Changes in Gray cast iron over the last century-An initial study

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Foreword

The experiments are carried out at the laboratories at the department of Mechanical Engineering at LTH. The required gray cast iron samples were supplied by the division of Production and Materials Engineering.

The analysis was carried out in both theoretically and practically in order to write this thesis. Thereafter analysis and sample investigation and mechanical testing are performed.

I would like to express my gratitude to my examiner, Jan-Eric Ståhl for providing me the opportunity to do master thesis at LTH.

My supervisor Filip Lenrick, whose patience, diligence, and knowledge of scholarly writing helped me get through the master thesis process, and my co-supervisor Rebecka Lindvall, whose optimistic outlook and appreciation of student's point of view were equally critical in completing the thesis.

Last but not least, I would like to extend my sincere thanks to my parents for showing immense love and believing me during my whole college career.

Lund – 2021-06-09

Puneeth Kumar Shivarudrappa

Abstract

This thesis report summarizes the research on the cold aging of gray cast iron samples dating back 100 years, and how researchers looked at the phase history and amount of impurities and trace metals generated by recycling. Initially, the topic of the thesis is introduced, with an explanation and general information on gray cast iron. The chemistry and structure of gray cast iron are both discussed. The impact of the various elements in the composition is briefly described. Then, the concept of aging has been explained also the influence of carbides, oxides and nitrides with aging is described. Gray cast iron has excellent machinability due to the inclusion of almost constant graphite flakes in the microstructure. Moving forward, the methods like x-ray fluorescence, Vickers hardness, and optical microscope with the Alicona Infinite 3D microscope are used for analysis are explained one by one. In methodology section, the detailed explanation of sample preparation and the required procedure for preparation is discussed. The data obtained from the various experiments are collected and analyzed. We obtained data from x-ray fluorescence as it shows the percentage of concentration of different materials in the gray cast iron. By the aid of Vickers hardness, we got the hardness value of each sample at different load. With the help of optical microscope, we are able to get the images of graphite structure of GCI at different magnifications. Finally, the analysis is done by the data what we got from various methods.

Keywords: Gray cast iron, age strengthening, and machinability.

Tabel Of Contents

List of Figures

List of Tables

1. Introduction

Gray cast iron (GCI) continues to be the most significant casting material, accounting for more than 70% of global production tonnage [1]. It has long been used in various industrial applications due to its versatility, superior castability, inexpensive cost (20–40 percent cheaper than steel), and wide range of mechanical qualities [1].

Cast iron is classified as lamellar (flake) or spherical (nodular) graphite iron based on graphite form. Numerical simulation and computer-aided modeling of casting solidification have been produced in recent years. Graphite lamellas scatter through the ferrous matrix, which defines the microstructure of CI. The foundry can influence the nucleation and growth of graphite flakes, and the size and type of graphite flakes can improve the desired properties. In evaluating the mechanical behavior of CI, the volume of graphite and the scale, morphology, and distribution of graphite lamellas are essential [2].

GCI is reputation stems from its superior machinability, damping adsorption, castability, and adequate strength and ductility. Surface interactions with external load and relative motion are every day in some GCI applications, such as gears, pumps, cylinder valves, cylinder bores, and cylinder liners for diesel engines [3]. Gray cast iron combines iron, carbon, silicon, manganese, phosphorus, and sulfur. In addition to these components, gray cast iron contains several trace elements. The elements found in traces in gray cast iron have a significant impact on the graphitic structure and characteristics. When trace element levels are lower or greater than the typical value, their impact on characteristics and graphitic structure becomes significant [4].

Since graphite serves as a chip-breaker and lubricates the cutting equipment, graphite flakes have excellent damping properties and machinability. Graphite is advantageous in wear applications because it aids in the retention of lubricants. Graphite pellets, on the other hand, function as tension concentrators, resulting in a lack of hardness. Liquid gray iron's fluidity, along with its expansion during solidification due to graphite deposition, has made it suitable for the cost-effective manufacture of complex, shrinkage-

free castings such as engine blocks. The flake-like form of graphite heavily influences gray iron's mechanical properties. The graphite flakes serve as stress raisers, causing localized plastic flow at low stresses and matrix breakup at higher stresses. Gray iron, as a result, has no elastic properties and fails under stress without substantial plastic deformation, but it has excellent damping properties [5].

1.1. Problem Description

What effect do impurities and trace elements have on machinability, and how can the awareness of ITEs increase an industry cost savings?

1.2. Purpose

The purpose of this thesis is to examine the phase development and amount of impurities and trace elements generated by recycling in 100-year-old gray cast iron samples. This knowledge will aid the manufacturing sector in developing new material standards to lessen the machinability impact of ITEs. Knowledge of the ITEs and strategies to compensate for their influence on machinability may help an industry like autos and trucks save a lot of money.

1.3. Scope

The project will be multi-disciplinary in nature and have a greater advantage to the manufacturing industry to develop new materials for the betterment of the industry. And produce new gray cast iron parts by enhancing the properties of the material.

1.4. Limitations

For the analysis and sample investigations, there are only four different methods that were used. For the hardness test it is Vickers hardness and for the microstructure of the samples we used optical microscope before and after etching. And to find the amount of concentration of various elements we have only XRF.

2. Theory

2.1. Gray cast iron

Gray cast iron, the most common variety of cast iron used to make industrial components, has better machinability than other cast iron forms and requires less lubrication from the metalworking fluid. Compared to other types of cast iron, gray cast irons are often alloyed with more significant quantities of sulfur and manganese. It has been discovered that during machining, sulfur and manganese may mix to generate manganese sulfide inclusions, which act as solid lubricants and add to the metal's machinability as well as the lifespan of the tool [6].

Gray cast iron is a generic name for various cast irons with flake graphite in the ferrous matrix as part of their microstructure. Carbon ranging from 2.5 percent to 4%, silicon ranging from 1% to 3%, and manganese additions ranging from 0.1 percent to 1.2 percent are common in such castings. The position of graphite in the matrix determines the strength of gray cast iron. The matrix might be made up of ferrite, pearlite, or a mixture of the two. Because large graphite flakes diminish ductility and strength, inoculants are employed to promote fine flakes [7].

The eutectic that occurs in grey cast iron is made up of flakes of graphite and austenite. The presence of silicon and slow cooling conditions encourage the development of graphite rather than iron carbide. If the casting is made up of different portions, the thin portions will be 'chilled' and cool faster than the thick portions, resulting in just the broad areas forming gray cast iron [8].

The majority of the carbon in grey cast iron comes in graphite flakes, making it softer, more machinable, and less brittle than white cast iron. As its name implies, cast iron is highly fluid when melted, making it ideal for producing complex castings. Offshore, it was primarily used in the building of flameproof enclosures. Its corrosion resistance appears to be highly varied.

A galvanized coating is recommended to be exposed to salt spray, such as in flameproof control stations on lower-deck railings. The variance in corrosion effects is most likely due to making cast iron, which requires remelting pig iron in cupolas [9].

2.2. Microstructure

The microstructure of cast iron is one of the most significant markers of its machinability. The number, size, shape, and distribution of graphite, the presence of inclusions, and the matrix coherence of ferrite and pearlite are all directly connected to material machinability metrics, including tool life and workpiece roughness [10]. In gray cast irons, carbon is typically found in the form of graphite flakes. Because these flakes are generally soft and disturb the matrix, chip breakage during machining is possible. The graphite also acts as lubricants between the chip and the tool and between the workpiece and the tool, extending tool life. Even though graphite flakes are a crucial component in increasing material machinability, the alloy's machinability is also heavily influenced by its matrix, which determines its hardness and mechanical strength [11]. Cementite (or ferrite, depending on the grain boundary structure and composition) nucleates on austenite grain boundaries during pearlite production. The carbon content of the austenite surrounding the nucleus decreases, increasing the driving force for ferrite precipitation, and a ferrite nucleus develops close to the cementite nucleus. The colony will extend sideways along the grain boundary if this practice is repeated. As with eutectic solidification, the carbon rejected from the developing ferrite diffuses through the austenite to the cementite in front of it. To form a lamellar structure of cementite embedded in ferrite, nucleation of pearlite necessitates cooperative development between the two phases, ferrite, and cementite [12].

2.3. Gray cast iron composition

The elements found in gray cast iron are classified into three groups. They are main components, smaller components, and trace elements.

2.3.1. The main components

Iron, carbon, and silicon are the three primary elements of gray cast iron.

Carbon

Carbon makes up around 2.5 to 4% of the weight of gray cast iron. There are two types of carbon: elemental carbon in the form of graphite and combined carbon in iron carbide (Fe3C). %Total Carbon =%Graphitic Carbon+ %Combined Carbon is used to determine the degree of graphitization. The proportion of total carbon and the percentage of graphitic carbon are identical if graphitization is complete. The proportion of graphitic carbon is 0 if no graphitization has happened. If the gray iron has a combined carbon content of 0.5–0.8%, the microstructure is predominantly pearlitic [13].

Silicon

Silicon makes up around 1.0 to 3.0% of the weight of gray iron. The influence of silicon on graphitization is a significant one. As the silicon proportion increases, the eutectic point of the iron-carbon diagram moves to the left [13].

2.3.2. The smaller components

Phosphorus, as well as the two linked elements manganese and sulfur, are minor components in gray iron.

Phosphorus

All gray irons include phosphorus. It is seldom added on purpose and usually comes from pig iron. It improves the fluidity of iron to some extent. In gray iron, phosphorus creates a phase with a low melting point known as steadite (Fe_3P). It enhances shrinkage porosity at high levels, enhancing metal penetration and finning defect at low levels (below roughly 0.05 percent) [13].

Sulfur

Sulfur is commonly found in the range of 0.08–0.18 percent in irons melted in the acid cupola and 0.03–0.08 percent in irons generated by electric melting. Sulfur's influence must be evaluated about its interaction with manganese in iron. During freezing, sulfur forms iron sulfide (FeS), which segregates on grain boundaries and precipitates during the last stage of freezing [13].

Manganese

Manganese sulfide (MnS) is generated when manganese is present, and it neutralizes the action of sulfur. Chemically similar sulfur and manganese ratios to make MnS. % Mn 1.7 % S The manganese proportion will produce a maximum of ferrite, and a minimum of pearlite is % Mn 1.7 % S+0.15. The manganese proportion that will generate a pearlitic microstructure is % Mn= 3 % S+ 0.35 [13].

Chromium

Gray irons can contain up to 0.3 % chromium. In gray irons, it increases cold and pearlitic structure. The strength of the material increased by forming carbides. Nickel plates, steel waste, and Ni–Mg alloys found in the initial charge materials are the significant sources of chromium [13].

Nickel

Gray irons can contain up to 0.5 % nickel. When present in negligible amounts (up to 0.1 %), it does not affect, but when present in significant amounts, it promotes graphitization. Nickel is primarily obtained from nickel plates, steel waste, and nickel-magnesium alloys found in the initial charge materials [13].

Copper

Gray irons may contain up to 0.5 percent copper. In ductile irons, it promotes pearlitic structure, increases strength, and inhibits fertilization. Copper wires, copper-based alloys, and steel waste are the primary sources of copper in the initial charge materials [13].

Tin

Tin is a strong pearlite promoter; hence increasing the tin concentration of gray and nodular irons will assure that structures are pearlitic or ferrite-free. Tin is generally found in gray cast iron at concentrations of less than 0.02 %. Nonferrous contamination or the usage of tin-coated steels during melting may result in higher levels. A maximum of % tin will assure an entirely pearlitic matrix and boost the tensile strength of both gray and nodular irons where purposeful tin additions are applied. Increased hardness and lower tensile strength are the results of additions of more than 0.1 % [13].

2.3.3. The trace elements

Elements found in gray cast iron in tiny levels can have a significant impact on the characteristics and graphitic structure. When trace element levels are lower or more significant than usual, the influence on characteristics and structure becomes significant. Boron, Lead, Bismuth, Titanium, and other trace elements are commonly found in gray cast iron [13].

Boron

Because of its strong carbide stabilizing characteristics, boron is an undesired ingredient in gray cast iron. Gray cast iron is often suggested to have a boron content of less than 0.005%. When boron levels are over the trace, pig iron is typically undetectable; this is usually due to enameled scrap in the furnace charge by mistake.

It is suggested that a furnace charge contain no more than 5% enameled scrap. When this limit is surpassed, boron can be present in the iron up to 0.055 %, causing cold, cracking issues in thin sections, a drop in tensile strength, and undesired graphite forms such as D graphite formation gray cast iron [13].

Lead

The trace elements in charge materials, like lead, accumulate to a point where the structure and mechanical qualities of castings are significantly harmed during the melting of gray cast iron. Various researchers have observed the

inclusion of tiny quantities of lead in gray iron to enhance the creation of aberrant graphite such as bayonet-shaped, widmanstatten, mesh, or spiky graphite. Tensile strength, impact strength, thermal shock, and fracture resistance all suffer from aberrant graphite formation. Any lead-bearing item thrown into the melting furnace might contaminate it with lead. Scrap containing lead or covered with lead-based paint, leaded steel scrap, and lead-bearing fluxes such as fluorspar Scrap containing lead or covered with lead-based paint, leaded steel scrap, and lead-bearing fluxes such as fluorspar, vitreous enameled scrap and non-ferrous metal scrap are the primary sources of lead in gray iron [13].

Bismuth

Bismuth level in gray iron can be as low as 0.002%. Pig irons, bismuth-containing mold, and core coatings are all sources of bismuth in gray cast iron. Due to the production of free carbide, type D, spiky, mesh, and widmanstatten graphite, residual bismuth levels in flake graphite irons over 0.0035 % cause a considerable loss in all mechanical characteristics. Bismuth inhibits eutectic cell development, promotes undercooling, raises chill (carbide network), and lowers the number of eutectic cells. The addition of roughly 0.10 percent cerium to the gray iron melt has been shown in the literature to counterbalance the adverse effects of bismuth on mechanical characteristics [13].

Titanium

Titanium may be found in gray irons in concentrations ranging from 0.005 to 0.05 %. Higher amounts of titanium are frequently the consequence of purposeful additions to counteract nitrogen's influence. Pig irons are the natural sources of titanium in gray cast iron and contain up to 0.2 % titanium. The influence of nitrogen on structure and characteristics is significant when it comes to GCI. Pearlite development can be aided by a high nitrogen level, leading to a white iron structure. Nitrogen's influence can be mitigated by the inclusion of nitride-forming elements like titanium and aluminum. The addition of titanium to the level of 0.04 percent in gray cast iron can remove

the nitrogen impacts. Titanium reacts with nitrogen in the melt to generate titanium nitride (TiN), preventing compacted graphite iron from forming. Titanium is high concentrations causes the production of unfavorable graphite [13].

2.4. Graphite structure

The distribution and morphology of graphite directly influence the characteristics of GCI. The graphite in GCI may be considered a void, and the micro notch stress concentration causes fractures to form at the tips of the graphite flakes. The improved microstructure of the deformed graphite flakes lowered stress concentration and prevented fracture expansion at the graphite tip. The weak interface and internal stress concentration caused by incompatible deformation of graphite–matrix next to the interface, according to the theory, lead to graphite–matrix cracking along the interface [14].

This section of ISO 945 describes how to use comparative visual analysis to categorize the microstructure of graphite in cast irons. The goal of this section of ISO 945 is to offer information on graphite categorization methods. It is not meant to advise the appropriateness of different cast-iron kinds and grades for different applications. The chemical composition of austenitic cast irons and the results of tensile tests and hardness testing determine the material grade. The statistical validity of a statement about the fulfillment of the standards provided in the applicable material standard is not possible due to the interpretation of graphite shape and size. The material qualities are influenced by the structure of the metallic matrix (e.g., ferrite, pearlite). This section of ISO 945 is not intended to be interpreted in this way [15].

Graphite in cast irons is classified using a classification scheme.

When graphite is studied under a microscope following this section of ISO 945, it is categorized by:

a) Its form, which is indicated by Roman numerals I to VI Figure 1 and

b) Its distribution, which is identified by capital letters A to E Figure 2.

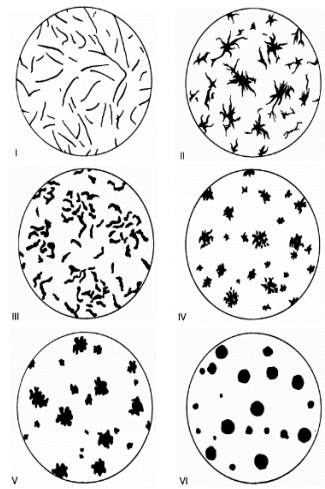

Figure 1: *Graphite form [15]*

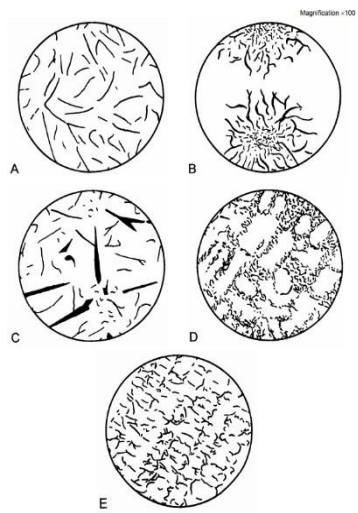

Figure 2: *Graphite distribution [15]*

2.5. Aging

Ebner announced the age strengthening of gray cast iron for the first time in 1963. Later, Nicola and Richards (1999) used statistics to show that most gray cast iron alloys experience considerable age strengthening. Additionally, nitrogen over the stoichiometric volume to mix with Ti as

titanium nitrides were a critical factor influencing the extent of age strengthening during this study period. In the presence of nitrogen above needed for a stoichiometric titanium nitride complex, titanium did not seem to improve or retard age strengthening. It is worth noting that gray iron machinability improves in tandem with its age-strengthening process [16]. Nitrogen seldom reaches the solubility level in cast iron, so increasingthe solubility limit would typically not result in a rise in nitrogen content in the melt. However, by reducing nitrogen supersaturation of the ferrite near room temperature, reductions in aging could be seen with a rise in the solid solubility limit of nitrogen [17]. When nitrogen is more than that necessary for stoichiometric titanium nitride compound, the addition of titanium does not appear to increase or delay age strengthening. When there is a substantial surplus of titanium relative to nitrogen, age strengthening does not occur. It is worth noting that the strengthening of gray iron co-occurs as the increase in machinability. With a rise in free nitrogen, age strengthening increased [18].

2.6. Carbides, oxides and nitrides

Normal aging of cast iron is linked to Fe-BCC strengthening due to iron nitride precipitation. Chromium, for example, facilitates the reduction of ferrite in cast iron and thereby decreases the overall potential strengthening effect. A microstructure from an as-cast machinability research article made of cast iron containing 0.2 percent Cr. The Cr-alloyed steatite eutectic (P-(FenCr1- n)3C) was included in the metal matrix, which had an utterly pearlitic composition with some white spots. Compared to ferrite or even pearlite, this process has a considerably higher micro-hardness and is called machinability detrimental. Iron nitride precipitate strengthening can be entirely suppressed by nitride forming elements like Ti, Al, and B. The amount of equilibrium iron nitride is influenced by both the nitrogen content of iron and the concentration of nitride-forming elements, especially titanium, which has a strong affinity for nitrogen. As titanium and nitrogen are present in the same iron alloy, they react to form titanium nitride, resulting in less "free" nitrogen in the solid solution. [19].

2.7. Machinability

Machinability tests are used to determine whether or not a material can be machined to an acceptable industrial level. The machinability rating is an index number that represents the relative efficiency (MR). The machinability value of AISI 1112 steel, which is the industry standard, is 1.0. This means that products that are more difficult to machine are given a lower grade. Materials that are easier to machine, on the other hand, have a higher ranking. Tool life, cutting forces, absorbed cutting strength, surface roughness, dimensional stability, metal removal rate, and chip control are some of the metrics used to assess machinability. Working machine, cutting tools, workpiece materials, and cutting conditions (speed, feed, and depth of cut) communicate dynamically [20]. Gray iron castings must be machinable in order to be used. Most structural engineers assume that cast irons are free-machining and that machinability would contribute to the cost savings associated with gray iron castings. For highly machined sections, the cost of machining gray iron can be ten times that of the casting. Setting and retaining optimum machine speeds requires consistent metal structure from batch to batch, from casting to casting, and within any single gray iron casting. Furthermore, the widespread use of numerically operated machine tools that use pre-programmed feed rates and cutting speeds reduces the need for operator interference. Specifying gray irons with an explicit microstructure is critical for the cost-effective machining of gray iron castings. Castings that do not machine reliably can suffer slowdowns or downtimes due to excessive tool wear, tool breakage, poor surface finish, and scrap, resulting in higher costs. Carbide content, pearlite content, pearlite hardness, non-metallic inclusions, the character of the casting skin, and alloy segregation are all factors that affect machinability in gray irons, according to studies. While these experiments explicitly show that the microstructure of gray irons affects machinability, the micromechanics of chip formation is less well understood [21].

2.8. Properties of gray cast iron

The properties of the gray cast iron listed below.

2.8.1. High compressive strength

This strength is determined by a metal's or alloy's ability to endure compressive forces. Grey Cast Iron has high compressive strength, so it is commonly used in building posts and columns. Furthermore, their compressive strength is comparable to that of certain Mild Steels [22].

2.8.2. Resistance to deformation

Grey Cast Iron has a good deformation resistance and offers a sturdy structure. However, if there is a flaw with the building, even a Grey Cast Iron building might fail [22].

2.8.3. Low melting point

Grey Cast Iron has a low melting point, ranging from 1140 to 1200 degrees Celsius [22]

2.8.4. Resistance to oxidation

Rust, generated by the interaction of oxygen and iron, is very resistant to grey cast iron. It is an excellent method for preventing corrosion [22].

2.9. Applications of GCI

Gray cast iron is used in many applications such as Engine blocks and heads for automobiles, internal combustion engine manifolds, gas burners, machine tool bases, cylinder liners, intake manifolds, soil pipes, counterweights, enclosures, and housing where it requires several strength classes, vibration damping, low rate of thermal expansion and resistance to thermal fatigue, lubricant retention, and superior machinability are all features of this material [23].

2.10. Methods and resources

Here are some of the methods and resources that have been used to assess the properties of gray cast iron. The powder x-ray diffractometer, x-ray fluorescence, Vickers hardness tester, and scanning electronic microscope

are all used to determine the chemical composition of inclusions in the workpiece material.

2.10.1. X- Ray Diffractometer

X-ray diffraction analysis (XRD) is a method for determining a material's crystallographic composition. XRD is a technique that involves irradiating a sample with incident X-rays and then calculating the intensities and scattering angles of the X-rays that exit the material. The detection of materials based on their diffraction pattern is one of the most popular applications of XRD analysis. XRD provides detail about how the current configuration differs from the optimal one due to internal strains and faults, in addition to step detection [24]. X-rays are beams of electric radiation, whereas crystals are ordinary clusters of atoms. The association of incident X-rays with the electrons of crystal atoms scatters incident X-rays. Elastic scattering is the name for this phenomenon, and the electron is the scatterer. A standard scatterer array generates a regular array of spherical waves. These waves cancel each other out in most directions due to disruptive interference, but they add constructively in a few directions, as determined by Bragg's law: $2d\sin\theta = n\lambda$ where d is the distance between diffracting planes,theta is the incident angle, n is an integer, and is the wavelength of the beam.The basic directions show up as reflections on the diffraction pattern. As a product of electromagnetic waves impinging on a standard series of scatterers, X-ray diffraction patterns emerge. Since their wavelength is oftenthe same order of magnitude as the spacing, d, between the crystal planes, X-rays create the diffraction pattern (1-100 angstroms) [25].

2.10.2. X-Ray Fluorescence

For the identification of major and trace elements in solids, X-Ray Fluorescence analyses samples. Minerals, polymers, catalysts, liquids, deposits, metals, and other materials will be analyzed using XRF. XRF provides clients with fast quantitative and semi-quantitative factor analysis in samples [26]. An X-ray fluorescence (XRF) spectrometer is a non-destructive x-ray instrument used for regular chemical analyses of rocks,

salts, sediments, and fluids. It operates on the same wavelength-dispersive spectroscopic concepts as an electron microprobe (EPMA). An XRF, on the other hand, is unable to perform analyses at the small spot sizes typical of EPMA function (2-5 microns). X-ray spectroscopy (e.g., SEM-EDS), X-ray diffraction (XRD), and wavelength dispersive spectroscopy all depend on basic concepts that are similar to many other instrumental approaches, including correlations between electron beams and x-rays with samples (microprobe WDS). The behavior of atoms as they interact with radiation allows x-ray fluorescence to analyze primary and trace elements in geological materials. As high-energy, short-wavelength radiation (e.g., X-rays) is used to excite objects, they may become ionized. If the radiation's energy is high enough to dislodge a closely bound inner electron, the atom becomes unstable. A missed inner electron is replaced by an outer electron. When this occurs, energy is emitted due to the inner electron orbital's lower binding energy relative to the outer one. The released radiation is called fluorescent radiation since it has lower energy than the primary incident X-rays. The resulting fluorescent X-rays will be used to detect the abundances of present elements in the sample since the energy of the emitted photon is typical of a transition between specific electron orbitals in a single element [27]. XRF instruments examine everything from minerals to fluids over a measuring spectrum of magnesium (Mg) to uranium (U). They examine all main and trace elements, including Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, and Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn [28].

2.10.3. Vickers Hardness Tester

The Vickers hardness test involves indenting the test material with a diamond indenter with a square base in the shape of a right pyramid and a 136-degree angle between opposite faces under a load of 1 to 100 kgf. Usually, the entire load is applied for 10 to 15 seconds. A microscope is used to determine the two diagonals of the indentation left in the material's surface after the load is removed, and the average is determined. The area of the indentation's sloping surface is measured. The Vickers hardness is calculated by dividing the kgf load by the indentation area in square mm.

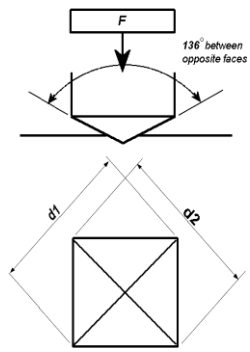

Figure 3 : Vickers hardness test

$$HV = \frac{2F\sin\frac{136^{o}}{2}}{d^{2}} \qquad HV = 1.854\frac{F}{d^{2}} \text{ approximately}$$

F= Load in kgf

d = Arithmetic mean of the two diagonals, d1 and d2in mm

HV = Vickers hardness

The Vickers hardness can be measured using the formula until the indentation's mean diagonal has been determined. The advantage of the Vickers hardness test is to take exact measurements and using only one kind of indenter for both metals and surface treatments [29].

2.10.4. Scanning Electron Microscope

Scanning electron microscopy (SEM) photographs the sample surface by scanning it in a raster scan pattern using a high-energy electron beam. The primary electron beam is screened over the surface of a specimen in a high-vacuum environment. As electrons strike the specimen, a signal variance creates an impression of the rock or its elemental composition combined with energy dispersive x-ray [30]. An electron gun creates and fires electrons as they speed down the microscope, traveling through a collection of lenses and

apertures to form a directed beam that interacts with the surface of a sample. Before the sample is placed on a stage in the microscope's chamber, a vacuum is produced in the chamber using a series of pumps. The vacuum level is determined by the microscope's design; specific microscopes are designed to work in low vacuum conditions, eliminating the need to evacuate the room. Scan coils regulate the direction of the electron beam above the objective lens. These coils allow the beam to scan over the sample's surface, allowing data about a specific region to be collected [31].

3. Methodology

The methods for gathering and evaluating data are discussed in this chapter. The information was gathered in three distinct methods. At first, the gray cast iron pieces with three different ages were collected. Then the pieces were cut, and samples were prepared. Then, the samples were examined, and analysis has been done with the help of X-ray fluorescence, SEM, Vickers hardness.

3.1. Collection of material

The gray cast iron samples that ranges from a century back are collected from the division of Production and Materials Engineering. Then the samples were cut into pieces with the help of cutting machine for sample preparation.

Figure 4: *Image of cutting machine.*

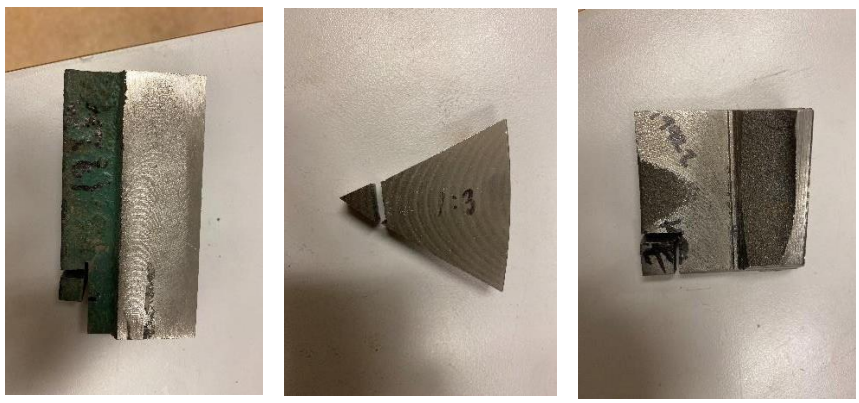

Figure 5: *From left, images of gray cast iron from 1920, 1990 and 2018 after being cut by the machine.*

3.2. Sample preparation

Sample preparation is carried out through different operations.

3.2.1. Mounting

The material samples were put in epoxy to look like the one in Figure. The mounting makes polishing and studying material samples in microscopes simpler.

Figure 6: *To left, image of samples after mounted by epoxy. To the right, image of mounting machine.*

3.2.2. Grinding

Grinding of the sample is done followed by mounting in order to keep the samples very flat so that it doesn't leave the graphite in relief.

Figure 7: *To the left, image of grinding machine. To the right, image of polishing machine.*

3.2.3. Polishing

Polishing is done followed by grinding so that the graphite structure could be examined under the microscope. Some of the parameters used while polishing is shown in the below table 1.

Table 1: *Parameters required for polishing [32]*

Abrasive/surface	Lubricant	Force/ sample	Speed (Head/base)	Time	Individual Force mode	Central Force mode
120 grit SiC paper 240 grit SiC paper*	Water	5-10 lbs	200/200 rpm	Planar 1 min		
360 grit SiC paper 600 grit SiC paper 800 grit SiC paper 1200 grit SiC paper	Water	5-10 lbs	200/200 rpm	1 min 1 min 1 min 1 min		
1 um DIAMAT diamond on GOLDPAD polishing pad	DIALUBE Purple Extender	5-10 lbs	200/200 rpm	2 min		
0.05 um Nanometer alumina on TRICOTE polishing pad		5-10 lbs	100/100 rpm	30 sec		

3.2.4. Cleaning

Because many cast irons corrode swiftly, cleaning samples must be done quickly and with cold water at all times. Water should never be allowed to come into contact with the samples. It is advised to rinse thoroughly with ethanol and dry quickly with a vigorous stream of warm air. Cleaning and washing with water-free alcohol alone are advised if corrosion persists.

3.2.5. Etching

Unetched cast iron samples are first inspected microscopically to determine the form, size, and distribution of graphite, as well as any cast porosity. Following this first assessment, the sample is etched for microstructure using 1 to 3 % Nital.

3.3. Scanning Electronic Microscope

Once the samples are prepared, initially they are inspected using SEM to find the distribution of graphite, form size. Here, the samples were examined one by one using various magnifications. Then the pictures obtained from the inspection are saved in the TIFF format and used to determine the distribution in the samples. Later, the samples are examined once after etching is finished. Again, the distribution pictures are saved and inspected.

3.4. X-Ray Fluorescence

Further, the samples are examined using XRF gun and the data obtained from the experiment has been recorded. Here, we can identify the major and trace elements which are present in the samples. We can get the quick quantitative factor analysis in the samples.

Figure 8: *Image of using XRF.*

NOTE: The samples have to be examined by the aid of XRD and the analysis needed to be done from the data obtained by XRD. But due to the malfunctioning of the XRD equipment the experiment is carried out using XRF instead of XRD as per the guidance of our supervisor and co-supervisor.

3.5. Vickers hardness

Here the sample is placed on the tester and the diamond indenter is pressed into the surface to perform the inspection. With a square base and a 136-degree angle between opposite sides, the indenter is pyramid-shaped. Loads usually range from 1 to 100 kgf. Normally, the entire load is applied for 10 to 15 seconds. Once loading and unloading is completed, the lengths of both diagonals formed on the test surface are determined, and the average is used to calculate the hardness, which is calculated using the F/A ratio (where F is the force or load, in kgf; and A is the surface area of the indentation, in sq. mm.). Vickers Hardness is the measurement of hardness (HV).

4. Results and discussion

The outcomes of the tests and examinations are reported in this chapter. The chemical composition of different samples and the concentration of inclusions, the graphite structure, and the hardness of the material is shown. There are also photographs of the graphite structure of the material samples and typical wear patterns on the cutting tools.

4.1. Graphite structure

Here, the type of distribution of graphite in each sample with different magnifications are shown.

Magnification 5x

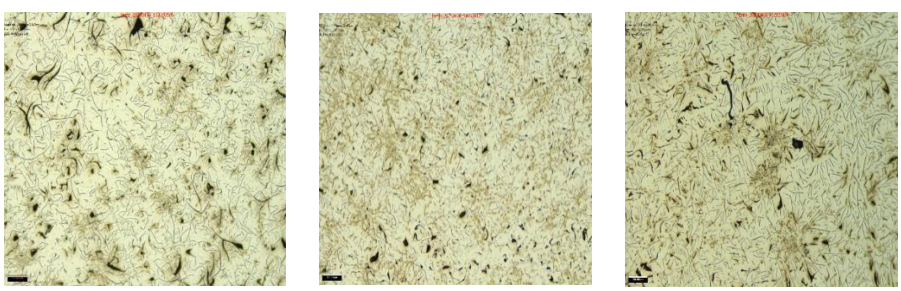

Figure 6: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are unetched at magnification 5x.*

Magnification 5x

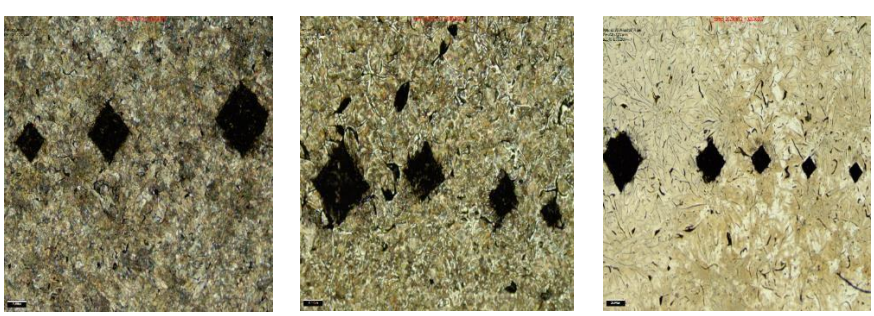

Figure 7: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are etched at magnification 5x.*

Magnification 10x

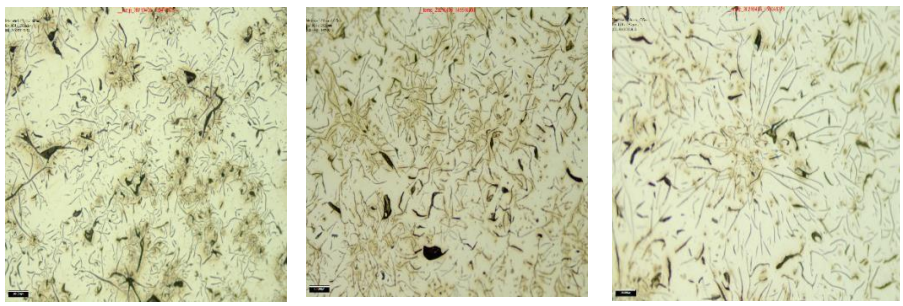

Figure 8: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are unetched at magnification 10x.*

Magnification 10x

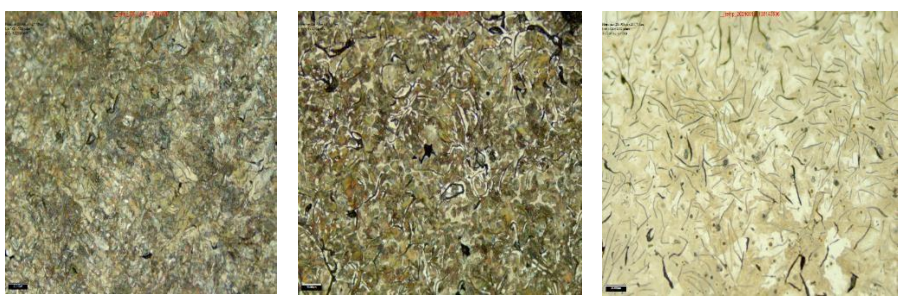

Figure 9: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are etched at magnification 10x.*

Magnification 20x

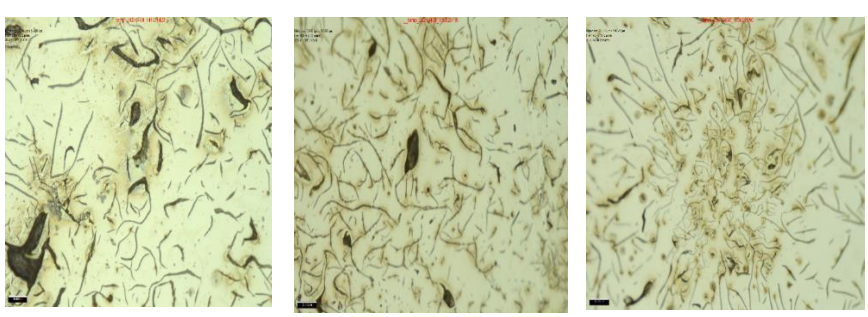

Figure 10: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are unetched at magnification 20x.*

Magnification 20x

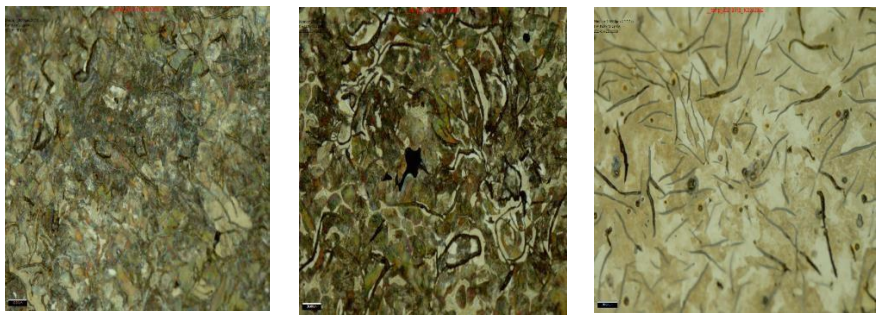

Figure 11: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are etched at magnification 20x.*

Magnification 50x

Figure 12: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are unetched at magnification 50x.*

Magnification 50x

Figure 13: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are etched at magnification 50x.*

Magnification 100x

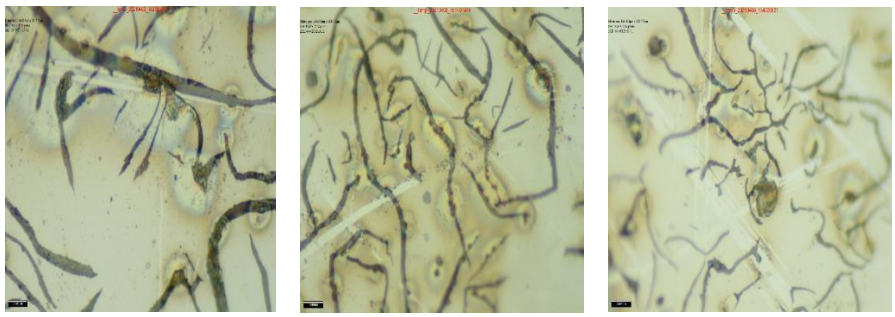

Figure 14: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are unetched at magnification 100x.*

Magnification 100x

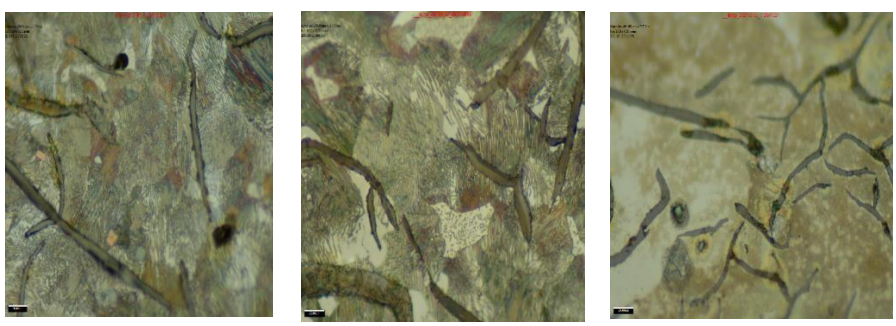

Figure 15: *From left, images showing graphite structure of samples from 1920, 1990 and 2018 which are etched at magnification 100x.*

The above figures from figure 6 to figure 14 shows the graphite structure of gray cast iron samples at different magnifications before and after etched. Because of the exposed graphite, the surface appears gray. Because graphite serves as a chip breaker and lubricates the cutting tools, graphite flakes have high damping properties and machinability. Graphite is advantageous in wear applications because it aids in the retention of lubricants. Graphite flakes, on the other hand, act as stress concentrators and cause poor toughness. The matrix in which these graphite particles are placed determines the strength of gray cast iron. Also, the size of graphite is significant, as well as its form, because it is directly connected to strength,

with more good flake sizes resulting in better strength in gray irons. Here, we can observe that the graphite structure of samples is different from each other. The matrix of graphite particles in 1920 sample is not close to each other and the size of the graphite is quite bigger compared to other samples. Accordingly, the sample from 2018 as the finer graphite structure which tends to have the better strength than the other samples. When we examine the graphite structure of the samples, we can say that according to ISO standard they are ISO 185 and ISO 2892 where the particles are interconnected within eutectic cells, and it has lamellar graphite with sharp ends. There occurrence will be the principal form in gray cast iron, austenitic cast iron with lamellar and flake graphite and occur in the rim zone of other cast iron materials. We can also observe that larger graphite flakes are surrounded by the smaller one with randomly oriented eutectic graphite.

4.2. Data obtained from XRF

This section shows the data obtained from the experimentation done by the X- ray fluorescence of the samples.

Sample	1920	1990	2018
Element	Concentration in %		
Cr	0.21	0.26	0.31
Ni	<0.00	<0.00	<0.00
Mo	<0.00	0.00	0.01
Cu	<0.00	<0.00	<0.00
Mn	0.66	0.60	0.37
Fe	99.01	99.2	99.58

4.2.1. Sample 1920

Analyte	Concentration in %	STD
Cr	0.21	0.031
Ni	<0.00	0.000014
Mo	<0.00	0
Cu	<0.00	0.0000076
Mn	0.66	0.1
Fe	99.01	0.26

Grade: 1000 series, 9260
Reference: LOW ID / C-1117

4.2.2. Sample 1990

Analyte	Concentration in %	STD
Cr	0.26	0.034
Ni	<0.00	0.000015
Mo	0.00	0.01
Cu	<0.00	0.0000083
Mn	0.60	0.1
Fe	99.2	0.27

Grade: 1000 series, 9260
Reference: LOW ID / C-1020

4.2.3. Sample 2018

Analyte	Concentration in %	STD
Cr	0.31	0.026
Ni	<0.00	0.000012
Mo	0.01	0.011
Cu	<0.00	0.0000064
Mn	0.37	0.057
Fe	99.58	0.16

Grade: 1000 series, 9260
Reference: LOW ID / C-1020

The above data shows the concentrations of elements which are present in the gray cast iron samples. We know that each element has its own characteristic, and it can impact the property of the gray cast iron. Even if the concentration of the elements varies slightly, it will result in different

properties. Pig iron, nonferrous metal scrap, vitreous enamelled scrap, leaded steel scrap, acquired scrap containing lead, and lead-based paint are all sources of trace elements in gray cast iron. To eliminate trace element contamination in charge materials, every scrap should be inspected before stockpiling to ensure that any unwanted charge materials are eliminated. We can observe, the concentration of iron and chromium is slightly increased over the years, but the concentration of the manganese is reduced. If the concentration of iron and chromium increases, then simultaneously the strength and hardness of the material will increase by increasing the cold and pearlitic structure by forming carbide. It also increases the elevated temperature properties of the gray cast iron. To eliminate trace element contamination in charge materials, every scrap should be inspected before stockpiling to ensure that any unwanted charge materials are eliminated.

4.3. Data obtained from Vickers hardness

In this section, the data obtained by the Vickers hardness is shown.

4.3.1. Sample 1920

Load	HV
0.3	250.3
0.5	162.5
1	199.8
2	178.1
5	161.7
10	169.2
20	167.4

4.3.2. Sample 1990

Load	HV
0.3	181.7
0.5	194.1
1	209.4
2	199.8
5	186.1
10	196.4
20	197.8

4.3.3. Sample 2018

Load	**HV**
0.3	205
0.5	227.9
1	193.5
2	210.9
5	198.4
10	222
20	199.1

4.3.4. Samples at load 2 kg

	Sample 1920	**Sample 1990**	**Sample 2018**
Test	**HV**	**HV**	**HV**
1	164.6	193.9	198.3
2	166.1	209.7	200.4
3	165.9	206.9	203
4	171.9	197.4	209.9
5	173.5	190.6	205.8
Average	**168.4**	**199.7**	**203.48**

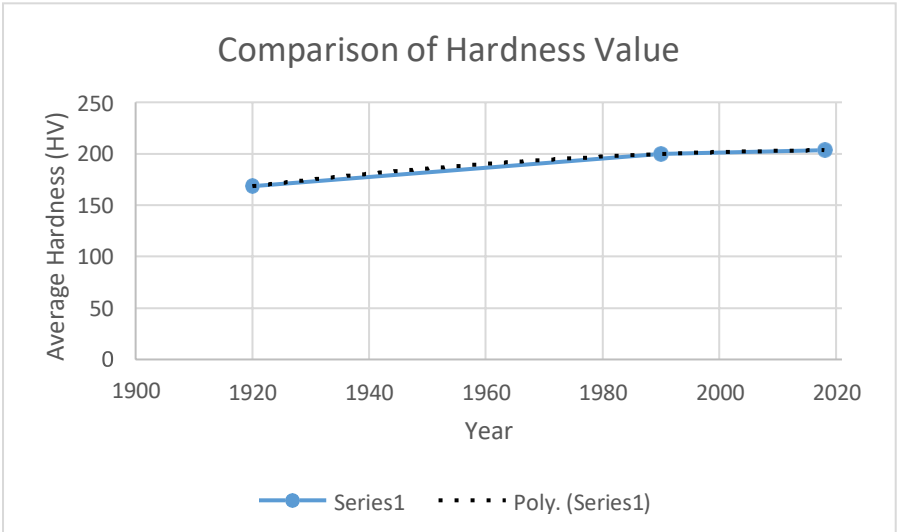

Figure 16: *Comparision of hardness values*

The above data is obtained from the Vickers hardness test. Initially, each sample has been tested using Vickers hardness at different load conditions and the data has been recorded as shown in the above tables. Again, the samples are tested by keeping the load constant at 2kg and the average is calculated. With the data obtained Figure 16 it is analyzed that the sample 2018 has the highest hardness followed by sample 1990 and sample 1920. Also, the standard deviation is 15.69 which demonstrates how widely your data is dispersed around the mean or average.

5. Conclusions

Gray cast iron is the material which is widely used in every industry. Gray cast iron is an ideal foundation material for various engineering components such as cylinder blocks, cylinder heads, oil cooler covers, brake drums, etc. Its outstanding castability, good mix of mechanical and physical qualities, low cost, and ease of manufacturing. Tensile strength, modulus of elasticity, impact strength, and damping capacity are essential mechanical qualities for such castings. The elements found in traces in gray cast iron have a significant impact on the graphitic structure and characteristics. As a result, users and producers of such data need to understand the ramifications. When trace element levels are lower or greater than the typical value, their impact on characteristics and graphitic structure becomes significant.

In this thesis, three different samples from 1920, 1990 and 2018 were chosen. All the three samples are varyingly differently from each other with their microstructure, the properties, and the various amount of concentration. The properties are analyzed and studied with the help of various experiments using XRF, optical microscope and Vickers hardness test.

Over the years, the microstructure, concentration of various elements in the GCI and the hardness has been changed. We can see, the sample 2018 has more hardness and strength because of the amount of chromium concentration and the test results done by the Vickers hardness followed by sample 1990 and sample 1920. This is because of the chemical composition and effect of impurities over the years.

6. Future works

In the future, as the industries like cars, trucks, and many automobiles increasing rapidly they should have the significant knowledge about the impurities, trace elements and to compensate the impact on the industry. Further, research can be done along the production of various parts using gray cast iron which results in increased properties of the material. We know many properties have the direct impact on the machinability so future works can be made to analyze this. Also, effect of graphite structure and the concentration of various elements on the properties of materials can be examined and studied for betterment of industries.

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