AGING BEHAVIOUR OF COPPER BEARING HSLA-100 (GPT) STEEL

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
METALLURGICAL AND MATERIALS ENGINEERING
(With Specialization in Physical Metallurgy)

By

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JUNE, 2006

CANDIDATE'S DECLARATION

I hereby declare that the work presented in this dissertation entitled as "**AGING BEHAVIOUR OF COPPER BEARING HSLA-100 (GPT) STEEL**"in the partial fulfillment of the requirements for the award of the degree of **"MASTER OF TECHNOLOGY"** in **"METALLURGICAL & MATERIALS ENGINEERING"** with specialization in **"PHYSICAL METALLURGY"**, at Indian Institute of Technology, Roorkee is an authentic record of my own work carried out between July 2005 to June 2006, under the guidance of Dr. D. B. Goel, Professor and Dr. S. Singh, Associate Professor, Department of Metallurgical & Materials Engineering, Indian Institute of Technology Roorkee, Roorkee. I have not submitted the matter presented in this dissertation for the award of any other degree of this institute or any other institute.

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Certificate

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ACKNOWLEDGEMENT

I express my deep sense of gratitude to my guide **Dr. D. B. Goel,** Professor and **Dr. S. Singh,** Associate Professor, Department of Metallurgical & Materials Engineering, Indian Institute of Technology Roorkee, for their keen interest, consistent guidance and encouragement throughout the course of this work. Their experience and deep insight of the subject helped this work on a smooth and steady course. Useful criticism and personal help in hour of need had been immensely useful.

I am also thankful to **Dr. P. S. Mishra,** Professor and Head, Department of Metallurgical & Materials Engineering, Indian Institute of Technology Roorkee for his encouragement in the course of this work.

I would also like to thank Shri Sanjay Panwar Research scholar, who helped me during the course of entire investigation.

I would also like to thank all the laboratory staff of Metallurgical and Materials Engineering Department especially Shri Samsher Singh of Heat Treatment Lab, Shri Vidya Prakash and Shri S. K. Seth of Metallography Lab, Shri R. K. Sharma and Shri S. M. Giri of Fabrication Lab who helped me to carry out the experimental work. Lastly I am thankful to all near and dear ones for their kind cooperation in completing this dissertation work.

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LIST OF ABBREVIATIONS

HSLA (Steel)	High Strength Low Alloy Steel (Steel)
AR	As Received
OQ	Oil Quenched
PA	Peak aged
OA	Over aged
SEM	Scanning electron microscopy
VHN	Vicker's hardness number
CVN	Charpy V-notch

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ABSTRACT

Investigations have been carried out on the development of copper bearing HSLA-100 (GPT) steel with composition (weight percent): C-0.05, Cu-1.23, Ni-1.77, Mo-0.51, Al-0.025, Mn-1.00, V-.004, P-.009, S-0.01, Si-0.34, Cr-0.61, Ti-0.003, Al-0.025, Nb-0.037, Sb-0.003, As-0.005, which was received from Naval Research Laboratory, Washington (USA) under an Indo-US Technical Collaboration Programme.

The steel was given treatment, which comprise of solution treatment/austenitization followed by oil quenching and tempering/aging at various temperatures. The effects of various processing parameters have been described with the help of mechanical property measurement, optical microscopy and scanning electron microscopy (SEM).

The HSLA-100 (GPT) steel was first austenitized at temperatures 1000°C for 180 minutes and then oil quenched. The austenitized specimens at 1000°C were tempered/aged at 400°C for varying lengths of time, from as low as 1 minutes to as high as 1200 minutes. As a result of aging, martensite is transformed into acicular ferrite and precipitation of carbide takes place at grain boundaries as well as within the laths/grains. The precipitation of microalloying element preferably Nb(Nb,Ti)C carbide particles initially form at the lath/grain boundaries in the peak aged condition and later on in the laths/grains. The content of Nb in precipitates increases with increasing aging time. Copper is always present in the carbides precipitates, retained austenite and in the matrix, where no separate precipitation of copper in this steel could be observed. Peak hardness is observed after aging for a particular aging time of 360 minutes. The microstructure at peak aged condition shows ferrite structure along with coherent precipitates of carbides of microalloying elements containing copper. Highest concentration of carbides particles has been observed in the peak aged condition of this steel. At the peak hardness level good hardness is observed at the cost of toughness. It has been observed that prolonged aging (aging beyond peaks) causes the formation of polygonal/acicular ferrite and coarse carbide particles. These precipitates particles in the over aging condition are rendered incoherent with the matrix of ferrite causing restoration of toughness by promoting homogeneous deformation and retarding early initiation of quasi-cleavage fracture.

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CHAPTER 1

LITERATURE REVIEW

1.1. INTRODUCTION

Those steel alloys known as high-strength low-alloy (HSLA) steels provide increased strength-to-weight ratios over conventional low-carbon steels for only a modest price premium. Because HSLA alloys are stronger, they can be used in thinner sections, making them particularly attractive for transportation-equipment components where weight reduction is important. HSLA steels are available in all standard wrought forms sheet, strip, plate, structural shapes, bar-size shapes, and special shapes .Typically, HSLA steels are low-carbon steels with up to 1.5% manganese, strengthened by small additions of elements, such as columbium, copper, vanadium or titanium and sometimes by special rolling and cooling techniques. Improved-formability HSLA steels contain additions such as zirconium, calcium, or rare-earth elements for sulfide-inclusion shape control. Since parts made from HSLA steels can have thinner cross sections than equivalent parts made from low-carbon steel, corrosion of HSLA steel can significantly reduce strength by decreasing the load-bearing cross section. While additions of elements such as copper, silicon, nickel, chromium, and phosphorus can improve atmospheric corrosion resistance of these alloys, they also increase cost. Galvanizing, zinc-rich coatings, and other rust-preventive finishes can help protect HSLA-steel parts from corrosion.

Grades known as "improved-formability" HSLA steels (sheet-steel grades designated ASTM A715, and plates designated ASTM A656) have yield strengths up to 80,000 psi, yet cost only about 24% more than a typical 34,000-psi plain-carbon steel. Because these alloys must compete with other structural metals such as AISI 1010 steel and aluminum, they must be as inexpensive as possible. However, formulating and rolling steel that meets this cost requirement is not easy, and the finished product presents a number of trades-offs. For example, the increase in strength from 35,000 to 80,000 psi may be accompanied by a 30 to

40% loss in ductility [1]. Earlier the major alloying element was carbon and we use HY-80 and HY-100 further the strength was increased by increasing the content of carbon but this causes the decrease in the weldability because it raises the hardenability, changes the properties of transformation products in heat affected zones enhances residual stresses in the vicinity of the weld. For good weldability it is desirable to keep the carbon contents low. This is also desirable for good toughness. Unfortunately, reducing the carbon content in the interests of improving the weldability and toughness decreases the volume fraction of pearlite in the steels this reduces the yield strength [2]. To compensate the reduce in the strength we replaced the carbon with the molybdenum and then further on as the advances took place we add other elements which strengthen material by the precipitation hardening and lead to the development of HSLA steels. Thus HSLA steels or microalloyed steels are basically low carbon steels with addition of low quantity of alloying elements to provide better mechanical properties (yield strength >275 MPa) and/or greater resistance to atmospheric corrosion than conventional carbon steels [3]. They are not considered to be alloy steels because they are designed to meet specific mechanical properties rather than chemical properties.

Improved-formability HSLA steels were developed primarily for the automotive industry to replace low-carbon steel parts with thinner cross-section parts for reduced weight without sacrificing strength and dent resistance. Typical passenger-car applications include door-intrusion beams, chassis members, reinforcing and mounting brackets, steering and suspension parts, bumpers, and wheels. Trucks, construction equipment, off-highway vehicles, mining equipment, and other heavy-duty vehicles use HSLA sheets or plates for chassis components, buckets, grader blades, and structural members outside the body. For these applications, sheets or light-gage plates are specified. Structural forms (alloys from the family of 45,000 to 50,000-psi minimum yield strength HSLA steels) are specified in applications such as offshore oil and gas rigs, single-pole power-transmission towers, railroad cars, and ship construction. In equipment such as power cranes, cement mixers, farm machinery, trucks, trailers, and power-transmission towers, HSLA bar, with minimum yield strengths ranging from 50,000 to 70,000 psi is used. Forming, drilling, sawing, and other machining operations on HSLA steels usually require 25 to 30% more power than do structural carbon steels. Most HSLA alloys have directionally sensitive properties. For some grades, formability and impact strength vary significantly depending on whether the material is tested longitudinally or transversely to the rolled direction. For example, bends parallel to the longitudinal direction are more apt to cause cracking around the outside, tension-bearing surface of the bend. This effect is more pronounced in thick sheets [1].

They are classified as separate steels category, which is similar to as-rolled mild-carbon steels with enhanced mechanical properties obtained by addition of small amount of alloying elements, and special processing technique such as controlled rolling and accelerated cooling methods. Initially the great progress has been made in developing HSLA steels based on relationship between microstructure and properties [3]. Now it has turned to factors, which control ductility, toughness, and formability. The HSLA steels have been developed on following criteria

1. Initially the design was based on tensile strength, with little cognizance being taken of yield strength, toughness and weldability and riveting being used for joining structural fabrication. Thus steel with high C content of 0.3% was used.
2. As the use of welding being used rather than riveting for joining which necessitated reducing carbon content and strength was maintained by increasing Mn.
3. The failure by brittle fracture of welded structure resulted in a recognisition that impact or fracture toughness was essential, and thus need for low transition temperature become apparent. Also it was recognized that higher yield strength was more important than high tensile strength thus carbon was lowered further and Mn was maintained at higher levels.
4. Refinement of grain size by grain–refining additions, such as Al-N introduced which results in increase in yield stress from 225 to 300 MN/$_m^2$ and ITT below 0°C.
5. Further increase in yield stress was then achieved by precipitation hardening. The low rolling finishing temperature were used for producing a fine grain size, also maintained low C & high Mn which increased strength to 450-525 MN/m^2 and ITT to –80°C.

6. The most recent development has been to improve general formability and in particular to improve the through thickness ductility and toughness. The occurrence of localized planar array of non-metallic inclusion is reduced by adding Zr, Ce, and Ca.

The structure of HSLA steels comprises mainly ferrite and pearlite. Other than HSLA steels may also have ferrite-bainite, tempered martensite or bainite structure.

Leslie [4] stated precipitation strengthening is the next most preferred mode of strengthening HSLA steels other grain refinement. This is because of fact that particles that form at high temperatures in austenite, although they are effective in controlling grain growth, do not cause strengthening, because they are too large and widely spaced. The strengthening particles are those that form at low temperature in austenite, at γ-α interface during transformation and in ferrite during cooling.

1.2. TYPES OF HSLA STEELS

1.2.1. Weathering Steels

These steels contain small amounts of alloying elements such as Cu and P and no painting may be required .As these steels rust Cu^{+2} and PO_4^{3-} are slowly concentrated at the rust-metal interface. These ions catalyze the oxidation of Fe(II) –hydroxyl complexes to amorphous δ FeOOH, which forms as a cohesive , crack–free layer at metal surface ,thereby limiting the access of O_2 and H_2O to metal surface and migration of Fe^{+2} ions away from the metal.[5]. These have ferrite-pearlite microstructures and gain their increased strength principally through elements in solid solution. Yield strengths are usually slightly in excess of 345 MPa, as compared to 248 MPa for C steels. Because of this greater strength are much higher than those obtainable in ferrite-pearlite structures, as the yield strength increases from 550 - 825 MPa, the impact transition temperature increases from -100°C to above room temperature. Thus the strength which can be achieved is limited by toughness requirement [6].

1.2.2. Dual Phase Steels

These steels having microstructure containing island of martensite (normally 10-20%), or dispersion of martensite in a ferrite matrix., resulting in a product with low yield strength and a high rate of work hardening, thus providing a high strength steel of superior formability. These steels do not show yield point elongation. The low yield stress is a consequence of the tessellated residual stresses arising from the transformation of the austenite pools to martensite; the high rate of work hardening is typical of alloys containing a dispersion of relatively hard particles in a softer matrix [7].

The dual-phase steels strengthen rapidly during deformation, because of their high work hardening rate. In addition, they can be markedly strengthened by static or dynamic strain aging. The high work hardening rate and strain aging response are attributed to the dispersion of hard phase, the presence of tessellated residual stresses before straining, and the ready availability of C to pin dislocations. After forming, the yield strength of dual-phase steels can be increased sharply by tempering at 300 to 400°C [4].

1.2.3. Acicular Ferrite Steels

These are low-carbon (less than 0.05% C) steel with an excellent combination of high yield strength (690 MPa), weld ability, formability and good toughness. This low carbon steel with sufficient harden ability it transforms on cooling to a very fine high-strength acicular ferrite structure rather than usual polygonal ferrite structure. The structure, of the ferrite grains is highly irregular in shape with a high dislocation density, about 10^{10} cm^{-3}, forms by either a bainitic or massive transformation of austenite to ferrite. This transformation can be achieved by quenching, or by alloying so that transformation during air-cooling is retarded. If the C and Mn contents are reduced to 0.05 and 1.85 % respectively, the structure becomes predominantly polygonal ferrite, and at still lower concentrations of these elements it becomes entirely polygonal ferrite. The acicular ferrite provides a large supply of mobile dislocations and the martensite islands provide residual stresses; the combination gives continuous yielding and high impact properties [7].

1.2.4. Microalloyed Steels

These are mild steels with carbon 0.03 to 0.15% Mn around 1.5%and less than 0.1% Nb, Ti, V, and also Al, which have been controlled rolling, controlled cooling to obtain ultra-fine ferrite grains of size below 5 µm to attain yield strength of 290 to 550 MP and tensile strength of 415to 700 MPa with ductile-brittle transition temperature at -70°C .So it gives high strength, good toughness and good weldability also. The finely dispersed precipitates of carbides or carbonitrides of these element cause refinement of grain size as well as precipitation hardening, both of which increase yield strength, and decrease the ductile-brittle transition temperature [7].

1.2.5. As –Rolled Pearlitic Steels

They may include C-Mn steel but which may also have additions of other alloying elements to enhance strength , toughness , formability and weld ability .

1.2.6. Inclusion –Shape Controlled Steels

They provide ductility and through – thickness toughness by small additions of Ca, Zr, Ti or perhaps rare earth elements so that shape of sulfide inclusion is changed from elongated stringers to small, dispersed almost spherical globules.

1.3. STRENGTHENING MECHANISMS IN HSLA STEELS

Following strengthening mechanisms have been observed in HSLA steels.

1.3.1. Grain Refinement

Refinement of the polygonal grain size increases the yield stress and decreases the impact transition temperature .Grain refinement, however, is generally only achieved in the normalised condition. This accounts for the extensive use of steels which are grain refined, for example, by Nb, V, Ti, or Al Ferrite grain refinement in ferrite-pearlite steels is accomplished through restricting the growth of austenite grains during hot rolling and/or by inhibiting the recrystallization of austenite during hot rolling so that the γ-cc transformation occurs in unrecrystallized austenite [3].

In most instances, all Nb, C and N are in solution at the start of hot rolling of austenite, but precipitation occurs during the rolling as the temperature of the steel drops. The precipitate particles hinder growth of austenite grains, and at still lower temperatures the particles (or precipitate clusters) inhibit recrystallization of the deformed austenite grains.

1.3.2. Solid Solution Strengthening

Substitutional solutes causes' symmetrical distortion of the solvent lattice and this leads to relatively moderate strengthening effects, whereas asymmetrical distortion, as induced by interstitial solutes in α-iron, gives rise to much more intense solid solution hardening [3]. However, the intensity of solid solution hardening by substitutional solute atoms associated in the form of dipoles, thus introducing some degree of asymmetrical distortion. By introducing asymmetrical lattice distortion, interstitial solutes such as carbon and nitrogen in α-iron exert a much greater strengthening effect than substitutional solutes. This is further augmented by the very strong interaction that occurs between the interstitial solute atoms and dislocations, coupled with the fact that the solute atoms tend to segregate to the dislocations. Again it has been shown that the strengthening is proportional to the square root of the solute concentration and the markedly increased strengthening is illustrated in Fig 1.1

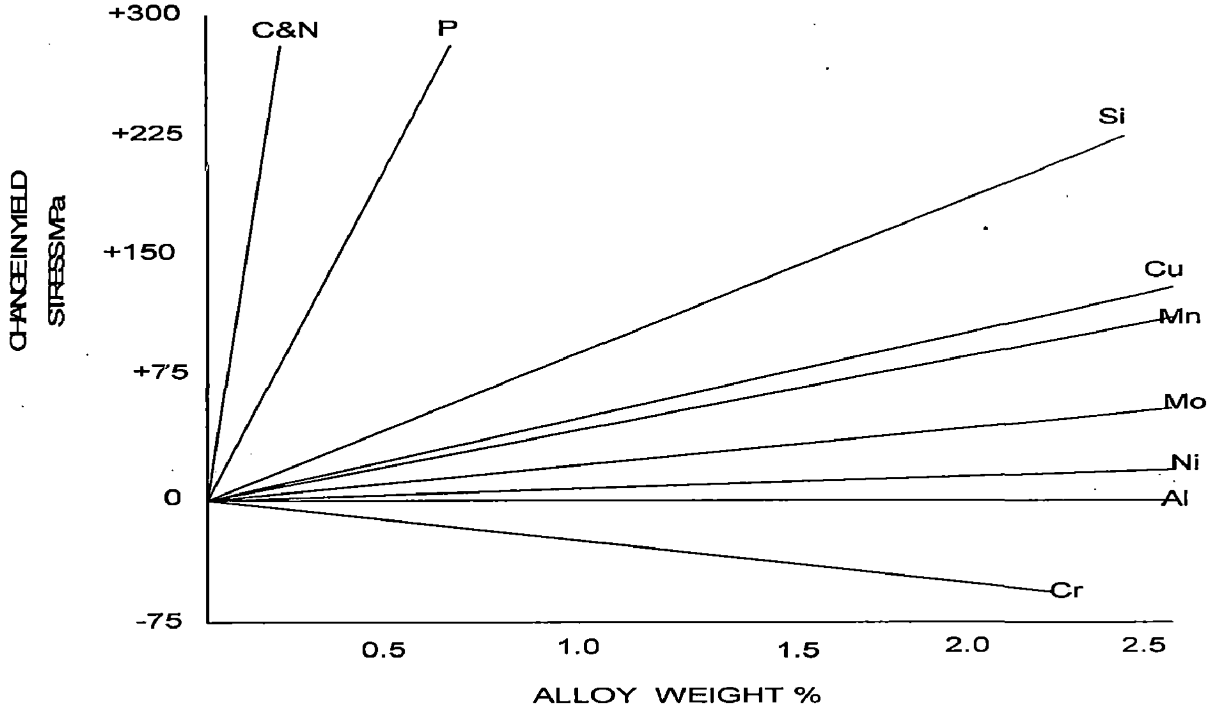


Fig: 1.1. Solid solution strengthening effects in ferrite-pearlite steels [3]

1.3.3. Precipitation Strengthening

Precipitation effects markedly increase the strength but lower the impact resistance. Recent developments have combined precipitation hardening with grain refinement, by the use of niobium, vanadium or titanium. The effectiveness of these elements depends on their solubility in austenite, which controls how much can be dissolved and is thus available for precipitation. Cooling rate also affects the intensity of precipitation strengthening by altering the transformation temperature. Fast cooling rates can prevent precipitation. Intermediate cooling rates cause maximum age hardening, whilst slow cooling rates give overaging. Precipitation strengthening is the next most preferred mechanism. The particles that form at high temperatures in austenite, although they are effective in controlling the grain growth, do not cause strengthening because they are too large and widely spaced. The strengthening particles are those that form at low temperatures in austenite, at the α-γ interface during transformation, and in ferrite during cooling. Precipitation effects markedly increase the strength but lower the impact resistance

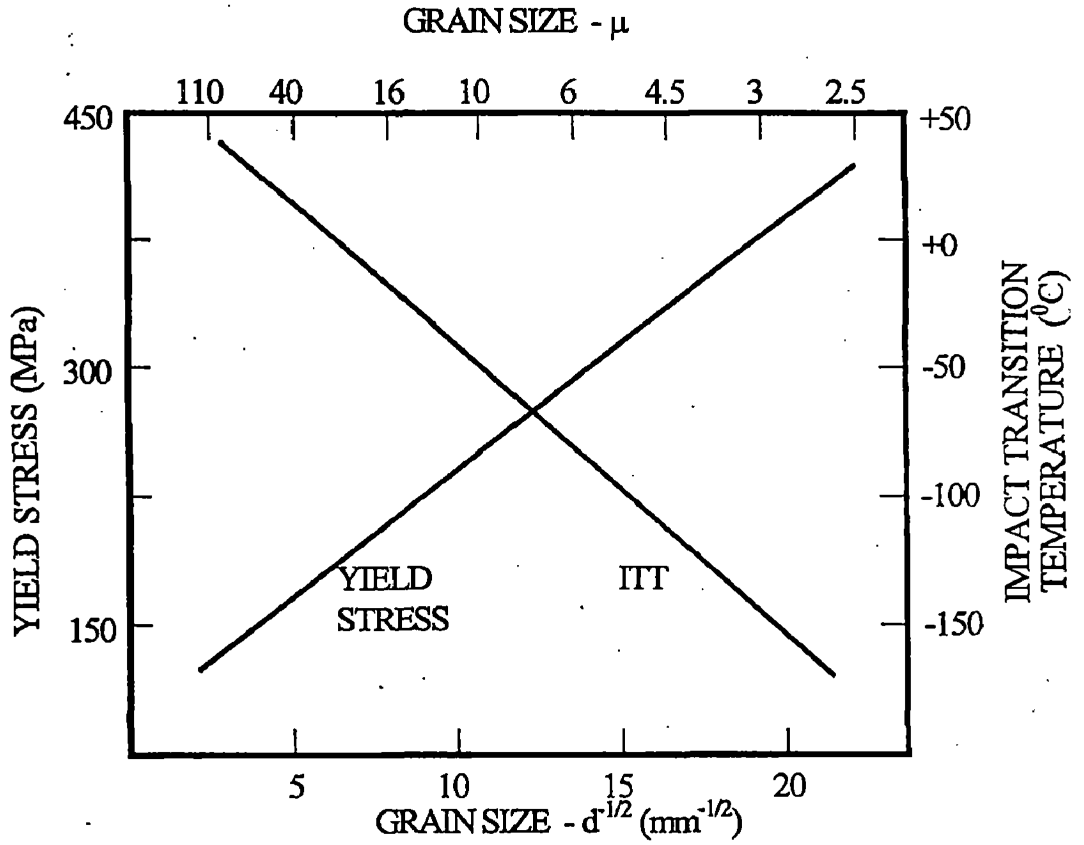


Fig 1.2. Effect of ferrite grain size on the yield stress and impact transition temperature of 0.1 % carbon steel [6]

Precipitation reactions have a very marked effect in increasing the yield strength, but they have definite limitations because they have a deleterious effect on the impact-transition temperature, often raising it markedly. The effects of precipitation on the strength and impact behaviour depend greatly on the degree of supersaturation, which will affect the volume fraction and also the size and spacing of the precipitate, and also on the aging time and temperature, which markedly affect the size and spacing of the precipitate particles. These structural features are the major variables that influence the tensile and impact properties of the steel in the precipitation- strengthened condition, but they are not easy to determine for the multitude of very fine particles present in precipitation-strengthening systems [6].The main precipitation strengthening systems used in commercial HSLA Steels are listed in the Table1.1

Table 1.1. Important precipitation –strengthening mechanisms in HSLA Steels [6]

Element(s)	Main precipitates
Niobium	Nb(C,N), Nb_4C_3
Vanadium	V(C,N), V_4C_3
Niobium + Vanadium	Nb(C,N), V(C,N), Nb_4C_3, V_4C_3
Vanadium +Nitrogen	VN
Copper	Cu
Copper + Niobium	Cu, Nb(C,N)
Titanium	Ti(C,N), TiC
Aluminium + Nitrogen	AlN

All of these precipitates, except for Cu, strengthen low C steels appreciably in the as-hot-rolled condition; with Cu, a subsequent aging treatment is mandatory if precipitation is to be effective. However, for a given addition of any of these elements, maximum strengthening can be achieved only by solution treating, quenching to retain the element in supersaturated solid solution, and then aging at the optimum intermediate temperature for a suitable time to precipitate particles of the optimum size. If the aging temperature is too high or aging is carried out for a long time, over aging results. Over aging is the condition in which the precipitate particles have grown too large (and at the same time become too few) for maximum strengthening.

The ferrite grain size refinement leads to an increase in both strength and toughness. The optimum reduction in ferrite grain size is generally achieved through heavy controlled rolling combined with accelerated cooling. For a simple steels composition in plate rolling this can reduce the ferrite grain size from 10 μm for hot rolling and air cooling to 5 μm for controlled rolling and water cooling, increasing the yield strength by about 80 MPa. At the same time there has been some evidence that strain induced transformation (i.e. transformation during rather than after deformation) could lead to significant ferrite refinement [8].

The copper containing age hardening steels have been of interest for a number of years owing to their desirable combination of strength and impact behavior [9].The design philosophy underlying such steels is to reduce the C content to approximately 0.05 wt%, to. increase toughness and weldability and increases strength via the precipitation hardening effects associated with the high (1-2 %) Cu contents, Ni is also added to eliminate the hot shortness effects associated with copper. Copper forms coherent clusters on tempering of austenitized steels, which becomes a major source of hardening in these steels. Since the GPT steels used in this investigation contains Cu, its effect should be emphasized to great extent.

1.3.4. Dislocation Strengthening

The flow stress, i.e. yield stress is related to the dislocation density (ρ) by:

$$\sigma_f = \kappa \sqrt{\rho}$$

Where σ_f = yield stress, ρ = dislocation density, k = constant

In general, decreasing the transformation temperature by either alloying or increasing the cooling rate both refines grain size and increases the dislocation density. This increased dislocation density increases the yield stress by about 50 MPa. Generally, increasing dislocation density decreases both tensile ductility and the toughness, as measured by DBTT. It has also been suggested that uniformly distributed dislocations are less detrimental to toughness than dislocation arrays. Also it has been suggested that mobile i.e. unlocked dislocations are less detrimental to toughness than are dislocations locked by precipitates or solute atmospheres [3].

1.4. STEPS IN AGE-HARDENING TREATMENT

Controlled precipitation from a supersaturated solid solution hardens the alloys, while its critical-cooling causes extensive hardening. The following are the steps in age-hardening treatment after choosing proper composition of the alloy [7].

1.4.1. Solutionzing

It is the process of heating the alloy just above the solvus temperature to obtain a single phase solid solution. The alloy should not be heated above solidius temperature as melting and oxidation shall occur to cause adverse effect on ductility. Heating the alloy much above the solvus temperature is also not advised as it causes grain-growth in the alloy, and the refinement in grain size later is a difficult process as no phase-change occurs during heating in these alloys. Many problems are faced while effectively solutionizing the Al-Cu-Mg alloys within a few degrees of the solidus temperature. If coring is present in the alloy, then the solutionizing temperature close to the solidus causes 'burning', *i.e.,* melting and oxidation caused at the grain boundaries seriously decreases the ductility of the alloy.

1.4.2. Quenching

The solutionised alloy is cooled fast to retain the high temperature single phase solid solution at room temperature as metastable supersaturated solid solution. As this supersaturation is normally required even in the centre of the section of a part, cold, hot or boiling water, or even air cooling may be used. As cold water gives maximum supersaturation, it may be used for thick sections.

1.4.3. Ageing

It is the process of controlled decomposition to form finely-dispersed-precipitates usually at one and sometimes at two intermediate temperatures for a suitable time period. A. Wilm's natural-ageing is the process of age-hardening by holding the quenched alloy at room temperature. Artificial-ageing is the process of ageing by holding the alloy at slightly higher temperature than room temperature.. If at any given temperature, ageing is allowed to take place for much longer time, then coarsening of the precipitates occurs, *i.e.*, precipitates grow in size at the cost of dissolution of smaller precipitates, so that the numerous fine precipitates are gradually replaced by a few coarse precipitates which are quite widely placed. The alloy in this state becomes softer after attaining peak hardness. This is called overageing.

1.5. TYPE OF PRECIPITATES

Depending on the structure of the boundary between the precipitate and the matrix, precipitates could be classified as [7]:

(i)Coherent precipitate
(ii) Semi-or partially coherent precipitate
(iii) Incoherent Precipitate

1.5.1. Coherent precipitate

With a coherent precipitate, its whole interface with the matrix is coherent, *i.e.*, there is a one-to-one matching of the lattice planes across the interface. This generally produces elastic lattice strains called coherency strains around the boundary where the lattice planes must be 'bent' to give this one-to-one matching. In an incoherent boundary, there is no regularity of lattice-plane matching across the boundary, *i.e.*, there is no coherent boundary. This is a large angle boundary between the precipitate and the matrix, *i.e.*, normal interface boundary.

1.5.2. Semi-or partially coherent precipitate

The formation of semi-coherent boundary is held. When two crystal lattices (i.e. α and β) touch each other to form an interface, the lattice planes like to have one-to-one matching across this interface. As the lattice parameters of two lattices are different elastic lattice strains are produced by dashed positions but this creates an edge dislocation at the point where the β plane is located symmetrically between two α-planes. It clearly illustrates that on both sides of this edge dislocation, there are coherency strains. On such an interface, the edge dislocation is obtained almost periodically with a spacing D between the two neighbouring dislocations Thus a semi-coherent boundary consists alternately of region of coherency and region of disregistry (region around dislocation).

1.5.3. Incoherent precipitate

In this case, there is no one-to one matching of the lattice planes. across the lattice parameters of two lattices are different elastic lattice strains developed

1.6. EFFECT OF ALLOYING ELEMENTS ON HSLA STEELS

Unlike the use of C and Mn, the use of microalloying to improve the strength and toughness of HSLA steels did not come about by accident. On the contrary, it was the result of purposeful methodical research. The use of Nb (200-400 ppm) was a way of usurping, in large part, the strengthening role of C. Microalloying with 1000 ppm V, however, was found to be more a way of exploiting C (and N) accidentally present in steels. Similarly microalloying with Ti (150-200 ppm) was found to be a way of almost entirely eliminating the effects of accidental N, because of very powerful high temperature affinity between these two elements. All three elements had the effects of augmenting or replacing the role of Mn, depending on circumstances.

1.6.1. Effect of Copper (Cu) on HSLA Steels

Copper can be used to give an added measure of precipitation strengthening. Copper additions can give 150MN/m^2 increase in yield stress, which is appreciable, and can be made to occur in air-cooled condition without a separate aging treatment if 3% Cu is added. Such an effect, however, requires that the transformation temperature is higher than that at which the copper precipitates. High copper minimizes the martensite transformation strains and thus inhibits distortion and quench cracking. Copper not only improves the hardenability, but also retards tempering and can introduce a precipitation-hardening reaction [3].

Copper precipitates as solute rich coherent bcc zones in Fe-lattice [10].The maximum solubility of copper in α-Fe is 2.1wt% at 851°C. When Fe-Cu alloy is quenched from a high temperature in the α-phase and then aged at a lower temperature (e.g. 400°C), the Cu atoms form spherical clusters in the Fe-lattice. These clusters can be detected when they are only about 0.8 nm in diameter. At this stage in a 1.4% Cu alloy their density is about 10^{18}/c.c. The clusters grow to a diameter of about 2.4 nm at which point the strength of the alloy is maximized. These clusters are not pure Cu; the earliest clusters contain about 50% Fe. As the particles grow they become richer in Cu. At a size of about 5 nm they transform insitu from bcc to fcc becoming non-coherent. At that point the alloy is overaged with respect to yield strength. Only in the overaged condition do the particles approach the equilibrium composition of ε-phase, which is essentially pure Cu. The rate of growth is controlled by rate of volume diffusion of Cu. Because of the decrease in solubility of Cu with decrease in temperature, ε-phase can be precipitated by aging supersaturated α-phase which has been formed upon rapid cooling. The Cu precipitates as spheres because the strain energy of the coherent particles is very small. The atomic radii of Cu & Fe differ by only about 0.3%. The precipitation of Cu from solid solution in ferrite continues to attract interest because of the possibility of controlling texture and strength by this process [11].

For specific purposes Cu can be added to increase strength by precipitation [12] but there are likely to be production problems involving surface quality and ingot breakup. The criteria for maintaining a high level of weldability are really the Ms Temperature and hardness of the martensite. Too low a Ms temperature and too high a hardness of martensite leads to heat affected zone or weld cracking.

Krishnadev and Le May [13] observed that ε-phase precipitation takes place along dislocations and throughout the matrix. This is in contrast to the predominant nucleation along dislocations observed by Cox [14] in 0.3%C, 1.5%Cu steels, but the greater carbon content may increase the degree of supersaturation sufficiently to alter the energy criterion for nucleation. Uniform precipitation was also reported by Hornbogen and Glenn [15]. The change from initial spherical rod-like morphology on prolonged aging is due to either minimization of strain energy or anisotropy of surface energy.

Considerable increase in strength of ferrite can be obtained from Cu-precipitation, an increment of up to 248 MPa per 1% Cu being obtainable [16] .Hornbogen and Glenn [15] suggested that the major part of the strengthening of an alloy containing Cu clusters might be due to vacancies causing jogs on screw dislocation mobility rather than to the cutting of the clusters. Hornbogen [15] also suggested that, in the stages between clustering and overaging, clusters and particles together produce hardening the clusters gradually disappearing as the non-coherent precipitates nucleate and grow. When small, the particles can be cut by dislocations since the slip systems in the bcc and fcc matrix and particles can be parallel, strengthening being by particle cutting.

Hurley and Shelton [17] reported the effect of Cu content on tensile properties of a 0.05%C, 0.5%Mn, 0.2%Si, 0.8%Ni, 1.25%Cu, and 0.03% Nb steels in the as-rolled or as-rolled and tempered condition. Snape [18] reported the results of thermomechanical treatment of same steels and observed the best balance of strength and toughness by hot rolling between 900°C and 750°C, especially with a final pass rolling, warm rolling at 650°C and aging at 570°C for 1 hour. DePaul and Kitchen [19] studied the mechanical properties of steels with base composition 0.05%C, 0.04%Mo and 0.25%Si, and Cu, Ni and Nb were added separately or together to this steel. With 1.3%Cu addition, the yield strength increases were 110 MPa and 210 MPa in as rolled and as rolled and tempered (560°C, 1hour) conditions respectively, but the upper shelf energy decrease considerably. In a study of low carbon Cu-containing HSLA steels the quenched and temper treatment was conducted[20] Niobium carbide particles reported in as quenched structure tempering this steels at 605°C for 1 to 3 hours yielded a heterogeneous distribution of Cu much of which was associated with the lath boundaries.

Skoufari et al [21] studied the strength and impact behavior of Cu containing steels. They observed that Cu free steels showed no response to any of aging treatments, its hardness, and lower yield strength and impact properties remaining almost constant. However, on aging, the hardness and strength of Cu containing steels is increased, reached a peak and then declined. The major influence of Cu on the microstructure is to produce a large amount of precipitation, this being present even in the un aged state. They concluded the following results:

(i) Addition of the Cu was found to have a grain refining effect on C-Mn-Al steels that was slowly cooled after austenitizing at 910°C.

(ii) Copper was precipitated out in a relatively coarse form (40-50 nm) during this slow cooling however, because of the large volume fraction precipitated, considerable strength substantially and even gives a small improvement in toughness.

(iii) Fully aging the Cu containing steels resulted in a further substantial increase in strength, but this time at the expense of the impact behavior similarly to normal precipitation hardening.

(iv) The higher Cu content in the steels lead to coarser incoherent precipitation, resulting in a slightly lower strength even though the volume fraction of incoherent precipitation was increased.

(v) The impact behavior of the Cu containing steels under investigation was good because the incoherent Cu containing particles were able to deform and absorb the impact energy without permitting cracks to be formed.

1.6.2. Effect of Vanadium (V) on HSLA Steels

Development of vanadium containing steels occurred shortly after the development of weathering steels, and flat-rolled products with up to 0.10% V are widely used in the hot-rolled condition. Vanadium-containing steels are also used in the controlled-rolled, normalized, or quenched and tempered condition. Vanadium contributes to strengthening by forming fine precipitate particles (5 to 100 nm in diameter) of V (CN) in ferrite during cooling after hot rolling. These vanadium precipitates, which are not as stable as niobium precipitates, are in solution at all normal rolling temperatures and thus are very dependent on the cooling rate for their formation. Niobium precipitates, however, are stable at higher temperatures, which is beneficial for achieving fine-grain ferrite The strengthening from vanadium averages between 5 and 15 MPa (0.7 and 2 psi) per 0.01 wt% V, depending on carbon content and rate of cooling from hot rolling (and thus section thickness). The cooling rate, which is determined by the hot-rolling temperature and the section thickness, affects the level of precipitation strengthening in a 0.15% V steel. An optimum level of precipitation strengthening occurs at a cooling rate of about 170 °C/min (306 °F/min) At cooling rates lower than 170 °C/min(306 °F/min), the V(CN) precipitates coarsen and are less effective for strengthening. At higher cooling rates, more V(CN) remains in solution, and thus a smaller fraction of V (CN) particles precipitate and strengthening is reduced [3]

1.6.3. Effect of niobium (Nb) on HSLA Steels

Like vanadium, Niobium added in small amounts (0.03% to 0.05%) increases yield strength by combination of precipitation strengthening and grain refinement. However, niobium is also a more effective grain refiner than vanadium. Thus, the combined effect of precipitation strengthening and ferrite grain refinement makes niobium a more effective strengthening agent than vanadium. The usual niobium addition is 0.02 to 0.04%, which is about one-third the optimum vanadium addition. Strengthening by niobium is 35 to 40 MPa (5 to 6 psi) per 0.01% addition. This strengthening was accompanied by a considerable impairment of notch toughness until special rolling procedures were developed and carbon contents were lowered to avoid formation of upper bainite. In general, high finishing temperatures and light deformation passes should be avoided with niobium steels because that may result in mixed grain sizes or Widmanstätten ferrite, which impair toughness. Niobium steels are produced by controlled rolling, recrystallization controlled rolling, accelerating cooling, and direct quenching. In a study of the aging kinetics of 0.02%C, 0.11 %Nb and 1.86%Cu steels, Krishnadev and Galibo [22] is observed a single hardness peak. Although two precipitation hardening elements Cu & Nb were present and the age hardening response was classic, the peak hardness and the time to reach it increases with decrease in aging temperature. However; when compared with the aging response of a plain Cu-containing steels (0.05%C, 2%Cu, and 1.5% Ni), the duration of the peak hardness plateau appeared to be greater and the rate at which overaging occurred lower for the Cu-Nb steels than for the plain Cu-containing one. In addition, the level of hardness achieved was higher throughout for the Cu-Nb steels. Even in a complex Cu containing steels containing Nb and Ti, both of which give rise to precipitation strengthening, single peak have been observed except at a low aging temperature of 500°C [23]. The hardness levels achieved were relatively high. The alloying elements Mo, Ni, Mn and Cr retard the precipitation of Cu because of their effect in delaying the austenite to ferrite transformation.

1.6.4. Effect of Titanium (Ti) on HSLA Steels

Titanium in low-carbon steels forms into a number of compounds that provide grain refinement, precipitation strengthening, and sulfide shape control. However, because titanium is also a strong deoxidizer, titanium can be used only in fully killed (aluminum deoxidized) steels so that titanium is available for forming into compounds other than titanium oxide. Commercially, steels precipitation strengthened with titanium are produced in thicknesses up to 9.5 mm (0.375 in.) in the minimum yield strength range from 345 to 550 MPa (50 to 80 psi), with controlled rolling required to maximize strengthening and improve toughness. It provides both precipitation strengthening and sulfide shape control .Small amounts of Ti (<0.025%) are also useful in limiting austenite grain growth [3]

Like niobium and/or vanadium steels, titanium microalloyed steels are strengthened by mechanisms that involve a combination of grain refinement and precipitation strengthening; the combination depends on the amount of alloy additions and processing methods. In reheated or continuously cast steels, small amounts of titanium (δ0.025% Ti) are effective grain refiners because austenite grain growth is retarded by titanium nitride. Small amounts of titanium are also effective in recrystallization controlled rolling because titanium nitride retards the grain growth of recrystallized austenite. In conventional controlled rolling, however, titanium is a moderate grain refiner, causing less refinement than niobium but more than vanadium.

In terms of precipitation strengthening a sufficient amount of titanium is required to form titanium carbide. Small percentages of titanium (<0.025% Ti) form mainly into TiN, which has an effect on austenite grain growth but little effect on precipitation strengthening because the precipitates formed in the liquid are too coarse. Increasing the titanium content leads to the formation first of titanium-containing manganese sulfide inclusions (Mn,Ti)S, and then of globular carbosulfides, $Ti_4C_2S_2$ (which provide sul-fide shape control). The formation of $Ti_4C_2S_2$ is accompanied by and followed by titanium carbide (TiC) formation, which can be used for the precipitation strengthening of low-carbon steels [3].

Krishnadev and Galibo [24] is observed very limited precipitation in Cu-Ni-Nb-Mo steels after being air-cooled from a finish rolling temperature of 760°C. They suggested that lowering of the transition temperature due to the presence of the additional alloying elements retards the premature precipitation of Cu because of its greater solubility in austenite than in ferrite.

Kong [25] studied the effect of precipitate on recrystallisation of Nb containing HSLA steels and softening behavior observed during interrupted 2-stage deformation. It was confirmed that, when Nb was in solute state, softening kinetic curve appeared as a plain sigmoidal shape. However, when precipitation occurred, sigmoidal curve contained a hump in initial stage. The nucleation of strain induced precipitate was found to be a very rapid process. Under the present experimental conditions at 850 °C and 900°C, recrystallisation took place at coarsening stage of precipitate. At 950°C, growth of precipitate and progress of recrystallisation occurred simultaneously. At 1000°C, recrystallisation was completed before precipitation started.

Of all the alloying elements commonly used, Mo appears to have the greatest effect in intensifying the strengthening response due to Cu precipitation In one commercial Cu-containing steels (IN-787), additions of both Mo and Cr were used to retard the premature precipitation so that further strengthening by aging can be obtained, even in thick sections [26].In this steels, more than half an hour was required to reach peak hardness at 600°C and considerable hardening taking place even at 700°C. In contrast, in plain Cu-containing steels, it takes about 10 min at 600°C to reach peak hardness and at 700°C little increase in hardness occurs with softening taking place after only 5 minutes aging [27].

Manganese (Mn) is the principal strengthening elements in plain carbon high-strength structural steels when it is present in amounts over 1% It functions mainly as a mild solid-solution strengthener in ferrite, but it also provides a marked decrease in austenite to ferrite transformation temperature [2]. Manganese additions [28] can improve the toughness as well as strength in pearlite reduced steels by lowering the Ar_3 temperature [29]. The decreased Ar_c temperature mitigate the embrittlement which accompanies precipitation strengthening, by refining the Nb(C, N) and VN, precipitated in the α-matrix and by refining the α-grains more effectively after the same rolling conditions and also by making it possible to intensify controlled rolling at non-recrystallisation temperature in the γ [30]The increase of Mn content over 1.8 % under a reduced C content less than 0.06 pct causes the microstructural transition from polygonal α-pearlite to acicular α, which consists of the mixed structure of a and bainite. The strengthening in the acicular a structure depends mainly on the volume fraction of bainite with high dislocation density, and this in turn, is associated with a lowering of γ-α transformation temperature of the steel. Therefore, the strength of acicular a steel largely depends on C, Mn or Mo content, and the effects of Cu, Ni and Cr are supplementary.

Carbon(C) is used solely as strengthening element .Its content is generally maintained at low level so as to provide good weldability and ductility. The maximum carbon content allowed in any of the ASTM grades is 0.28%, but materials with these higher carbon contents are intended primarily for use in construction of riveted bolted bridges [2] Since C is the basic alloying element in HSLA steels, all such elements which interact with C will affect the structure and properties of these steels. A carbide forming element such as W, if present in only moderate amount in a high-C composition, is found almost wholly in the carbide phase. If it is present in high concentration in a low-C steel, it is largely dissolved in ferrite. However, such moderately strong carbide former may be found largely in ferrite in high-C steel if a large amount of a still stronger carbide forming element is present. Thus, Cr, and to some extent W and Mo, are forced into ferrite solid solution by Ti or Nb unless the C is sufficient to combine both with most of the Ti or Nb and with much of the other less active elements. Some elements such as Ni, Al, Si, Cu and Co are not found extensively in the carbide phase. Although Si may combine to a small extent with oxygen, these elements will be found largely dissolved in ferrite. Copper, having a limited solubility in ferrite, will be found as a nearly pure Cu dispersion (saturated with Fe) when more than about 1 % is present [6].

Phosphorus (P) is an effective solid-solution strengthener in ferrite .It also enhances corrosion resistance but causes decrease in ductility at low levels (<0.05%P) can also cause embrittlement through segregation to prior austenite grain boundaries [2]

Silicon (Si) is used as a deoxidizer in molten steels .It is usually present in fully deoxidizer in molten steels. It is usually present in fully deoxidized structurally steels in amounts up to 0.35%, which ensures the production of sound, dense ingots. It has a strengthening effect in low-alloy structural steels. In larger amounts, it increases resistance to scaling at elevated temperature. It has a significant effect on yield strength enhancement by solid-solution strengthening [2].

Chromium (Cr) is often added with copper to obtain improve atmospheric-corrosion resistance .Upon exposure to the atmosphere a steels composition of 0.1% P, 0.85% Cr and 0.4% Cu, steels develop a particularly adherent, dense oxide coating [2].

Nickel (Ni) is added about 1%. It moderately increases strength by solution hardening of ferrite .It enhances atmospheric–corrosion resistance when present in combination with copper or phosphorus [2] Nickel is generally known to influence the toughness; this is brought about by lowering of transition temperature rather than by raising the energy absorbed in ductile fracture (shelf energy). Nickel lowers the transition temperature due to promotion of cross slip of screw dislocations. This characteristic of Ni, unique among commercial alloying elements, accounts for its use in high strength steels in concentrations from 1 to 10 %. As a constant grain size and Ni content, the transition temperature increases with increasing yield strength. Therefore, once the possibilities of grain refinement have been exhausted, the only way to maintain a low transition temperature is to increase the Ni content as the yield strength increases [6].

Boron (B) addition in high Mn steels, under a further reduction of C content below 0.04 %, can yield the ultra low-C bainite structure [31]. This microstructure is different from acicular-α in respect of a single structure of bainite without α and the bainite is formed directly from the deformed austenitic grain boundaries stabilised by B because of the extremely reduced C content. Bainite in this type of steel has superior low-temperature toughness and ductility, and weldability such as cold cracking susceptibility is remarkably improved. Under a given basic composition of 0.25 % Si - 2 % Mn - 0.05 pet Nb, B free steel forms the acicular α and the addition of Ti gives rise to ultra low-C bainite structure. In the latter steel, 0.02 % Ti is simultaneously added to protect B against BN formation. The decrease of strength with reducing C content in B free steel is due to the decrease of the volume fraction of bainite formed in the acicular a products. Conversely, B added steel results in a relatively small dependence of the strength content of less than 0.02 %. The starting temperature of bainite transformation in this steel is very low, e.g. 630°C in 0.02 % C steel, preventing completely the α-formation.

1.7 EFFECT OF AGING ON HSLA STEELS

In general term aging is defined as the phenomena when the precipitation of certain alloying elements took place in the certain temperature range [32] .We can use this phenomenon for our purpose of strengthening the sample. For aging in HSLA steels we generally use Cu Nb, Ti, and V etc (these elements control austenite grain size as well as subsequently strengthen the transformed structure of ferrite, bainite or martensite). If we add Cu to the HSLA steels and cold working treatment is given after austenitization the dense dislocation–cluster network on aging should provide effective hindrance to the mobility of dislocations. The steels precipitate strengthen with Cu must be aged at temperature in range of 427-650°C, subsequent to hot rolling to develop increase in yield strength. The temperature used will depend on aging time (very long times are required at low temperature). Most of the substitutional and interstitial solutes are detrimental to the impact properties, especially interstitial solutes. Solutes may have other effects such as altering ferrite: pearlite ratio, refining grain size by decreasing transformation on cooling (Mn) producing precipitation effects (C&N) and withdrawing interstitial from solution (Al).

Hornbogen [33] observed that, on deforming a quenched Fe-Cu alloy, dislocations originated at grain boundaries and sub-boundaries. As strain increased they formed tangles, then cell walls, the interiors of which were comparatively free of dislocations. After slight aging to form clusters, dislocation still originated at grain boundaries but ceased to have random orientation, lying preferably along <111> directions, also the concentration of dislocations within cell walls increased after deformation. After prolonged aging, dislocations formed a uniform grid along <111> directions they were heavily jogged and many rings were observed. Upon further aging until ε-phase particles were formed no changes were observed in the dislocation configuration after deformation, nor were there any indications of concentric dislocations around particles or of dislocation pile-ups against them. When heavily overaged material was deformed the dislocation loops emitted from the matrix / precipitate interfaces led to a uniform distribution of dislocations if the interparticle spacing λ was $\approx 0.1\mu m$. The dislocations were randomly oriented if precipitates were more widely spaced $\lambda \geq 1\mu m$ and cell walls were formed linking the particles. As the temperature of deformation was decreased, the formation of cells was inhibited.

Krishnadev and Le May [34] studied the effect of tensile deformation as well as cold rolling on the appearance of ε-phase precipitates. After tensile deformation no internal structure or deformation of precipitates was detected, but on severe cold rolling a complex dislocation structure was evident within the deformed precipitates. Hornbogen and Glenn [33] studied the deformation behavior of ε-phase precipitates by subjecting the specimens of Fe-Cu alloy to different degrees of cold rolling and by examining the structure of the extracted particles using replica techniques. The spherical ε-phase particles appeared to be unaffected by small reductions, but with increasing deformation they contained an increasing number of straight lines. It was suggested that these were due to narrow twins or stacking faults within the particles, which had been created by the deformation, rather than being dislocations. After extensive cold rolling (90% reduction), the precipitates were rolled out and their structural details could not be resolved. Hornbogen [33] suggested that it is more likely that dislocations pile up outside a particle, leading to deformation of the particle on its own slip systems, than that they cut through it.

Robert [35] reported that by rapidly quenching low carbon steels from the controlled rolling temperature produces the best combination of strength and toughness. The lower the finishing rolling temperature, the better are the properties due to finer prior austenite grain size which gives rise to a very fine acicular ferrite grain size, and a defect structure induced by the deformation, which is not annealed out. This latter is very attractive in increasing the strength when the final rolling occurs at temperatures where the austenite-ferrite transformation takes place in very low carbon steels. However the impact properties may be impaired.

Leslie [36] reported that the precipitation strengthening is the most preferred mode of strengthening in HSLA steels. This is because of the fact that particles that form at high temperature in austenite, although they are effective in controlling grain growth, do not cause strengthening, because they are too large and widely spaced. The strengthening particles are those that form at low temperatures in austenite, at γ-α interface during transformation and in ferrite during cooling. Studies of precipitation in HSLA steels led to the discovery of interphase precipitation, which has since been shown to occur in many systems. At the phase transformation γ->α there is a discontinuous decrease in solubility of the carbide or nitride. Precipitate nucleation and growth occurs at the γ->α interface, which normally moves discontinuously.

Interphase precipitation also has been seen in steels containing V, W, Mo, Ti and Cr. Davenport and Honeycombe [37] have given a model to include a build up of carbon in the austenite ahead of the moving boundary, which aids nucleation of carbides at the boundary. Such nucleation also can be assisted by drag of substitutional solutes by the advancing boundary. When carbides precipitate, the carbon content of austenite adjacent to the boundary is depleted, this increases the driving force for transformation to ferrite [38]. On cooling, V_4C_3 or Nb (CN) precipitate at the ferrite austenite interface during the transformation [37], which produces rows of fine precipitates, which cause strengthening. Due to the higher solubility of V_4C_3 compared with NbC, Vanadium steels can age-harden from conventional normalizing temperatures such as 950°C whereas Niobium steels do not because the solubility of NbC at 950°C is too small. Thus on normalizing, Niobium steels are only grain refined, whilst Vanadium steels are both grain refined and precipitation-hardened. Niobium steels can precipitation-harden if they are heated to higher austenitizing temperatures at which more NbC is dissolved, but this also dissolves the grain-refining precipitates (or coarsens them) so that the grain refinement is no longer achieved. Thus, whilst the strength is increased the impact properties are very detrimentally affected.

Hamano [38] reported the effect of precipitation of coherent and incoherent precipitates on the ductility and toughness of high-strength steels. He concluded that the coherent precipitates strengthen the material and decrease its toughness by promoting in homogenous deformation and increasing stress concentration. Those precipitates that are rendered incoherent with overaging cause the restoration of the toughness by promoting homogeneous deformation and retarding the early initiation of quasi-cleavage fracture. He stated that the roles of coherent precipitates in strengthening the matrix and the roles of incoherent precipitates in promoting the homogeneous deformation can be expected to allow increase of both strength and toughness of materials, independent of compositions of the precipitates.

Baczynski et al [39] studied the influence of rolling practice on notch toughness and texture development in high-strength line pipe steels. They determined the mechanical properties and notch toughness of an X80 line pipe steels for various test directions in the plane of steels that had been finish rolled in the γ and in the intercritical ($\alpha+\gamma$) regions. They observed that intercritical rolling of steels with lower carbon content led to higher yield stress values and lower toughness values along with higher intensities of the transformation component. They observed that a higher yield strength (YS) and ultimate tensile strength (UTS) were obtained along the transverse direction (TD) than along the longitudinal direction (RD). YS changes from about 580 MPa along RD to about 620 MPa along the TD. The lowest ductility was observed in the TD, intermediate and higher values correspond to the longitudinal and 45° test directions.

Patel and Wilshire [40] studied the effect of controlled hot rolling of Nb–HSLA strip steels has been done. It was found that by decreasing the soak temperature from 1250°C to 1150°C strength was developed as NbC precipitate is not fully dissolved. Finish rolling near but above austenite to ferrite transformation temperature with a reduced coiling temperature of about 600°C has resulted in a marked improvement in consistency of mechanical properties. Application of high coiling temperature will result in strength loss due to precipitate coarsening.

Dhua et al [41] studied the effect of cooling rate on as-quenched microstructure and mechanical properties of HSLA-100 steels plates using cooling media such as brine, water, oil and air. While quenching in oil, water, brine resulted in lath martensite structure, granular bainite and martensite–austenite constituents were found in air or furnace cooled. The average lath spacing increased slightly on decreasing cooling rate from brine to water. Precipitates of Cu and Nb(C, N) were observed in all quenching condition except brine quenched. The as-quenched strength, toughness of brine, water and oil were higher than air and furnace cooled due to closer lath spacing and more alloy retention owing to faster cooling from austenitizing temperature.

Lee et al [42] studied the effect of plastic deformation on transformation of austenite to acicular ferrite in a Fe-Mn-Si-C alloy steels containing NMI. An acicular ferrite microstructure has potential of combining high strength & high toughness. This is because the plates of acicular ferrite nucleate intragranulary on NMI within large austenite grains, and then radiate in many different orientations from those inclusions whilst maintaining an orientation relationship with austenite. The resulting microstructure is less organized when compared with ordinary bainite, where there is tendency to form pockets of parallel plates which are identically oriented. A crack has to follow a more tortuous path through an acicular ferrite microstructure, thereby leading to improvement in toughness without comprising strength. When an externally applied stress exceeds yield strength of austenite, it is possible in principle for transformation of austenite to bainite retarded via process known as mechanical stabilization.

Sivaprasad et al [43] studied that as the HSLA steels are produced in quenched and tempered condition they can neither be hot worked, for structural fabrication, nor be heat treated to relieve the stresses developed during cold forming. As a consequence, the material enters into service in cold deformed condition. Cold deformation is essentially a prestrain condition. He studied HSLA-80 & HSLA-100 steels quenched and aged shows acicular ferrite and tempered bainite structure respectively. The effect of tensile prestraining on ductile fracture toughness remains invariant up to 2% and further prestraining of material result in deleterious deterioration of toughness. The HSLA-80 steels shows yield behavior due to shortage of mobile dislocations and HSLA-100 do not shows yield behavior as majority of dislocation is mobile.

N.Banerjee et al [44] studied the role of thermo mechanical processing on microstructure and mechanical properties of low C (0.07%) Cu bearing HSLA steels. Boron lowers the austenite transformation to ferrite. DSC technique is used to study the precipitation behavior i.e. temperature of formation of Cu in HSLA steels. The 1st peak is obtained at 200°C shows formation of Cu atoms clusters and the 2nd peak is obtained at 350°C shows formation of Cu precipitate. The microstructure of TMCP alloy consists of laths of martensite and bainite with some evidence of granular ferrite. MA constituents appear ribbon like along lath boundary. MA of this type promotes nucleation of crack and decreases impact properties. High strength is achieved by fine dispersion of microalloyed carbides and copper in strong matrix of lath martensite.

Dhua et al [45] studied the influence of thermomechanical treatment i.e. Controlled rolling and direct quenching as a function of rolling temperature and deformation on microstructure and mechanical properties of HSLA-100 steels have been studied. Optical microstructure of 800°C & 900°C rolled steels with 50 % reduction tempered bath at 450°C and 650°C shows slightly elongated deformed prior austenite grains. While complete equiaxed grains structure was found in 1000°C. In general mechanical properties of DQ (direct quenched) steels with large deformation (50 %) was found to be more superior then less-deformed (25 %) steels in both tempering condition. The YS, UTS, VHN in the DQ steels is more than RQ steels.

Hong et al [46] studied the strain induced precipitation of NbC in Nb and Nb-Ti microalloyed HSLA steels. The precipitate start time of strain induced NbC carbides is delayed in Nb-Ti steels in comparison to the case of Nb steels. In Nb-Ti steels, super saturation of Nb in austenite was reduced by both the insufficient solution of Nb due to stable (Ti, Nb) (C, N) carbonitride. The reduced super saturation of Nb can result in delay of precipitate of strain–induced NbC carbides forming in matrix of Nb-Ti steels.

Dhua et al [47] studied the effect of tempering temperature on mechanical properties and microstructure of HSLA-100 copper bearing steels. Two types of HSLA steels similar to HSLA-100 were made (i) air induction furnace and other by (ii) vacuum induction furnace which changes the characteristics of NMI. Few small size globular oxides and lenticular sulphides and complexes of MnS and Al_2O_3–SiO_2 were observed in steel 1 and in steel 2 and small globular oxides and inclusions of Fe and Si and few stringers of oxy-sulphide were also observed. Slight improvement in mechanical properties and microstructure of as-quenched and tempered plates were observed. Higher volume fraction and elongated morphology of NMI in steel 1 was found to be responsible for its lower CVN energy value.

Hong et al [48] studied the effect of cooling rate and isothermal holding on precipitation behavior during continuous casting of Nb-Ti bearing HSLA steels. The morphology of precipitate in industrial slab was dendrite, semi-dendrite and rod-shaped type Nb-rich (Nb, Ti) (C, N). The precipitate amounts of samples after solidification and cooling down to 800°C are smaller than those industrial slab regardless of cooling rate. Most of Nb & Ti were precipitate during isothermal holding between 900°C and 1000°C. Those precipitate were dendritic or semi-dendritic type Nb rich (Nb, Ti) (N, C). The precipitate during continuous casting consists following stages.

(i) Small nuclei are found during solidification in high temperature region.

(ii) And then, nuclei continuously grow during isothermal holding with equilibrium composition (Nb rich) at around 1000°C

Mishra [49] studied the types of precipitates on quenching from different austenitizing temperature in range of 950°C to 1200°C have been carried out for HSLA-100[GLE] and HSLA -80[GPQ] HSLA steels. Both steels show bainite structure. TEM, SEM studies shows Nb-rich precipitate in form of carbonitride. The solutionizing temperature has been found to be 1140°C and 1150°C for these steels respectively.

Thompson [50] studied the microstructures formed during continuous cooling of low C (0.06 % C) HSLA steel plate containing significant additions of Mn, Cu, Ni, Cr and Mo. Two types of ferrite, acicular and granular, were observed to form by the decomposition of austenite at intermediate cooling rate. Polygonal ferrite and Widmanstaetten ferrite formed at high temperatures during slow cooling. It showed that the optical microscopy did not reveal any ferrite, upper bainite, or undissolved carbides in the microstructures for all heat treatments from 900°C to 1200°C. With these exceptions, the changes in microstructures included by high temperature austenitizing treatment are similar to those reported in literature. It is observed that prior austenite grain size and martensite lath packet size increase rapidly with increasing the austenitizing temperature. In addition, the lath size, especially lath length, is longer in high temperature aistenitized structure. No significant difference is observed in the volume fraction of retained austenite (RA) for any of the structures.

CHAPTER 2

FORMULATION OF PROBLEM

Precipitation strengthening is the most preferred mode of strengthening in HSLA steels because it is held along with grain refinement. The temperature of austenitization controls the grain growth in this steel. If the austenitization temperature is high then there will be grain coarsening occurs, so that it will affect upon the strengthening process. So there should be held low temperature austenitizaion in order of transformation of ferrite in the γ-α interface during cooling. At the present work the austenitization is held at 1000°C.So further study will be held by doing austenitization at various temperatures in order of getting good strengthening. When carbides precipitate, the carbon content of the austenite adjacent to the boundary is depleted, this increases the driving force for transformation to ferrite.

The main aim of this study is to characterize the aging behaviours of HSLA-100(GPT) steel and to identify microstructural effects on strengthening and hardness and impact properties of these steels. In present work the HSLA-100(GPT) steel is austenitized at 1000°C for 180 minutes followed by oil quenching. Then it is aged at 400°C for varying length of time from 1 minute to 1200 minutes. The aging time for 360 minutes gives high hardness of 330 VHN. In this case only single peak is observed due to mainly the precipitation of carbides of Ti and Nb. But these precipitates contain some amount of copper precipitates. The copper precipitates in single peak are suppressed by Ti. The present study is not held by giving aging time beyond 1200 minutes. But increasing aging time beyond 1200 minutes give second peak which mainly contain copper precipitates with small amount of carbides of Ti and Nb. The impact energies are observed in as received (AR), oil quenched (OQ), peak aged (PA), and over aged (OA) conditions. The impact energy increases with the aging time. The variation in hardness as a result of aging has been recorded and the microstructural studies have been conducted using light microscopy. The results have been analyzed to formulate the mechanism of aging in this steel.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. MATERIAL USED

The present work was undertaken to study the aging behavior of an HSLA-100(designated as GPT steels) and to identify microstructural effects and variation of hardness of this steels. The composition of HSLA (GPT) steels is shown in Table.3.1

Table 3.1: Composition of HSLA-100 (GPT) Steel (wt %)

C	Mn	P	S	Ti	Al	Sb	Cu	Si	Ni	Mo	V	Nb	As
0.05	1.0	0.009	0.001	0.003	0.025	0.003	1.23	0.340	1.77	0.51	0.004	0.037	0.005

3.2. HEAT TREATMENTS

The HSLA steel was given following heat treatments:

1. Solution treatments at the temperature of 1000°C for 180 minutes followed by oil quenching.
2. The specimens which have been solution treated at 1000°C were tempered at the temp of 400°C followed by water quenching immediately.
3. Solution treated specimens (1000°C, 180 minutes) were aged at 400°C for various times ranging from 1 minute to 1200 minutes followed by water quenching.

3.3. MECHANICAL PROPERTIES

3.3.1. Hardness Measurement

Hardness (Vickers) measurements were conducted in all stages of various treatments by employing a 30 kg load. At least five indentations were made and the average of hardness (Vickers) was noted and hardness curve for each treatment was established.

3.3.2. Impact (Charpy V-Notch) test

The specimens, which were aged at 400°C after solution treatment at 1000°C, were chosen for impact property measurements. The charpy V-notch test were conducted as per ASTM E23 standard on the specimens as received (AR), solution treated (oil quenched) condition, peak aged (400°C, 360 minutes) and over aged (400 °C, 1200 minutes).

3.4. OPTICAL MICROSCOPY

Specimens were prepared for metallographic examinations by conventional techniques. Reichert-Jung MeF_3 optical microscope and AXIOVERT 200 MAT were utilized for recording microstructures. Metallographic studies were carried out on the various heat treated fine polished samples. After removing scratches by polishing on emery papers, the polished sample were then subjected to wheel polishing with the alumina paste on the wheel followed by etching. Etchant used to etch the surface was 2% nital solution, etching time was 10 to 12 seconds and then photographs were taken at various magnifications. The metallographic study of the given sample had been carried out to observe and photograph the microstructure so that changes occurred in microstructure of HSLA steels during processing can be compared and analyzed, to explain the changes in mechanical properties.

3.5. SCANNING ELECTRON MICROSCOPY

Extensive investigations were carried out on the fractured surface of impact specimens. A LEO 435 VP scanning electron microscope operating at 15 KV was utilized Secondary electron technique was adopted to study the fracture behavior. The fractured specimens in which impact test is carried out are cleaned with the acetone and SEM photographs were taken at the fractured surface and the photographs were analyzed to judge the results.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. GENERAL

This section deals with the experimental techniques in this study. Conventional techniques were used for the measurement of mechanical properties, hardness, charpy V-notch (CVN) impact strength, optical microscopy, scanning electron microscopy (SEM) were used for microstructural characterization. Scanning electron microscopy (SEM) and hardness values were used for analysis of the precipitates.

4.2. EFFECT OF VARIOUS TREATMENTS ON MECHANICAL PROPERTIES

4.2.1. Hardness

The hardness values of the various specimens with ageing time are given in the following table

Table 4.1: Variation of hardness with aging time at 400°C

Ageing time(minutes)	1	5	10	30	60	240	360	600	1200
Hardness Values(VHN)	266	288	289	297	302	303	330	314	306

The HSLA-100(GPT) steel in the as received (AR) condition shows a hardness value of 249 VHN. Solution treatment at 1000^0C for 180 minutes followed by oil quenching gives a hardness value of 288 VHN. Aging at 400^0C causes multistage hardening in this steel. Fig 4.1 shows the variation of hardness with aging time. In general on aging hardness first increases, attains a peak value and then decreases on further ageing. The hardness on aging for 1 minutes decreases to 266 VHN due to the transformation of martensite from oil quenched(OQ) to ferrite in the aging condition.

After 1 minute, the hardness on aging increases, then attain a peak value for 360 minutes as 330 VHN then decreases and get minimum hardness for 1200 minutes as 306 VHN. The hardness value increases with ageing time up to 360 minutes. Then on further aging there is decrease in hardness it is due to dissolution of precipitates at 1200 minutes. At peak hardness precipitates are in finely dispersed phase. When ageing time increases after peak hardness precipitates become coarsen. Thereby the hardness decreases up to the minimum value of 306 VHN at 1200 minutes. Here the inter particle distance increases.

The maximum hardness is at 360 minutes as more fraction of precipitates seen as compared to 1200 minutes. The precipitates phase is coherent with the matrix. The coherent precipitates are not the cause for peak hardness but due to fine precipitates of Cu & Nb. The occurrence of single age hardening peaks suggests that the precipitation hardening is primarily due to the presence of Ti and Nb. The microstructures observed at this stage consist of ferrite and tempered martensite. When ageing time increases precipitate particles are nucleated. So the hardness value increases. At 360 minutes which shows peak hardness more precipitates in the matrix as well as in grain boundaries as compared short time of ageing. The peak hardness is held due to fine precipitation of precipitates particles.

In HSLA-100 (GPT) steel the main alloying elements are Cu, Ti and Nb. The peak in the aging curve are held due to precipitation of (Nb,Ti)C with Cu rich precipitates. But the single peak is held due to precipitation of (Nb,Ti)C containing some amount of Cu. The main alloying element for single peak is Ti, which completely suppress the Cu precipitation. Ti substantially activates the precipitation process in Nb-containing HSLA-100 (GPT) steel. Here second peak aged has not come due to the suppression of copper precipitates by Titanium. The kinetics of precipitation of (Nb,Ti)C is substantially faster than that of Cu. Aging in general causes the conversion of martensite to ferrite. Large ferrite areas results in softening .It is seen that continuous aging at 400^0C causes simultaneous coarsening of existing precipitates and nucleation of fresh (Nb,Ti)C precipitates, which results in which results in continued increase in hardness up to peak aged stage observed after 360 minutes . The network of fine precipitates is observed at the grain boundaries as well as grains.

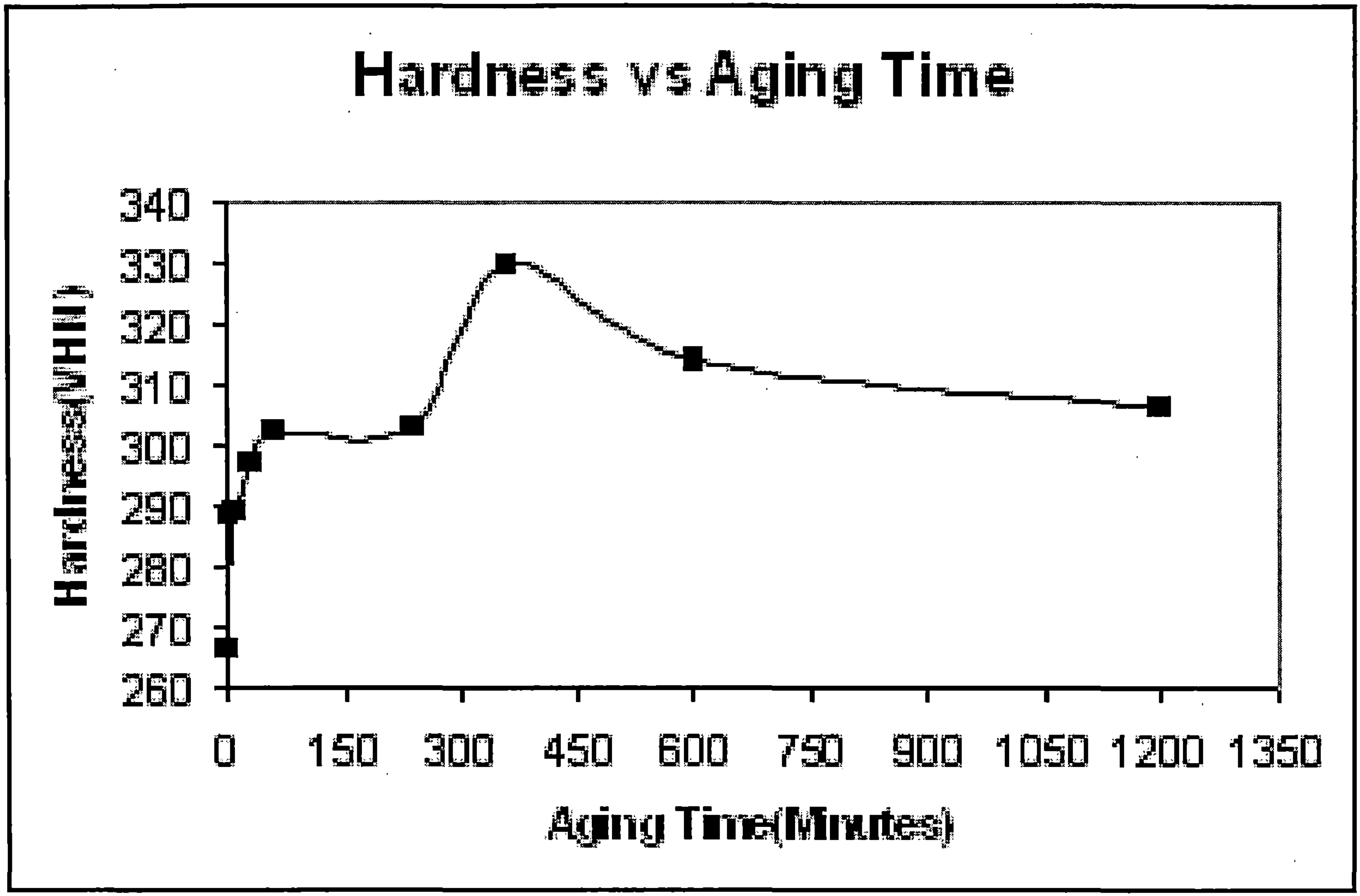
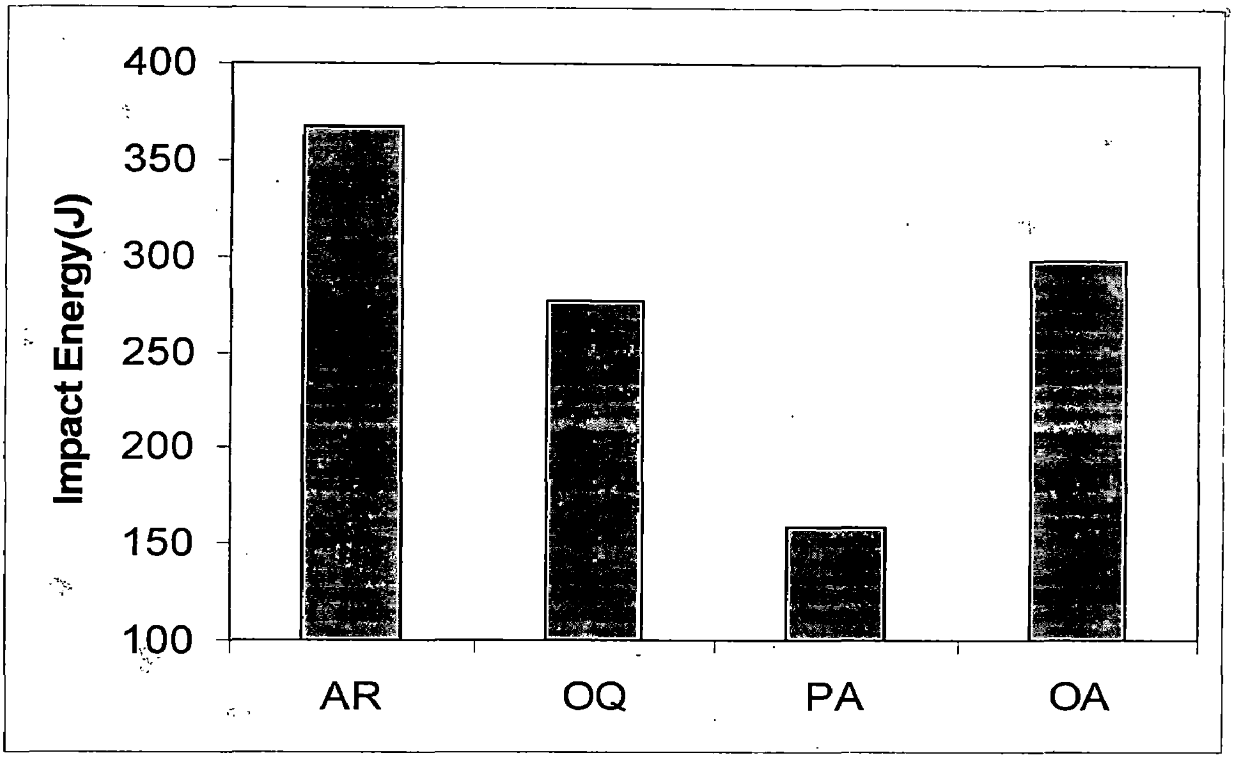


Fig 4.1. Showing Variation of Hardness with Aging Time at 400^0 C

4.2.2. Impact (Charpy V-Notch) test

The impact strength (charpy V-notch) as affected by various treatments is shown in figure. In as received condition we get impact energy value of (367.5 J).After austenitization at 1000°C for 180 minutes (followed by oil quenching) the impact value decreases to (277.3 J), it is due to presence of martensite. Now for aging at 400°C for 360 minutes (peak ageing) impact value goes down to (158.7 J), it is due to formation of coherent precipitates of copper which causes decrease in toughness as makes the matrix stronger, whereas on further aging causes increase in impact energy as due to coarsening of copper precipitates occurred as in aging at 400°C for 1200 minutes (over ageing) shows impact value of (298.9 J).



AR: As received

OQ: Oil quenched from 1000°C (180 minutes).

PA: Peak Aged at 400°C for 360 minute

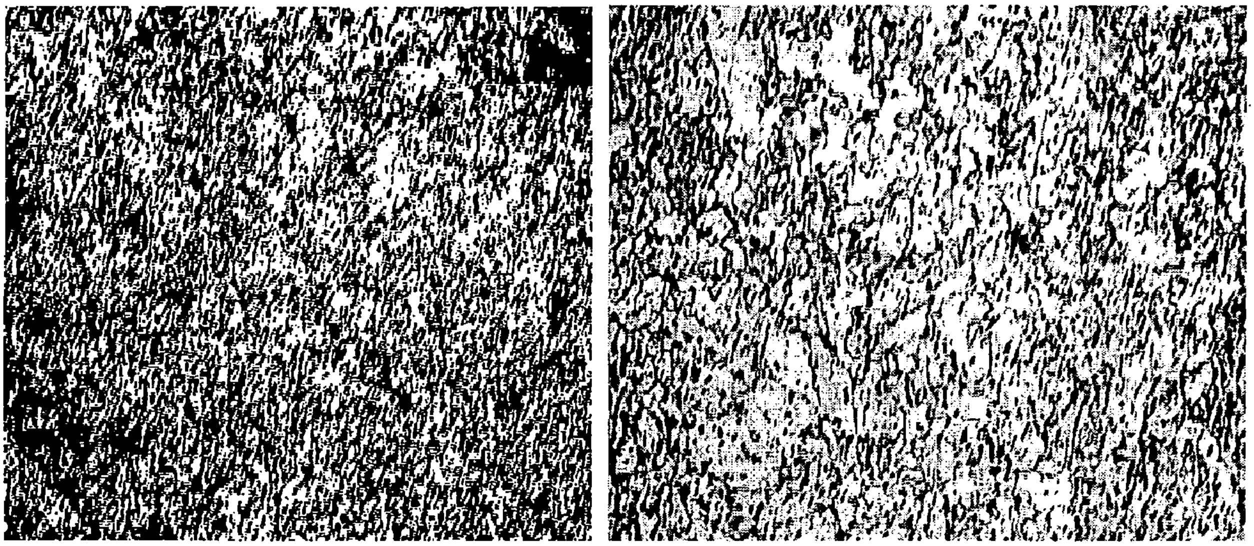
OA: Over Aged at 400°C for 1200 minutes

Fig. 4.2: Impact energy in various conditions

4.3. OPTICAL METALLOGRAPHY

4.3.1. As Received (AR) condition

This HSLA-100(GPT) steel in the as received condition shows the microstructure consist of predominantly ferrite and large concentration of coarse carbide particles within the matrix. It shows a high density of dislocations together with traces of retained austenite. Cu is always present in the precipitates, retained austenite and in general in the matrix. So it shows lower hardness (249 VHN).

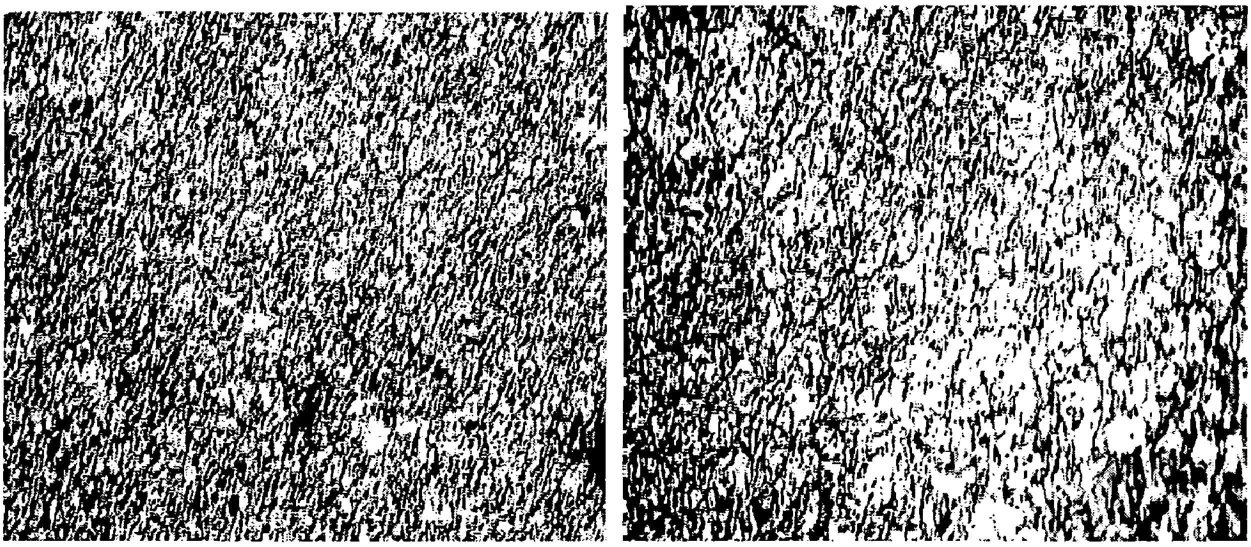


Mag. 330x Mag. 620x

Fig. 4.3: Optical microstructure of HSLA-100 (GPT) steel in the as received (AR) condition

4.3.2. After Oil Quenched (OQ) condition

In the oil quenched (OQ) condition the microstructure shows martensite plus ferrite together with a few fine carbide particles at grain boundaries. Due to the presence of lath martensite in the matrix of ferrite the hardness (288 VHN) of the oil quenched (OQ) is than that of the as receive (AR) condition. The OQ treatment results in the precipitation of carbides predominantly at the grain boundaries. These carbides particles are primarily (Nb, Ti) C .Due to the presence of Ti, carbides are not completely dissolved in the austenitizing temperature.



Mag. 330x

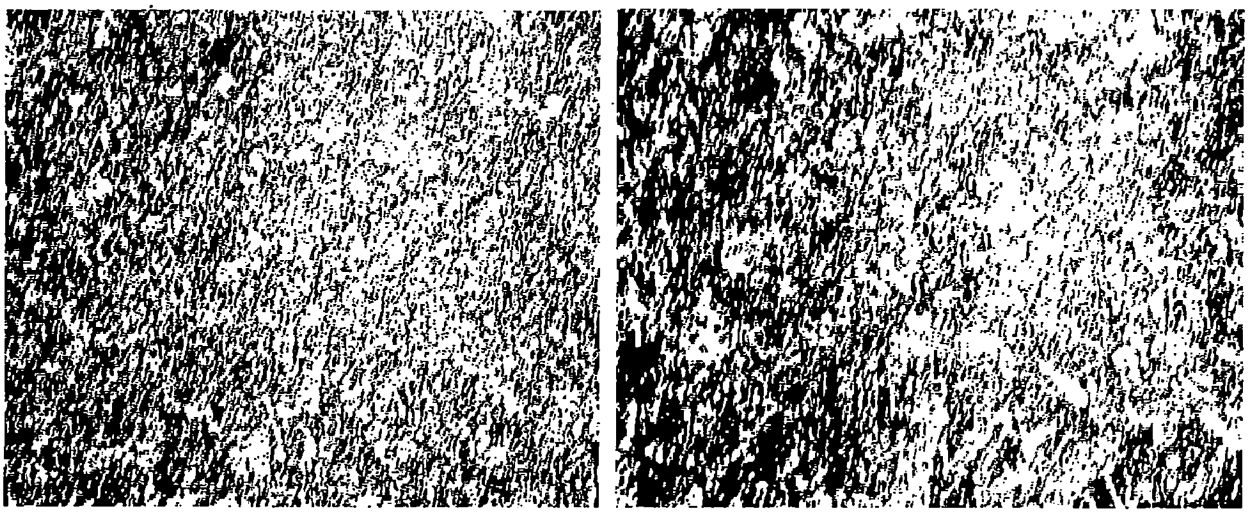
Mag. 620x

Fig. 4.4: Optical microstructure of HSLA-100 (GPT) steel in the oil quenched (OQ) condition

4.3.3. After various aging treatment

Aging in general, causes the conversion of martensite into ferrite. Coarsening of existing carbides particles occurs, which is noted by decrease in the number of density and increase in average size. In addition to coarsening of existing particles fresh nucleation of carbides also takes place on aging there will be the decrease in hardness due to the conversion of martensite into ferrite and coarsening of particles, the resultant increase in hardness is due to the fresh nucleation of fine carbides at grain boundaries as well as within the grains. It is seen that continuous aging at 400^0C causes simultaneous coarsening of existing precipitates and nucleation of fresh (Nb,Ti)C precipitates, which results in which results in continued increase in hardness up to peak aged stage observed after 360 minutes

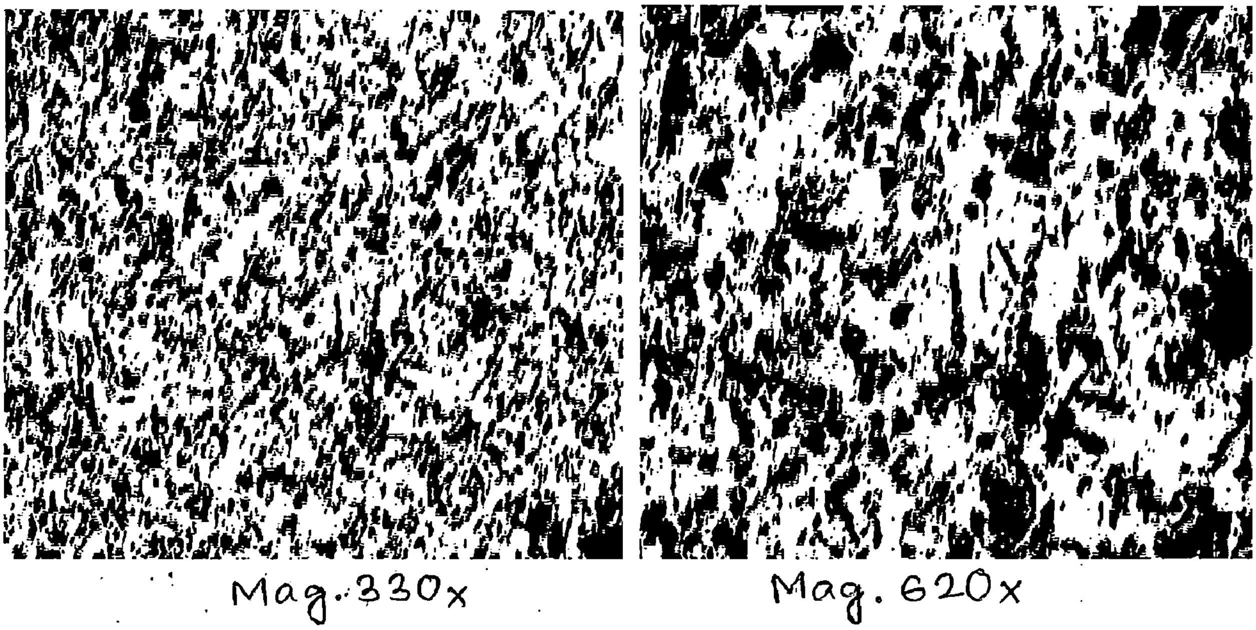
After oil quenching when the HSLA-100(GPT) is subjected to aging at 400^0C with no time it shows microstructure of coarse carbides particles in the matrix of large area of ferrite. In this case the martensite is converted into ferrite. The large area of ferrite decreases the hardness. After aging of 5 minutes shows the microstructure of coarse carbide particles with the fresh nucleation of fine precipitates of carbides in the matrix of ferrite. In this way up to 360 minutes (PA)of aging the existing coarse carbides particles decreases with the increase in fine distribution of fresh nucleation of fine precipitates of carbides in the matrix of ferrite in the matrix of ferrite. The microstructure in the peak aged stage shows fine distribution of carbides together with coarse carbides precipitates. The network of fine precipitates is observed at the grain boundaries as well as grain .Large ferrite areas results in softening, but the high hardness in peak aged (PA) is due to the fine precipitates. Ageing treatment may cause precipitation of Manganese sulfides and Vanadium Carbides in addition to formation of Cu-rich particles. Copper improves hardenabilty and introduces precipitation hardening. Although two precipitate hardening elements (Cu and Nb) are present in this steel, the occurrence of simple age hardening peaks suggest that the precipitate hardening is primarily due to presence of Nb. As a result it is observed that the formation of age hardening peaks is not necessarily due to the existence of coherent carbides precipitates alone but due to copper On further aging coarsening of carbides leads to fall in hardness after peak aged (PA) condition, which is seen in microstructure after 600 minutes. It shows the structure of coarse carbides in the matrix of ferrite. After aging of 1200 minutes the hardness is lower than that of 600 minutes aging due to the high density of coarse carbides .Overageing may be due to dislocation of Cu atom's cluster. The grain boundary precipitates a complex carbide structure but the structure of carbides is not ascertained



Mag. 330x

Mag. 620x

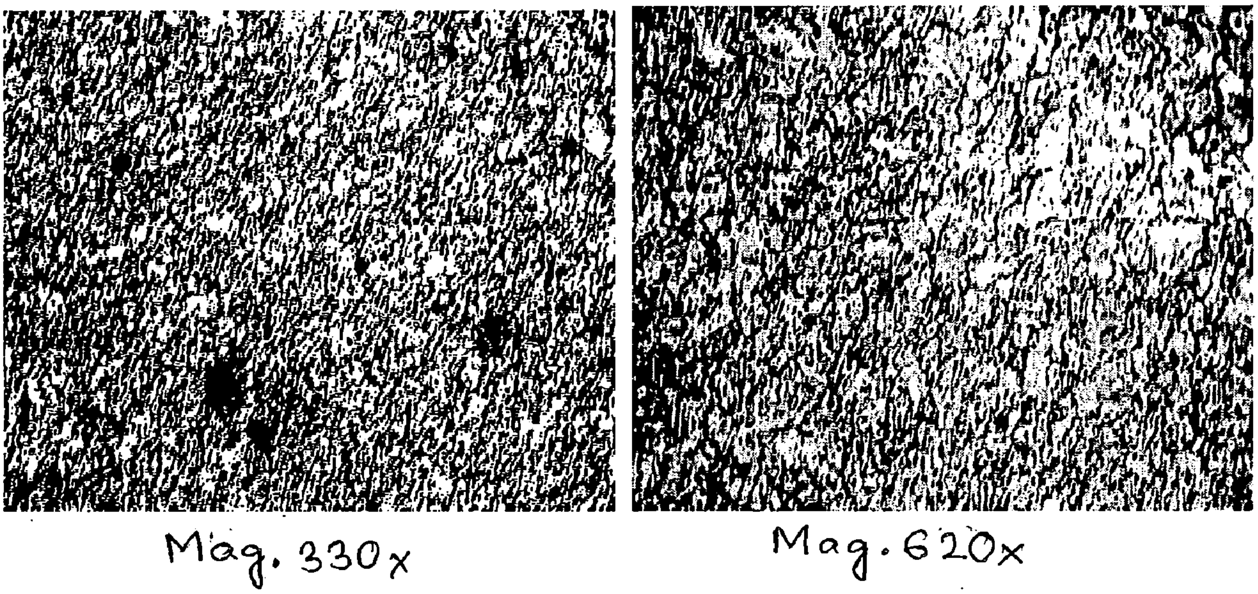
Fig. 4.5: Optical microstructure of HSLA-100 (GPT) steel after 1 minutes of aging at 400°C



Mag. 330x

Mag. 620x

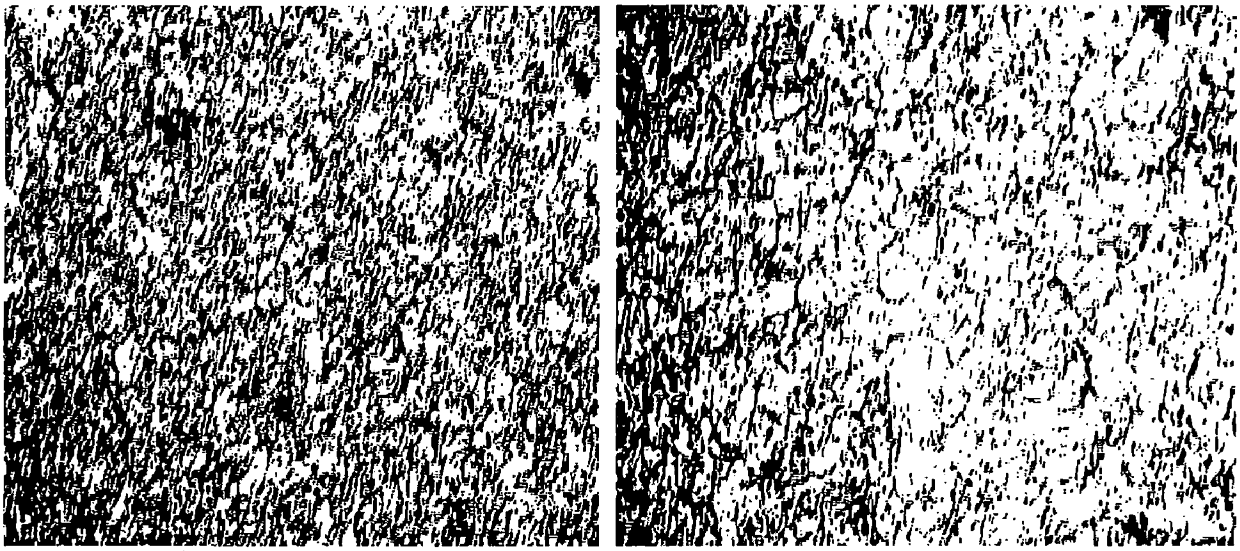
Fig. 4.6: Optical microstructure of HSLA-100 (GPT) steel after 5 minutes of aging at 400°C



Mag. 330x

Mag. 620x

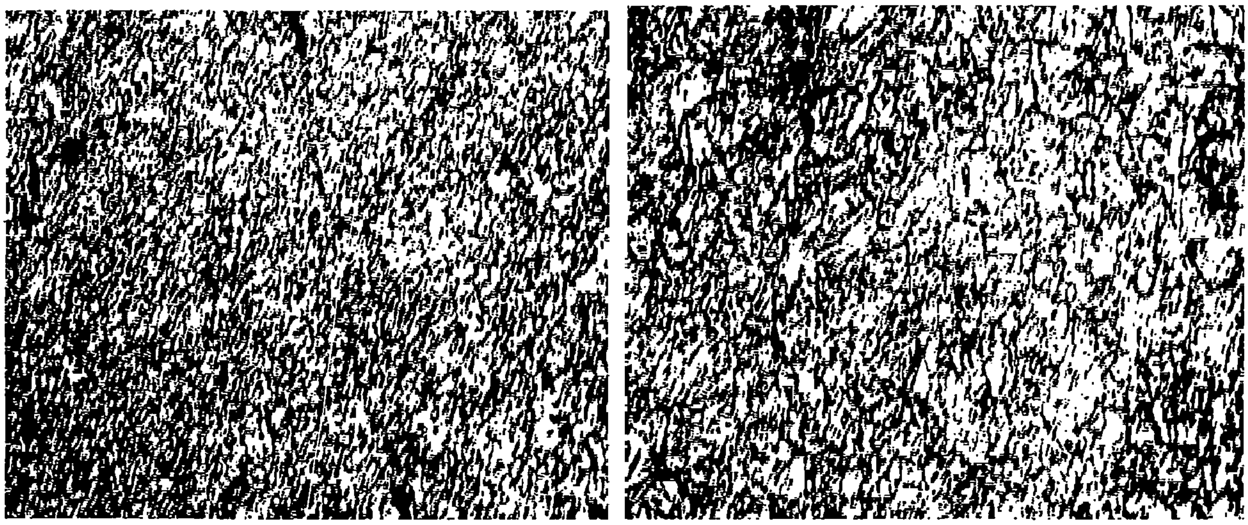
Fig. 4.7: Optical microstructure of HSLA-100 (GPT) steel after 10 minutes of aging at 400°C.



Mag. 330x

Mag. 620x

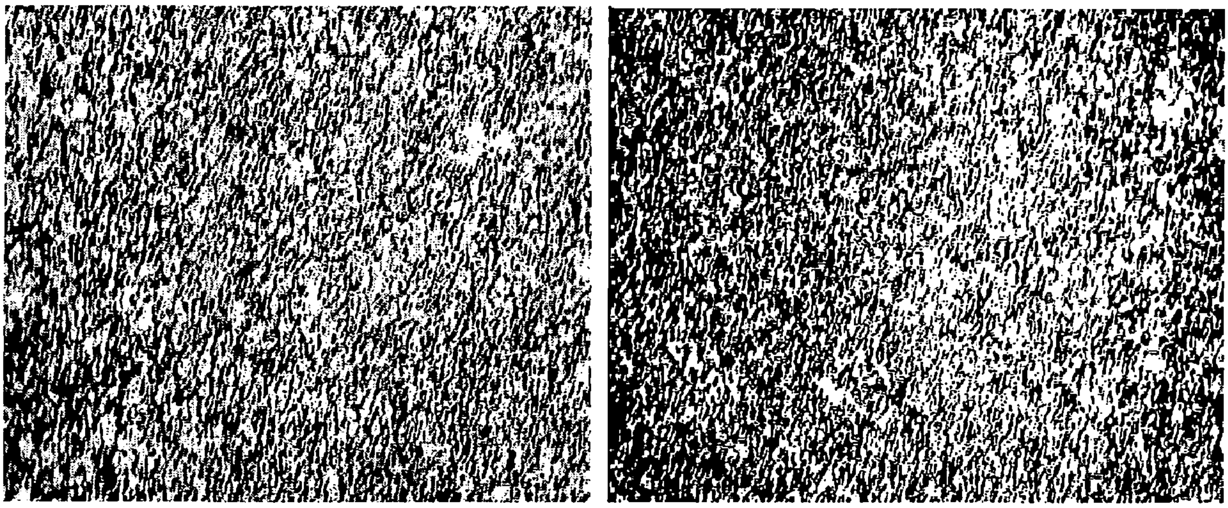
Fig. 4.8: Optical microstructure of HSLA-100 (GPT) steel after 30 minutes of aging at 400°C



Mag. 330x

Mag. 620x

Fig. 4.9: Optical microstructure of HSLA-100 (GPT) steel after 60 minutes of aging at 400°C

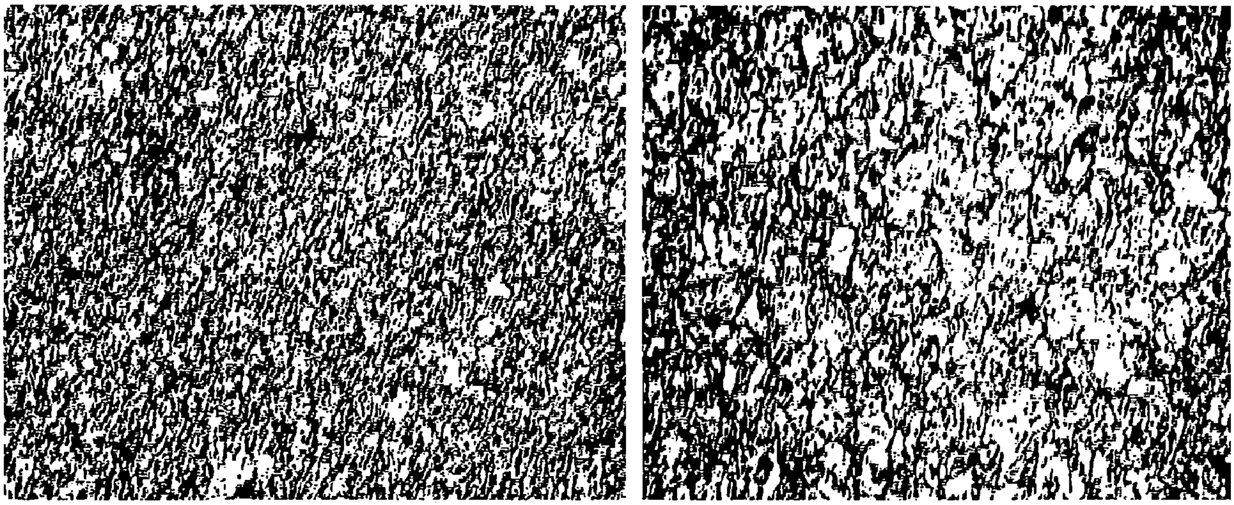


Mag. 330x Mag. 620x

Fig. 4.10: Optical microstructure of HSLA-100 (GPT) steel after 240 minutes of aging at 400°C.

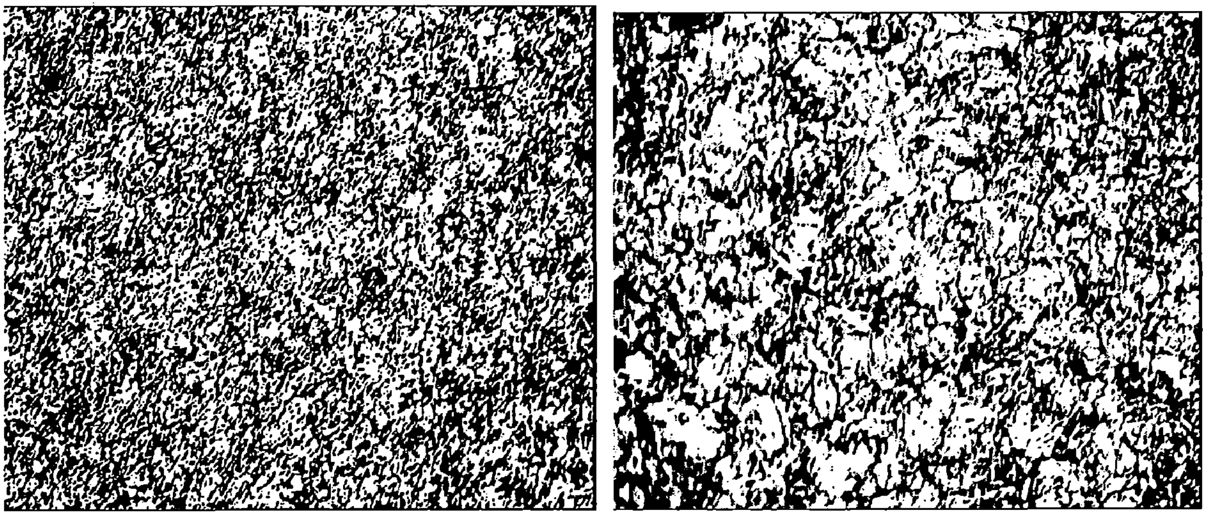
Mag. 330x Mag. 620x

Fig. 4.11: Optical microstructure of HSLA-100 (GPT) steel after 360 minutes of aging at 400°C showing peak hardness (PA).



Mag: 330x Mag. 620x

Fig. 4.12: Optical microstructure of HSLA-100 (GPT) steel after 600 minutes of aging at 400°C.



Mag: 330x Mag. 620x

Fig. 4.13: Optical microstructure of HSLA-100 (GPT) steel after 1200 minutes of aging at 400°C showing over aging.

4.4. SCANNING ELECTRON MICROSCOPY

Extensive SEM study of fracture surfaces of Charpy V-notch specimens was conducted. The fractographs in various conditions are given in Figures 4.14 - 4.17

4.4.1 Impact Specimens

Figures 4.14 - 4.17 show the scanning electron micrographs of impact fracture surfaces after various treatments. The SEM study after various stages shows that on impact loading the fracture occurs by the formation of dimples, nucleation and growth of voids at the precipitate/inclusion sites, and development and propagation of cracks. The high impact energy values are characterized by fine network of ductile dimples and closely spaced coarse voids, which are linked by several finer voids; whereas low impact energy values are characterized by (i) shear dimple networks, (ii) coarse voids, (iii) quasi-cleavage facets, (iv) intergranular cracks and (v) stepped fracture appearance.

High impact strength is observed in AR condition (367.5 J) is characterized by fine network of ductile dimples and closely spaced fine voids (Figure 4.14), which is indicative of a high resistance to cleavage fracture. Aging, in general, reduces the impact energy in various treatments. Figure 4.16 shows the scanning electron micrographs in PA condition of various treatments. The drastic fall in impact energy value (158.7 J) in PA condition of OQA treatment is characterized by a relatively coarse network of ductile dimples and coarse voids as shown in Figure 4.16

4.4.1.1. As received (AR) condition

The SEM of impact fracture surface of HSLA-100 (GPT) steel in the as received (AR) shows a very fine distribution of micro dimples indicating a high resistance to cleavage fracture with fine distribution of micro voids. It gives the high impact energy (367.5 J)

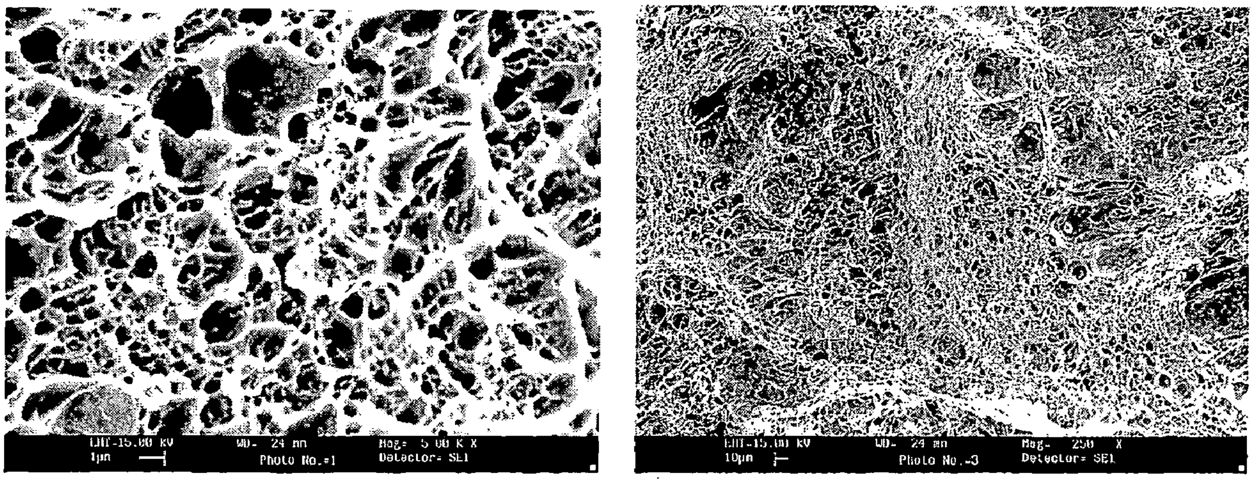


Fig. 4.14: Scanning electron micrographs of impact fracture surface of HSLA-100(GPT) steel in the as received (AR) condition.

4.4.1.2. Austenitized at 1000°C for 180 minutes followed by oil quenching (OQ)

The SEM of impact fracture surface of HSLA-100(GPT) steel after austenitization at 1000°C for 180 minutes shows a fine network of ductile dimples impinged upon one another. This is the reason for high impact value (277.3 J).

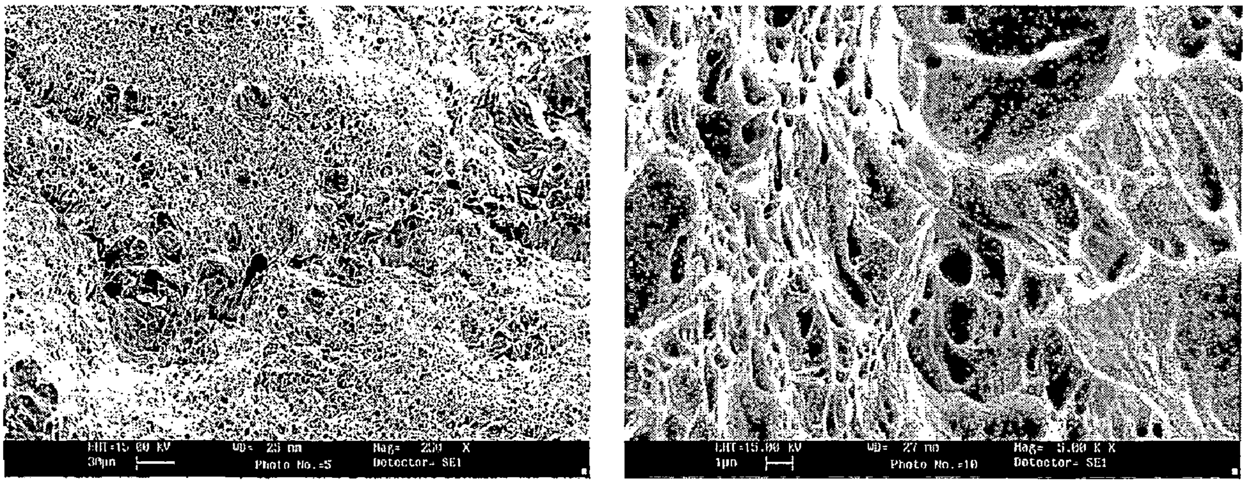


Fig. 4.15: Scanning electron micrographs of impact fracture surface of HSLA-100(GPT) steel after austenitization at 1000°C for 180 minutes

4.4.1.3. Aging at 400°C for 360 minutes in the peak aged (PA) condition

The SEM of impact fracture surface of HSLA-100 (GPT) steel after aging at 400°C for 360 minutes after water quenching shows a coarse and faceted network of dimples and large voids thereby giving low impact energy (158.7 J).

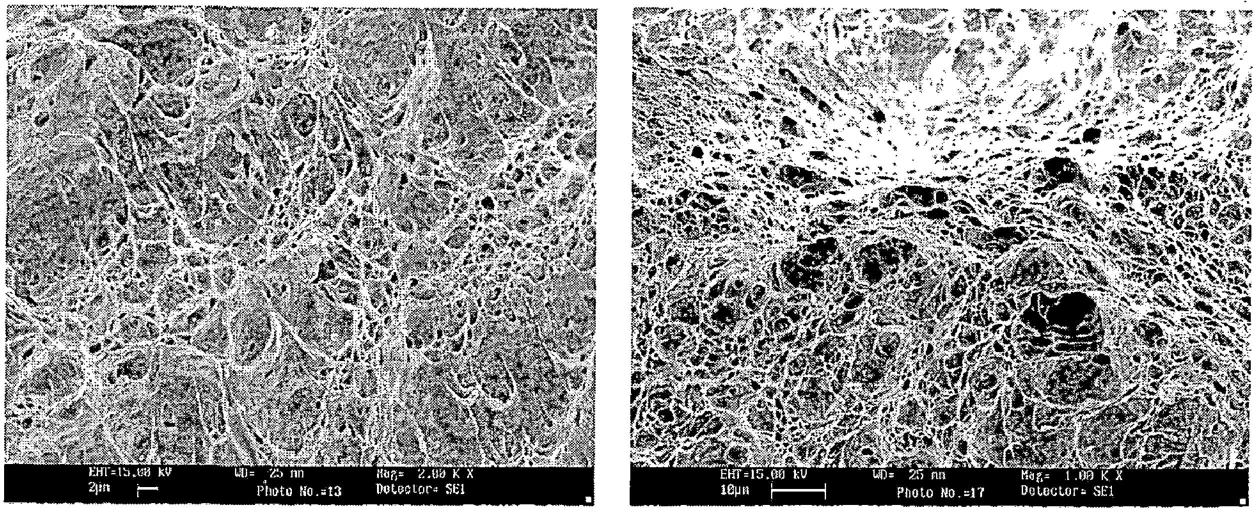


Fig. 4.16: Scanning electron micrographs of impact fracture surface of HSLA-100(GPT) steel after aging at 400°C for 360 minutes (Peak Ageing).

4.4.1.4. Aging at 400°C for 1200minutes in the over ageing (OA) condition

The SEM of impact fracture surface of HSLA-100 (GPT) steel after aging at 400°C for 1200 minutes (peak Ageing) after water quenching shows coarse & fine distribution of micro voids and fine dimples which shows good impact energy(298.9 J).

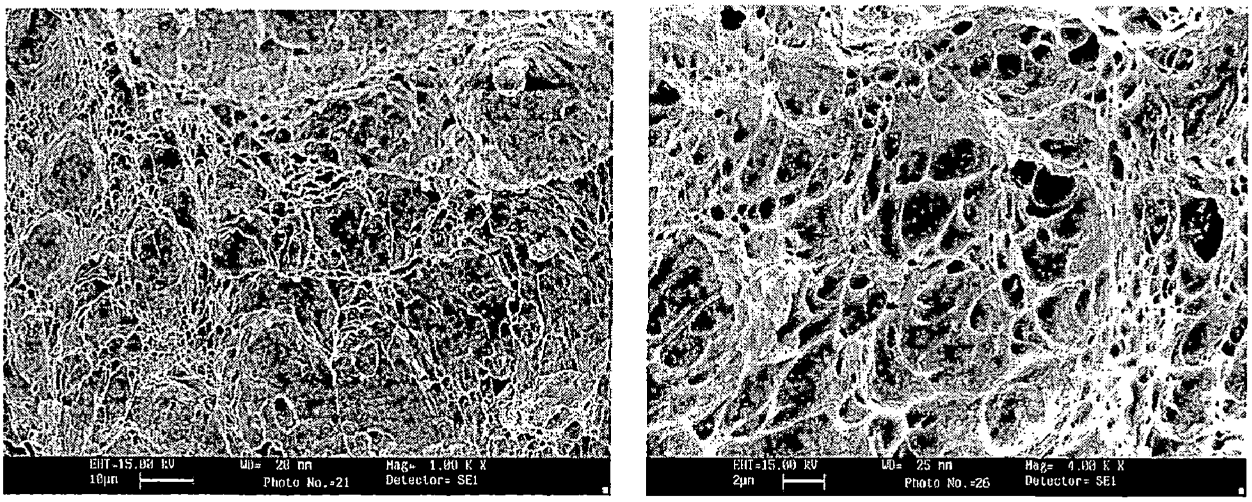


Fig. 4.17: Scanning electron micrographs of impact fracture surface of HSLA-100(GPT) steel after aging at 400°C for 1200 minutes (Over Ageing)

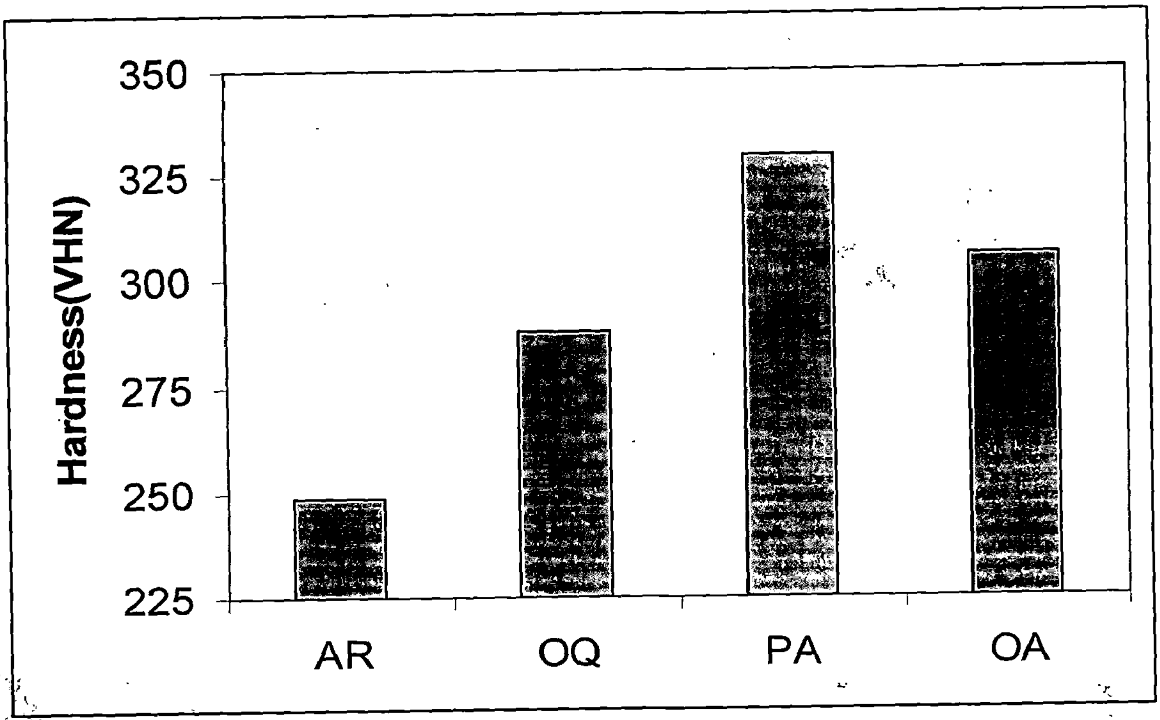
4.5. FACTORS AFFECTING MECHANICAL PROPERTIES

The experimental results indicate that the mechanical properties are significantly influenced by the process of aging. Aging allows further increase in hardness and, but at the cost of ductility and impact toughness.

4.5.1. Hardness

Aging in general, causes the conversion of martensite into ferrite. Coarsening of existing carbides particles occurs, which is noted by decrease in the number of density and increase in average size. In addition to coarsening of existing particles fresh nucleation of carbides also takes place on aging there will be the decrease in hardness due to the conversion of martensite into ferrite and coarsening of particles, the resultant increase in hardness is due to the fresh nucleation of fine carbides at grain boundaries as well as within the grains. It is seen that continuous aging at 400^0C causes simultaneous coarsening of existing precipitates and nucleation of fresh (Nb,Ti)C precipitates, which results in which results in continued increase in hardness up to peak aged stage observed after 360 minutes .The microstructure in the peak aged stage shows fine distribution of carbides together with coarse carbides precipitates. The network of fine precipitates is observed at the grain boundaries as well as grain .Large ferrite areas results in softening, but the high hardness in peak aged (PA) is due to the fine precipitates. The grain boundary precipitates a complex carbide structure but the structure of carbides is not ascertained. On further aging coarsening of carbides leads to fall in hardness after peak aged (PA) condition, which is seen in microstructure after 600 minutes. It shows the structure of coarse carbides in the matrix of ferrite. After aging of 1200 minutes the hardness is lower than that of 600 minutes aging due to the high density of coarse carbides These are the stages of over aging (OA).

Hardness increases with increasing aging time up to peak hardness then it decreases due to overaging The resultant increase in hardness is attributed to the coarsening, and fresh nucleation and growth of fine (Nb,Ti)C carbide particles in the matrix. The figure shows variation in hardness with aging time in specimens. The structure shows ferrite and tempered martensite with carbides. On aging ferrite percentage increases. Overaging results in polygonal ferrite. The hardness on aging for 5 minutes decreases to 288 VHN. After 5 minutes, the hardness on aging increases, attain a peak value for 360 minutes as 330 VHN then decreases and get minimum hardness for 1200 minutes as 306 VHN. There is decrease in hardness first at 5 minutes due to formation of ferrite. The maximum hardness is at 360 minutes as more fraction of precipitates seen as compared to 30 minutes. Then on further aging there is decrease in hardness it is due to dissolution of precipitates at 1200minutes. Overaging may be due to coarsening of Cu rich cluster and carbides of Nb. The coherent precipitates in peak aged condition are easily cut by moving dislocation, gives poor ductility and impact strength.



AR: As received

OQ: Oil quenched from 1000°C (180 minutes).

PA: Peak Aged at 400°C for 360 minute

OA: Over Aged at 400°C for 1200 minutes

Fig. 4.18. Hardness values in various conditions

4.5.2 Impact

4.5.2.1. Mechanical Properties

Impact energy is the function of hardness. In general, the impact toughness decreases with increase in hardness whereas its correlation with ductility shows a general increase with increasing ductility. The large scatter in the data predicts that no single parameter is solely responsible for any increase or decrease in toughness; it also depends on other parameters such as microstructure, distribution of precipitates and dislocation density.

4.5.2.2. Existence of Coherent Precipitates

Literature review indicates that existence of coherent particles in peak aged condition is detrimental to impact strength in several alloy systems. Such alloys have to be used in over aged condition for improved impact properties. In order to obtain high levels of both hardness and impact strength, it was felt necessary to study a situation in which both coherent and incoherent precipitates may coexist. Figure 2.3 also indicates variations of impact strength after various treatments. The impact strength suffers a serious setback as a result of various treatments studied in this investigation. The impact energy is very sensitive to the presence of coherent precipitates and the dislocation network in the matrix. It is now well established that presence of coherent precipitates causes inhomogeneous deformation leading to crack nucleation. Coarse precipitates are not as much dangerous to impact strength as the fine coherent precipitates, since the stress concentration around coarse precipitates is always much lower than that in the vicinity of coherent precipitates. At the same time coarse precipitates do not result in inhomogeneous deformation. Therefore in all treatments substantially low impact energy values are obtained on aging to PA stages.

Hamano [38] reported the effect of precipitation of coherent and incoherent precipitates on the ductility and toughness of high-strength steel. He concluded that the coherent precipitates strengthen the material and decrease its toughness by promoting inhomogeneous deformation and increasing stress concentration. Those precipitates that are rendered incoherent with overaging cause the restoration of the toughness by promoting homogeneous deformation and retarding the early initiation of quasi-cleavage fracture. He also stated that the roles of coherent precipitates in strengthening the matrix and the roles of incoherent precipitates in promoting the homogeneous deformation can be expected to allow increase of both strength and toughness of materials, independent of compositions of the precipitates. Among the various elements that contribute to age hardening, Cu has been considered as the most promising element and has provided a base for development of various grades of Cu bearing HSLA steels.

4.5.2.3. Other parameters

The other parameters affecting impact properties are types of solutes, alloying element, precipitation behavior etc.

The effects of solutes on impact toughness of HSLA-100(GPT) are not understood clearly. Substitutional solutes which show appreciable strengthening are detrimental in that they increase the impact transition temperature. The effect of interstitial solutes, carbon and nitrogen, are perhaps less clearly established because of complication arising from interaction with dislocation or substitutional solutes, but these effect are more detrimental than those of substitutional solutes. But Ni has a better effect on impact properties due to deformation twinning in the ferrite.

Robert [35] reported that by rapidly quenching low carbon steels from the controlled rolling temperature produces the best combination of strength and toughness. The lower the finishing rolling temperature, the better are the properties due to finer prior austenite grain size which gives rise to a very fine acicular ferrite grain size, and a defect structure induced by the deformation, which is not annealed out. This latter is very attractive in increasing the strength when the final rolling occurs at temperatures where the austenite-ferrite transformation takes place in very low carbon steels. However the impact properties may be impaired.

Manganese additions [28] can improve the toughness as well as strength in pearlite reduced steels by lowering the Ar_3 temperature [29] The decreased Ar_3 temperature mitigate the embrittlement which accompanies precipitation strengthening, by refining the Nb(C, N) and VN, precipitated in the α-matrix [29] and by refining the α-grains more effectively after the same rolling conditions and also by making it possible to intensify controlled rolling at non-recrystallisation temperature in the α [30]. The increase of Mn content over 1.8 pet under a reduced C content less than 0.06 % causes the microstructural transition from polygonal α-pearlite to acicular a, which consists of the mixed structure of a and bainite. The strengthening in the acicular a structure depends mainly on the volume fraction of bainite with high dislocation density, and this in turn, is associated with a lowering of γ-α

transformation temperature of the steel. Therefore, the strength of acicular a steel largely depends on C, Mn or Mo content, and the effects of Cu, Ni and Cr are supplementary.

Nickel is generally known to influence the toughness; this is brought about by lowering of transition temperature rather than by raising the energy absorbed in ductile fracture (shelf energy). Nickel lowers the transition temperature due to promotion of cross slip of screw dislocations. This characteristic of Ni, unique among commercial alloying elements, accounts for its use in high strength steels in concentrations from 1 to 10 %. As a constant grain size and Ni content, the transition temperature increases with increasing yield strength. Therefore, once the possibilities of grain refinement have been exhausted, the only way to maintain a low transition temperature is to increase the Ni content as the yield strength increases.

Vanadium can be used to grain refine by VN particles, this lowers the amount of V available for precipitation of V. Thus a combined addition of (Al +V + N) grain refines by AlN, removes N to improve further the impact properties, and allows more of V to be available for precipitation. Certain steels contain higher (V+N) additions to increase the grain refinement and give more precipitation, resulting in excellent strength and impact properties. Vanadium increases the lattice parameter of M02C and stabilizes the carbide. This results in a greater intensity of secondary hardening, which occurs at higher tempering temperatures. Thus the tempering resistance is increased by V, which therefore is beneficial. However, too much V cannot be used due to its low solubility and the need for high austenitizing temperatures, and so the V must be limited to 0.5 pet. Taylor and Hansen [51] in their study of 0.1C-1.4Mn- 0.5Mo-B steels containing from 0-2.4 % V found that V additions to the base composition increase hardenability, the largest effects were observed when samples were hot rolled prior to direct quenching. Vanadium additions were also observed to provide significant strengthening in the quenched and tempered condition as the result of the precipitation of fine V-Mo carbides. The strengthening increments due to these precipitates were approximately 100 MPa/0.1 wt % V.

Davenport and Honeycombe [37] have given a model to include a buildup of C in the austenite ahead of the moving boundary, which aids nucleation of carbides at the boundary. Such nucleation also can be assisted by drag of substitutional solutes by the advancing boundary. When carbides precipitate, the C content of austenite adjacent to the boundary is depleted, which increases the driving force for transformation to ferrite [36] on cooling, V_4C_3 or Nb(C,N) precipitates at the ferrite austenite interface during the transformation [37], which produces rows of fine precipitates which cause strengthening. Due to the higher solubility of V_4C_3 compared with NbC, V steels can age-harden from conventional normalizing temperatures such as 950°C, whereas Nb steels do not because the solubility of NbC at 950°C is too small. Thus on normalizing, Nb steels are only grain-refined, whilst V steels are both grain refined and precipitation-hardened. Niobium steels can precipitation-harden if they are heated to higher austenitizing temperatures at which more NbC is dissolved, but this also dissolves the grain-refining precipitates (or coarsens them) so that the grain refinement is no longer achieved. Thus, whilst the strength is increased the impact properties are very detrimentally affected.

Dhua et al [41] studied the effect of hot rolling on microstructure and mechanical properties of HSLA-100 Cu-bearing steels. They noticed substantial improvements in strength at the expense of impact toughness on tempering at 500°C owing to profuse precipitation of Cu in the matrix. However, considerable improvements in notch toughness were observed with increase in tempering temperature. Partially recovered matrix and coarsened Cu precipitates in the temperature range of 650 - 700°C presumably enhanced the dislocation movement and notch toughness. In another investigation on HSLA-100 steel (with C-0.04, Mn-0.87, Cu-1.77, Cr-0.58, Mo-0.57, Ni-3.54, and Nb-0.038 pet) Dhua [41] reported the influence of tempering on the microstructure and mechanical properties. They observed profuse precipitation of Cu on tempering at 450°C, which enhanced the strength of the steel significantly, though at the cost of notch toughness. The precipitates became considerably coarsened and elongated on tempering at 650°C, resulting in a phenomenal rise in impact toughness at the expense of yield strength and ultimate tensile strength.

4.6. EFFECT OF MICROALLOYING ON PRECIPITATION BEHAVIOUR

The most important alloying element in GPT steel is Ti, which restricts effectively the grain growth of austenite by forming stable nitrides or carbonitrides and finally results in fine grained steel. This study shows that presence of Ti changes the complete precipitation behaviour of Cu-bearing HSLA-100(GPT) steels.

4.6.1 Precipitation Behaviour

The presence of Ti in GPT steel makes dissolution of carbide precipitates on solution treatment at 1000°C difficult. It is seen that on oil quenching undissolved carbides of (Nb,Ti)C still exist in the quenched matrix. In a recent study on the strain-induced precipitation of NbC in Nb and Nb-Ti microalloyed steels, Hong [49] reported complete dissolution of all the precipitates in Nb steel at 1250^0C, whereas undissolved precipitates have been observed in Nb-Ti steel. The undissolved precipitates are identified as Ti-rich (Ti,Nb)(C,N) carbonitrides. In the GPT steel it is shown that the undissolved precipitates contain both Nb and Ti. The concentration of Nb is higher than that of Ti in all stages of aging.

This study also shows that the presence of Ti in this steel accelerates the precipitation of (Nb,Ti)C particles on subsequent aging in all treatments. This is in agreement with the observation of Hong [48] who observed enhancement in precipitation kinetics in HSLA steels microalloyed with both Nb and Ti. They have concluded that the undissolved (Nb,Ti)C particles are relatively very stable and act as potential sites for the nucleation of (Nb,Ti)C carbides. According to Hong [48] the fresh (Nb,Ti) C carbides are precipitated coherently on the pre existing (Nb,Ti)(C,N) precipitates. The lattice mismatch between the pre existing carbide particles and freshly nucleating (Nb,Ti)C particles is very small .The strain energy arising from this small lattice misfit is thus negligible in comparison to the large decrease of interfacial energy between pre existing undissolved carbide particles and the nucleating (Nb,Ti)C precipitates. Thus heterogeneous nucleation of (Nb,Ti)C precipitates occurs on pre existing carbides due to the decrease of energy barrier for nucleation.

The present study also reveals that the Nb content in carbide precipitates forming on aging is higher as compared to the same in undissolved carbides. Also, it is observed that as the aging process advances, the concentration of Nb in freshly nucleating precipitates generally increases. This is supported by the observations of Hong [48], who observed that only about 8 pet of total Nb content of the steel was tied up within the undissolved (Ti,Nb)(C,N) carbonitrides, whereas after a pre strain of 0.3 at 950°C followed by holding for 8 s, about 14 pet of total Nb content of the steel was available in (Nb,Ti)(C,N) carbides precipitating coherently at the undissolved carbonitrides. This obviously is due to a very sensitive role of Ti in the precipitation kinetics inHSLA-100 (GPT) steel. The presence of Ti significantly accelerates the precipitation process and as a significant portion of Ti already gets combined to the undissolved carbide particles; the relative concentration of Ti in precipitates forming on aging steadily decreases and the concentration of Nb increases as the aging progresses. Hong et al [48] also showed that the incubation period of Nb-rich precipitates increased by addition of Ti in HSLA steels. In the present study also it is observed that in the undissolved (Nb,Ti) C precipitates, the Nb content is low. The content of Nb in the nucleating precipitates increases as the aging advances. At the end of aging process, a much higher Nb concentration is observed as compared to that in the initial stages of aging.

Addition of Ti is believed to cause austenite grain refinement in HSLA steels. It may be argued that the influence of Ti on precipitation kinetics in this steel is through its effect on austenite grain refinement as reported by Dutta and Sellars [52]. However, in deformed steels, the effect of austenite grain size is not likely to influence the precipitation kinetics of (Nb,Ti)C carbides, since in deformed matrix a nucleation of strain induced precipitates is more likely to take place mainly at dislocations and sub boundaries developed by deformation. Presence of dislocations causes development of potential nucleation sites and as such the rate of precipitation of (Nb,Ti)C carbides is expected to increase with increasing deformation.

A major observation made in this study is that precipitation coarsening begins at very early stage of aging and leads to a significant decrease in precipitate number density. It is also seen that growth and coarsening occur simultaneously during the precipitation of fine (Nb,Ti)C precipitates. A comprehensive analysis of the precipitation kinetics involving nucleation, growth and coarsening of precipitates in this steel poses a very complex challenge. Earlier work has shown that the presence of dislocations causes a significant acceleration in nucleation, growth and coarsening of precipitates. The early occurrence of coarsening is assumed to be an essential feature in strain induced. Dutta [52] have shown that the coarsening of precipitates leading to growth of bigger precipitates at the expense of smaller precipitates cannot occur if the diffusion is dominated by volume diffusion. In this study the continuous growth and coarsening of existing (Nb,Ti)C precipitates together with nucleation of fresh (Nb,Ti)C precipitates indicate that bulk diffusion cannot be the dominant mechanism for precipitation and coarsening. These observations can only be explained by considering the effect of accelerated solute diffusion along the dislocations, whereby coarsening can easily occur since the precipitates are interconnected through the dislocation networks. Due to increasing enhancement of precipitation kinetics as a result of prior deformation, both coarsening of existing precipitates and nucleation of fine (Nb,Ti)C precipitates will accelerate with degree of cold work .Charleux [53] studied the precipitation behaviour of a commercial HSLA steel with 0.086 wt % Nb and 0.047 wt % Ti using transmission electron microscopy (TEM) and mechanical testing. They observed cubic TiN nitride precipitates with sizes in the range of 1 nm, grain boundary precipitates with diameters of approximately 10 nm and very fine spherical and needle-like shaped precipitates with sizes of the order of 1 run. The needle-like precipitates, found on dislocations in ferrite, appear to be responsible for precipitation strengthening. They observed three types of precipitates on aging. The largest precipitate in the range of 200 to 2000 nm in size and square shaped were observed with typical morphologies of TiN nitride (type I). The second type of precipitates is observed on grain and subgrain boundaries with more or less spherical shape and approximately 10 nm in diameter (type II). These precipitates contain Nb and Ti. Further very fine precipitates classified into two main types. The most numerous of these precipitates were needle shaped (type III), while a smaller number of precipitates were spherical (type IV). These smaller precipitates were assumed to be responsible for the observed precipitation hardening. Ghosh [54]), in their investigation on ultra low-C Cu-bearing HSLA steel with Nb and Ti, reported that dislocation substructures act as nucleation sites for precipitates. Maximum density of precipitates has been observed near the dislocation networks. The precipitation has been suppressed by faster cooling except when the formation of a few carbides/carbonitrides of Ti/Nb has been observed near a dislocation. Marked increase in the density of fine precipitates of approximately 5-25 nm in size has been observed on air cooling. On the other hand, sand cooling resulted in profuse distribution of precipitates of 1- 55 nm in size with some large 110 - 125 nm spherical and 150 - 165 nm cuboids particles. They also found that the precipitates near dislocation substructure and lath boundaries are getting coarsened.

4.6.2 Effect on copper precipitation

Copper forms coherent clusters on tempering of austenized steel, which becomes major source of hardening in these steels Copper precipitates as solute rich coherent bcc zones in Fe-lattice. The maximum solubility of Cu in alpha ferrite is 2.1% at 851°C. When Fe-Cu alloy is quenched from a high temperature in alpha phase and then aged at lower temperature (e.g. 500°C), the Cu atoms from spherical clusters in Fe- lattice. At a size of 5 nm. They transform insitu from bcc to fcc. Becoming non-coherent, at that point the alloy is overaged w.r.t. Yield strength. Only in averaged condition do particles approach equilibrium composition of ε -phase, which is essentially pure Cu. The rate of growth is controlled by rate of volume diffusion of Cu. Because of decrease in solubility of Cu which decreases in temperature ε-phase can be precipitated by aging supersaturated α phase, which has been formed upon rapid cooling. On aging, the hardness and strength of Cu containing steel is increased, reached a peak and then declined. A remarkable feature observed in GPT steel is that aging in any treatment does not cause formation of Cu rich precipitates. The HSLA-100 GPT steels contain Cu, Nb and Ti. The major difference in the chemistry of these steels is the presence of Ti in GPT steel. Thus complete suppression of Cu precipitation in GPT steel is attributed to the presence of Ti. As mentioned earlier, presence of Ti substantially activates the precipitation process in Nb-containing HSLA steels. The plastic deformation induced prior to aging also accelerates the precipitation of (Nb,Ti)C particles. Some amount of Cu is always existing in (Nb,Ti)C precipitates. In the beginning the kinetics of precipitation of (Nb,Ti)C is substantially faster than that of Cu, due to which (Nb,Ti)C carbides precipitate in preference to Cu. As the aging progresses the concentration of Cu in the matrix is depleted due to continued precipitation of (Nb,Ti)C particles containing Cu in solution. The matrix therefore continuously depletes in Cu and the possibility of Cu precipitation dwindles as the aging process continues. This remarkable behaviour of (Ti + Nb) combine in suppressing the precipitation of Cu rich particles in this steel may seriously affect the work hardening characteristics and the resultant mechanical properties after various treatments in the GPT steel. Copper precipitates as solute rich coherent bcc zones in Fe-lattice .The maximum solubility of Cu in α-Fe is 2.1 wt % at 851°C. When Fe-Cu alloy is quenched from a high temperature in the α-phase and then aged at a lower temperature (e.g. 500°C), the Cu atoms form spherical clusters in the Fe-lattice. These clusters can be detected when they are only about 0.8 nm in diameter. At this stage, in a 1.4 wt % Cu alloy their density is about 10^{18}/cc. The clusters grow to a diameter of about 2.4 nm at which point the strength of the alloy is maximized. These clusters are not pure Cu; the earliest clusters contain about 50 % Fe. As the particles grow they become richer in Cu. At a size of about 5.0 nm, they transform in-situ from bcc to fcc, becoming non-coherent. At that point the alloy is overaged with respect to yield strength. Only in the overaged condition do the particles approach the equilibrium composition of e-phase, which is essentially pure Cu. The rate of growth is controlled by rate of volume diffusion of Cu. Because of the decrease in solubility of Cu with decrease in temperature, α-phase can be precipitated by aging supersaturated a-phase, which has been formed upon rapid cooling. The Cu precipitates as spheres because the strain energy of the coherent particles is very small. The atomic radii of Cu and Fe differ by only about 0.3 %. The precipitation of Cu from solid solution in ferrite continues to attract interest because of the possibility of controlling texture and strength by this process [11]. Considerable increase in strength of ferrite can be obtained from Cu-precipitation, an increment of up to 248 MPa per 1 % Cu being obtainable [16]. Hornbogen [33] suggested that the major part of the strengthening of an alloy containing Cu clusters might be due to vacancies causing jogs on screw dislocation mobility, rather than to the cutting of the clusters. Hornbogen [34] also suggested that, in the stages between clustering and overaging, clusters and particles together produce hardening, the clusters gradually disappearing as the non-coherent precipitates nucleate and grow. When small, the particles can be cut by dislocations since the slip systems in the bcc matrix and fee particles can be parallel, strengthening being by particle cutting. The alloying elements, Mo, Ni, Mn and Cr retard the precipitation of Cu because of their effect in delaying the austenite to ferrite transformation. Krishnadev and Galibois [24] observed very limited precipitation in Cu-Ni-Nb-Mo steel after being air-cooled from a finish rolling temperature of 760°C. They suggested that lowering of the transition temperature due to the presence of the additional alloying elements retards the premature precipitation of Cu because of its greater solubility in austenite than in ferrite. Of all the alloying elements commonly used, Mo appears to have the greatest effect in intensifying the strengthening response due to Cu-precipitation [22]. In a commercial Cu-containing steel (IN-787), additions of both Mo and Cr were used to retard premature Cu-precipitation so that further strengthening by aging can be obtained, even in thick sections (IN-787 1978). In this steel, more than half an hour was required to reach peak hardness at 600°C, and considerable hardening taking place even at 700°C. In contrast, in plain Cu-containing steel, it takes about 10 min at 600°C to reach peak hardness and at 700°C little increase in hardness occurs with softening taking place after only 5 min aging [9].

CHAPTER 5

CONCLUSIONS & SUGGESTIONS FOR FUTURE WORK

5.1. CONCLUSIONS

1. The aging treatments causes increase in hardness with a decrease in impact energy, which is primarily due to increase in rate of nucleation of coherent (Nb,Ti)C precipitates.

2. The microalloying combination of (Nb+Ti) alters drastically the mode of precipitation. Presence of Ti activates the formation of (Nb,Ti)C carbide precipitates and completely suppresses the precipitation of Cu.

3. Even a solution treatment temperature of 1000°C is not sufficient to completely dissolve Nb and Ti in the matrix and undissolved (Nb,Ti)C precipitates are observed in oil quenched state. Although aging at 400°C is not sufficient for nucleation of fresh coherent (Nb,Ti)C precipitates.

4. The undissolved (Nb,Ti)C particles act as heterogeneous nucleation sites for fresh (Nb,Ti)C precipitates as coherent particles at their interface.

5. Aging at 400°C causes simultaneous coarsening of existing precipitates and nucleation of fresh (Nb,Ti)C precipitates.
6. The concentration of Nb in (Nb,Ti)C precipitates nucleating on aging increases with duration of aging process. Consequently. The carbide precipitates forming all through the aging process contain some concentration of Cu.
7. The aging treatments causes increase in hardness with decrease in impact energy, which is primarily due to increase in rate of nucleation of coherent (Nb,Ti)C precipitates.

5.2. SUGGESTIONS FOR FUTURE WORK

1. The study of aging treatment shows that single peak is observed within the aging time of 1200 minutes. So there is need to do observe any other peak aged values by increasing aging time beyond 1200 minutes.
2. This study shows that some concentration of Cu is always available in the (Nb,Ti)C precipitates which are mostly observed from peak aged (PA) condition. Solubility of Cu in (Nb,Ti)C is of critical importance for changes in the precipitation behaviour of Cu in Cu bearing HSLA-100(GPT) steels. In view of this, there is need to investigate critically all the factors affecting precipitation of Cu in such steels.
3. There is a drastic fall of impact strength at peak aged (PA) condition in these steels. So it may impose serious restrictions on the use of these steels. It is necessary to investigate more thoroughly the factors responsible for poor impact toughness. So there is need to do concentrated study of the suitable solutionizing and aging temperature for developing high levels of hardness together with high impact energy.
4. In Copper bearing HSLA-100 (GPT) steel, (Nb,Ti)C carbide precipitates are nucleated coherently at the interfaces of undissolved or pre existing carbide particles. Detailed experimental studies involving sophisticated methodology are however necessary to verify this aspect of nucleation. The role of interfaces of undissolved (Nb,Ti)C precipitates in the nucleation of fresh (Nb,Ti)C precipitates needs to be systematically studied.

CHAPTER 6

REFERENCES

1. http://www.machinedesign.com/BDE/materials/bdemat6/bdemat6_7.html
2. F. B. Pickering: Physical Metallurgy and the design of Steels, Applied Science Publishers, London: 1978, pp.60.
3. High-Strength Structural and High-Strength Low-Alloy Steels, Properties and Selection: Irons, Steels, and High-Performance Alloys, Vol 1, ASM International, Metal Hand book, 1990, pp.389–423
4. W. C. Leslie: The Physical Metallurgy of Steels, Hemisphere Publishing Corp.: New York: 1981.
5. V.Raghavan, Physical Metallurgy, Principle and practice, June 2000 Edition, pp.217.
6. Panwar S: 2005, Ph.D Thesis, Thapar Institute of Engineering and Technology Patiala-147 004(India)
7. Vijendra Singh, Physical Metallurgy, 2002 edition, pp.643-645.
8. B. Mintz, S. Yoo & J. J. Jonas: Int. Mater. Rev; 1991, Vol 36, pp.187.
9. M. R. Krishnadev: Proc.Conf.on "HSLA Steels Technology & Applications, USA
10. S. R. Godman, S. S. Brenner and S. S. Low Jr: Met.Trans.1973, vol. 4, pp.2363-2371.
11. W. B. Hutchison and B. J. Duggan: Met. Sci.: 1978, 1, pp.340.
12. R. A. DePaul and A. I. Kitchen: Met.Trans; 1970, vol.12, pp.389.
13. M. R. Krishnadev and J. Le May: JISI, 1970, 208, pp.458.

14. A. R. Cox: in "Copper in Iron and Steels"; edt.Le May and L.McDonald Schetky John-Wiley and Sons, New York; 1982.

15. E. Hornbogen and R. C. Glenn: in "Copper in Iron and Steels"; edt. I. Le. May and L. McDonald Schetky John-Wiley and Sons, New York; 1982.

16. E. E. Fletcher and A. R. Elsar: Precipitation-Strenthned, Weldable, Low Carbon Structural Steels for Line-pipe Applications, NG-18, Report No. 101, Battel, Columbus Ohio; Dec.1975.

17. H. Hurley and C. H. Shelton: in "Copper in Iron and Steels"; edt. I. Le May and L. McDonald Schetky John-Wiley and Sons, New York; 1982.

18. . E. Snape in "Copper in Iron and Steels"; edt. I. Le May and L. McDonald Schetky John-Wiley and Sons, New York; 1982.

19. R. A. DePaul and A. I. Kitchen in "Copper in Iron and Steels"; edt. I. Le May and L. McDonald Schetky John-Wiley and Sons, New York; 1982.

20. R. Varughese and P. R. Howell: Application and Metallographic Techniques to study the Tempering of HSLA -100 steels, Materials Characterization, July 1993, vol.30, No-4, pp.261.

21. 21. L. Skoufari Themistou, D. N. Crowther and B. Mintz: Mater. Sci. Technology: 1999, col. 15, pp.1069-1079.

22. M. R. Krishnadev and A.Galibois: Met. Trans., 1975, 6A, pp.282.

23. L. R. Cutler: Thesis, Laval University; 1979.

24. 25 M. R. Krishnadev and A.Galibois: Mater. & Tech., 1974, pp.300.

25. K. B. Kong, W. B. Lee and C. G. Park: Scripta Mater.Vol 36 No-11, pp1303-1308(1997).

26. IN-787 A precipitation Hardening Alloy Steels, Properties and applications, INCO Ltd., New York; 1978.
27. M. R. Krishnadev: in "Copper in Iron and Steels"; edt. I. Le May and L. McDonald Schetky John-Wiley and Sons, New York; 1982.
28. Duckworth W L, Philips R and Chapman JA: 1988, in "Thermomechanical Processing of High Strength Low Alloy Steels"edt. I.Tamura, C.ouchi, T.tanaka and Sekine, Butterworth co. (publ.), London
29. Sekine H and Maruyama T: 1988, in "Thermomechanical Processing of High Strength Low Alloy Steels"edt. I.Tamura, C.ouchi, T.tanaka and H.Sekine, Butterworth co. (publ.), London
30. .Kazasu I and Tanaka J: 1975,Sulfide Inclusions in Steel, American society of Metallurgists,
31. Nakasugi H, Matsuda H and Tamehiro H:1980, Steel Inst. Japan, p.1028
32. E. E. Fletcher: High-Strength, Low-Alloy Steels: Status, Selection & Physical Metallurgy: Ohio (1979).
33. E. Hornbogen: Trans. ASM: 1964, pp.120
34. M. R. Krishnaedev and I. Le May: Proc. 2nd Int. Conf. on the Strength of Metals and Alloys, ASM Metals Park, Ohio; 1970, pp.611.
35. J. E. Roberts: Strong and Tough Structural Steels, Iron and Steels Institute; 1967, pp.104.
36. W. C. Leslie: The Physical Metallurgy of Steels, Hemisphere Publishing Corp.: New York: 1981.

37. A. T. Davenport and R. W. K. HoneyCombe: Proc. Roy. Soc; London; 1971, A322, pp.1991.

38. R. Hamano: Metal. Trans. A; 1993, vol 24A, pp.127-139

39. G. J. Baczynski, J. J. Jonas and L. E. Collins: Metall. and Mater. Trans. A; 1999, vol.30A, pp.3045-3054.

40. J. K. Patel, B. Wilshire: Journal of Mater Process. Tech. 120 (2002) pp.316.

41. S. K. Dhua, D. Mukherjee and D. S. Sharma, Metal. and Mater Trans A; 2003.vol34A, pp.241-253.

42. C. H. Lee, H. K. D. H. Bhadesia, H. C. Lee, Mater. Sci. and Engg. (2003), vol30A, pp 249-257.

43. Sivaprasad, S. Tarafder, V. R. Ranganath, K. K. Ray Mater. Sci. and Trans. A284 (2000), pp.195-201.

44. M. K. Banerjee, P. S. Banerjee and S. Datta. ISIJ International, Vol41 (2001), No-3, pp.257-261.

45. 46 S. K. Dhua, D. Mukherjee and D. S. Sarma, Metall. and Mater. Trans. A; 2003, vol34A, pp.241-253.

46. S. G. Hong, H. J. Jun, K. B. Kang, C. G. Park, Scripta Mater. 48(2003), pp. 1201-1206.

47. S. K. Dhua, Amitava Ray and D. S. Sarma, Metal. and Mater. Trans A318 (2001), pp.2493-2504.

48. S. G. Hong, K. B. Kong: Scripta Mater. 46(2002), pp.163.

49. S. K. Mishra, S. Ranganathan, S. K. Das and Samar Das: Scripta Materialia Vol39(1998), No.2, pp.253-259.

50. Thompson S W, Colvin D J and Krauss G: 1990, Metall. Trans. A, 21A, pp.1493.

51. Taylor K A and Hansen S S: 1991,Metall.Transaction A, 22A,PP.2359.

52. Dutta B and Sellars C M :1987,Material Science Technology ,3,pp197.

53. Charulex M,Poole W J, Militzer M and Deschamps A :2001,Metall.Trans.A,32, PP.1635.

54. Ghosh A, Das S, Chatterjee S, Mishra B and Ramchandra Rao P: 2003, Material Science. Eng. A, 348, PP.299.