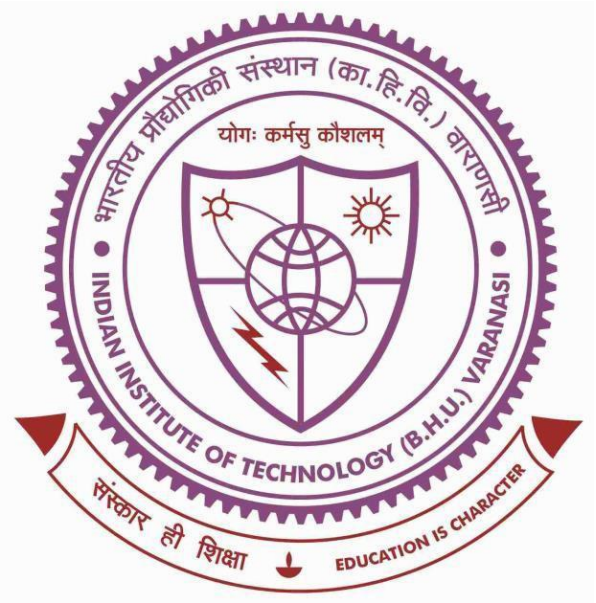
Microstructure, Mechanical and Corrosion Behaviour of Indigenously Developed Carbide-free Nanostructured Bainitic Steel



Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

By

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CERTIFICATE

It is certified that the work contained in the thesis titled ***"Microstructure, Mechanical and Corrosion Behaviour of Indigenously Developed Carbide-free Nanostructured Bainitic Steel"*** by ***Sandeep Kumar Gupta*** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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I, ***Sandeep Kumar Gupta***, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***Dr. Kausik Chattopadhyay*** and ***Dr. Rampada Manna*** from ***July 2017*** to ***July 2023***, at the ***Department of Metallurgical Engineering***, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

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Dedicated

To

My Family

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SANDEEP KUMAR GUPTA

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
BCC	Body Centred Cubic
CPE	Constant Phase Element
CR	Corrosion Rate
TRIP	Transformation Induced Plasticity
SIM	Strained-induced Martensite
EBSD	Electron Back Scattered Diffraction
EDS/EDX	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FCC	Face Centred Cubic
FESEM	Field Emission Scanning Electron Microscope
HCP	Hexagonal Closed Packing
HRTEM	High Resolution Transmission Electron Microscope
LCF	Low Cycle Fatigue
OCP	Open Circuit Potential
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscope
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
BFI	Bright Field Images
DFI	Dark Field Images
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

IQ	Image Quality
IPF	Inverse Pole Figure
LAGB	Low Angle Grain Boundary
HAGB	High Angle Grain Boundary
KAM	Kernel Average Misorientation
YS	Yield Strength
UTS	Ultimate Tensile Strength
TE	Total Elongation
UE	Uniform Elongation
PSE	Product of Strength and Elongation

SYMBOLS

°C	Degree Centigrade
µm	Micrometre
nm	Nanometre
α	Ferrite
α_b	Bainite
α′	Martensite
ϒ	Retained Austenite
Υ_F	Filmy Retained Austenite
Υ_B	Blocky Retained Austenite
P	Pearlite
♦	Cementite
$V°_{RA}$	Volume Fraction of Initial Retained Austenite
V_{RA}	Volume Fraction of Retained austenite After SIM Transformation
V_B	Volume Fraction of Bainite
V_M	Volume Fraction of Martensite
θ	Theta
C_Υ	Carbon Concentration in Retained Austenite
λ	Inter Lamellar Spacing
kHz	Kilo Hertz
mHz	Milli Hertz
mg	Milligram
mm	Millimetre

ml	Millilitre
t_B	Bainite plate thickness
t_{RA}^F	Thickness of Filmy Retained Austenite
t_{RA}^B	Size of Blocky Retained Austenite
a	Lattice Parameter
B	Crystallite Size
k°	Scherrer Constant
cm	Centimetre
s	Second
k′	Constant
K	Strength coefficient
K_1	Strength coefficient
n	Strain Hardening Exponent
kN	kilo Newton
kV	kilo Volt
λ	Wavelength
ε	Root mean square of micro-strain
$\Delta\varepsilon_{t/2}$	Total strain amplitude
$\Delta\varepsilon_{p/2}$	Plastic strain amplitude
$\Delta\varepsilon_{e/2}$	Elastic strain amplitude
MPa	Mega Pascal
Ra	Average Surface Roughness
HV	Vickers hardness
$2N_f$	Number of reversals to failure

ε'_f	Fatigue ductility coefficient
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
βa	Anodic Tafel slope
βc	Cathodic Tafel slope
ρ	density
E	Elastic Modulus
μA	Microampere
Δw	Weight Loss
t	Immersion Period
Z''	Impedance Imaginary Component
Z'	Impedance Real Component

PREFACE

Nanostructured bainitic steels represent a major advance in technology for producing very large quantities of three-dimensional objects like rail, armor, transmission shaft and bearing. The nanostructure bainitic steel usually is a mixture of slender plates of bainite embedded in a matrix of carbon enriched austenite. This austenite is stable under ambient conditions. Previous researchers found that nanostructured bainitic steel can be made carbide-free by adding sufficient amount of silicon concentration and by adding elements like Mn and Ni that increase the thermodynamic stability of the austenite at room temperature. However, that makes the transformation kinetics sluggish. Accelerated transformation of bainite can be obtained by adding small amount of Al and Co. The evaluation of nanostructured bainitic steel reports low toughness, reasonable fatigue, wear and corrosion resistance. Very less study is available on the effect of higher amount of retained austenite on tensile properties of high carbon carbide-free nanostructured bainitic steels. No study is available on the low cycle fatigue behaviour of high carbon carbide-free nanostructured bainitic steel. Tribological study at low and medium carbon bainitic steel shows that with increasing percentage of carbon wear resistance increases. However, there is hardly any literature on tribological behaviour of high carbon carbide-free nanostructured bainitic steels. There is no significant study available in literature on corrosion behaviour of high carbon carbide-free nanostructured bainitic steel with high amount of retained austenite as well as with variation of austempering time. Therefore, the objectives of the present investigation are to produce high carbon carbide-free nanostructured bainitic steel with improved strength, toughness, fatigue, wear and corrosion resistance.

The present thesis is divided into eight chapters.

Chapter 1 accounts literature survey on synthesis and characterization of nanostructured bainite and its resultant mechanical properties like tensile, fatigue and wear behaviour and corrosion properties to find scientific gaps. Chapter ends with the objectives of the present investigation. The objectives of the present investigation are:

1. Design and characterization of ultrahigh strength carbide-free nanostructured bainitic (NSB) steel at lowest possible austempering temperature.
2. Ductilization, strengthening and toughening of the NSB steel.
3. Evaluation of low cycle fatigue behaviour of NSB steel.
4. To study the influence of microstructure and mechanical properties on dry sliding wear behaviour of nanostructured bainitic steel.
5. To study the effect of microstructure on Electrochemical and immersion Corrosion behaviour of nanostructured bainitic steel.

Chapter 2 describes the design, synthesis and processing of materials and procedures of characterization of phases, microstructure, mechanical and corrosion properties. Three alloy compositions were designed using Jmat-pro database to get three different levels of martensite start temperature (much below room temperature, below room temperature and above room temperature). The selected compositions except manganese was melted in vacuum in an induction furnace at 1600°C. The temperature of melt was dropped to 1575°C and vacuum was replaced by argon atmosphere. Ferro-manganese and manganese were added to the melt. The homogeneous melt was maintained at 1550°C and was cast as plate in a copper mold. The cast materials were homogenized at 1200°C for 24 h in vacuum followed by furnace cooling. The homogenized plates were hot rolled

at 1050°C for 75% reduction in thickness and air cooled. The chemical analysis of hot-rolled plates was characterized by optical emission spectroscopy. The rolled sheets were austenitized at 950°C for 30 minutes. One set of austenitized samples was austempered at 250°C for different time periods to get required amount of bainite and another set of samples was patented at 550°C for 1 h for fully fine pearlitic structure. The austempered and patented steels are characterized by x-ray diffraction for phases and its quantification, crystallite size, micro strain, dislocation density and carbon content of retained austenite. Morphology and distribution of coarse phases were imaged in optical microscope. Scanning electron microscopy (SEM) was utilized for morphology of bainite, retained austenite, pearlite and size of blocky austenite. The chemical composition of phases was determined by EDS. Morphology, size and its distribution of bainite and filmy austenite, carbides if any were studied using transmission electron microscopy. Selected area diffraction patterns were analysed for confirmation of phases. Further hardness, tensile, Charpy impact toughness and low cycle fatigue testing were conducted on austempered steels. Also, dry sliding wear and corrosion behaviour of austempered steels were conducted and compared with patented steels of the same composition.

Chapter 3 illustrates the synthesis and microstructural characterization of high carbon high silicon carbide-free nanostructured bainitic steel. XRD and TEM studies confirm that the investigated steels are carbide-free. Austempering of specially designed B12VA, B14VA, and B15VA steels at 250°C results in carbide-free nanostructured bainite with plate thickness in the range of 24-36 nm along with filmy and blocky retained austenite. For a given composition and austempering temperature, increasing austempering time increases volume fraction of bainite, increases amount of filmy austenite but decreases blocky retained austenite. Austempering of B12VA, B14VA and B15VA steels for a

respective optimized period of 96 h, 48 h and 50 h at 250°C temperature produces ~65 % bainite and ~35% retained austenite.

Chapter 4 describes in detail the strengthening behaviour of high carbon high silicon carbide-free nanostructured bainitic steel. Yield strength of nanostructured bainite increases with increasing bainite content but ultimate tensile strength is mainly controlled by strain-induced martensite (SIM). Hardness of the austempered samples increases with increasing bainite content. XRD and TEM analysis confirmed that chemically stable but mechanically unstable blocky retained austenite undergo strain-induced martensitic transformation in all three compositions with decreasing order from B15VA, B14VA and B12VA as carbon percentage is in increasing order. SIM leads to high ductility with increasing strength and hardness. Among selected three compositions, B15VA-1 shows highest total elongation of 29.2%, Yield strength of 1281 MPa, highest ultimate tensile strength (UTS) of 1889 MPa, tensile toughness (U_T) of 492 MJ/m^3, hardness of 602 HV and product of strength and elongation (PSE) value of 55.16 GPa%. Work hardening behaviour of the selected nanostructured bainitic steel matches with the Swift model of three stages of deformation mechanism with increasing strain. Bainitic-austenitic steel of selected composition fails by mixed mode of fracture; however, the ductile fracture predominates.

Chapter 5 describes the low cycle fatigue and Charpy impact behaviour of high carbon high silicon carbide-free nanostructured bainitic steel. The low cycle fatigue (LCF) tests were conducted at 5×10^{-3} s^{-1} strain rate and ±0.50%, ±0.60%, ±0.70% and ±0.80% strain amplitudes. It was observed that fatigue life decreases with increasing strain amplitude. B15VA-2 steel revealed excellent fatigue life (11322 cycles) at strain amplitude of ±0.50% amongst the studied steels (B12VA-2, B14VA-2 and B15VA-2). Cyclic

hardening was observed in all the strain amplitudes for all samples. XRD studies of fatigue tested samples reveal the formation of new phase, martensite. During cyclic loading, blocky retained austenite which is chemically stable but mechanically unstable, is transformed to martensite and contributed to cyclic hardening. The crack initiation takes place at the surface in all the fatigue tested samples. The striations are very fine and are visible on some transgranular facets of some samples. B15VA-1 and B15VA-2 samples reveal better impact energy among the studied steels (15-18 J/cm^2). Charpy impact samples reveal typical quasicleavage fractography, indicating a specific pattern of fracture morphology. The crack propagation predominantly occurred through interlath cracking, suggesting a specific mechanism of crack growth within the material.

Chapter 6 discusses the sliding wear behaviour of high carbon high silicon carbide-free nanostructured bainitic steel and compared it with that of patented steel. Patenting of the steels at 550°C results in a fine pearlitic structure. X-ray diffraction and transmission electron microscopy (TEM) were used to confirm the presence of nanostructured bainite and retained austenite in austempered steels, as well as ferrite and cementite in patented steels. In patented steels, the optical, scanning, and transmission electron microscopy revealed the presence of lamellar pearlite. The hardness and tensile strength of patented steels are much less than that of austempered steels. The mass loss is linearly dependent on the load and the specific wear rate as well as coefficient of friction decreases with the rise in load from 10 N to 50 N. The hardening volume of B15VA-1 sample is greater than that of B15VA-2 and P15VA, and it is mainly due to the transformation of blocky retained austenite to strain-induced martensite. The austempered and patented samples of B12VA and B14VA reveals similar trends but higher specific wear rate than the B15VA. The bainitic pins exhibited superior tribological response than the pearlitic one. SEM analysis

of worn surfaces confirmed that at lower load (10 N), abrasive wear occurs but at higher load (50 N), the wear mechanism changes to adhesive along with abrasive in bainitic steel and oxidative wear along with adhesive and abrasive wear in pearlitic steel.

Chapter 7 discusses the effect of microstructure on electrochemical and immersion corrosion behaviour of high carbon high silicon carbide-free nanostructured bainitic steel and patented steel. Electrochemical and immersion corrosion tests are conducted in an aqueous 3.5% NaCl solution. The corroded surfaces are analysed with the scanning electron microscope (SEM) and X-ray photoelectron spectrometer (XPS). Corrosion resistance increases with increasing carbon percentage due to the formation of magnetite (Fe_3O_4), provided the content of other alloying elements remains the same. The presence of Ni decreases corrosion rate significantly, i.e., enhances corrosion resistance, charge transfer resistance (R_{ct}) and polarization resistance (R_p). Reducing retained austenite in nanostructured steel decreases the corrosion rate due to the lesser area of galvanic couples and the formation of uniform, compact, and non-porous passive layer. The bainitic steel samples demonstrated superior corrosion resistance to that of the pearlitic steel due to lesser cell formation. The corrosion mechanisms of high-carbon bainitic and pearlitic steel are discussed.

Chapter 8 presents major conclusions drawn from the present investigation along with suggestions for the future work.