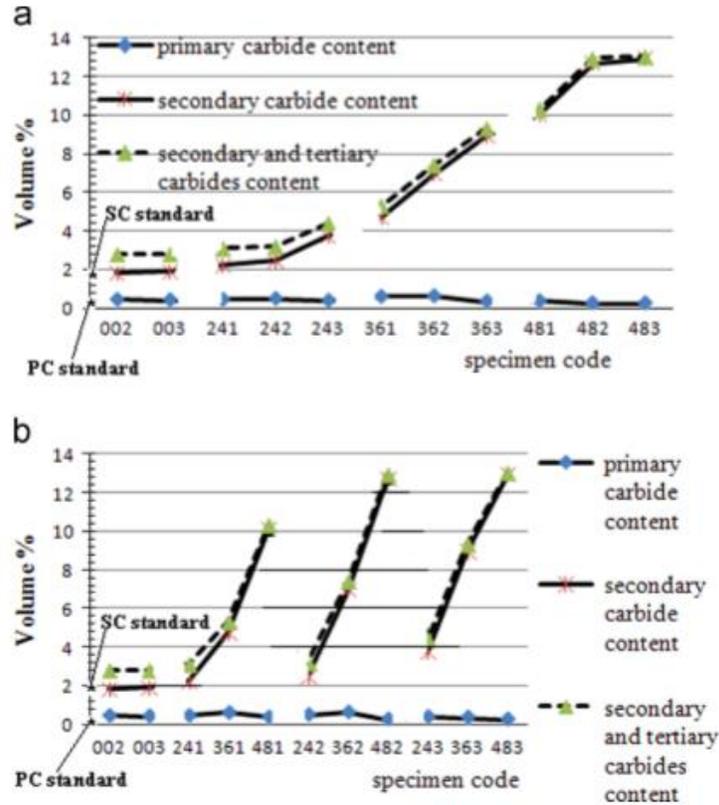


Fig. 19 PC, SC and tertiary carbide volume fraction (a) tempering time trend and (b) soaking time trend

Seyed Ebrahim Vahdat et al. [22] mentions that, according to Fig. 19, volume fraction of the secondary carbides increases with the tempering time. Greater effect on the increase of the secondary carbides is given by soaking time, due to defect density around the PCs in the phase matrix. However, volume fraction of the primary carbides remains constant irrespective of tempering and soaking time. Another point worth mentioned is that specimens 002, 003 have the volume fraction of SCs almost constant, since the conditions of formation of SC were not facilitated. In conclusion, cryogenically treated samples showed precipitation of fine secondary carbides. This subzero procedure increased their volume fraction and their population density, causing the formation of more homogenous and refined microstructure.

B. Podgornik et al. [9] used high C and V content cold-work steel A2, cold work tool steel A1 lower C and high W and Co content and high speed tool steel B1 and examined the microstructure after conventional heat treatment (Fig. 20) and deep cryogenic treatment at -196 °C for 25 h. Three groups of the materials were formed (Table 11).

Table 11 Different treatment cycles for tool steels A1, A2, B1

Group	Austenitizing		DC Treatment		Tempering	
	Temp [°C]	Soaking time [min]	Temp [°C]	Immersion time [h]	Temp [°C]	Time [h]
A1						
1	1130	6	-	-	520/520/500	2/2/2
2	1100	20	-	-	500/500/480	2/2/2
3	1070	20	-	-	585/585/565	2/2/2
1P	1130	6	-196	25	520	2
2P	1100	20	-196	25	500	2
3P	1070	20	-196	25	585	2
A2						
1	1180	6	-	-	540/540/510	2/2/2
2	1180	6	-	-	560/560/530	2/2/2
3	1180	6	-	-	500/500/480	2/2/2
1P	1180	6	-196	25	540	2
2P	1180	6	-196	25	560	2
3P	1180	6	-196	25	500	2
B1						
1	1180	2	-	-	530/530/500	2/2/2
2	1100	20	-	-	560/560/530	2/2/2
3	1030	20	-	-	570/570/540	2/2/2
1P	1180	2	-196	25	530	2
2P	1100	20	-196	25	560	2
3P	1030	20	-196	25	570	2

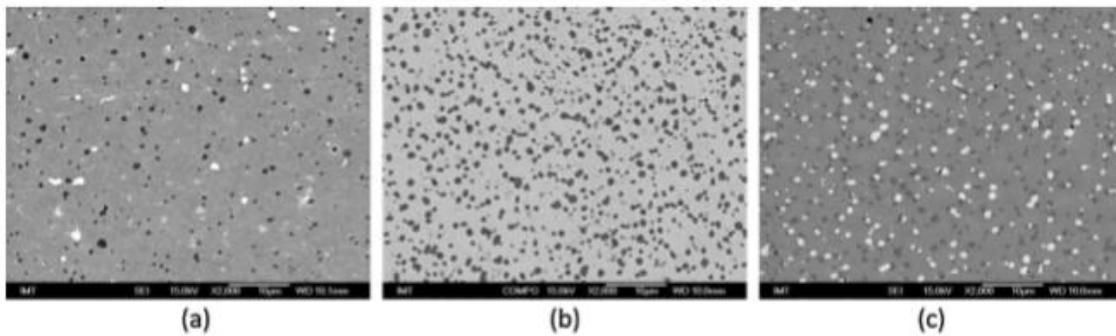


Fig. 20 Typical SEM images for analysis of undissolved eutectic carbides (MC—grey/black and M6C—white) after conventional heat treatment from the highest austenitizing temperature (1180 °C) for (a) tool steel A1, (b) tool steel A2 and (c) tool steel B1 tool steel A2

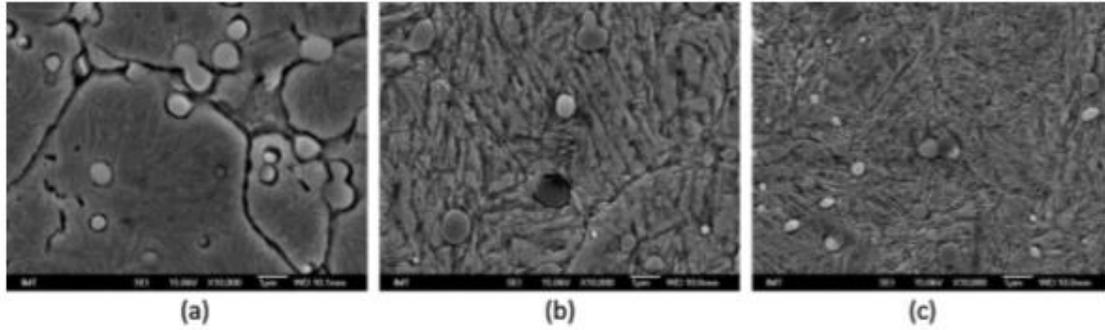


Fig. 21 Microstructure of A1 cold work tool steel after (a) quenching, (b) conventional triple tempering (group 1) and (c) DCT and single tempering (group 1P)

Table 12 Quantitative metallographic analysis (^a below the detection limit)

Group	Conventional heat treatment				Deep Cryogenic treatment (P)			
	Grain size		Volume Fraction [%]		Grain size		Volume Fraction [%]	
	[μm]	ISO 643	Carbides	RA	[μm]	ISO 643	Carbides	RA
A1								
1	3.7	G13	4.43±0.37	<1.0 ^a	3.8	G13	4.38±0.27	<1.0 ^a
2	2.9	G14	4.85±0.43	<1.0 ^a	2.9	G14	4.98±0.38	<1.0 ^a
3	2.6	G14	5.05±0.36	<1.0 ^a	2.8	G14	5.50±0.27	<1.0 ^a
A2								
1	2.1	G15	19.40±1.33	<1.0 ^a	2.0	G15	19.25±0.53	<1.0 ^a
2	1.8	G15	19.25±0.65	<1.0 ^a	1.8	G15	18.20±1.43	<1.0 ^a
3	2.2	G15	19.30±0.63	<1.0 ^a	1.5	G15	18.76±0.99	<1.0 ^a
B1								
1	2.3	G15	16.82±1.21	<1.0 ^a	2.1	G15	16.20±1.41	<1.0 ^a
2	2.1	G15	18.17±2.06	<1.0 ^a	1.8	G15	17.84±1.59	<1.0 ^a
3	1.9	G15	20.49±1.70	<1.0 ^a	2.0	G15	20.72±1.70	<1.0 ^a

As it can be seen from Table 12, for tool steel A1, the grain size of the prior-austenite stayed between 2.6 and 3.8 μm in the microstructure. Moreover, volume fraction of the fine uniformly distributed carbides (eutectic carbides of MC – grey/black, M_6C – white) reached the value of 5%. As far as the retained austenite is concerned, the volume fraction after cryogenic treatment and tempering was below the detection limit (1%) (Fig. 21). It is essential to notice that decrease in tempering temperature caused increase in the volume fraction of the carbides. However, deep cryogenic treatment had no significant effect on both retained austenite and volume of carbides.

In the case of tool steel A2, the increased content of C and V caused reduction to prior-austenite grain size, in contrast with A1. Moreover, the grain size of the undissolved eutectic carbides showed great increase, being mainly of MC type. Similar results were observed for the high speed steel B2, although the carbides are both MC and M_6C . However, none of the three types of

tool steels showed significant effect in grain size and carbide volume fraction after deep cryogenic treatment.

The advantage of cryogenic treatment is the formation of fine uniformly distributed carbides, which have significant positive effects in strength, fracture toughness and structure homogeneity. Strength and fracture toughness are described in the next paragraph.

As discussed above, in tool steels there are three types of carbides morphologies: large carbides, which do not dissolve during austenitization, secondary microcarbides, distributed during quenching, and secondary nanocarbides, formed during tempering. Thus, cryogenic treatment affects only the nanocarbides during tempering, and let primary and secondary carbides keep their characteristics.

For cryogenically treated tool steel H13 samples, microstructural analysis exhibited expected tempered martensite, involving fine spherical homogeneously dispersed carbides [28]. Marcos Pérez and Francisco Javier Belzunce presented that there is a significant difference in the carbides precipitation between the treated and non-treated samples (Fig. 22). HT1 treatment cycle exhibited a relatively coarse and sometimes elongated appearance. However, samples subjected to cryogenic treatment in cycle HT4 showed a more uniform distribution of finer carbides. Thus, cryogenic treatment provided a homogeneous distribution of finer carbides and increases their volume fraction. It is important to mention that the characteristics of the carbide network have a positive effect in toughness of H13.

According to the study, the precipitation of fine η -carbides (transition carbides) was observed in the structural defects created during the quenching and cryogenic stages. Moreover, there was an in-situ nucleation of M_3C carbides (cementite) on η -carbides. The final formation of alloy carbides was responsible for secondary hardening. In the case of chromium containing tool steels, M_3C carbides transform to M_7C_3 , whereas in tool steels containing molybdenum, M_3C carbides transform to M_2C . As H13 steel has both chromium and molybdenum, M_3C carbides are supposed to transform into M_7C_3 and M_2C .

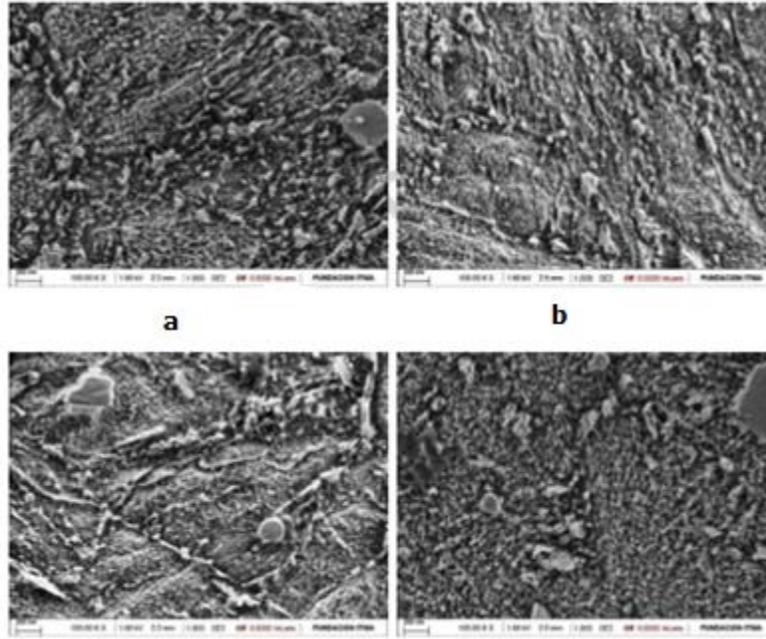


Fig. 22 H13 steel microstructure at 100000x magnification (FEG-SEM): a) HT1, b) HT2, c) HT3 and d) HT4

On Table 13, volume fraction of carbides for the four different heat treatments is presented. Tool steel H13 kept the volume up to 10%. In cases HT3 and HT4, the cryogenically treated samples showed increase in volume fraction, in comparison with the non-treated samples, as expected. Comparing the HT1-HT2 and HT3-HT4, it was observed that the increase in carbide percentage of H13 tool steel reached 22.3% and 8.2% respectively. Moreover, the effect of more severe quenching medium, such as oil quenching, was great and resulted in increase in carbide content of 30% between HT1 and HT4.

Table 13 Volume fraction of carbides (%) measured in the different heat treatments (HT)

Heat treatment	HT1	HT2	HT3	HT4
Carbide content V_c (%)	11.2	13.7	13.4	14.5

Thus, increase in carbide content provides increase in toughness, since the carbon content of the martensitic matrix phase will be lower. Thus, deep cryogenic treatment affects microstructure of materials in a significantly positive way. Homogenization and stabilization of internal microstructure benefits mechanical properties of tool steels, including hardness and wear resistance and improve quality and production control of tool parts.

Mahdi Koneshlou et al.^[10] confirmed the above statement by examining the characteristics of carbides during cryogenic treatment at -72°C and deep cryogenic treatment -196°C . H13 tool steel holds a microstructure of large carbide particles inside the matrix. After tempering stage,

precipitation of finer carbides was observed, in case of deep cryogenic treatment. Moreover, through the scanning electron microscope picture (Fig. 23), there were two different types of carbides: (a) chromium (black), (b) and molybdenum (white) carbides. The chromium carbides were the dominant carbides in the microstructure.

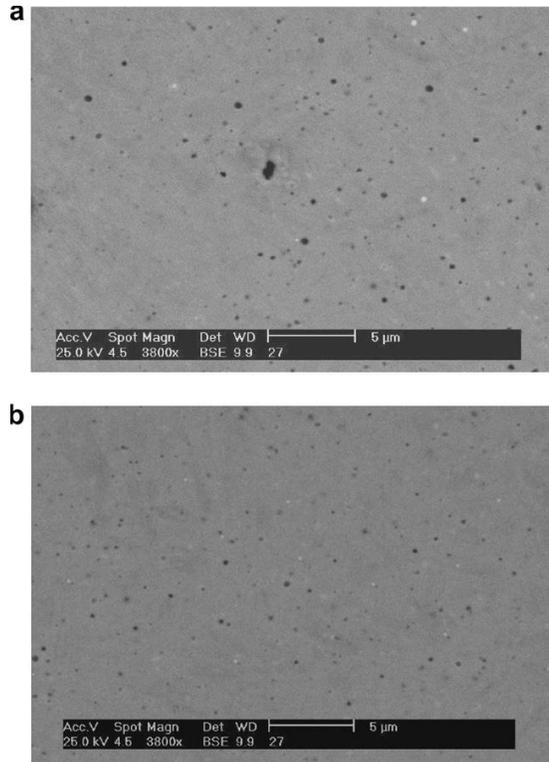


Figure 23 Scanning electron microscopy images showing the effect of deep cryogenic treatment on the chromium (black) and molybdenum (white) carbides distribution of sample 1 (a) and sample 4 (b)

The sample, which was subjected to deep cryogenic treatment, showed a fine and more uniform distribution of spherical carbides in the microstructure after tempering. The percentage of carbides was measured to be 5.8% for the non-treated sample. For shallow cryogenic treatment, the percentage was not affected and remained similar. However, the deep cryogenically treated sample showed an increase in value which reached 6.9%. The increase in volume fraction is caused by the transformation of the retained austenite to martensite and the precipitation of more carbides. The more spherical and uniform carbides benefit hardness, which is an essential factor in tool steel applications. Furthermore, it is confirmed that deep cryogenic treatment results in the formation of finer martensite laths in the microstructure. This formation is a main factor which initiates nucleation sites for the precipitation of fine carbide particles, resulting in the enhancement of mechanical properties of the H13 tool steel.

Section 3: Hardness and Fracture Toughness

Cryogenic treatment affects microstructure of tool steel, enhancing mechanical properties, especially hardness and wear resistance. In general, materials with a face-centered cubic (fcc) lattice keep their ductility at cryogenic temperatures, whereas body-centered cubic (bcc) and hexagonal-closed packed (hcp) materials become brittle (jawahir2016). The increase in hardness is caused by the transformation of austenite to martensite, resulting in great martensite content. Another factor is the precipitation of finer carbides, uniformly distributed in matrix.

A. Akhbarizadeh et al.^[11] proved the above statement by subjecting D6 tool steel to cryogenic treatment. According to mechanical properties of D6, hardness without heat treatment reaches the value of 46 Rockwell C. After carrying out the different types of hardening treatments, it was observed that deep cryogenic treatment provided greater increase in hardness of material (Table 4). Although, shallow cryogenic treatment showed higher hardness than conventional treatment, in the case of deep cryogenic process, the combination of transformed retained austenite with more homogenized chromium carbide distribution and higher chromium carbide percentage exhibited better results. Compared with the non-stabilized samples, the stabilized ones did not show significant increase in hardness.

Table 14 The hardness (HRC) of the heat-treated D6 tool steel samples after and before temper

Sample	After tempering	Before tempering
SHT	62±0.5	64±0.7
SCT20	62.5±0.6	65±0.5
SSCT20	63.3±0.4	65.5±0.4
SCT40	63±0.5	65.5±0.3
SSCT40	63.5±0.6	66±0.5
DCT	64±0.4	66.7±0.4
SDCT	64.2±0.3	67±0.5

Hardness and fracture toughness have an inversely proportional relationship. In fact, deep cryogenic treatment causes increase in hardness but decrease in toughness. Debdulal Das et al.^[18] came to the conclusion that fracture toughness decreases almost linearly with increase in both macrohardness and microhardness (Fig. 24). The specimens were subjected to the below heat treatments:

- CHT – Conventional HT
- CT – Cold Treatment at -75°C for 5 min
- SCT – Shallow Cryogenic Treatment at -125°C for 5 min
- DCT – Deep Cryogenic Treatment at -196°C for 36 hrs

The deep cryogenically treated samples of D2 tool steel showed moderate fracture toughness, in contrast with higher value of hardness. The variations of the fracture toughness between the different heat treatments were due to alterations of the matrix microstructure. The matrix of all of the studied specimens consisted of secondary carbide particles in the tempered martensite, while the presence of retained austenite had been identified only for the conventionally treated and cold treated specimens. Since the characteristics of the secondary carbides were modified by the conditions of the heat treatments, the variations were related to these microstructure alterations.

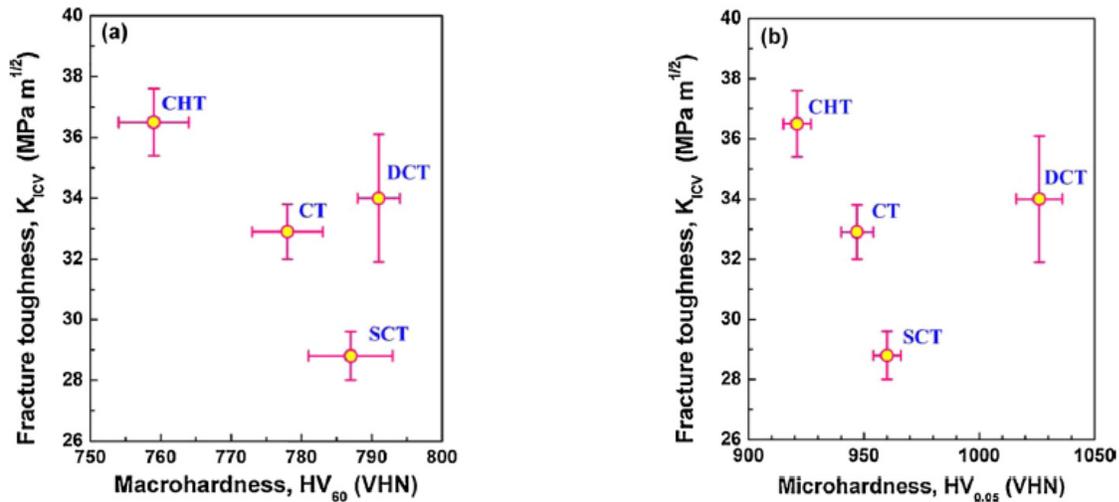


Fig. 24 Variations of fracture toughness with Vickers (a) macrohardness and (b) microhardness of the investigated specimens. CHT: conventionally heat treated, CT: cold treated, SCT: shallow cryogenically treated, DCT: deep cryogenically treated.

It can be seen that the degree of improvement in hardness varies with the type of cryogenic treatment (Fig. 25). Deep cryogenic treatment shows higher value of hardness than shallow type. Moreover, it can be seen that the subzero treatment has a more significant effect in case of microhardness, compare to macrohardness. In fact, study ^[27] shows that the improvement in microhardness over conventional treatment reaches 8.1%, in contrast with 11.4% for bulk hardness. The increase in bulk hardness can be related to reduction of austenite, improvement of amount of secondary carbides and tough tempered martensite.

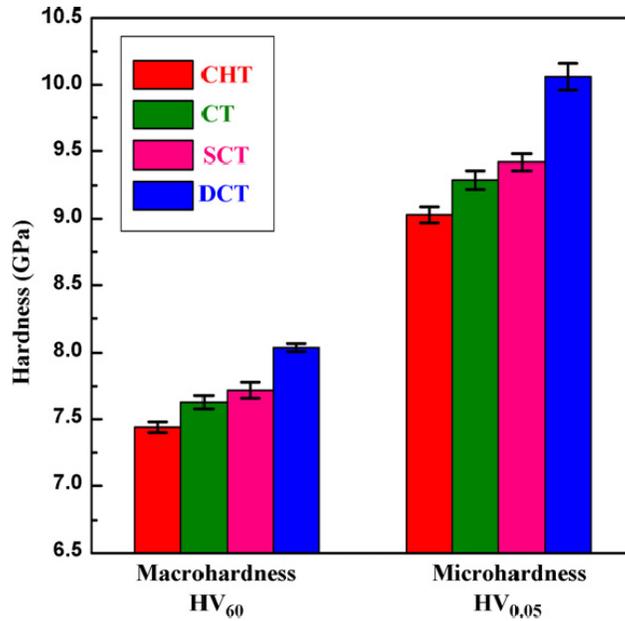


Fig. 25 Effect of heat treatment schedules on the variation of macrohardness (HV₆₀) and microhardness (HV_{0.05}) values. CHT: conventionally heat treated; CT: cold treated; SCT: shallow cryogenically treated; DCT: deep cryogenically treated of tool steels D2.

Cord Henrik Surberg, Paul Stratton and Klaus Lingenhole ^[30] suggest that deep cryogenic treatment between hardening and tempering process improves mechanical properties and dimensional stability. The samples of D2 tool steel were subjected to cryogenic treatment at -50 °C, -120 °C, and -150 °C. As it can in Table 15, the treated samples at -120 °C for 2h show improve in hardness since the percentage of retained austenite is reduced.

Table 15 The effect of cryogenic treatment at -120 °C for 2 h on position dependent retained austenite for an austenitising temperature of 1070 °C

Position	Before cryogenic treatment		After cryogenic treatment	
	RA (%)	Hardness (HRC)	RA (%)	Hardness (HRC)
Core	15	65.2	10	66.0
Surface	16	64.2	6	66.4
Edge	17	64.6	6.5	66.5

Lowering the cryogenic temperature results in less significant change in hardness of the material. During the study of microstructure and mechanical properties of H13 tool steel after cryogenic treatment ^[10] Mahdi Koneshlou et al suggested that deep cryogenic treatment showed higher value of hardness, although the change was not great compared to shallow type. The main reason was the fact that a significant percentage of the retained austenite had been transformed. The tempered samples, after cryogenic treatment, show the highest hardness, since the process resulted in better distribution of martensite laths along with the more uniform and finer exhibition of carbides (Table 16).

Table 16 Ultimate tensile strength and hardness of samples H13 tool steel

Samples	Ultimate tensile strength (MPa)	Hardness (HRC)	Impact energy (J)
1	1580	49	15.4
2	1640	51	16.1
3	1695	55	17.3
4	1720	59	18.2

Although, it seems that cryogenic treatment affects in a positive way the hardness of the material, the degree of improvement is related to austenitization temperature. B. Podgornik et al.^[9] suggested that the higher austenitization temperature provides the highest value of hardness (Fig. 26). A1 tool steel reached the highest hardness, but the lowest fracture toughness at the highest austenitizing temperature of 1130 °C. On the other hand, A1 tool steel has the highest toughness and lowest hardness value at the lowest austenitizing temperature of 1070 °C and high tempering temperature of 500 °C. As far as B1 high speed steel is concerned, similar result are observed, reaching the highest value of hardness at the highest austenitizing temperature of 1180 °C and the highest value of fracture toughness at the lowest austenitizing temperature of 1030 °C and high tempering temperature of 530 °C. In the case of A2, austenitizing temperature remains constant for all three groups at 1180 °C. Maximum hardness and maximum toughness is reached at tempering temperature of 540 °C.

In conclusion, it can be seen that deep cryogenic treatment at -196 °C has no significant effect in hardness of A1 tool steel, although there is improvement in fracture toughness. In Group 1, fracture toughness increased at almost 70%, for an extremely small drop of hardness. For Group 2, hardness is maintained at the same level and the increase in fracture is lower than Group 1. The lower degree of change is observed in Group 3, in which toughness increases only about 10%, whereas hardness remains constant. According to the study, this behavior can be related to plastic deformation of primary martensite accompanying martensitic transformation, partial dissolution of carbide particles and formation of carbon clusters. This plastic deformation, in combination with reduced amount of dissolved carbon in the martensite and finer and more homogeneous carbides precipitation improved fracture toughness. In the case of B1, improvement of toughness reaches 10% in Group 1 at the highest value of hardness, whereas in two other groups increase reaches 5%. Thus, deep cryogenic treatment had no effect on B1 high speed steel hardness and fracture toughness. The small effect can be attributed to very small volume fraction of retained austenite in B1 steel after quenching, but mainly to high volume fraction of undissolved eutectic carbides. Finally, for A2 tool steel, deep cryogenic treatment had negative effect, since in all three groups, it led to reduction in fracture toughness. In fact, in two of the three groups, reduction in hardness is observed. This behavior is justified by the presence of undissolved eutectic carbides, as for B1.

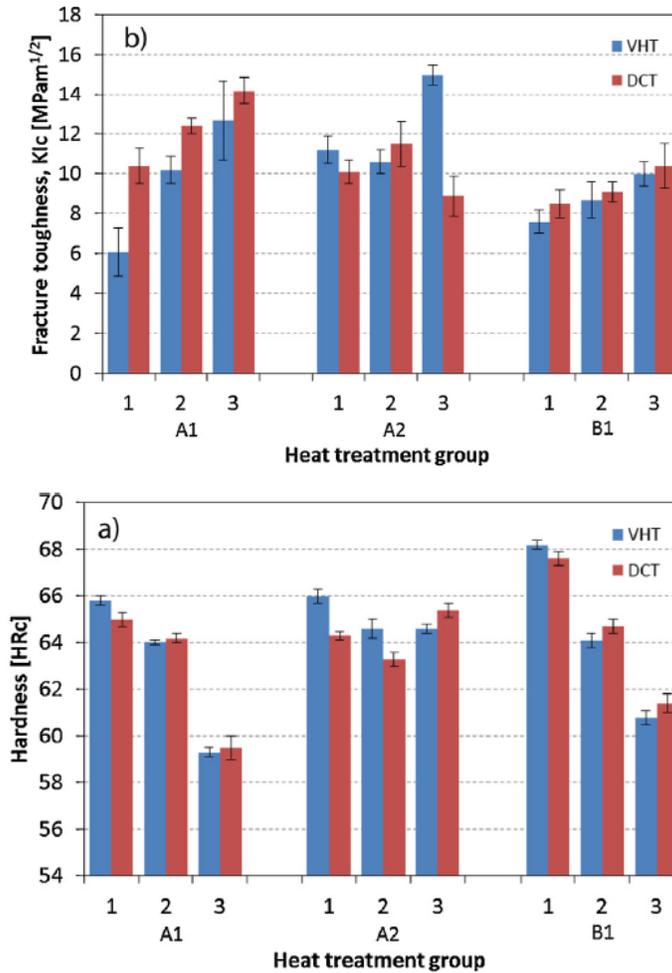


Fig. 26 Effect of deep cryogenic treatment on (a) hardness, (b) fracture toughness

Seyed Ebrahim Vahdat et al.^[22] compared the treated specimens with the non-treated ones, for tool steel 45WCrV7, and discovered that hardness of DCT specimens showed 9-12% increase. The non-treated material was subjected to oil quenching and tempering at 450 °C, whereas the deep cryogenically treated samples were quenched in water prior to DCT. Improvement in both toughness and hardness was observed in specimens, which were subjected to cryogenic treatment at -196 °C for 36h and tempering at 200 °C for 1h and specimens subjected to cryogenic treatment at -196 °C for 48h and tempering at 200 °C for 2h.

For the treated 45WCrV7 tool steel, maximum toughness is achieved by simultaneously increasing soaking and tempering times. However, it is essential to value time and cost of production. Thus, specimens, subjected to cryogenic treatment at -196 °C for 36h and tempering at 200 °C for 1h, is a more feasible option. On the other hand, maximum hardness is obtained by increasing either soaking or tempering times. In this case, a more feasible option would be the specimens which were subjected to cryogenic treatment at -196 °C for 24h and tempering at 200 °C for 3h.

3 Cryogenic treatment in different stages and in combination with surface treatments

Microstructure and mechanical properties can be affected by the conditions on which cryogenic treatment is carried out. In many cases, cryogenic treatment is held after tempering procedure. In other cases, surface treatment, especially TiN coating is used before or after cryogenic treatment. The effect of these combinations is examined in multiple studies, which are presented below.

The process of nitriding is a ferritic thermochemical treatment and usually involves the introduction of atomic nitrogen into the ferrite phase in the temperature range 500-590 °C and consequently no phase transformation occurs on cooling to room temperature. The method was first used at the end of the 1920s and since then its application has continuously spread, due among other things to the fact that the process has been further developed and can now be applied to a much larger number of steels than was originally thought possible

D. Mohan Lal et al.^[7] used samples of M2, T1, D3 tool steels and subjected them to cryogenic treatment before and after tempering, as well as coating with titanium before and after the subzero process (Table 17). The study showed that the samples with prior tempering exhibited 69% and 33.9% improvement on M2 and D3 respectively. However, post tempering procedure improved the above tool steel samples at a percentage of 86.6% and 48% respectively. Hence, tempering procedure after cryogenic treatment is a more desirable option. This can be attributed to stabilization of carbides and microstructural phases during tempering process, which inhibits further transformation during cryogenic treatment. Moreover, cryogenic treatment is carried out at a very slow rate for cooling and heating. In that way, the process itself relieves the brittleness and stress accumulated. As a result, a post tempering procedure relieves any brittleness remaining.

Table 17 Different hardening treatment cycles

Cases	Nomenclature followed
Hardened and tempered	SHT
Cryotreated at 93 K for 24 h	CT (93/24)
Cryotreated at 133 K for 24 h	CT (133/24)
Cryotreated at 163 K for 24 h	CT (163/24)
Cryotreated at 93 K for 6 h	CT (93/6)
Cryotreated at 93 K for 6 h and quenched in LN ₂ for 2 h	CT (93/6) + LN ₂ /2
Tempered and cryotreated at 133 K for 24 h	TCT (133/24)
Tempered and cryotreated at 93 K for 24 h	TCT (93/24)
Titanium nitride coated	TiN
Cryotreated (CT 93/24) and then coated with Titanium	CT + TiN
Titanium nitride coated and then cryotreated (CT 93/24)	TiN + CT

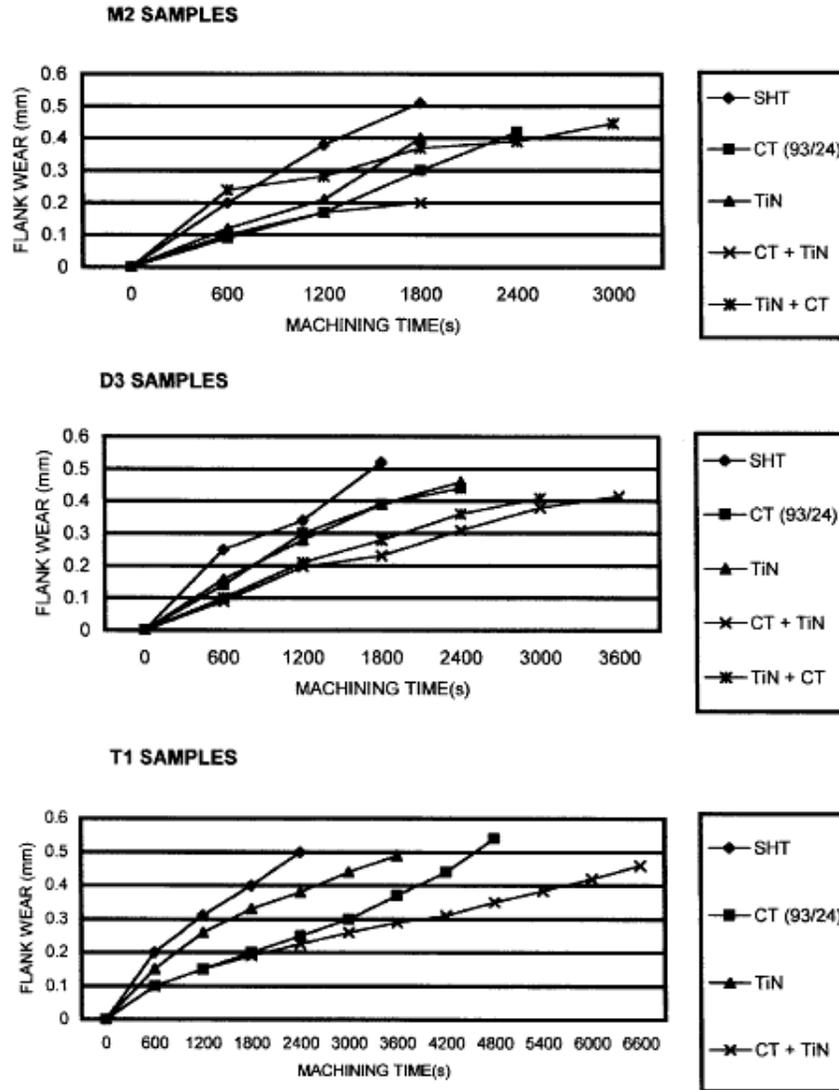


Fig. 27 Flank wear versus machining time for different cases

From Fig. 27, it can be observed that TiN-coating caused 48.4%, 42%, 41% improvement while cryogenic treatment showed 110.2%, 86.6% and 48% in T1, M2, D3 steels, respectively. Thus, it is observed that cryotreated tools outperformed TiN-coated tools, while the cost of TiN coating and cryogenic treatment were 25% and 10% of the tool cost, respectively. The case of coating the cryogenically treated samples showed improvement of 205.3%, 153% and 146% for T1, M2, D3 respectively. On the other hand, a prior coating treatment at the treated samples caused less improvement, reaching the percentage of only 104% and 109% in M2, D3 respectively. Hence, cryogenic treatment on TiN coated samples is not favorable, since it results in shorter tool life. This may be attributed to the uneven contraction during cryotreatment of the coating material and the substrate leading to incipient cracks at the interface. Hence cryotreatment should not be done after TiN coating.

The process of Nitriding was, also, carried out for four tool steel grades: X38CrMoV5-1, 55NiCrMoV6 and Swedish steel grades Uddeholm HOTVAR and Uddeholm QRO 90 Supreme. [Error! Reference source not found.] The samples were nitrided both before and after cryogenic treatment. The impact in hardness of X38CrMoV5-1 tool steel is distributed on Fig. 28.

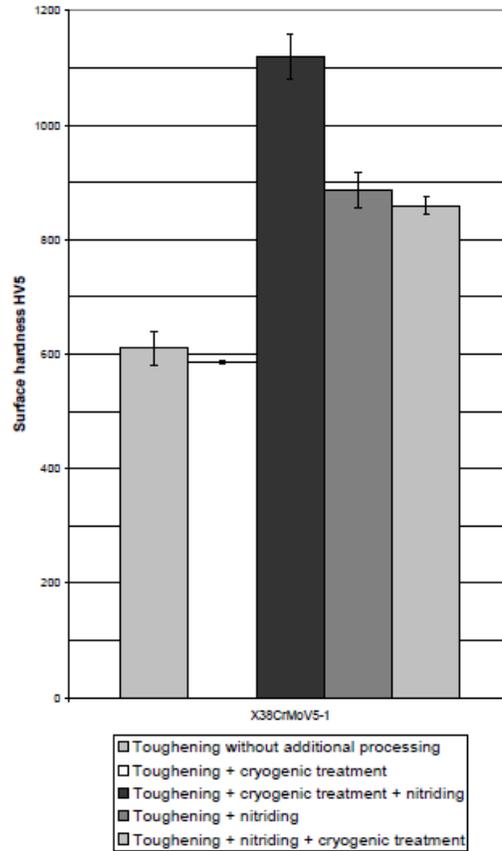


Fig. 28 Averages and 95% confidence intervals of surface hardness HV5 of X38CrMoV5-1 tool steel specimens after hardening and tempering and after various types of additional treatment

It can be observed that, in comparison with the prior nitriding hardening process, post nitriding treatment exhibits greater value of hardness for the particular tool steel sample. Moreover, in the case of conventional heat treatment and then nitriding, the samples show higher value of hardness than the process of hardening + nitriding + cryogenic treatment. However, according to researchers the drop in hardness for the second case mentioned was insignificant and fell within statistical error. Similar relations between the different hardening processes are shown on the below distribution (Fig. 29). In the case of the combination of cryogenic treatment followed by nitriding, extremely high value of hardness was achieved at great depth from surface. Similar changes in microhardness were seen for the HOTVAR and QRO 90 Supreme steel as well. The process of cryogenic treatment carried out prior to nitriding and structural transformations associated with this process seem to facilitate diffusion nitriding, thus affecting both the depth and the hardness of the internal nitrogen hardening zone.

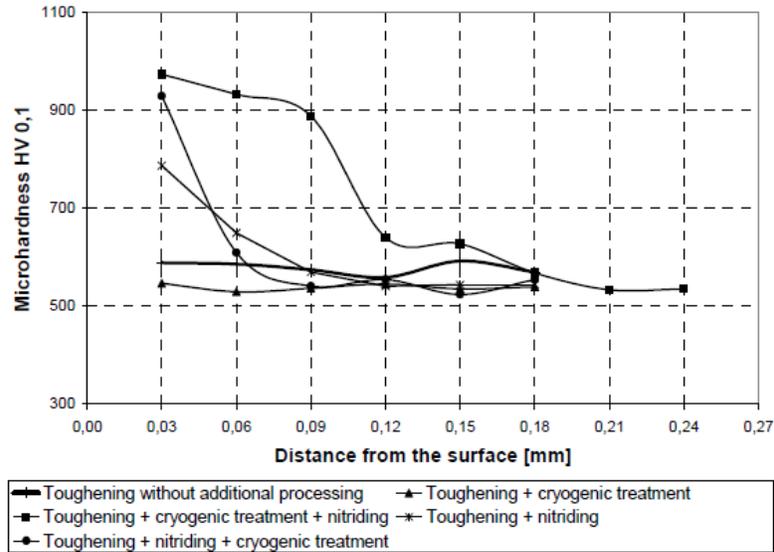


Fig. 29 Microhardness profiles of X38CrMoV5-1 tool steel specimens after hardening and tempering and after various types of additional treatment

The volume fraction of retained austenite in samples treated by DCT is related to the sequence between cryogenic treating and tempering. The above statement is justified by the study of microstructure and hardness of tool steel Cr8Mo2SiV, during different heating treatments and cycles. [17] The cryogenically treated samples were austenitized at 1040 °C, quenched in oil and then DCT treated in different cycles at -196 °C in liquid nitrogen, whereas the non-treated ones were subjected to conventional hardening and tempered at 210 °C in a vacuum furnace under flowing argon atmosphere (Table 18).

Table 18 Different cycles of heat treatment for tool steel Cr8Mo2SiV

Groups	Details of treatment	Nomenclature
No.1	Hardening & tempering (2 times)	HT
No.2	Hardening & DCT (2h) & tempering (2 times)	HCT2
No.3	Hardening & DCT (24h) & tempering (2 times)	HCT24
No.4	Hardening & tempering (2 times) & DCT (24h)	HTC
No.5	Hardening & DCT (3 times, 1h) & tempering (2 times)	HC3T
No.6	Hardening & tempering (1 time) & DCT (24h) & tempering (1 time)	HTCT

As it was discussed in previous paragraphs, the higher hardness of the cryogenic treated samples is due to the decrease of the retained austenite. Fig. 30 shows the XRD profiles associated with the martensite reflections and the carbon content of martensite for all DCT treating cycles. The results show the carbon content in the martensite decreased when prolonger the soaking time in the liquid nitrogen for the quenched samples. Executing the deep cryogenic treatment after tempering, increases the volume fraction of retained austenite in a higher level in contrast with

the case of subzero treatment prior to tempering (Table 19). The possible reason is the retained austenite stabilized after tempering and the stabilized retained austenite is beneficial to toughness.

Table 19 Retained austenite percentage according to every cycle

Nomenclature	Retained austenite percent (%)
HT	23.25
HCT2	2.87
HCT24	2.79
HTC	4.65
HC3T	3.05
HTCT	5.72

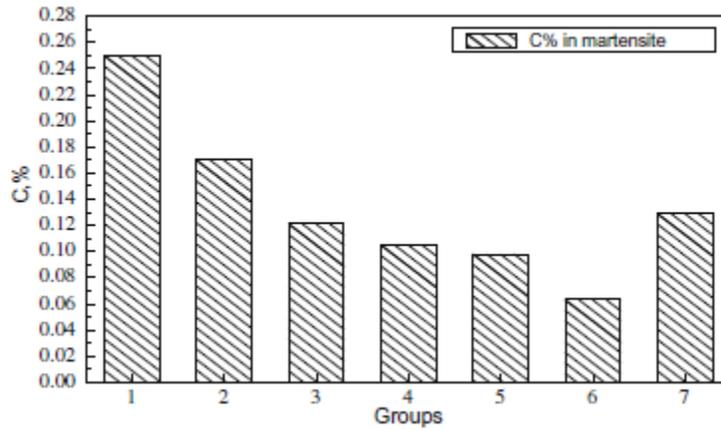


Fig. 30 The carbon content in martensite for all heat treatment cycles

Shaohong Li, et al. observed that deep cryogenic treatment after tempering achieves increase in toughness, whereas hardness is not affected. The reason can be found in the precipitation of carbides during tempering. Moreover, the samples, which were subjected to deep cryogenic treatment before tempering, show higher value of hardness [HCT2 (+2.5HRC) and HCT24 (+3.5HRC)] than the ones in the case of prior tempering. When the samples repeated several times in the liquid nitrogen, the hardness increased as high as carrying out the deep cryogenic treatment between quenching and tempering for 2 h, and the lower toughness was obtained. The reason is probably the internal stress increased and micro cracks produced when the samples repeated several times in the liquid nitrogen. It is indicated that the hardness obviously increased when carried out the deep cryogenic treatment between quenching and tempering.

The effects of the subzero treatment with prior tempering are observed in the microstructure of the tool steel W9Mo3Cr4V high speed steel [13]. Cryogenic treatment with prior tempering led to less increase in the volume fraction of the secondary carbide particles, compared to subzero treatment with subsequent tempering (Fig. 31). Moreover, the subsequent tempering process resulted in more secondary carbides, especially in the increase in the amount of small secondary carbides (Fig. 32).

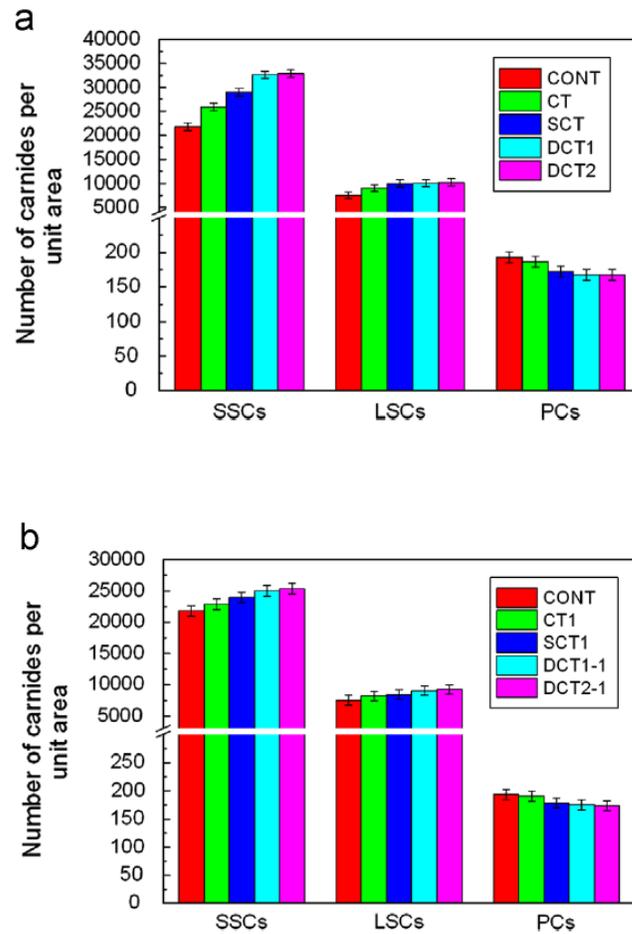


Fig. 31 Quantitative information on the volume fractions of carbides in samples experienced different sub-zero treatments for W9Mo3Cr4V. The volume fraction of carbides is represented by the number of carbides per unit area: (a) sub-zero treatment with subsequent tempering; (b) sub-zero treatment with prior tempering

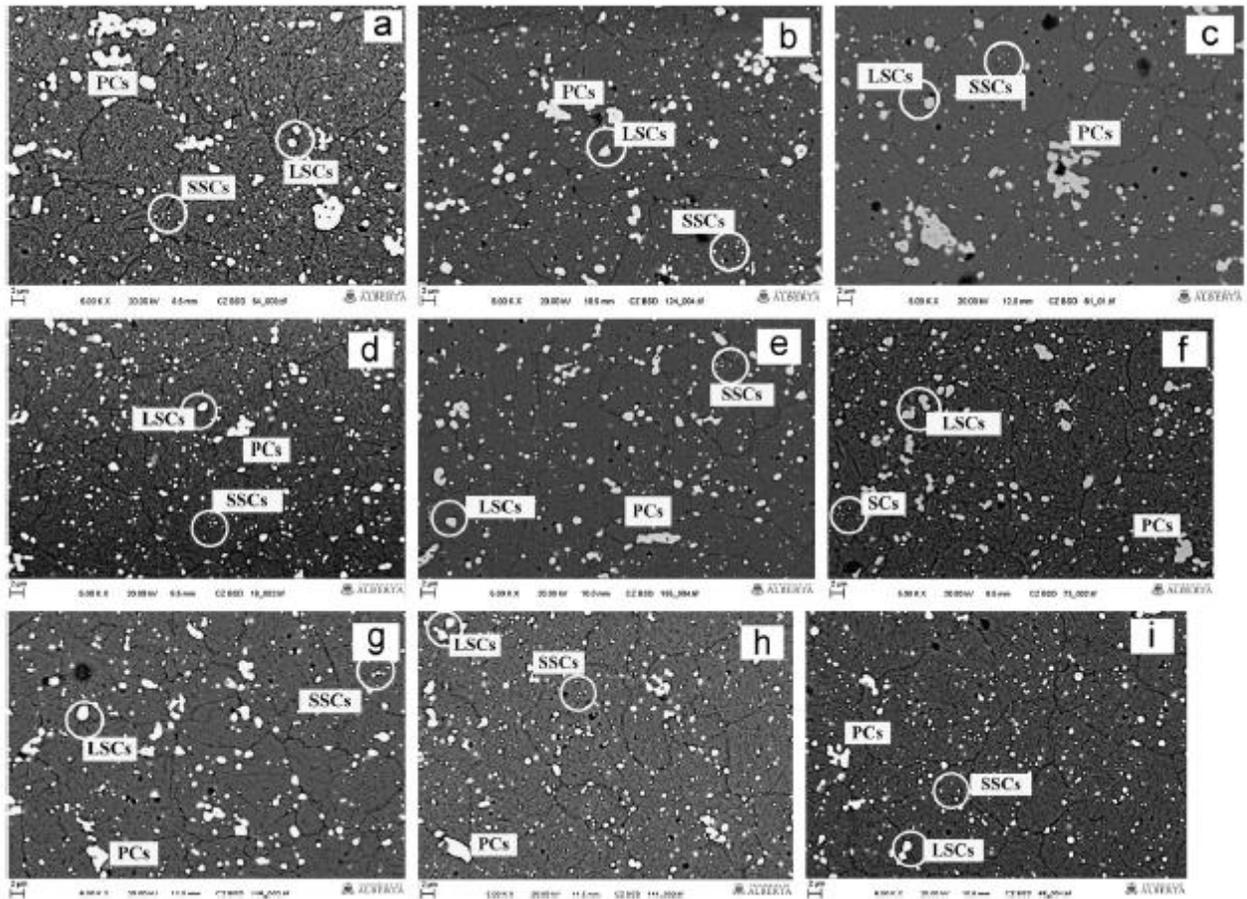


Fig. 32 SEM micrographs of samples W9Mo3Cr4V experienced different heat treatment processes. The microstructure of the W9HSS samples generally consists of a matrix of tempered martensite and carbides, including primary carbides (PCs: size 45 μm) and secondary carbides (SCs: size 5 μm), which are further sub-classified as large secondary carbides (LSCs: 1 μm < size < 5 μm) and small secondary carbides (SSCs: size < 1 μm): (a) SEM micrograph of CONT; (b) SEM micrograph of CT; (c) SEM micrograph of CT1; (d) SEM micrograph of SCT; (e) SEM micrograph of SCT1; (f) SEM micrograph of DCT1; (g) SEM micrograph of DCT1-1; (h) SEM micrograph of DCT2; (i) SEM micrograph of DCT2-1.

As far as hardness is concerned, subzero treatment with prior tempering led to slight improvement, compared to conventional heat treatment. On the other hand, cryogenic treatment with subsequent tempering showed significant increase in hardness. Fig. 33 exhibits the difference in hardness between the two heat treatments.

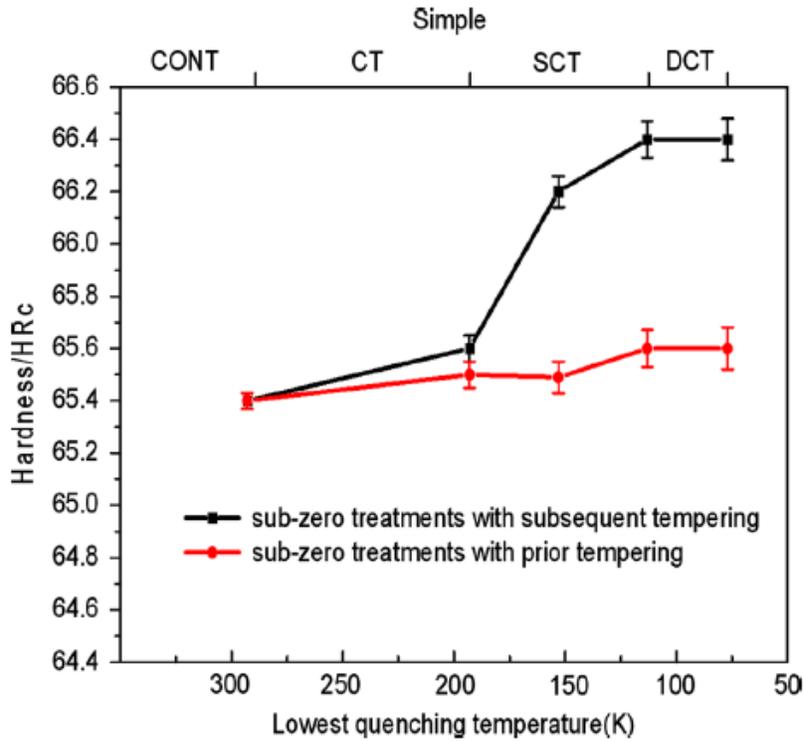


Fig. 33 Hardness values of samples experienced different heat treatment processes in different temperature ranges (CONT, CT, SCT, and DCT) for W9Mo3Cr4V

As illustrated, the sub-zero treatment with subsequent tempering is more effective in strengthening the material than in the case with prior tempering. For sub-zero treatments with subsequent tempering, SCT W9 HSS samples showed significantly higher hardness than CONT samples. The increase in hardness of DCT1 and DCT2 samples is trivial when compared with the SCT sample. The shallow cryogenic treatment boosted the sample hardness due to near complete transition of soft retained austenite to relatively hard martensite. However, when the sample was subjected to deep cryogenic treatment, no further improvement in hardness was observed as compared to SCT sample. The reason is that the deep cryogenic temperature produced smaller secondary spherical carbides, which could be more beneficial to the fracture toughness but may not lead to significant improvement in hardness. For sub-zero treatments with prior tempering, the improvement in hardness is slight, compared to CONT samples.

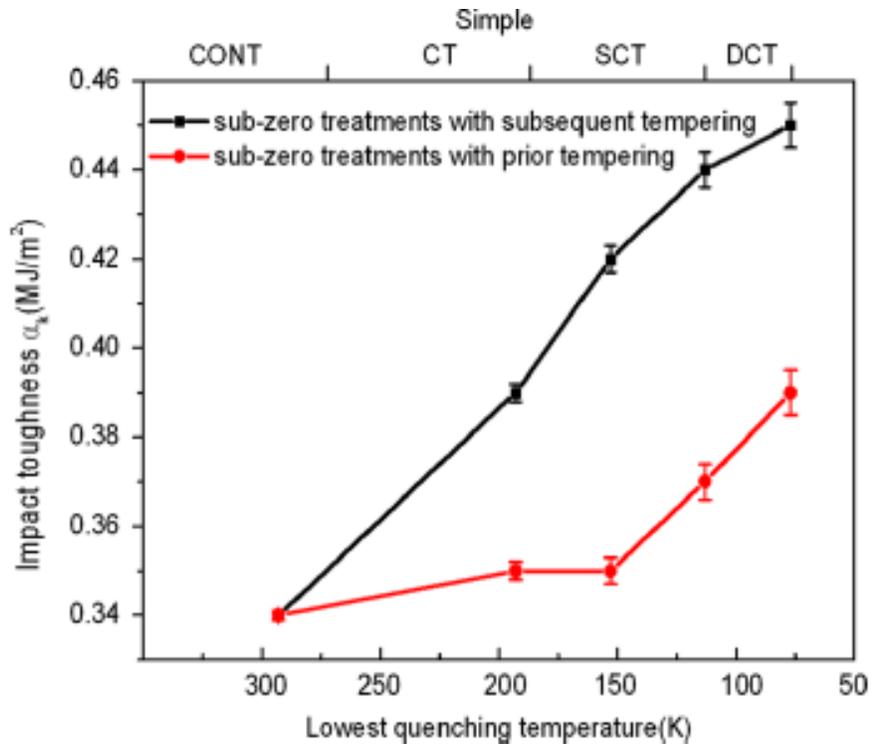


Fig. 34 Impact toughness values of samples experienced different treatment processes in different temperature ranges (CONT, CT, SCT, and DCT)

After the sub-zero treatment with subsequent tempering, W9 HSS showed significantly higher impact toughness, compared to the CONT sample (Fig. 34). The lower temperature of sub-zero treatment resulted in increased impact toughness by 29% (DCT1 sample) relative to the CONT samples. As shown, the impact toughness was also improved when sub-zero treatment with prior tempering was carried out. However, this improvement was not significant compared to the case of the sub-zero treatment with subsequent tempering.

In conclusion, through research, it has been observed that cryogenic treatment affects significantly microstructure and mechanical properties of tool steels. The subzero treatment generates more secondary carbides, increasing their volume fraction. Moreover, the retained austenite inside the matrix is transformed into martensite. As a result, improvement in microhardness and macrohardness is caused. However, as the retained austenite is transformed, the fresh martensite increases the residual stress inside the matrix and the brittleness of the material. With subsequent tempering or subsequent surface treatment, such as nitriding, stress relief and dimensional stability are achieved. Finally, the tool steel is characterized by increased hardness and toughness, decreased wearing rate and improved service life. The effect of the heat treatment on the microstructure and mechanical properties of tool steels depends on the type of the tool steel (properties, carbon content) and the conditions on which the procedure is carried out. Especially, cryogenic treatment temperature and soaking time have an influencing role on the properties of the final material.

Chapter IV – Experimental Procedure

Section 1: Introduction

In the present thesis, the behavior of hot work tool steel Uddeholm Orvar 2M (AISI H13/W. Nr. 1.2344, 0.39%C, 1%Si, 0.4%Mn, 5.3%Cr, 1.3%Mo, 0.9%V) at tempered condition after cryogenic treatment was studied. Experiments aimed at investigating the effect the cryogenic treatment on microstructure and mechanical properties (micro-hardness) of tool steels. The specific grade of tool steel was subjected to two different types of cryogenic treatments, as follows:

- Deep Cryogenic Treatment (DCT) at -196 °C for 24hrs. This temperature is considered to be the lowest limit of temperature of cryogenic treatment, since it is the boiling point of Nitrogen.
- Shallow Cryogenic Treatment (SCT) at -130 °C for 20 min. According to studies, the destabilization of austenite starts at this temperature^[39]. For the particular experiment, 20 minutes are the minimum duration of cryogenic treatment.

It is essential to point that cryogenic treatment was carried out prior to tempering for both experiments. After Cryogenic Treatment, the specimens were separated into pairs, each one of them referred to a different Tempering Temperature (TT). For every TT, the average value of hardness was measured, producing thus a curve of hardness as a function of TT. Furthermore, changes in microstructure in each pair were observed. A comparative study was performed between cryogenic and non-cryogenic processed specimens in relation to microstructure and microhardness.

1.2 Specimens' preparation

Twenty (20) specimens of tool steel H13 have been chosen for the experiment. All specimens were prepared by the following procedure:

- i. Cutting:* Specimens were cut as rectangular pieces of 40x15x15 mm from a tool steel bar.
- ii. Milling:* The final shape of the specimens is complete by the milling process.
- iii. Preparation for the experiment*

Before inserting the 20 specimens in the furnace, it was essential to organize the pairs in way to handle them during the process. Each one of the 20 specimens (Fig. 35, 36) has one through hole, for support purposes. As a result, they are tied in 4 groups of 5 with a metal wire of great resistance in high temperatures. After cryogenic treatment is completed, the pairs remain tied in the same way, being ready for the process of tempering.



Fig. 35 Indicative view of the Orvar 2M specimen before treatment



Fig. 36 Grouped specimens before inserting in furnace

1.3 Pre Treatment

1.3.1 Stage No 1: Austenitization

Temperature control is an integral step of heat-treating procedures, which generally consist of three separate functions: material movement, the application of energy, and the supervision of process conditions. In a typical heat-treat procedure, the specimen is placed into a furnace, heated according to a time-temperature program, cooled or quenched, and finally removed of the furnace or quench vessel. The temperature, and frequently the atmosphere, must be controlled precisely in order to achieve the desired metallurgical results.^[2]

Heat treatment furnaces are classified as batch, semicontinuous, or continuous. In batch furnaces, which are the most common and most versatile in the heat treatment industry, the specimen is typically held stationary in the furnace vestibule. The furnace is loaded or unloaded in a single (batch mode) operation.

Box Furnace

The box furnace is the simplest heat-treating furnace (Fig 37a). It is used for tempering, annealing, normalizing, stress relieving, and pack-carburizing. It is capable of operating over a wide range of temperatures, 95-1095°C (200–2000°F). In the particular project this type of furnace is used.



(a)



(b)

Fig. 37 (a) The Furnace used in procedure, **(b)** The box used for inserting the specimens in the furnace

Procedure

The 20 specimens, tied in groups of 5, put in a metal box (Fig 37b), wrapped in filter paper (Fig. 38) and inserted in the furnace. The austenitization procedure was carried out at 1030 °C. The initial temperature of the furnace was 13 °C and the procedure began by fixing its temperature up to 1040 °C, since there are thermal losses due to lack of insulation. The initial rate of heat transfer was set to be 6-7 °C/min.

The specimens remained in the austenitization conditions for 55 minutes, following the time chart which has been recorded. The first 20 minutes are the pilot, since the specimens need some time to absorb the heat. Another 30 minutes are required for austenitization and last 5 minutes are used as safety time in case the core of the specimen did not reach the appropriate temperature. It needs to be noticed that time inserting the box was measured about 6.86 sec.



Fig.38 The specimen are wrapped in filter paper inside the box

In the present thesis, two experimental procedures were carried out and are described below.

Experiment No1:

1. Austenitization at 1030 °C (Table 20)
2. Air Quenching
3. Deep Cryogenic Treatment at -196 °C for 24h
4. Tempering at 180 °C, 280 °C, 360°C, 450 °C, 500 °C, 525 °C, 550°C, 580 °C 600 °C, 630°C for 2 hrs each

Experiment No 2

1. Austenitization at 1030 °C (Table 21)
2. Air Quenching
3. Shallow Cryogenic Treatment at -130 °C for 20 min
4. Tempering at 180 °C, 280 °C, 360°C, 450 °C, 500 °C, 525 °C, 550°C, 580 °C 600 °C, 630°C for 2 hrs each

Table 20. Time table of austenitization process (DCT - Experiment No1)

Time	Furnace Temperature (°C)
11:30 (Start)	13 (Set rate to 6-7 °C/min)
12:06	245
12:19	292
13:16	457
13:25	590
13:33	672
13:38	715 (Change rate to 9-10 °C/min)
13:46	813
13:55	903
14:02	967
14:09	1004 (Insert the specimens)
14:22	1027
14:34 (Finish)	1040

Table 21. Time table of austenitization process (SCT - Experiment No2)

Time	Furnace Temperature (°C)
09:44 (Start)	13 (Set rate to 9-10 °C/min)
10:32	960
10:39	993
10:40	1005
10:46	1027
11:07	1022
11:12	T _{min} : 1022 T _{max} : 1029 Cycle duration : 43 sec
12:05	Fix: 1040
12:42	T _{min} : 1033 T _{max} : 1040 Cycle duration : 1 min 16 sec
12:54	T _{min} : 1033 T _{max} : 1040 Cycle duration : 1 min 18 sec
12:57	1034 – Specimens inserted
13:21	T _{min} : 1033 T _{max} : 1040 Cycle duration : 1 min 38 sec
13:23	1040
13:47	1040
13:48	T _{min} : 1033 T _{max} : 1040 Cycle duration : 2 min
13:53	1035
14:34 (Finish)	1035

The heat transfer process that occurs when a part is heated in a furnace is depicted in Figure.39. Typically, the heat transfer rate is rapid initially and decreases as the temperature of the center of the part reaches the surface temperature, which achieves the furnace temperature more rapidly. Heat transfer in furnaces occurs by convection, radiation, and conduction.

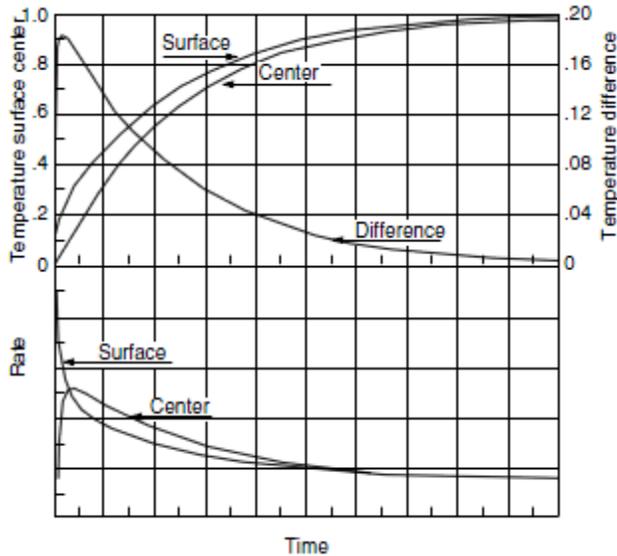


Fig.39 Relationship of temperature rise and heating rates with respect to time

1.3.2 Stage No2: Quenching

After austenitization is completed, the specimens remain outside the furnace to cool down (Fig. 40). The exportation endured 13.19 sec. at 15:08 followed by the process of quenching. Once the austenite is cooled below its critical temperature, it becomes unstable and transforms into martensite. By reheating, these crystallographic and microstructural changes result in the precipitation of finer carbides in the tempered microstructure, with consequent increase in toughness.

Cooling rate is a function of the thickness and geometry of the sample. Moreover, it is related to the quenching facility including the extent of agitation, racking procedure, extent of surface oxidation, and the effective heat transfer coefficient between the part and the quenchant. In this case, the quenchant is cold air from a blower. Following, a timetable recorded during quenching is presented.

Table 22. Time table of quenching process (DCT - Experiment No1)

Time	Quenching Temperature (°C)
15:09 (Start)	1030
15:24	65
15:28	45
15:45 (Finish)	25

Table 23. Time table of quenching process (DCT - Experiment No2)

Time	Quenching Temperature (°C)
13:58 (Start)	1030
14:24 (Finish)	25



Fig 40. (a) The box of specimens out of the furnace, (b) The specimens ready for quenching

After the process of quenching, the specimens were inserted in a secondary furnace and maintained at 100 °C for about 1 hour, in order to achieve temporary tempering (Fig. 41). This process is called snap tempering and is known as a precautionary interim stress-relieving treatment applied to high hardenability steels immediately after quenching to prevent cracking. The process started at 16:11, the temperature raised at 16:14 and thus tempering of the specimens began. At time 17:30, the specimens were exported form the furnace and left to cool down. Their temperature reached 40 °C at 17:49.



(a)



(b)

Fig.41 (a) The specimens after quenching, (b) The secondary Furnace for mini tempering

1.3.3 Stage No3: Cryogenic Treatment

Liquid nitrogen is most widely used in cryogenic treatment. It has a melting point and a boiling point of $-210.01\text{ }^{\circ}\text{C}$ (63K) and $-195.8\text{ }^{\circ}\text{C}$ (78 K), respectively. It is a most abundant gas: it composes about four-fifths (78.03%) by volume of the atmosphere. It is often abbreviated as LN2. It is colorless, odorless, tasteless, and nontoxic.

At the initial stage, conventional electrical cooling may also be used to reduce the temperature to about $-73\text{ }^{\circ}\text{C}$ (200K) which makes the process economical. At $-73\text{ }^{\circ}\text{C}$ (200 K), the liquid nitrogen system cuts in, to cool it further following a desired cycle. Liquid nitrogen is converted to a gas before it enters the chamber, so that at no time does liquid nitrogen come in contact with the parts to eliminate any danger of cracking of the specimen. This process refines and stabilizes the crystal lattice structure and distributes carbon particles evenly throughout the material, creating a stronger, more durable material. ^[5]

Figures 42a and 42b show the cryogenic processor of STL along with Liquid Nitrogen container.



(a)



(b)

Fig. 42 (a) Liquid Nitrogen, (b) Chamber of Cryogenic treatment

Initially, the two main valves of nitrogen were opened. The rate of decreasing temperature reached 2.5 °C/min, and the initial temperature was at 19 °C. When liquid nitrogen was converted to a gas and entered the chamber, creating cryogenic conditions, specimens were inserted in the chamber. The process endured 24 hours at temperature -196 °C.

In the end of the treatment, the final pressure reached the point of 56 PSI or 3.9 bar. Shutting off the valves, the temperature began to increase with rate of magnitude 2.74 °C/min. The gate of the chamber opened and the specimens were ready for cooling down until ambient temperature. The color of the specimens, from light grey due to low temperatures, began to fade and dark metal color was observed (Fig. 43). Below, a timetable of the procedure is exhibited.

Table. 24 Time table for Cryogenic treatment (DCT - Experiment No1)

Time	Temperature °C
17:53 (Start – Open Valves)	19
18:05	-2
18:11	-20
19:18	-196
19:18 (24h – Finish)	-196
19:20	-187
19:25	-178
19:30	-174
19:35 (Open the Gate)	-172

The second experiment was carried out with the same machine and instruments. Cryogenic treatment temperature is $-130\text{ }^{\circ}\text{C}$ with holding time of about 20 minutes, under the same conditions regarding the cooling rate.

Table. 25 Time table for Cryogenic treatment (SCT - Experiment No2)

Time	Temperature $^{\circ}\text{C}$
16:33 (Start – Open Valves)	19
16:39	11
16:41	7
16:42	1
16:47	-6
16:52	-21
16:55	-26
16:59	-39
17:03	-51
17:05	-58
Finish (20 min)	-130



(a)



(b)

Fig. 43 (a) Inside the Chamber of Cryogenic treatment, (b) The specimens after the process

1.3.4 Stage No4: Tempering

Structural Changes^[2]

Based on x-ray, dilatometric, and microstructural studies, there are three distinct stages of tempering, even though the temperature ranges overlap:

- Stage I: The formation of transition carbides and lowering of the carbon content of the martensite to 0.25% (100 to 250 °C, or 210 to 480 °F)
- Stage II: The transformation of retained austenite to ferrite and cementite (200 to 300 °C, or 390 to 570 °F)
- Stage III: The replacement of transition carbides and low-temperature martensite by cementite and ferrite (250 to 350 °C, or 480 to 660 °F)

An additional stage of tempering (stage IV), precipitation of finely dispersed alloy carbides, exists for high-alloy steels. It has been found that stage I of tempering is often preceded by the redistribution of carbon atoms, called autotempering or quench tempering, during quenching and/or holding at room temperature. Other structural changes take place because of carbon atom rearrangement preceding the classical stage I of tempering.

Dimensional Changes^[2]

Martensite transformation is associated with an increase in volume. During tempering, martensite decomposes into a mixture of ferrite and cementite with a resultant decrease in volume as tempering temperature increases. Because a 100% martensitic structure after quenching cannot always be assumed, volume may not continuously decrease with increasing tempering temperature.

The retained austenite in plain carbon steels and low-alloy steels transforms to bainite with an increase in volume, in stage II of tempering. When certain alloy steels are tempered, a precipitation of finely distributed alloy carbides occurs, along with an increase in hardness, called secondary hardness, and an increase in volume. With the precipitation of alloy carbides, the M_s temperature (temperature at which martensite starts to form from austenite upon cooling) of the retained austenite will increase and transform to martensite during cooling from the tempering temperature. As far as the specimens are concerned, they, as pairs, are inserted in the furnace. It is important to know that the tempering process is held in the same furnace the austenitization happened.

Before placing the specimens, the bath salt of the specific Tempering Temperature was inserted in the furnace in order to melt. When the bath salt reached expected temperature, the specimens were inserted. The temperature of the bath salts was measured with dual input thermocouple thermometer (Fig. 44). In Annex I and Annex II the timetables of the 20 tempering procedures are presented.

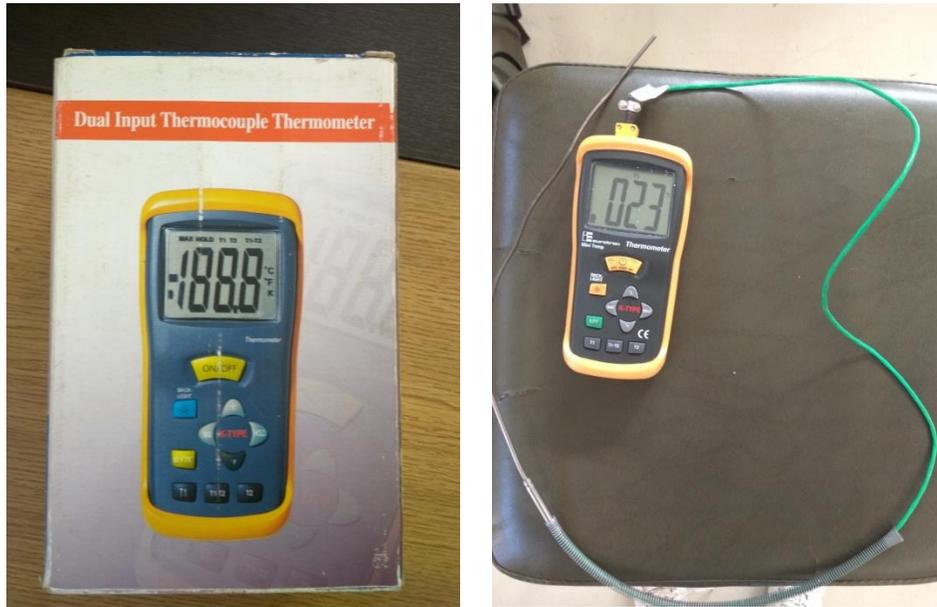


Fig. 44 Thermometer used for the experiment

1.4 After Treatment

After the experiments, specimens were prepared for microstructure analysis and microhardness measurement following the described procedure below

1.4.1 Cutting

Every one of the specimens was cut in two pieces with the follow dimensions (Fig. 46):

- One piece of 15x15x15 mm
- One piece of 25x15x15 mm

The cutting machine of Shipbuilding Technology Laboratory which was used is Discotom-5 manufactured by **Struers** (Fig. 45). Cutting procedure was performed with the following settings

- Propulsion speed fixed to 0.5 mm/s
- Rotational speed of disk set to 2300 RPM.



(a)



(b)

Fig. 45 (a) Cutting machine outside, (b) Cutting machine inside

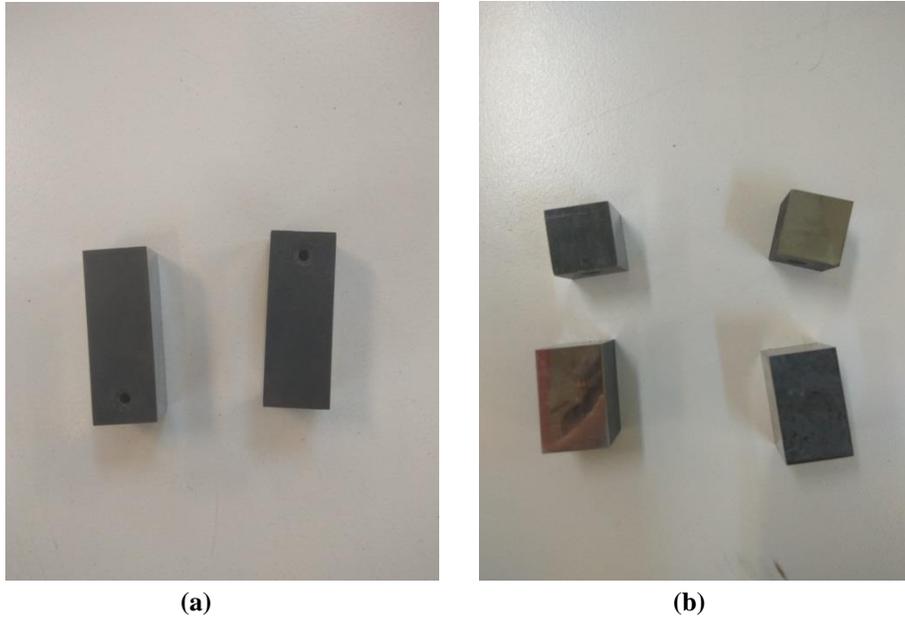


Fig. 46 (a) Specimens before cutting, (b) Specimens after cutting

1.4.2 Mounting

Mounting is a process, in which the specimens are inserted in plastic molds filled with epoxy resin, for 24 hours in order to form a solid disk or puck that can be used to handle the sample easier. For the procedure, EpoFix Resin, by Struers, was used. The forms are shown below (Fig. 47). In the mounting process, the specimens of dimensions 15x15x15 were used (Fig. 48).



Fig. 47 Specimens through mounting process

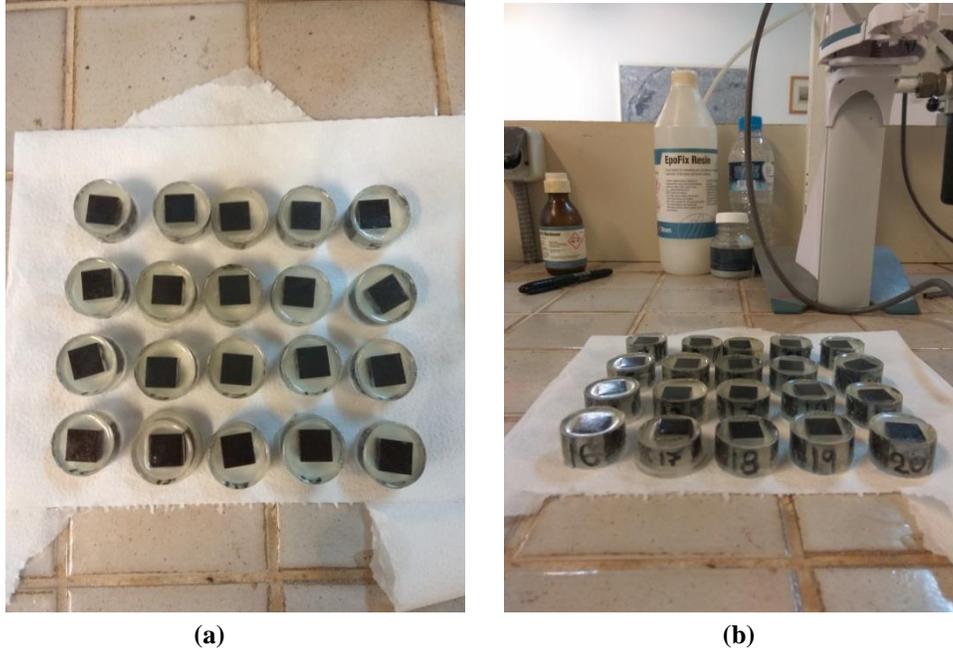


Fig. 48 (a), (b) Specimens being and numbered after mounting procedure

1.4.3 Grinding, polishing and etching

The mounted specimens were polished, in order to be used for metallographic analysis and microhardness measurement (Fig. 50). The polishing machine is type LaboPol-5, manufactured by Struers (Fig. 49a). The variable rotational speed of between 50 - 500 rpm is controlled by an electronic servo system that keeps the selected speed constant, independent of the load. The chosen speed was 300 rpm. The system is water cooled, with a 200mm in diameter platen while sample holder can hold three specimens of 30mm. Moreover, for the procedure multiple types of grinding papers were used, including, Grit 180, 220, 320, 500, 800, 1000, 2000. After grinding, polishing procedure was performed by using a velvet disk with two types of polishing pastes as lubricant, a) AP-A Suspension 1 μ m agglomerated alpha alumina, b) AP-A Suspension 0.3 μ m agglomerated alpha alumina (Fig 49.b). Finally, nital of concentration 3-4% was used as etchant for preparing the surface for microstructure analysis.



(a)



(b)

Fig. 49 (a) Grinding and polishing machine LaboPol-5, (b) Polishing pastes

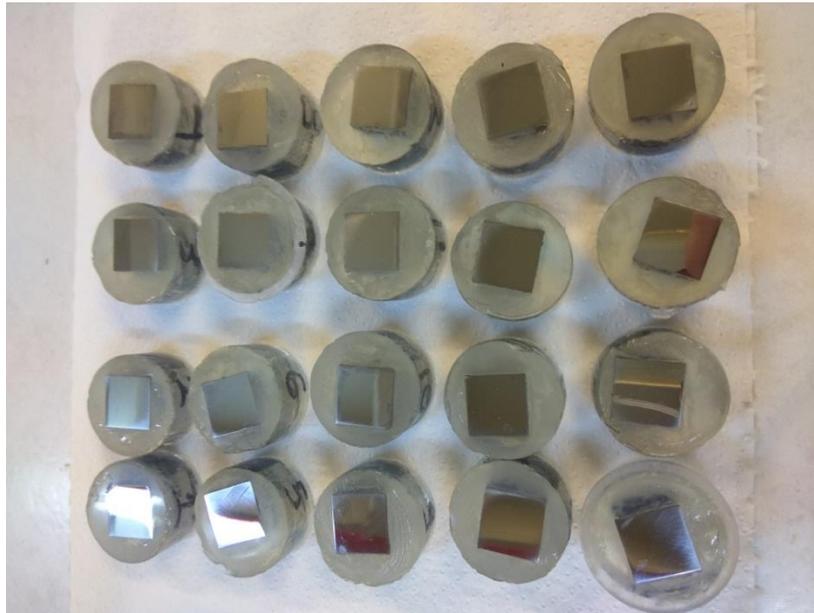


Fig. 50 Polished specimens

Section 2: Results

2.1 Microstructure

The treated samples were subjected to microstructure examination by using Leica DMIL optical microscope coupled with Leica DFC290 HD digital microscope camera and Leica Application Suite image analysis software. The microstructure of the material is presented in magnification of x10, x20, x50 and x100. Microstructures were compared to the corresponding ones from the untreated material. Figures below (Fig 51-54) show the microstructure of the specimen subjected to tempering at 180°C and at temperatures in the precipitation area, 450°C, 500°C, 525°C and 550°C, for the two experimental procedures.

As it can be observed, the below pictures show the expected structure of martensite along with the carbides, the density of which is noticeably increased at the temperatures around the area of precipitation. Even though, it is argued that the cryogenic treatment contributes to complete transformation of the retained austenite, a small percentage of remained austenite is expected to be found ^[40]. The white areas are expected to be carbide areas and are dispersed inside the matrix.

Comparing the aforementioned cryogenic treatment procedures, optical metallographic microscope shows no difference in microstructure. Thus, SEM microscope is needed to examine further the matrix of the samples. SEM photos are shown in the next paragraph.

Deep Cryogenic Treatment - *Experiment No 1*

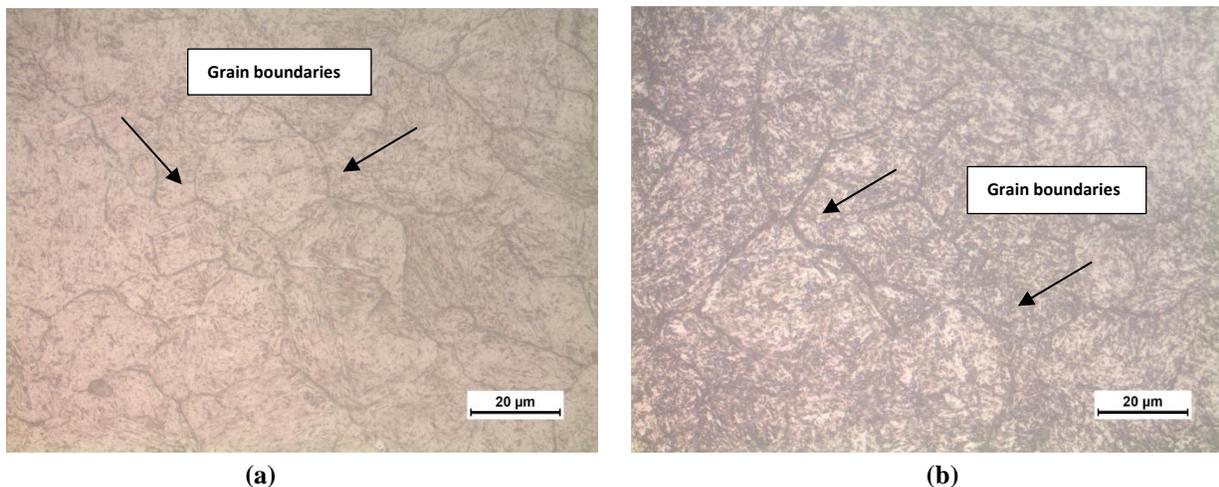


Fig. 51 Indicative microstructures of DCT (Experiment No 1) at various TT: **a)** Specimen No 4 – 180°C (x100), **b)** Specimen No 6 – 450°C (x100)

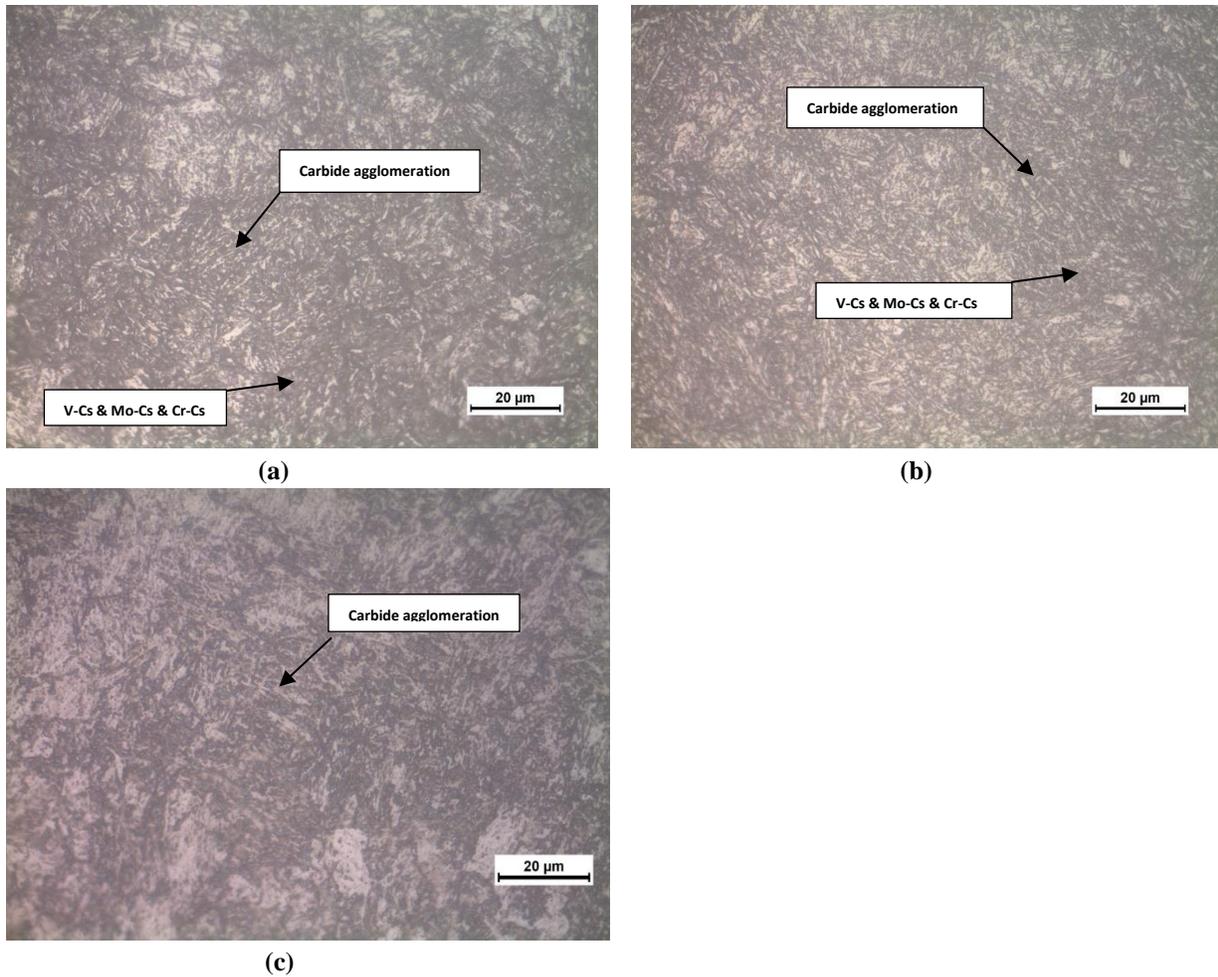


Fig. 52 Indicative microstructures of **DCT** (Experiment No 1) at various TT: **a)** Specimen No 8 - **500°C** (x100), **b)** Specimen No 12 - **525°C** (x100), **c)** Specimen No 13 – **550°C** (x100)

In the case of tempering at 180°C (Fig.51), it is observed that the microstructures after tempering are similar with clearly etched grain boundaries. The size of the coarse grains may indicate lower percentage of precipitated carbides inside the boundaries, in relation to the rest of the tempering temperatures. Taking into consideration the microstructures of the TT of 500 °C, 525°C and 550°C, the grain boundaries are not clearly etched. However, carbide agglomeration areas are observed, suggesting that microstructure is not typical tempered martensite. As TT increases, the agglomeration of carbides becomes greater and more obvious. Moreover, fine martensite laths and dispersed spherical carbides of Molybdenum and Vanadium (V-Cs, Mo-Cs) of size below 1μm are observed in all the above cases. The larger and wider carbides (size 1-3μm) are expected to be the Chromium carbides (Cr-Cs). Regarding the case of shallow cryogenic treatment, similar microstructures appear for TT of 180°C and 450°C. Nevertheless, microstructures for TT of 500°C and 525°C show reverse results in relation to DCT. Higher levels of carbide agglomeration are observed in the first case, suggesting increase in carbide content. For both DCT and SCT, microstructure of tempered martensite at 550°C shows similar results.

Shallow Cryogenic Treatment - Experimental No 2

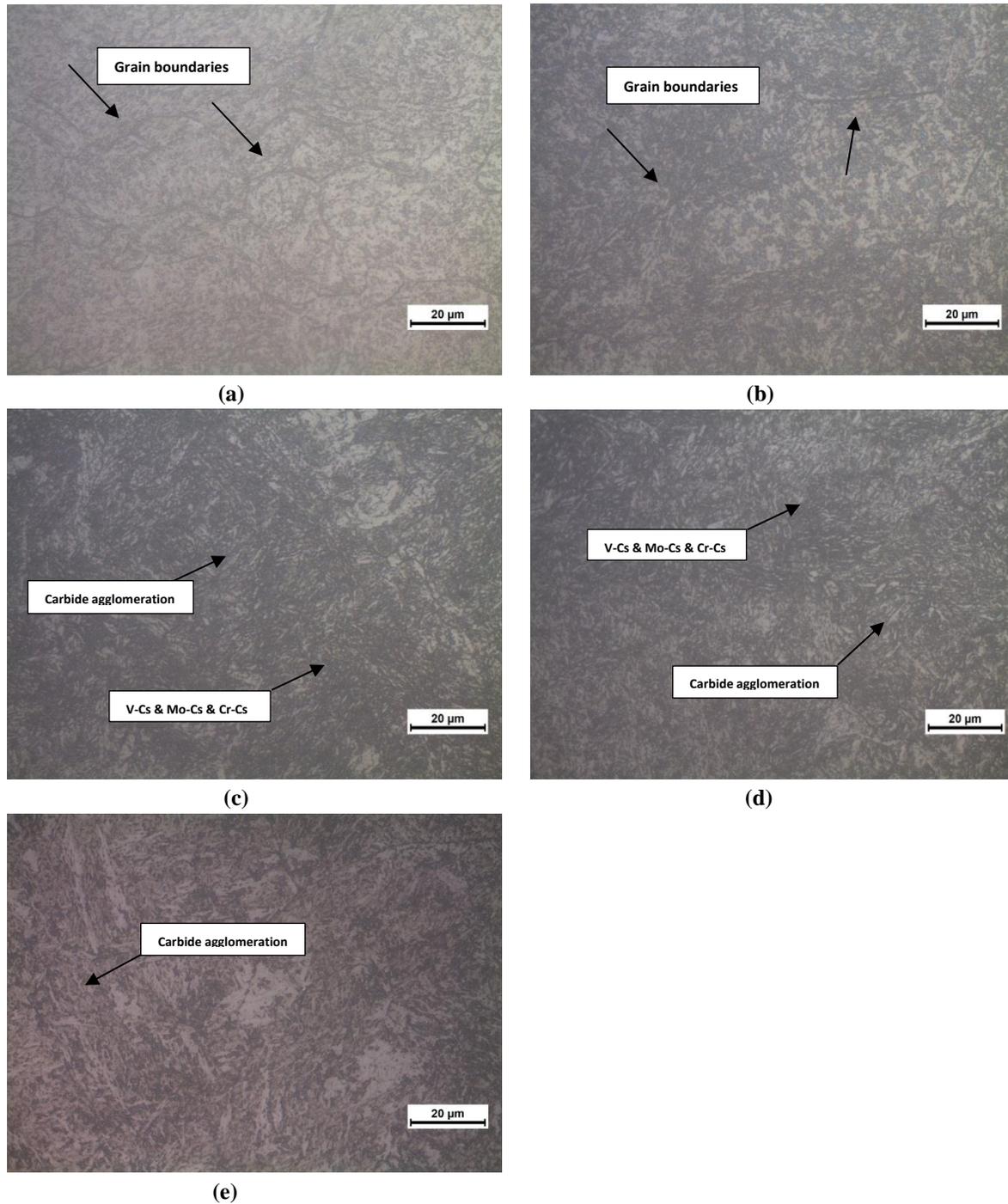


Fig. 53 Indicative microstructures of SCT (Experiment No 2) at various TT: **a)** Specimen No 21- **180°C** (x100), **b)** Specimen No 28 - **450°C** (x100) **c)** Specimen No 29 - **500°C** (x100), **d)** Specimen No 31 - **525°C** (x100), **e)** Specimen No 33 - **550°C** (x100)

Untreated specimen

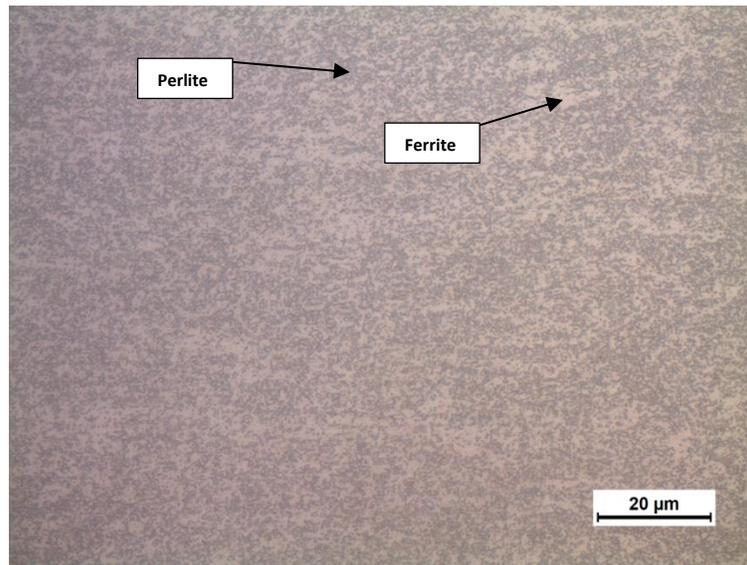


Fig. 54 Indicative microstructure of untreated specimen (x100)

Fig. 54 shows the microstructure of the material which was not subjected to any heat treatment. The untreated tool steel sample belongs to the category of hypoeutectoid steels. Thus, it contains perlite and ferrite microstructure and primary carbides are rarely observed. It can be seen that cryogenic treatment caused great impact on microstructure since the tempered martensite with the carbide precipitation is observed in higher content, in comparison with the untreated sample.

2.2 Carbide Precipitation

As it has been discussed above, cryogenic treatment contributes to the formation of finer martensite laths in the microstructure and initiates nucleation sites for precipitation of fine carbide particles. In order to observe the precipitated carbides inside the steel matrix, scanning electron microscope (SEM - Jeol JSM-6390), of STL was used. The SEM microscope produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The following pictures exhibit the microstructure of the H13 tool steel, including the presence of the carbides for the main tempering temperatures (180°C, 450°C, 500°C, 525°C and 550°C).

Deep Cryogenic Treatment - Experiment No 1

- Specimen No 4 (180°C)

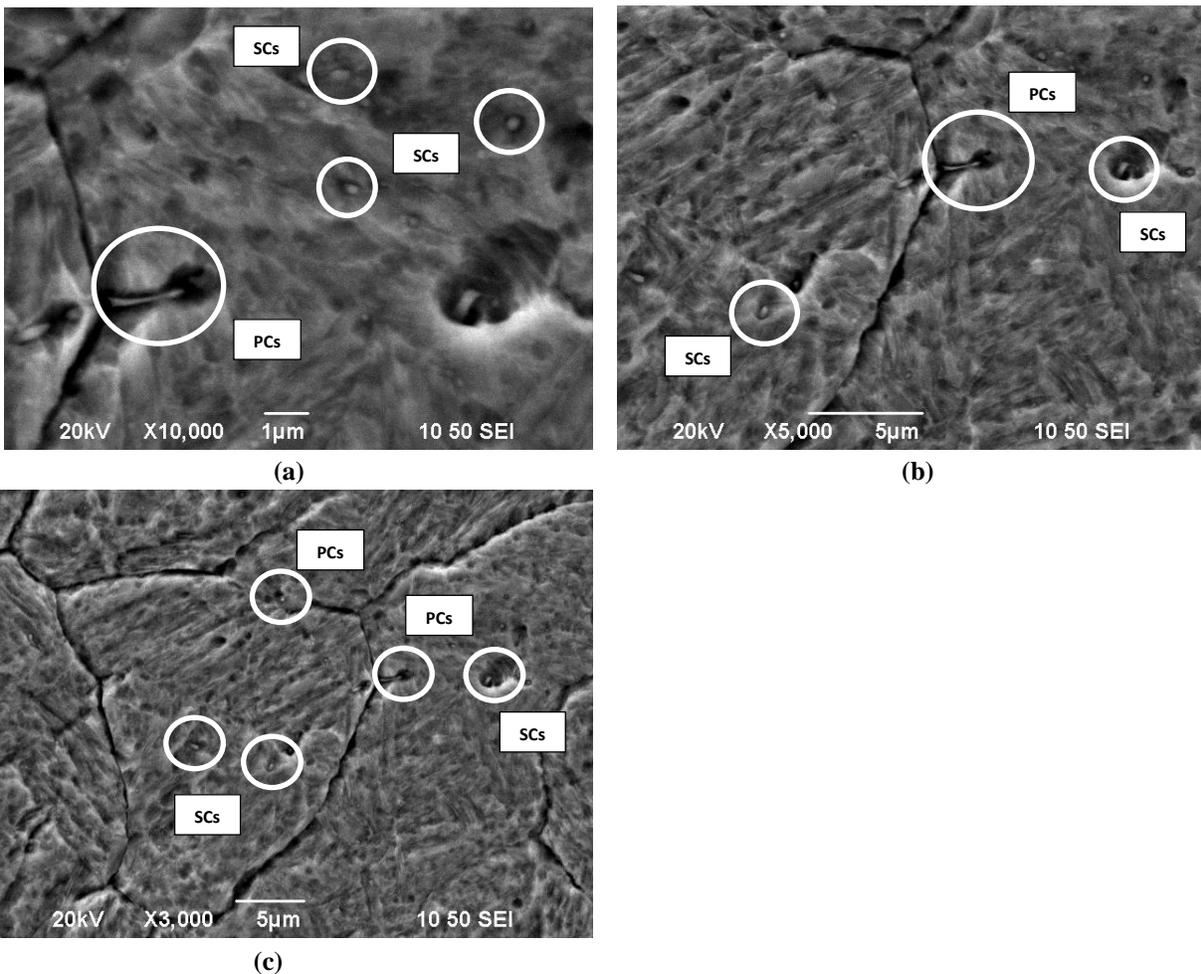


Fig. 55 Indicative SEM microstructures of DCT (Experiment No 1) at TT=180°C: **a)** x10,000, **b)** x5,000, **c)** x3,000

Carbides of various dimensions are depicted in the above photo, for tempering temperature of 180°C. The large carbide at the grain boundary is considered to be primary insoluble carbide. Additionally, a number of carbides are portrayed in the picture, with diameter up to 0.3 μm, which have been precipitated during tempering procedure at 180°C. It is essential to mention that the secondary carbides at TT of 180 °C are a combination of the transition carbides (ε-carbides and η-carbides), which were formed during tempering, and the carbides of Mo and V, which already exist inside the matrix of the untreated tool steel. Although, the Mo-carbides and V-carbides are part of the primal microstructure of the material, they cannot be considered as primary carbides due to their size.

- Specimen No 6 (450°C)

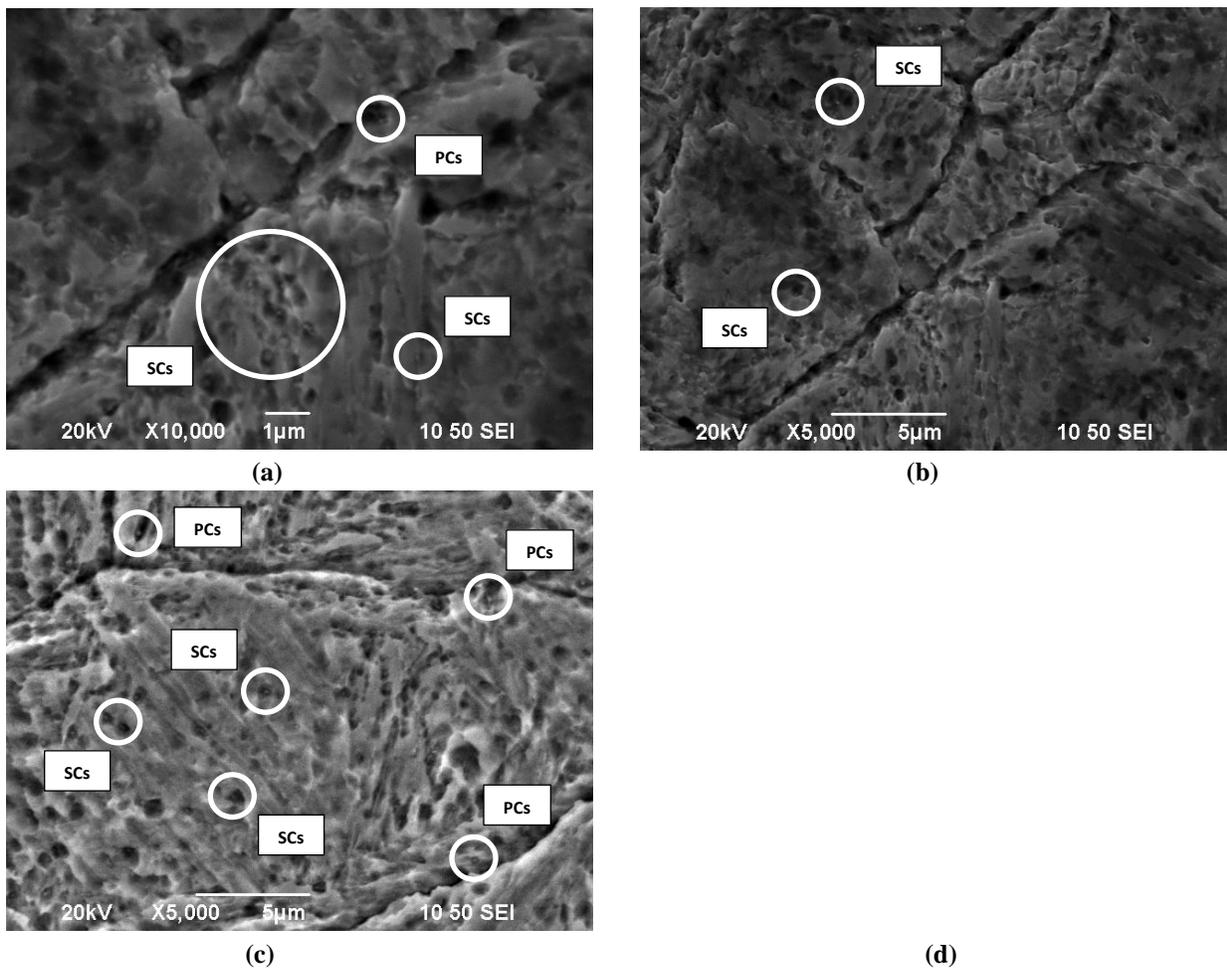


Fig. 56 Indicative SEM microstructures of DCT (Experiment No 1) at TT=450°C: a) x10,000, b) x5,000, c) x5,000

Tempered martensite microstructure is observed in the above photo. In contrast with the tempering temperature of 180°C (Fig. 55), there is higher content of carbides which are more uniformly dispersed.

- Specimen No 8 (500°C)

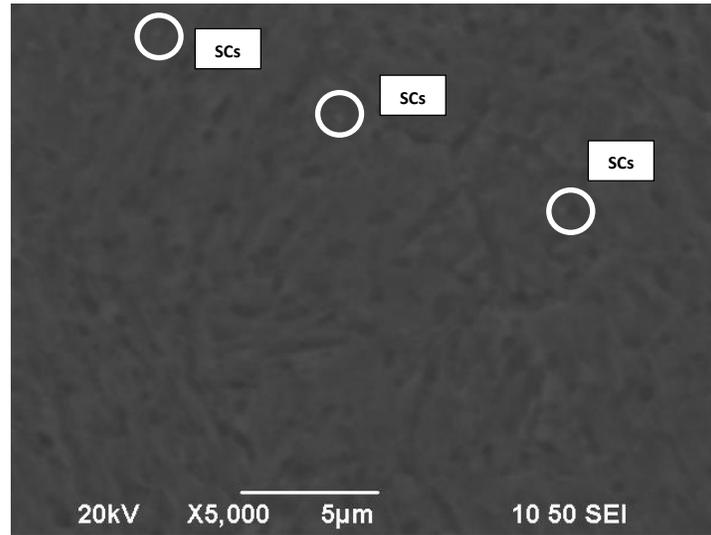


Fig. 57 Indicative SEM microstructures of **DCT** (Experiment No 1) at TT=500°C

- Specimen No 12 (525°C)

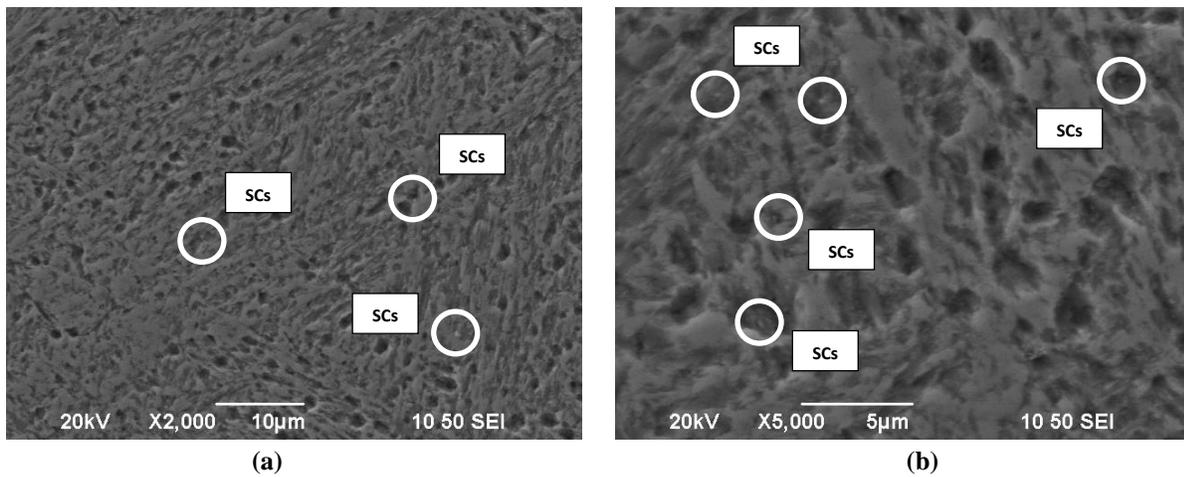


Fig. 58 Indicative SEM microstructures of **DCT** (Experiment No 1) at TT=525°C: **a)** x2,000, **b)** x5,000

- Specimen No 13 (550°C)

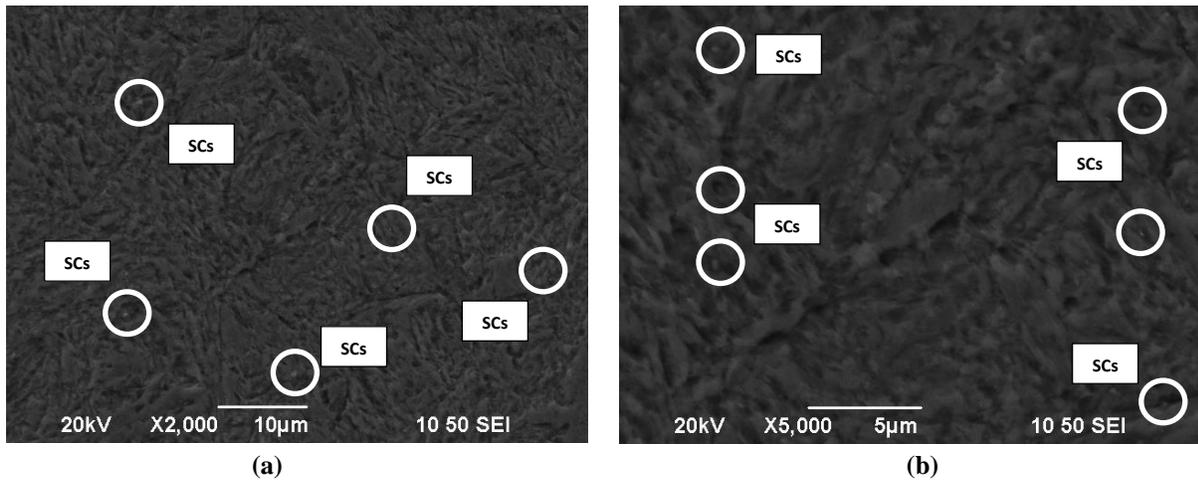


Fig. 59 Indicative SEM microstructures of **DCT** (Experiment No 1) at TT=550°C: **a)** x2,000, **b)** x5,000

Unfortunately, due to resolutions and magnification limitations with the equipment, it is still challenging to properly see these small carbides for the case of 500 °C, 525 °C and 550 °C. However, the size of these particles strongly suggests that they are secondary carbides. These carbides were precipitated during the secondary hardening process.

Shallow Cryogenic Treatment - Experimental No 2

- Specimen No 21 (180°C)

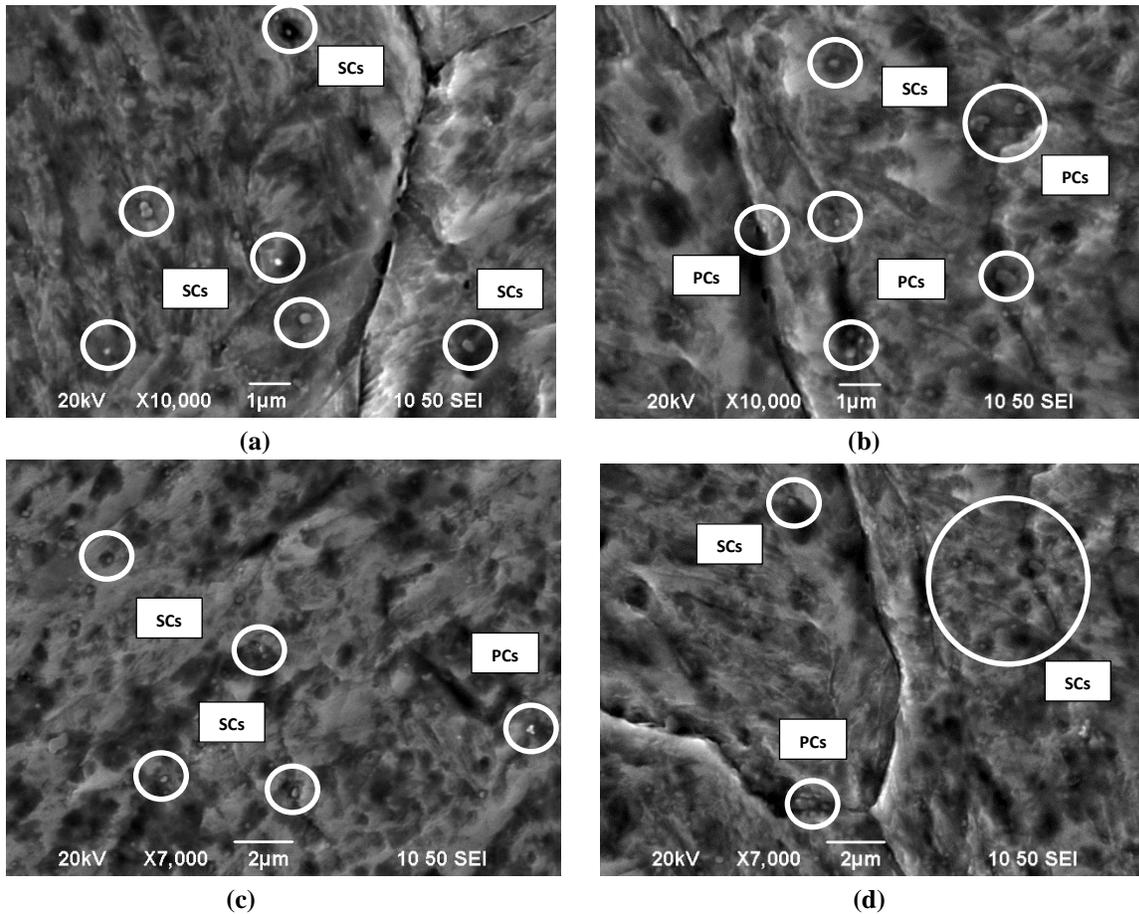


Fig. 60 Indicative SEM microstructures of SCT (Experiment No 2) at TT=180°C: **a)** x10,000, **b)** x10,000, **c)** x7,000, **d)** x7,000

In the above case (Fig. 60), uniform dispersion of carbides of the same size is observed. This microstructure is similar with the one in the case of deep cryogenic treatment. In picture 60(a), an agglomeration of carbides is observed, revealing that the thermodynamic conditions are such as to cause the merge of two carbides. In addition, the crowded areas of carbides (Fig. 60d) show that, despite the low TT of 180°C, the energy state of the material facilitates the initiation of the nucleation sites for precipitation of more fine carbide particles.

- Specimen No 28 (450°C)

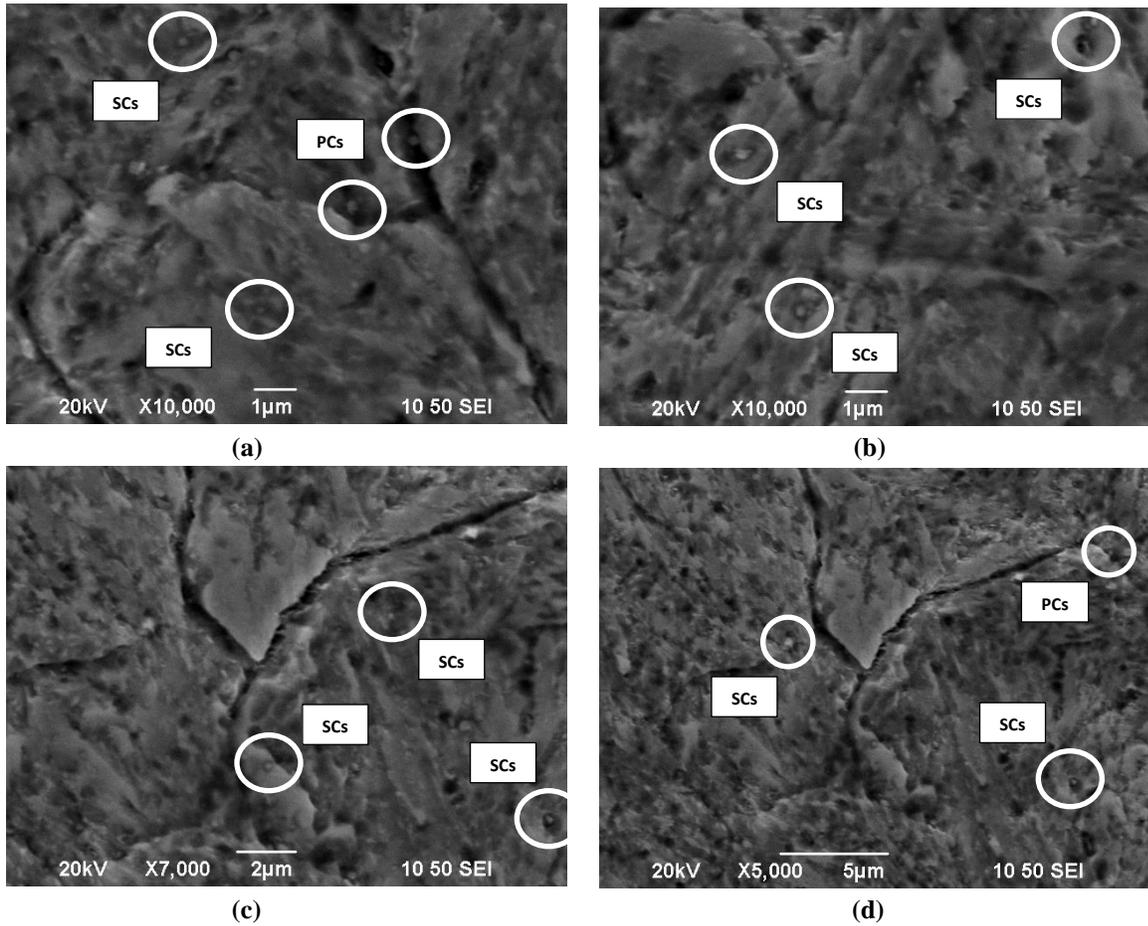


Fig. 61 Indicative SEM microstructures of SCT (Experiment No 2) at TT=450°C: **a)** x10,000, **b)** x10,000, **c)** x7,000, **d)** x5,000

Regarding the temperature of 450°C (Fig. 61), there is uniform dispersion and the carbide content is higher.

- Specimen No 29 (500°C)

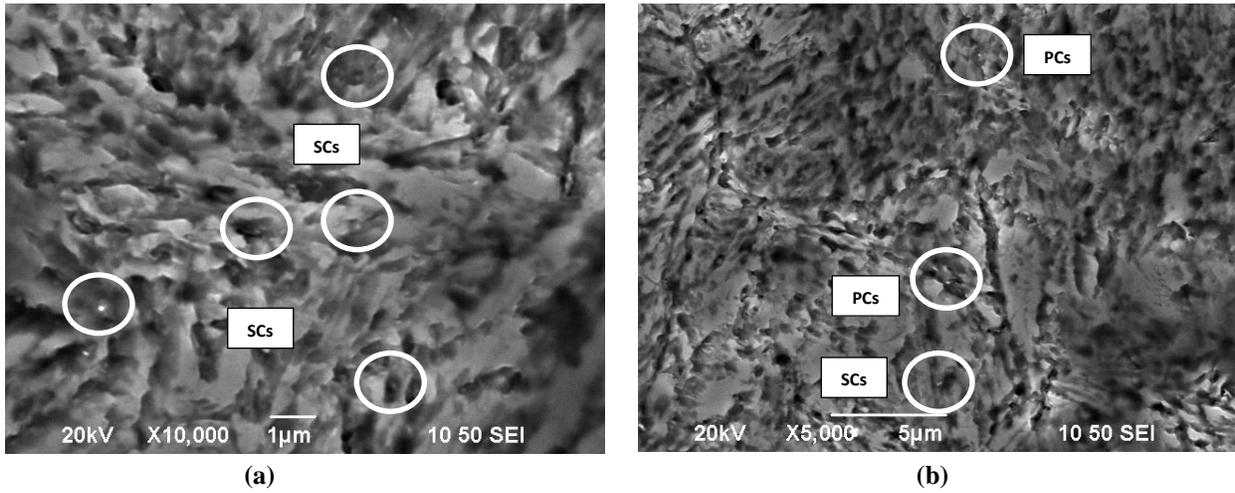


Fig. 62 Indicative SEM microstructures of **SCT** (Experiment No 2) at **TT=500°C**: **a)** x10,000, **b)** x5,000

- Specimen No 31 (525°C)

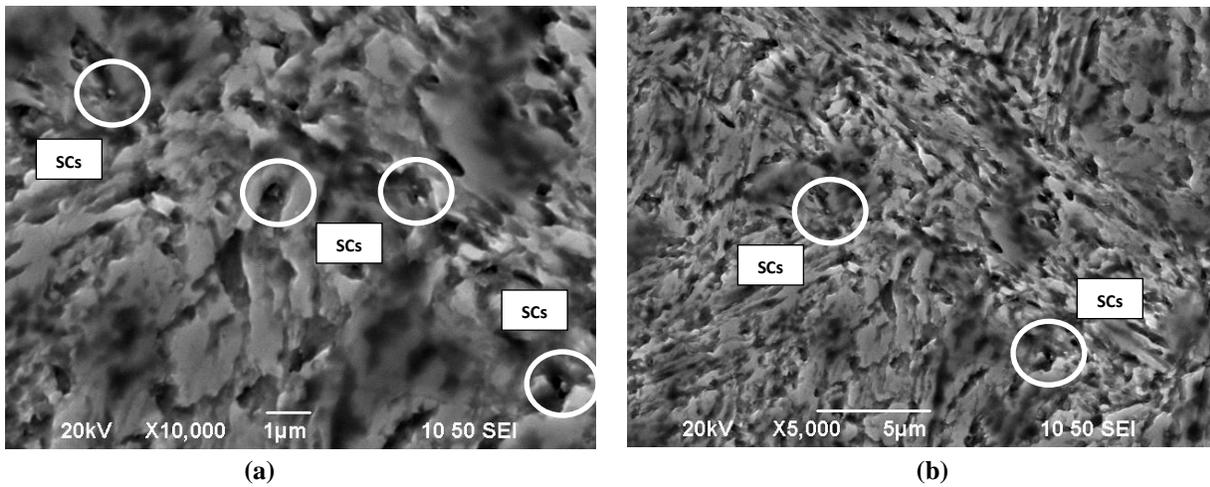


Fig. 63 Indicative SEM microstructures of **SCT** (Experiment No 2) at **TT=525°C**: **a)** x10,000, **b)** x5,000

For both of the above temperatures (Fig 62, 63), the microstructure is similar with the matrix of the samples subjected to deep cryogenic treatment and tempered at 450 °C.

- Specimen No 33 (550°C)

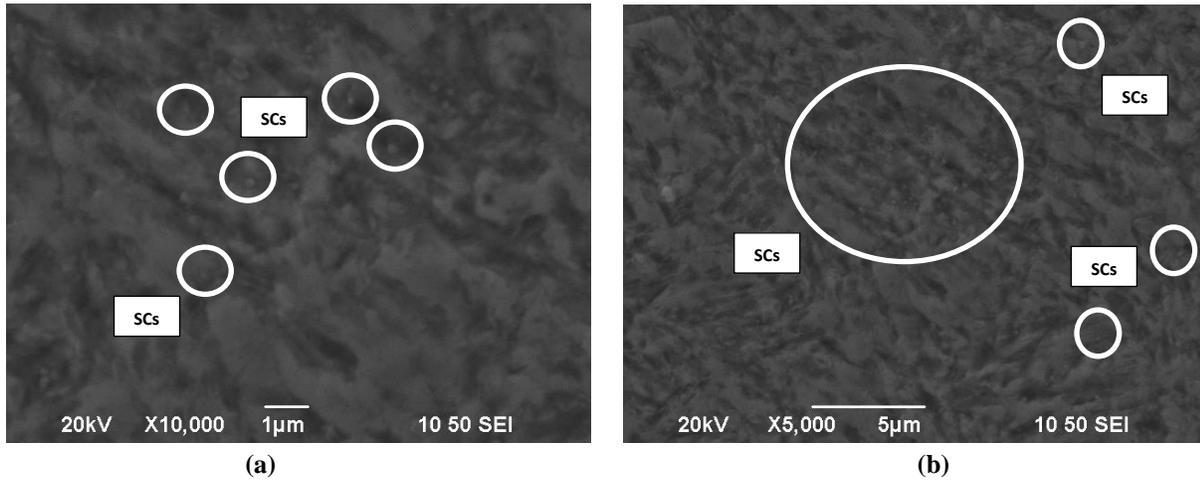


Fig. 64 Indicative SEM microstructures of SCT (Experiment No 2) at TT=550°C: **a)** x10,000, **b)** x5,000

In the particular case of shallow cryogenic treatment and tempering at 550°C, uniformly dispersed carbides of size up to 0.3 µm are observed. These carbides are considered to be carbides of secondary precipitation.

2.3 Hardness

For every pair for both of the experiments, one specimen was used for microhardness measurement. Method as per Vickers at 0.3kg weight was applied for the measurement of microhardness. It is essential to point out that, in each case, more than 10 values of microhardness was measured in order to avoid great deviation. Due to small measurement imprint and the existence of carbides, microhardness results showed some extreme values. At this point, the Boxplot diagram method was used so as to set aside values of high deviation. Moreover, the Shaphiro Wilk W method was applied in order to check the normalization of the remained values. It was proved that the microhardness measured values were within limits and approved.

Additionally, it shall be well noticed that microhardness was measured from the inside surface of the cut specimen and not the external. The extreme conditions due to the heat treatment have caused decarburization on the steel surface. Although, grinding and polishing have managed to clean and prepare the external surface, the percentage of decarburization could not be measured and it could be a risk for the values to be taken from this place. Finally, the tempering diagram in the case of conventional heat treatment (at the same austenitization temperature) was received from the manufacturing company in order to complete the comparison. For the conventional treatment, information regarding the process that was carried out, along with the cooling medium and the size of the samples are given through the corresponding material brochure of the manufacturer. Below are the mean values of hardness for every TT for the treatment procedures.

Table 26 Micro – Hardness of treated samples - DCT -196 °C for 24 hrs

Cryogenic Heat Treatment (24hrs)										
TT(°C)	181	280	362	450	501	523	550	580	600	630
Hardness	594.3	605.6	613.5	583.7	630.9	623.8	612.2	565.1	528.8	456

Table 27 Micro – Hardness of treated samples - DCT -130 °C for 0.3 hrs

Cryogenic Heat Treatment (0.3hrs)										
TT(°C)	180	290	370	450	501	526	548	577	602	630
Hardness	653.74	618.70	645.11	662.24	666.61	684.98	674.03	619.24	577.10	500.44

Table 28 Micro – Hardness of treated samples - Conventional HT

Cryogenic Heat Treatment (24hrs)										
TT(°C)	181	281	353	450	499	526	550	576	600	633
Hardness	569	563	572	595	610	620	602	535	500	413

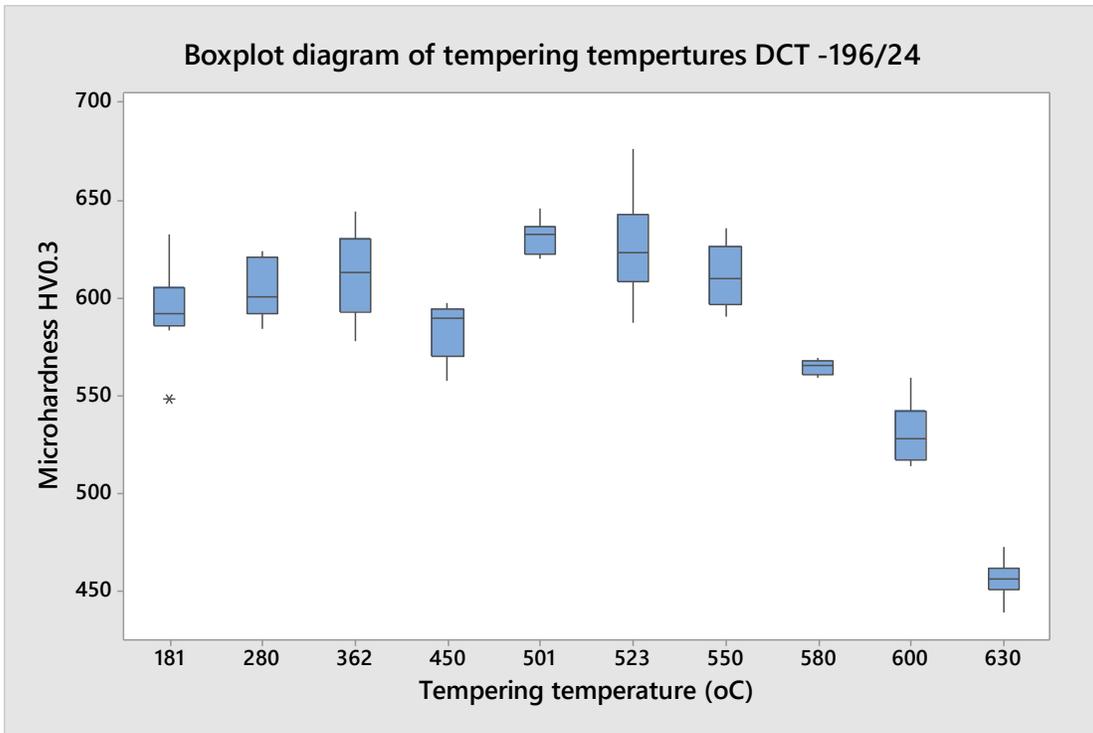


Fig. 65 Boxplot diagram of tempering temperatures DCT -196 °C for 24 hrs.

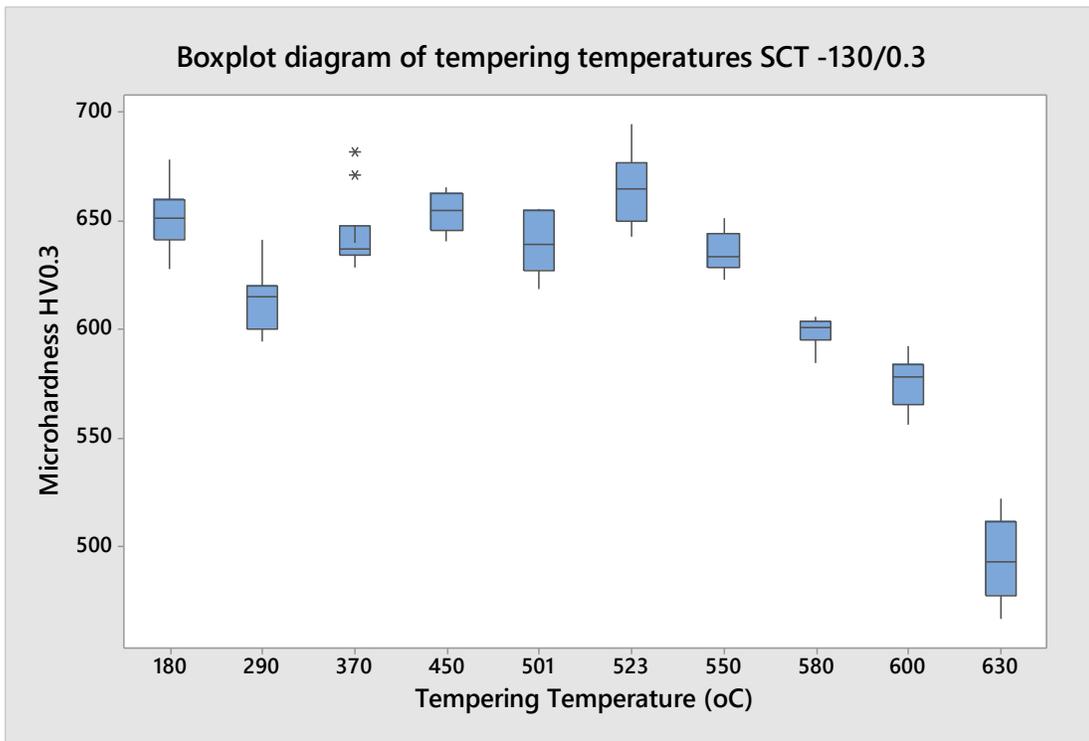


Fig. 66 Boxplot diagram of tempering temperatures SCT -130 °C for 0.3 hrs.

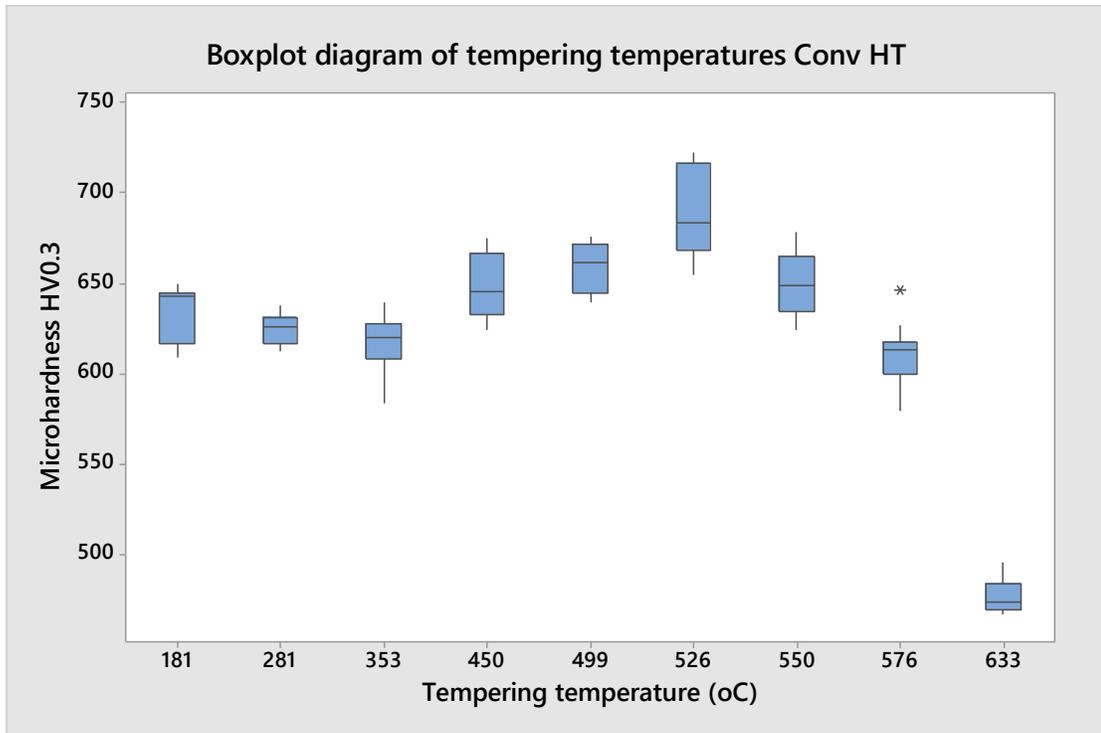


Fig. 67 Boxplot diagram of tempering temperatures Conventional HT

According to above Boxplot diagrams (Fig. 65-67), there are extreme values of microhardness for each of the tempering temperatures. The ones which exist far from the mean value are considered “invalid” since they represent values of hardness in the case of carbides. As a result, these values shall be excluded from the final chart.

It is essential to mention that the heating rate from the cryogenic temperature to ambient temperature was studied. In the case of deep cryogenic treatment, heating rate was higher (at -172°C, the specimens were taken out of the chamber in order to reach ambient temperature. On the other hand, in shallow cryogenic treatment, the samples remained inside the chamber until the expected temperature was reached.

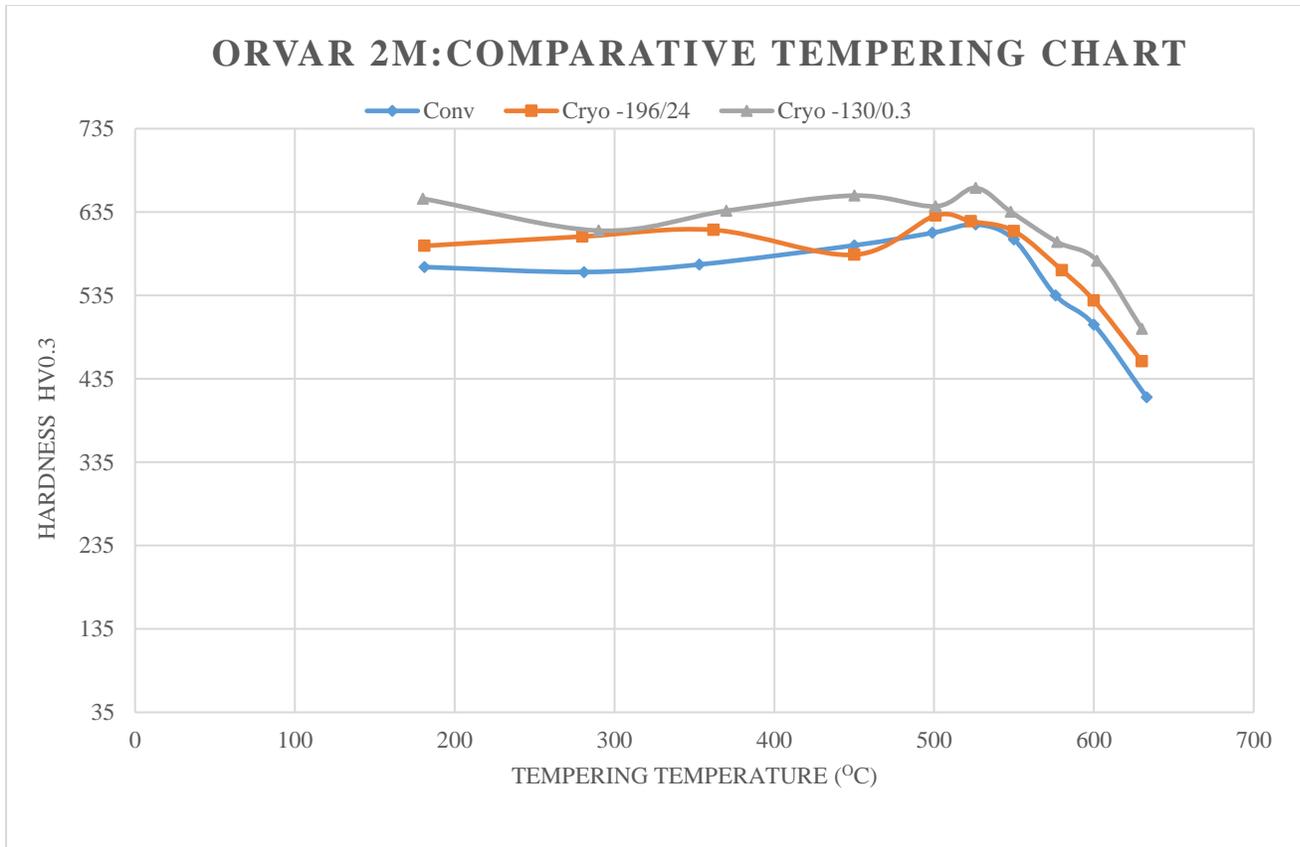


Fig. 68 Comparative Tempering Chart

Shallow Cryogenic Treatment -130°C/20min

From the tempering chart (Fig 68), increase in microhardness values of 50-80HV is observed through the temperature range, except for the area of secondary carbide precipitation where this difference is reduced to 20-40HV. According to Uddeholm manufacturing company [31] the difference is due to the more complete transformation of austenite into martensite, $\gamma \rightarrow \alpha$. For lower tempering temperatures, the difference in microhardness is 1-2 HRC, whereas less or no change is expected in the case of higher tempering temperatures. In the area of carbide precipitation, the complete austenite transformation contributes to increasing the carbide percentage and as a result hardness is increased. However, the difference in hardness, in the particular area, is lower, in relation to the conventional heat treatment due to the existence of the tempered martensite. Tempered martensite is more stable and characterized by lower hardness than the untempered. As far as the high tempering temperatures are concerned, the difference in microhardness between shallow cryogenic treatment and conventional treatment is greater since there is no carbide precipitation. Additionally, no difference is observed at the temperatures of secondary hardening between the two aforementioned heat treatments. The conditions, on which the shallow heat treatment was carried out, such as the temperature and the duration, did not contribute to carbide precipitation [32, 33, 34, 35]. Thus, the thermodynamic behavior of the material did not change.

Deep Cryogenic Treatment -196°C/24hrs

Regarding this type of cryogenic treatment, an increase in microhardness values of 20-40 HV is observed, across the whole TT range, except the area of the carbide precipitation (Fig. 68). This behavior is justified by the same reason as the ones in the case of the shallow cryogenic treatment. Moreover, it can be observed from the chart, that the temperature, at which the carbide precipitation takes place, is reduced by 20°C, resulting in transposition of the curve to the left. Deep cryogenic treatment accelerates the phenomenon of diffusion and as result the precipitation of the carbides is activated ta a lower tempering temperature. This shift is the macroscopic representation of the change in the thermodynamic behavior of the material.

In comparison with the shallow cryogenic treatment, it can be observed that microhardness, in the case of shallow, shows higher values than deep. This is considered to be in conflict with the theory of microcarbide formation during the subsidence temperatures ^[36]. This phenomenon is attributed to two specific reasons. One reason is related to carbon content inside the martensite matrix ^[37]. The under study material contains an average percentage of carbon. As a result, the process of carbide precipitation is restricted and there is great difficulty in observing huge changes in hardness. However, changes in wear resistance are expected. Another reason relies on increasing rate from the cryogenic temperature to the ambient temperature. In the case of shallow cryogenic treatment temperature rate was slow. On the other hand, deeply cryogenically treated samples showed higher rate of increasing temperature. According to researchers, this heating rate plays an important role on the performance of cryogenic treatment ^[38]. Based on thermodynamics rules, slow heating rate has as a result the material to pass through successive equilibrium states in relation to the rapid rate. Thus, the final state of the material is in a different intensive state.

Conclusion

The present experimental thesis was carried out in order to study the changes in microstructure and mechanical properties of Uddeholm Orvar 2M tool steel after cryogenic treatment. According to numerous studies, cryogenic treatment on tool steels contributes to complete transformation of retained austenite to martensite as well as precipitation and formation of finer carbides in the material. The above microstructural changes led to enhancement of mechanical properties of the material, including increase in hardness. The level of the changes depends on the type of the cryogenic treatment (Deep or Shallow) and the grade of the tool steel, especially the carbon content. Moreover, the level of contribution on the behavior of the material depends on the sequence of the treatment processes, the quenching medium as well as the application of additional surface treatment, such as nitriding.

Through the experimental procedure, Orvar 2M samples were subjected to deep and shallow cryogenic treatment prior to tempering and the results were compared to the conventional heat treatment behavior. As it was observed, both types of cryogenic treatment showed secondary hardening in the matrix, although higher values of microhardness were measured in the case of the shallow treatment. These results may be related to the heating rate from the cryogenic temperature for each procedure or the carbon content of the martensitic matrix of the tool steel. Moreover, through SEM and optical microscope, microstructure changes were observed. The retained austenite from quenching process has not been completely transformed into martensite and the percentage of precipitated carbides increased. The finer carbides are uniformly dispersed inside the matrix, increasing the microhardness. It is expected that wear resistance is also increased.

In conclusion, the present thesis gave the opportunity to understand cryogenic processing, a subject on which a number of published papers contain conflicting or specific, generally, conclusions and information. However, cryogenic treatment contributes in the enhancement of mechanical properties and structure stability of the material.

ANNEX I

Experiment No 1 (A – Q – CT (-195/24h) – T)

Tempering Temperature = 362 °C
Specimens 1 & 2

Table A.1 Tempering at 362 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
	The bathing box is inserted in the furnace	Fix : 220 °C Display : 276 °C Temperature of bath: 330 °C
	New Fix	Fix : 320 °C Temperature of bath: 336 °C
	Cycle	T _{min} : 317 °C T _{max} : 338 °C
17: 52	The specimens are inserted	Fix : 320 °C Display : 323 °C
17:54	Check	Display : 336 °C
17:56	Check	Display : 329 °C (Cold material in hot environment)
18:01	Check	Display : 320 °C
18:02	Check	Display : 317 °C
18:03	Check	Display : 330 °C Max : 333 °C
18:05	Check	Display : 331 °C
18:05	Cycle	T _{min} : 317 °C T _{max} : 333 °C Cycle duration : 12 min 18 sec
18:36	Check	Display : 318 °C
18:37	Check	Display : 317 °C (Re: ON)
18:49	Check	Display : 324 °C
18:51	Check	Display : 334 °C
18:55	Check	Display : 326 °C
19:01	Check	Display : 317 °C
19:02	Check	Fix : 320 °C Display : 333 °C Temperature of bath: 363 °C
19:02	Check	T _{min} : 317 °C T _{max} : 333 °C (10,44 min)
20:02	END of Tempering	Temperature of bath: 362 °C
20:03	Cooling	
20:09	END	T: 30 °C

Tempering Temperature = 180 °C
Specimens 3 & 4

Table A.2 Tempering at 180°C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
	The bathing box is inserted in the furnace	Fix : 220 °C Display : 218 °C Temperature of bath: 264 °C
	New Fix	Fix : 170 °C Display : 218 °C Temperature of bath: 246 °C
	New Fix	Fix : 150 °C
18:28	Check	Fix : 150 °C Display : 189 °C Temperature of bath: 221 °C
18:48	Check	Fix : 120 °C Display : 158 °C Temperature of bath: 204 °C
19:06	Check	Fix : 130 °C Display : 147 °C Temperature of bath: 198°C
19:22	New Fix	Fix : 100 °C Temperature of bath: 184°C
19:30	Check	Fix : 100 °C Display : 145 °C Temperature of bath: 181°C
19:33	New Fix	Fix : 135 °C
19:40	Check	Display : 142 °C Temperature of bath: 183°C
19:40	New Fix	Fix : 130 °C
19:40	The specimens are inserted	
19:47	Check	Display : 149 °C
19:57	Check	Fix : 135 °C Display : 146 °C
20:12	New Fix	Fix : 140 °C Display : 143 °C
20:38	Check	Fix : 140 °C Display : 135 °C Temperature of bath: 183°C
20:54	Check	Display : 155 °C
21:08	Check	Display : 149 °C
21:16	Check	Display : 147 °C
21:18	Check	Display : 140 °C Temperature of bath: 185°C
21:32	Check	Display : 141 °C
21:38	Check	Display : 140 °C
21:47	END of Tempering	Display : 139 °C Temperature of bath: 183°C

Tempering Temperature = 450 °C
Specimens 5 & 6

Table A.3 Tempering at 450 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
	The Furnace is ON	Fix : 415 °C Rate : 7-8 °C/min
	The specimens are inserted	
18:38	Check	Display : 426 °C Temperature of bath: 440°C
19:09	Cycle	T _{min} : 412 °C T _{max} : 425 °C Cycle duration : 8 min 14 sec
19:45	Check	Fix : 415 °C Display : 424 °C Temperature of bath: 448°C
20:38	Check	Fix : 415 °C Display : 415 °C Temperature of bath: 449°C
20:38	END of Tempering	
20:39	Cooling	
20:50	END	

Tempering Temperature = 500 °C
Specimens 7 & 8

Table A.4 Tempering at 500 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:46	The Furnace is ON	Fix : 465 °C Rate : 6-7 °C/min
10:04	Check	Display : 306 °C
10:08	New Rate	Rate : 9-10 °C/min
10:23	Check	Display : 459 °C (Re : ON) Display : 461 °C (Re : OFF)
10:25	Cycle	T: 462 °C(Re : ON) → T: 464 °C(Re : OFF) (38.7 sec)
10:28	Check	Display : 468 °C
10:28	Cycle	T _{min} : 462 °C T _{max} : 469 °C Cycle duration : 2 min 26 sec
10:33	Check	Display : 469 °C Temperature of bath: 371 °C
10:54	Check	Display : 468 °C
10:59	Cycle	T _{min} : 462 °C T _{max} : 473 °C Cycle duration : 3 min 55 sec
11:26	Check	Temperature of bath: 482 °C
11:37	Check	Fix : 465 °C Display : 466 °C Temperature of bath: 486 °C
11:53	Check	Temperature of bath: 488 °C
12:16	Check	Temperature of bath: 493 °C
12:40	Check – New Fix	Temperature of bath: 493 °C Fix : 470 °C
13:07	New Fix	Fix : 480 °C Display : 488 °C
13:09	The specimens are inserted	Fix : 480 °C Display : 482 °C Temperature of bath: 501 °C
13:32	Check	Display : 477 °C
13:50	Cycle	T _{min} : 476 °C T _{max} : 489 °C Cycle duration : 5 min 52 sec
14:30	Check	Display : 476 °C (Re : ON) Display : 481 °C (Re : OFF)
14:32	Check	Display : 489 °C (MAX)
14:56	Check	Fix : 480 °C Display : 492 °C Temperature of bath: 507 °C
15:10	END of Tempering	
15:16	Cooling	
15:21	END	

Tempering Temperature = 280 °C
Specimens 9 & 10

Table A.5 Tempering at 280 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
08:50	The Furnace is ON - The bath salts for 280 °C, 350 °C are inserted	
09:10	Check	Fix : 230 °C Rate : 6-7 °C/min Display : 85 °C
09:32	Check	Display : 204 °C
09:39	New Fix	Fix : 230 °C Display : 225 °C
09:42	New Fix	Fix : 240 °C
09:59	New Fix	Fix : 260 °C Display : 271 °C
10:05	Liquefaction of bath	
10:06	Check	Display : 257 °C (Re : ON)
10:07	Check	Display : 262 °C (Re : OFF)
10:16	Check	Display : 257 °C (Re : ON) Display : 262 °C (Re : OFF)
10:23	Check	Display : 273 °C (MAX)
10:52	Full Liquefaction of bath	
11:10	Check – New Fix – new Rate	Temperature of bath: 230°C Fix : 290 °C Rate : 10 °C/min
11:14	Check	Display : 309 °C
11:23	Cycle	T _{min} : 287 °C T _{max} : 301 °C Cycle duration : 5 min 26 sec
11:33	Check	Temperature of bath: 260°C
11:34	New Fix	Fix : 310 °C
12:22	Check – New Fix	Temperature of bath: 330°C Fix : 260 °C
13:10	Check	Temperature of bath: 316°C
13:20	New Fix	Fix : 225 °C
13:55	Check - The door of Furnace is opened	Temperature of bath: 302°C
14:03	Check - The door of Furnace is closed	Display : 197 °C
14:24	Check	Fix : 225 °C Display : 232 °C Temperature of bath: 283°C
14:40	The specimens are inserted	Fix : 225 °C Display : 232 °C Temperature of bath: 280°C
15:02	Check	Fix : 225 °C

15:14	Check	Display : 229 °C
15:24	Check	Display : 225 °C
15:24	Check	Display : 222 °C (Re : ON)
15:24	Cycle	Display : 226 °C (Re : OFF)
16:25	Check	T _{min} : 222 °C
16:42	END of Tempering	T _{max} : 240 °C
16:43	Cooling	Cycle duration : 27 min 9 sec
16:47	END	Temperature of bath: 270°C

Tempering Temperature = 525 °C
Specimens 11 & 12

Table A.6 Tempering at 525 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:53	The Furnace is ON	Fix : 490 °C Rate : 7-8 °C/min Display : 498 °C
09:56	Cycle	T _{min} : 486 °C T _{max} : 498 °C Cycle duration : 4 min 29 sec
10:20	Check	Display : 486 °C (Re : ON)
10:27	Check	Display : 495 °C
10:42	Check	Display : 498 °C (MAX)
10:51	Cycle	T _{min} : 486 °C T _{max} : 498 °C Cycle duration : 5 min 11 sec
10:56	Check	Fix : 490 °C Display : 490 °C Temperature of bath: 513°C Rate : 7-8 °C/min
11:56	Check	Fix : 490 °C Display : 498 °C Temperature of bath: 517°C
11:56	New Fix	Fix = 495 °C
12:05	Cycle	T _{min} : 491 °C T _{max} : 503 °C Cycle duration : 5 min 35 sec
12:13	Check	Temperature of bath: 521°C
12:59	Check	Fix : 495 °C Display : 503 °C
13:10	Check	Temperature of bath: 522°C
13:37	The specimens are inserted	Temperature of bath: 523°C
13:55	Check	Fix : 495 °C Display : 497 °C
13:55	Cycle	T _{min} : 491 °C T _{max} : 504 °C Cycle duration : 6 min 52 sec
15:04	Check	Display : 494 °C
15:14	Check	Display : 504 °C
15:27	Check	Display : 491 °C (Re : ON)
15:30	Check	Fix : 495 °C Display : 500 °C Temperature of bath: 525°C
15:37	END of Tempering	
15:38	Cooling	
15:46	END	

Tempering Temperature = 550 °C
Specimens 13 & 14

Table A.7 Tempering at 550°C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:52	The Furnace is ON	Fix : 520 °C Rate : 7-8 °C/min
11:41	Check	Display : 520 °C
11:43	Check	Display : 531 °C
11:43	Cycle	T _{min} : 517 °C T _{max} : 529 °C Cycle duration : 6 min 58 sec
12:04	Check	Fix : 520 °C Display : 518 °C Temperature of bath: 550°C
12:08	The specimens are inserted	
12:50	Check	Display : 519 °C
12:50	Cycle	T _{min} : 517 °C T _{max} : 529 °C Cycle duration : 6 min 51 sec
13:00	Check	Display : 527 °C Fix : 520 °C
13:36	Check	Fix : 520 °C Display : 524 °C
13:45	Check	Fix : 520 °C Display : 517 °C (Re : ON)
13:55	Check	Fix : 520 °C Display : 524 °C
14:02	Check	Fix : 520 °C Display : 529 °C Temperature of bath: 551°C
14:08	END of Tempering	
14:09	Cooling	
14:15	END	

Tempering Temperature = 580 °C
Specimens 15 & 16

Table A.8 Tempering at 580 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:41	The Furnace is ON	Fix : 550 °C Display : 498 °C Rate : 7-8 °C/min
10:01	Check	Fix : 550 °C Display : 548 °C
10:09	Cycle	T _{min} : 546 °C T _{max} : 553 °C Cycle duration : 2 min 20 sec
10:23	Check	Fix : 550 °C Display : 546 °C (Re : ON)
10:34	Check	Display : 552 °C Temperature of bath: 566°C
10:47	Cycle	T _{min} : 546 °C T _{max} : 557 °C Cycle duration : 3 min 20 sec
12:02	Check	Fix : 550 °C Display : 547 °C Temperature of bath: 569°C
12:02	New Fix - New Rate	Fix : 560 °C Rate : 8-9 °C/min
12:20	Cycle	T _{min} : 556 °C T _{max} : 567 °C Cycle duration : 4 min 12 sec
12:40	The specimens are inserted	Fix : 560 °C Display : 558 °C Temperature of bath: 580°C
13:00	Check	Fix : 560 °C Display : 563 °C
13:10	Check	Fix : 560 °C Display : 567 °C
13:34	Cycle	T _{min} : 556 °C T _{max} : 568 °C Cycle duration : 4 min 54 sec
14:22	Check	Fix : 560 °C Display : 568 °C
14:33	Check	Fix : 560 °C Display : 567 °C Temperature of bath: 585°C
14:43	END of Tempering	Fix : 560 °C Display : 564 °C Temperature of bath: 585°C
14:44	Cooling	
14:52	END	

Tempering Temperature = 600 °C
Specimens 17 & 18

Table A.9 Tempering at 600 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
	The Furnace is ON	Fix : 580 °C Rate : 9-10 °C/min
17:42	The specimens are inserted	Fix : 580 °C Display : 582 °C
17:42	Cycle	T _{min} : 576 °C T _{max} : 586 °C Cycle duration : 5 min 12 sec
17:42	Cycle	T _{min} : 412 °C T _{max} : 425 °C Cycle duration : 5 min 20 sec
19:47	Cycle	T _{min} : 412 °C T _{max} : 425 °C Cycle duration : 5 min 15 sec
19:47	Check	Fix : 580 °C Temperature of bath: 603°C
19:47	END of Tempering	
14:48	Cooling	
14:55	END	

Tempering Temperature = 630 °C
Specimens 19 & 20

Table A.10 Tempering at 630 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:34	The Furnace is ON	Fix : 650 °C Rate : 9-10 °C/min
11:08	Open the door – New Fix	Fix : 600 °C Temperature of bath: 657°C
11:12	Close the door	Fix : 600 °C Display : 570 °C
11:23	Check	Fix : 600 °C Display : 607 °C
11:23	Cycle	T _{min} : 596 °C T _{max} : 607 °C Cycle duration : 4 min 37 sec
11:52	Check – New Fix	Fix : 610 °C Display : 600 °C Temperature of bath: 615°C
12:03	Check	Fix : 610 °C Display : 613 °C
12:03	Cycle	T _{min} : 606 °C T _{max} : 616 °C Cycle duration : 3 min 31 sec
12:17	Check	Fix : 610 °C Display : 616 °C
12:25	Check	Fix : 610 °C Display : 615 °C Temperature of bath: 627°C
12:30	The specimens are inserted	
13:07	Check	Fix : 610 °C Display : 610 °C
13:07	Cycle	T _{min} : 606 °C T _{max} : 617 °C Cycle duration : 4 min 15 sec
14:06	Check	Fix : 610 °C Display : 607 °C
14:24	Check	Fix : 610 °C Display : 608 °C Temperature of bath: 632°C
14:30	END of Tempering	
14:31	Cooling	
14:40	END	

ANNEX II
Experiment No 2 (A – Q – CT (-130/20m) – T)

Tempering Temperature = 180 °C
Specimens 21 & 22

Table A.11 Tempering at 180 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:44	Furnace is ON	Fix : 120 °C Rate : 7-8 °C/min
09:52	Check-New rate	Fix : 120 °C Display : 61°C Rate : 9-10 °C/min
09:57	Bath of 190 °C is inserted	
10:13	Check	Fix : 120 °C Display : 133 °C
10:22	Cycle	T _{min} : 118 °C T _{max} : 137 °C Cycle duration : 11 min 33 sec
10:35	New Fix	New Fix : 220 °C Display : 119 °C
11:28	Check	Fix : 220°C Display : 226 °C
	Cycle	T _{min} : 217 °C T _{max} : 234 °C Cycle duration : 8 min 29 sec
12:10	Check – New Fix	Display : 228 °C Temperature of bath: 211°C New Fix : 200 °C
12:30	New Fix	Fix : 150 °C
13:50	Check	Fix : 150 °C Display : 187 °C
13:35	New Fix – Open door	Fix : 130 °C
14:20	Check	Fix : 130 °C Temperature of bath: 180°C
	The specimens are inserted	
15:00	Check	Display : 150 °C
15:25	Check	Fix : 130 °C Display : 143 °C
15:44	Check	Fix : 140 °C Display : 136 °C
16:07	Check	Display : 135 °C
16:20	END of Tempering	Display : 134 °C Temperature of bath: 180°C
16:26	Cooling	
16:31	END	

Tempering Temperature = 290 °C
Specimens 23 & 24

Table A.12 Tempering at 290 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:21	The Furnace is ON - The bath salts for 190 °C is inserted	Fix : 290 °C Rate : 9-10 °C/min
09:41	Check	Fix : 230 °C Display : 295 °C
09:59	Check	Display : 286 °C
10:31	Cycle	T _{min} : 286 °C T _{max} : 302 °C Cycle duration : 6 min 52 sec
10:40	Check	Fix : 290 °C Display : 289 °C Temperature of bath: 274°C
10:45	Cycle	T _{min} : 286 °C T _{max} : 302 °C Cycle duration : 6 min 58 sec
10:57	Check	Display : 294 °C (Re : ON)
11:07	Check	Display : 291 °C Temperature of bath: 300°C
11:11	New fix – Open door	Fix : 270 °C
11:47	Check	Fix : 270 °C Temperature of bath: 272°C
12:08	Cycle	T _{min} : 267 °C T _{max} : 284 °C Cycle duration : 11 min 7 sec
12:24	New Fix - Open Door	Fix : 260 °C Rate : 9-10 °C/min
12:30	Check	Temperature of bath: 283°C
12:30	Specimen are inserted	
13:22	Check	Display : 263 °C
	Cycle	T _{min} : 257 °C T _{max} : 275 °C Cycle duration : 17 min 59 sec
13:56	Check	Fix : 260 °C Display : 266°C
	Cycle	T _{min} : 257°C T _{max} : 275 °C Cycle duration : 18 min 3 sec
14:25	Check	Temperature of bath: 290°C
14:30	END of Tempering	
14:31	Cooling	
14:36	END	

Tempering Temperature = 370 °C
Specimens 25 & 26

Table A.13 Tempering at 370 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
14:38	The bathing box of 290 °C is inserted in the furnace	Fix : 330 °C Rate : 9-10 °C/min
15:08	Check	Display : 329 °C
15:30	Cycle	T _{min} : 326°C T _{max} : 342 °C Cycle duration : 5 min 38 sec
15:43	Check	Display : 334 °C
16:00	Check – New Fix	Temperature of bath: 288°C New Fix : 340 °C
16:19	Cycle	T _{min} : 336°C T _{max} : 353 °C Cycle duration : 8 min 51 sec
16:45	Check	Fix : 340 °C Temperature of bath: 355°C
16:45	The specimen are inserted	
17:21	Cycle	T _{min} : 336°C T _{max} : 353 °C Cycle duration : 11 min 55 sec
18:09	Check	Display : 344 °C
	Cycle	T _{min} : 336°C T _{max} : 353 °C Cycle duration : 12 min 21 sec
18:40	Check	Temperature of bath: 370 °C
18:45	END of Tempering	
18:46	Cooling	
18:54	END	

Tempering Temperature = 450 °C
Specimens 27 & 28

Table A.14 Tempering at 450 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:41	The Furnace is ON	Fix : 410 °C Rate : 9-10 °C/min
10:29	Check	Display : 415 °C Temperature of bath: 361°C
10:56	Check	Display : 412 °C Temperature of bath: 412°C
11:09	Cycle	T _{min} : 407 °C T _{max} : 421 °C Cycle duration : 5 min 54 sec
11:35	Check	Fix : 410 °C Temperature of bath: 434°C
12:51	Check	Fix : 410 °C Temperature of bath: 445°C
	The specimen are inserted	
14:07	Check	Display : 412 °C
14:28	Cycle	T _{min} : 407 °C T _{max} : 422 °C Cycle duration : 9 min 14 sec
14:43	Check	Temperature of bath: 444°C
15:51	END of Tempering	
14:53	Cooling	
15:00	END	

Tempering Temperature = 500 °C
Specimens 29 & 30

Table A.15 Tempering at 500 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
15:05	The Furnace is ON	Fix : 450 °C Rate : 9-10 °C/min
15:32	Check	Display : 460 °C Temperature of bath: 474°C
15:51	Cycle	T _{min} : 447 °C T _{max} : 461 °C Cycle duration : 7 min 35 sec
	Check	Temperature of bath: 480°C
16:20	Check – New Fix	Temperature of bath: 481°C New Fix : 460 °C
16:53	Check	Temperature of bath: 490°C
17:17	New Fix	Fix : 470 °C
17:41	Check	Temperature of bath: 500°C
	The specimen are inserted	
18:07	Check	Display : 480 °C T _{min} : 467 °C
18:36	Cycle	T _{max} : 480 °C Cycle duration : 7 min 48 sec
19:21	Cycle	T _{min} : 467 °C T _{max} : 480 °C Cycle duration : 7 min 53 sec
19:35	Check	Display : 501 °C
19:41	END of Tempering	
19:42	Cooling	
19:45	END	

Tempering Temperature = 525 °C
Specimens 31 & 32

Table A.16 Tempering at 525 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:31	The Furnace is ON	Fix : 490 °C Rate : 9-10 °C/min
10:15	Check	Display : 490 °C
10:15	Cycle	T _{min} : 486 °C T _{max} : 496 °C Cycle duration : 2 min 49 sec
12:09	Check – New Fix	Temperature of bath: 515°C New Fix : 500 °C
12:34	Check	Temperature of bath: 521°C
12:40	Cycle	T _{min} : 497 °C T _{max} : 509 °C Cycle duration : 2 min 49 sec
	Cycle	T _{min} : 486 °C T _{max} : 498 °C Cycle duration : 5 min 30 sec
12:51	Check	Temperature of bath: 524°C
	The specimen are inserted	
14:03	Check	Display : 500 °C
	Cycle	T _{min} : 497 °C T _{max} : 510 °C Cycle duration : 6 min 19 sec
14:45	Check	Temperature of bath: 526°C
14:51	END of Tempering	
14:52	Cooling	
14:59	END	

Tempering Temperature = 550 °C
Specimens 33 & 34

Table A.17 Tempering at 550 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:27	The Furnace is ON	Fix : 520 °C Rate : 9-10 °C/min
10:46	Check	Fix : 520 °C Display : 518 °C Temperature of bath: 550°C
11:03	Cycle	T _{min} : 517 °C T _{max} : 528 °C Cycle duration : 4 min
11:16	Check	Temperature of bath: 537°C
12:01	Check – New Fix	Temperature of bath: 540°C New Fix : 525 °C
12:41	Check	Temperature of bath: 548°C
12:42	The specimens are inserted	
13:57	Cycle	T _{min} : 522 °C T _{max} : 534 °C Cycle duration : 5 min 25 sec
14:38	Check	Temperature of bath: 547°C
14:42	END of Tempering	
14:43	Cooling	
14:51	END	

Tempering Temperature = 580 °C
Specimens 35 & 36

Table A.18 Tempering at 580 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
09:30	The Furnace is ON	Fix : 550 °C Rate : 9-10 °C/min
10:30	Check	Fix : 550 °C Display : 555 °C
10:49	Check	Display : 574°C
	Cycle	T _{min} : 546 °C T _{max} : 557 °C Cycle duration : 3 min 20 sec
11:14	Check	Fix : 550 °C Temperature of bath: 574°C
11:28	Cycle	T _{min} : 547 °C T _{max} : 558 °C Cycle duration : 4 min 3 sec
11:56	Check	Temperature of bath: 577°C
	The specimens are inserted	
13:02	Cycle	T _{min} : 552 °C T _{max} : 563 °C Cycle duration : 4 min 47 sec
13:32	Cycle	T _{min} : 552 °C T _{max} : 563 °C Cycle duration : 4 min 57 sec
13:49	Check	Fix : 560 °C Temperature of bath: 577°C
13:56	END of Tempering	
13:57	Cooling	
14:01	END	

Tempering Temperature = 600 °C
Specimens 37 & 38

Table A.19 Tempering at 600 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
14:03	The Furnace is ON	Fix : 580 °C Rate : 9-10 °C/min
15:09	The specimens are inserted	Fix : 580 °C Temperature of bath: 602°C
17:00	Cycle	T _{min} : 576 °C T _{max} : 587 °C Cycle duration : 5 min 12 sec
17:04	Check	Fix : 580 °C Temperature of bath: 602°C
17:09	END of Tempering	
17:10	Cooling	
17:15	END	

Tempering Temperature = 630 °C
Specimens 39 & 40

Table A.20 Tempering at 630 °C

<i>Time</i>	<i>Procedure</i>	<i>Temperature</i>
11:39	The Furnace is ON	Fix : 600 °C Rate : 9-10 °C/min
12:16	Check	Fix : 600 °C Display : 600 °C
	Cycle	T _{min} : 596 °C T _{max} : 604 °C Cycle duration : 2 min 5 sec
13:07	Check	Fix : 600 °C Temperature of bath: 614°C
13:39	Cycle	T _{min} : 596 °C T _{max} : 606 °C Cycle duration : 3 min 28 sec
13:44	Check – New Fix	Temperature of bath: 618°C New Fix : 605 °C
14:14	Check	Fix : 605 °C Display : 604 °C
	Cycle	T _{min} : 601 °C T _{max} : 611 °C Cycle duration : 4 min 2 sec
14:26	Check	Fix : 605 °C Temperature of bath: 626°C
14:27	The specimens are inserted	
16:09	Check	Fix : 605 °C Display : 607 °C
16:11	Cycle	T _{min} : 601 °C T _{max} : 612 °C Cycle duration : 4 min 27 sec
	Cycle	T _{min} : 601 °C T _{max} : 612 °C Cycle duration : 4 min 26 sec
16:22	Check	Fix : 610 °C Temperature of bath: 626°C
16:27	END of Tempering	
16:28	Cooling	
16:33	END	

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