Development of iron-iron carbide composite by planetary milling and conventional sintering

Thesis submitted in partial fulfilment of the requirements for the award of the degree of

Master of Technology

in

Mechanical Engineering

by

George Lenin T.M

212MM2419

[Specialization**:** Steel Technology]

Department of Metallurgical and Materials Engineering

National Institute of Technology

Rourkela-769008

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Under the guidance of

Prof. D. Chaira

Department of Metallurgical and Materials Engineering

National Institute of Technology Rourkela

Rourkela, Orissa-769008

May 2014

National Institute of Technology

Rourkela

Certificate

This is to certify that the project entitled **"Development of iron-iron carbide composite by planetary milling and conventional sintering"** submitted by George Lenin T.M (212MM2419) in Department of Metallurgical and Materials Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the report has not been submitted to any other University/ Institute for the award of any degree or diploma.

Date:

Prof. D. Chaira

Dept. of Metallurgical and Materials Engineering

National Institute of Technology Rourkela

National Institute of Technology Rourkela

Declaration

I certify that

a) The work contained in the thesis is original and has been done by myself under the general supervision of my supervisor.

b) The work has not been submitted to any other Institute for any degree or diploma.

c) I have followed the guidelines provided by the Institute in writing the thesis.

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Abstract

Fe-6.67 wt. %C and Fe-1 wt. %C powders were milled in a dual drive planetary mill for 40 h. It has been found that there is a formation of Fe_3C and other iron carbides after 40 h of milling. However, the formation of iron carbide is more in the case of Fe-6.67 wt. %C as compared to Fe-1 wt. %C. The reduction in particle size is very fast up to 10 h of milling and after that it remains constant. It has been found that after 40 h of milling particle size is 10.47μm and 10.59 μm for Fe-6.67 wt. %C and Fe-1 wt. %C respectively. It has been also found from SEM that the powder particles are flakey in nature at the initial milling period due to the ductile nature of iron but in later stages powder become brittle and breakage takes place. Maximum density was obtained 65.47 and 62.28 for Fe-6.67%C and Fe-1wt. %C sintered at 1250ºC for 1.5 h, similarly maximum Vickers hardness 836 and 780 are obtained for Fe-6.67 wt. %C and Fe-1 wt. %C sintered at 1250ºC for 1.5 h. From wear study it is established that wear depth is less for Fe-6.67 wt. %C as compared to Fe-1 wt. %C. It is also found that wear depth decreases with increase in sintering temperature and sintering time due to the higher density and hardness.

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1. Introduction

1.1. Background

The development of technology in every field demands modern materials which possess certain properties which cannot be met by conventional material processing techniques and conventional materials like ceramics, polymers, and metal alloys, development of composites are a way to achieve these materials with desired properties [1].

The ever increasing demand for materials with unusual properties has accelerated the development of advanced materials and it is well known that the structure and constitution of advanced materials can be better controlled by non-equilibrium processing methods like mechanical alloying, plasma processing, vapor deposition and rapid solidification technique [2]. The presence of iron carbides in steel improves the mechanical properties of steel but conventional route of carbide formation requires a huge instrumentation, mechanical milling is an efficient method to produce metal carbides at room temperature [3].

Iron, iron-carbide composites can be used in applications in which high strength, hardness and wear resistance are required. In a predominantly ferritic matrix the homogeneous distribution of carbide improves the wear resistance, its important applications are machine tool and die and it can also be used in applications like dump bed liners of huge trucks used in construction and mining, for excavation process (wear resistant plate), compression spring and high wear applications, rail steel, pre-stressed concerts, high strength bars etc.

1.2. Objectives of the project

1. Fabrication of Fe-Iron carbide composite by planetary milling

2. Study the effect of milling time on the formation of iron carbide

3. Characterization of iron-iron carbide composites and property evaluation

2. Literature review

The study of Fe-C system has received a greater attention because of its importance in steel industry. This leads to the necessity of development of high carbon content carbides like Fe_3C which influence the properties of the steel to a greater extent. These carbides are metastable and hence it is difficult to produce by conventional methods; hence ball milling or other high energy milling techniques are used to develop these carbides [4].

Mechanical alloying was started in 1960 to produce oxide dispersion strengthened super alloys, now a days this technique is widely used to develop a variety of non-equilibrium alloys like intermetallic, solid solution and glassy alloys, the recent developments of mechanical alloying are in the fields of formation of metallic glasses, use of metal particles in combustion and development of homogeneously dispersed nano composite, mechanical alloyed powder also be used to produce powder condition without consolidation like catalysis, pigments, solder, hydrogen storage materials etc [5].Mechanical alloying is a process in which the powder particles were subjected to repeated fracture cold welding and deformation, the new surface formed helps in reaggregation of the powder with the formation of powder particles, the microscopic techniques like SEM, TEM helps us to analyze the nanocrystelline size and particle size distribution [1].

2.1 Mechanism of mechanical alloying

During the high energy milling process as the grinding media (usually balls) colloids some powder particles gets trapped in between them, normally about .2g of powder which is around1000 particles get trapper in each collision, hence a large value of force is exerted on the entrapped powder particles and this leads to work hardening and fracture of the particle. In the initial stages of milling the particles are soft, the new surface created due to collision enables the particles to weld together and this leads to an increase in particle size, there for in early stages of milling the tendency to form large particle is high. At the initial stages the composite particle have a layered structure and this consist of various combination of starting composition, in this stage the size of the particles varies widely some particles formed may be have a size three times

bigger than initial particle size, as the milling proceeds the particles gets work hardened and fractured by fragmentation of fragile flakes or/and by the fatigue failure mechanism, in absence of strong agglomeration forces the fragments generated by this mechanism may continue to reduce in size, at this stage of milling the tendency to fracture predominates over cold welding and the particle size continuous to be same and the structure of the particle remains same due to the continued impact of grinding balls, as a result of this the inter lamellar spacing decreases and the number of layers in a particle increases. The important components of mechanical alloying process are raw materials and process variables [1].

2.2 Attributes of mechanical alloying

2.2.1 Production of dispersion of second phase (usually oxide) particles

2.2.2 Extension of solid solubility limits

2.2.3 Refinement of grain sizes down to the nanometer range

2.2.4 Synthesis of novel crystalline and quasicrystalline phases

2.2.5 Development of amorphous (glassy) phases

2.2.6 Disordering of ordered intermetallic

2.2.7 Possibility of alloying of difficult to alloy elements

2.3 Process variables

The parameters which affect the final composition of the powder is called process variables. They are listed as follows.

2.3.1 Type of mill

2.3.2 Milling container

2.3.3 Milling speed

2.3.4 Milling time

2.3.5 Type, size, and size distribution of the grinding medium

2.3.6 Ball-to-powder weight ratio

2.3.7 Extent of filling the vial

2.3.8 Milling atmosphere

2.3.9 Process control agent

2.3.10 Temperature of milling

2.3.1 Types of mill

Some important types of mills used to produce mechanically alloyed powder are given below [3]

1. Planetary ball mill
2. SPEX shaker mill
3. Attritor mill
4. Commercial mills

1. **Planetary ball mill**

   Because of the planet like motion of vial the name planetary ball mill, the vials are mounted on rotating disc and the vials also rotates its own axis. The centrifugal force produced due to the rotation of container and the disc acts on the vial contents. In this mill a few hundred grams of powder can be milled at a time.

2. **SPEX shaker mill**

   Usually it contains a single vial it clamped to the mechanism which swag back and forth and the ends of the vial have a lateral movement hence the vial describes a figure infinity as it moves. The capacity of the mill is about 10-20 grams.

3. **Attritor mill**

   Unlike the other mills here the milling vial is stationary, the powder to be milled is placed in the container and it is agitated by a shaft with arm rotating at high speed, attritor mills with capacity .5 to 40 kg are available.

4. **Commercial mills**

   Commercial mills are used for industrial applications, they are having much larger size and capacity. Commercial mills can process several hundred kilograms at a time.

As described above different types of mill is used for mechanical alloying, these mills very from one another in speed, capacity, ability to control temperature etc. hence a suitable mill can be choose depending on the requirement.

2.3.2 Milling container

Stainless steel, hardened steel, tempered steel, chromium steel, tool steel and WC-lined steel are the some of the common examples for milling container material, the selection of milling container is very important since the powder comes in direct contact with the inside surface of the container, if the mill material is different from the powder the contamination of the powder may occur, and if the milling vial material is different from powder there is a chance of alteration of the initial chemical composition of the powder.

2.3.3 Milling speed

It is obvious that as the milling speed increases the input energy to the powder increases but there is a limit to which the speed can be increased depending on the type of mill, in conventional ball mill if we increase the speed to a certain value the balls will pinned to the inner walls of the vial hence no more milling can be happen, therefore it is important to keep the speed of the mill below the critical value, the temperature developed inside the mill is also depend on the milling speed in some cases the temperature increase is advantageous but in other cases it adversely affect the final powder composition hence choosing of suitable speed is important.

2.3.4 Milling time

The milling time selection depends on factors like type of mill, intensity of mill, ball to powder ratio and the temperature of milling, usually milling time is chosen as the time required to establish a balance between cold welding and fracturing of the particle.

2.3.5 Grinding medium

The size of the grinding medium and the material of grinding medium are important parameters in MA, the commonly used materials are Stainless steel, hardened steel, tempered steel,

Chromium steel, tool steel and WC-lined steel etc. The size of the grinding medium also having an important effect on final composition of the powder as the size of the ball increases the energy transferred to the powder is also increases, and it is observed that the use of different sized grinding medium increase the efficiency of milling.

2.3.6 Ball to powder ratio

The commonly used BTPR is 10:1 but in certain cases it can be very from 1:1 to 200:1, for large size mills like attritor mill this ratio can be 50:1 to 100:1. Higher the BTPR shorter the time required for milling.

2.3.7 Extent of filling the vial

There should be enough room for the powder particles and balls to move freely inside the container, if the container is filled excessively the impacts will be less and if the filing of vial is less the production rate will be very less hence it is important to choose the right amount of powder in the vial, it is usually 50 % of the volume of the vial.

2.3.8 Milling atmosphere

Milling atmosphere has an important role hence it affect the contamination of the powder in a greater extent. Usually the milling vials are evacuated or filled with inert gas such as argon or helium and the loading and unloading should be carried out in atmosphere controlled glove box to avoid contamination, some investigators even conducted the milling in evacuated glove box to avoid contamination.

2.3.9 Process control agents

Process control agents used to control the cold welding occurring during the milling process, an efficient alloying can be occur between the powder particles only when a balance is maintained between cold welding and fracturing. The process control agents can be solid, liquid, gas they are mostly organic compounds.

2.3.10 Temperature of milling

Temperature of milling have an important effect in any alloy system, which is an important parameter influence the constitution of the milled powder.

2.4 Problems in mechanical alloying

Although mechanical alloying have so many advantages it also suffers from some problems, they are [6]

2.4.1 Powder contamination

2.4.2 Limited science content

2.4.3 Limited application

2.4.1 Powder contamination

The major factors contributes to the powder contaminations are time of milling, grinding vessel, intensity of milling, grinding media and milling atmosphere, formation of new surface during milling, availability of large surface area and the small size of the particle

Methods to prevent contamination

(a) Use of high purity atmosphere (b) Use of high purity metals (c) Self-coating of balls with the milled material (d) Use balls and container of the same material that is being milled, (e) Short milling time

2.4.2 Limited science content

Mechanical alloying is a complex process involving a large number of variables, although it is a famous method but it is not clear that how and why the technique works. It has been not possible to provide the final chemical composition for a given condition.

2.4.3 Limited application

The process mechanical alloying have a very few industrial applications, although many potential many potential applications have been suggested for mechanical alloying, many of them are not industrial related.

The technique mechanical alloying is originally developed to produce ODS super alloys around 1966 and it also used to produce PVD (physical vapor deposition) commercially for electronic

industry, the process of mechanical alloying starts with the mixing of powders at desired composition and which is then loaded to the milling container with suitable milling medium, and its milled for desired time period then the milled powder is consolidated to pellets and then heat treated to get required properties [2].

Aricet et al. [7] prepared Fe-Fe_3C by mechanical alloying from elemental iron and graphite powder and then powders were sintered at temperatures 1125, 1150 and 1175°C in argon atmosphere for 2h in a tubular furnace. They showed that milling results in finer powder particles with homogenous distribution of carbon in iron and the green density decreases due to work hardening during milling. As a result, Fe_3C is formed and the amount of Fe_3C increases with milling time. The transverse rupture strength and density also increases with sintering temperature. **Campbell** et al. [8] observed the formation of Fe_3C, Fe_7C_3 by ball milling powder of $Fe_{75}C_{25}$composition and they found amorphous Fe_3C phase could be produced within a milling time of 70 h. They noticed crystalline Fe_3C was produced in 140 h, extended milling up to 285 h results in the formation of crystalline Fe_7C_3 phase (75%).

Chaira et al. [9] studied the formation of iron carbide powder in a special type dual drive high energy planetary ball mill by milling elemental iron and graphite powder for 40 hours. They showed that dual drive planetary ball mill is more efficient than commercially available planetary ball mill. The conclusions obtained from this study are as follows, at the initial stage of milling (2 h) flattening of powder occurred, and the particle size is enhanced due to cold welding, during further milling work hardening of the powder takes place, in the final stage of milling fracturing of cold welded powder occurred and the morphology of sample has changed to spherical from flake. The stability of cementite formed was studied by DTA and annealing and it has been observed that the decomposition of meta-stable cementite phase taken place above 800^oC. **Gosh** et al. [10] milled pure iron and graphite powder in argon atmosphere and observed the formation of stoichiometric Fe_3C phase after 40 hours of milling without any contamination.

Chen et al. [11] prepared nanocrystelline Fe-C alloy with variable carbon concentration in a Fritsch planetary mill. They used zirconium grinding bowl and grinding balls. They found that nano crystalline ferrite crystals are formed whereas higher concentration of carbon formed a

mixture of Fe-Fe_3C. **Roblesh** et al. [12] milled 85% Fe and 15% graphite; 85% Fe and 15% fullerene separately. Then the powders were consolidated by spark plasma sintering technique (SPS) at 773 K and 100 MPa. They found that in Fe-$C_{graphite}$ composite FeC_3 was formed whereas in Fe-$C_{fullerine}$ composite, carbide was not formed. **Nowosielski** et al. [13] took Fe and graphite powder and mechanical alloying was carried out in a high energy Spex 8000 mill under inert (argon) atmosphere. The conclusions obtained from this study are massive iron carbide materials can be produced by mechanical alloying and impulse plasma sintering. The sintering temperature of 900^oC causes further crystallization of cementite. The hardness value of the sintered product obtained was 1300HV.

Kathikar et al. [14] milled high purity iron powder in a Fritsch P5 planetary high energy ball mill for 20 h, and XRD analysis shows that the peaks become substantially broadened after milling. This is due to the reduction of crystal size and introduction of defects. They found from SEM studies that at the initial stages of the milling, the particles become flat, and upon further milling the particle brakes and size reduction occurs. **Chen** et al. [15] studied the non-equilibrium transformation during high energy ball milling of iron powder. NH_3 was taken as nitriding atmosphere. XRD and Mossbauer spectroscopy revealed phase transformations during milling and subsequent thermal annealing. It was also found that a competition exist between the reaction with NH_3 and the decomposition reaction during milling process. **Wang** et al. [16] milled pure iron powder and activated carbon for 210 h in a high energy planetary ball mill and subsequently the milled powder were annealed at 500^oC. On examination of the sample it was shown that the metastable Fe_3C and Fe_7C_3 phases were formed during milling, and it is also found that the environment or state of carbon does not significantly affect the rate of formation of carbides.

Hussain et al. [17] investigated the microstructure of the milled Fe-C powder and studied the hardness of consolidated samples. They found that hardness increases with increase in milling time up to 6 h beyond which it was decreased. They also observed that the hardness value increased with increase in carbon concentration up to 2 % then it was found to decrease at 3 and 4 wt. % C because of the presence of more pores and residual graphite.

Hidaka et al. [18] studied the relationship between the hardness and microstructure of mechanically alloyed powder with initial composition Fe-.63 wt% C and small amount of Cr, Si and Mn. Milling was carried out in a planetary ball mill in argon atmosphere and they found that the hardness of the alloy depends on the grain size of ferrite not the volume fraction of retained cementite.

3 Experimental details

3.1 Development of iron-iron carbide composite

3.1.1 Mechanical alloying

The elemental powders of Fe and graphite (purity> 99%) of the compositions Fe-6.67 wt.% C and Fe-1 wt. %C were subjected to milling in a high energy dual drive planetary mill. The main shaft rotates at 275 and jar rotates at 620 rpm. Stainless steel ball of 8 mm diameter was used and milling was conducted under toluene to prevent oxidation. Powder samples were collected from the mill after 0, 1, 2, 5, 10, 15, 20, 30 and 40 h of milling for characterization. The milling parameters are mentioned in Table 1.

Table 1 Milling parameters used

Mill type	High energy dual drive planetary ball mill
Milling time	0, 1, 2, 5, 10, 15, 20, 30 and 40 h
Process control agent	Toluene
Milling speed Main shaft Jar	 275 620
Grinding media	Stainless steel ball
Ball diameter	8 mm
Ball to powder ratio by weight	5:1
Jar volume	1000ml

3.1.2 Compaction and sintering of milled powder

The 40h milled powder was subjected to compaction using a uni-axial hydraulic compaction press under a pressure of 665MPa. The pellets were then sintered in tubular furnace under argon atmosphere. Details of sintering parameters are mentioned in Table 2.

Table 2 Details of sintering parameters

Compaction pressure	665 MPa
Relaxation time in compaction	5 min
Sintering temperature	1000^{o}C, 1250^{o}C
Soaking time	1.5 h, 2h
Sintering atmosphere	Argon
Heating rate	10^{o}C/min

3.2 Microstructural characterization

3.2.1 X-Ray diffraction

The powder samples at different milling time and polished pellets at different sintering conditions were characterized by PAN analytical model: DY-1656 XRD machine by using Cu-Kα (=1.5418^{o}) radiation to determine the evolution of phases at different stages of mechanical milling and different sintering conditions. The scanning range was 20^{o}-100^{o} and step size was 3^{o}/min.

3.2.2 Scanning electron microscopy

The morphology of milled powder at different milling time was determined by a JEOL JSM-6480 LV scanning electron microscope. Micrographs are taken at suitable accelerating voltages for the best possible resolution.

3.2.3 Optical microscopy

The sintered pellets were polished to mirror like finish and then etched with nital (98% ethanol 2% nitric acid) to make the microstructure more clearly visible. The micrographs of the sample with different magnifications were taken for analysis.

3.3 Study of mechanical properties

3.3.1 Hardness measurement

The hardness of the samples was measured by using Vickers hardness tester (Leco Micro-hardness Tester LM248AT). A load of 50gf was applied for a dwell time of 10 seconds. Minimum 8 measurements were taken at equivalent location for each sample to get consistent results.

3.3.2 Wear study

To study the wear behavior of pellets sintered at different conditions Ball-on-plate wear tester (Ducom, TR-208 M1) was used. Stainless steel ball of 4 mm diameter rotates on pellet with a speed of 20 rpm for a time of 5 minutes and the experiment was carried out under constant load of 20 N.

3.4. Study of density

Density of the sintered samples were measure by the formula

$$D = \frac{\mathrm{M}}{V}$$

Where D=density

M=mass of pellet

V=volume of pellet

4 Result and discussion

4.1 Characterization of the milled powder

4.1.1. X-Ray diffraction study

Figure 1(a) shows the XRD spectrum of Fe-6.67 wt. %C milled for different time. It can be seen from the XRD spectra that peak width increases with increase in milling time. The increase in peak width is due to introduction of lattice strain and reduction in particle size during milling. It also can be found that graphite become amorphous after 10 h of milling; hence no peak of graphite is present after 10 h of milling. It is found that after 20 h of milling there is a formation of Fe_3C, Fe_7C_3 and Fe_2C.

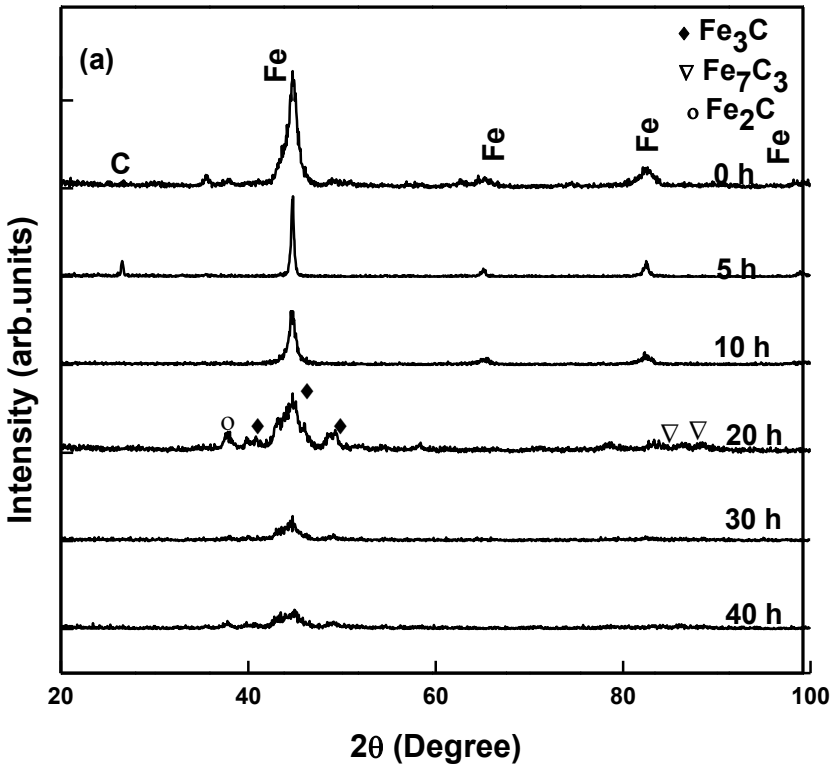

Figure 1(a) XRD spectra of powder of initial composition Fe-6.67 wt. %C Milled for 0, 5, 10, 20, 30, 40 h.

Figure 1 (b) shows the XRD spectra of Fe-6.67 wt. % C milled for 20 hours with very slow scan speed in the range of 2θ (30-50°). The spectrum shows the strong peaks of Fe3C along with Fe.

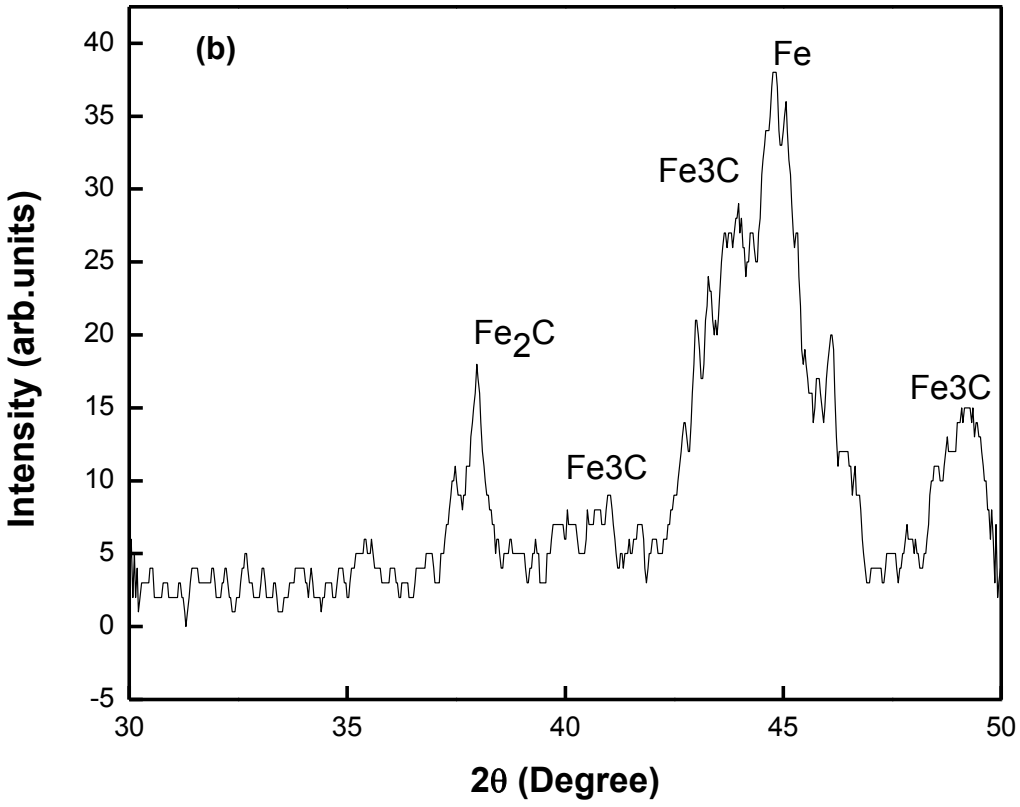

Figure 1 (b) XRD spectrum of strongest peak at slow scan for Fe-6.67 wt. % C milled for 20 hours.

Figure 2 shows the XRD spectrum of Fe-1wt. % C milled for different time. It is also observed here that peak width increases with milling time. However, formation of Fe_3C and other iron carbide is less as compared to Fe-6.67 wt. % C. Chaira et al. also showed that formation of iron carbide is highest for stoichiometric composition of Fe_3C (Fe-6.67 wt. % C).

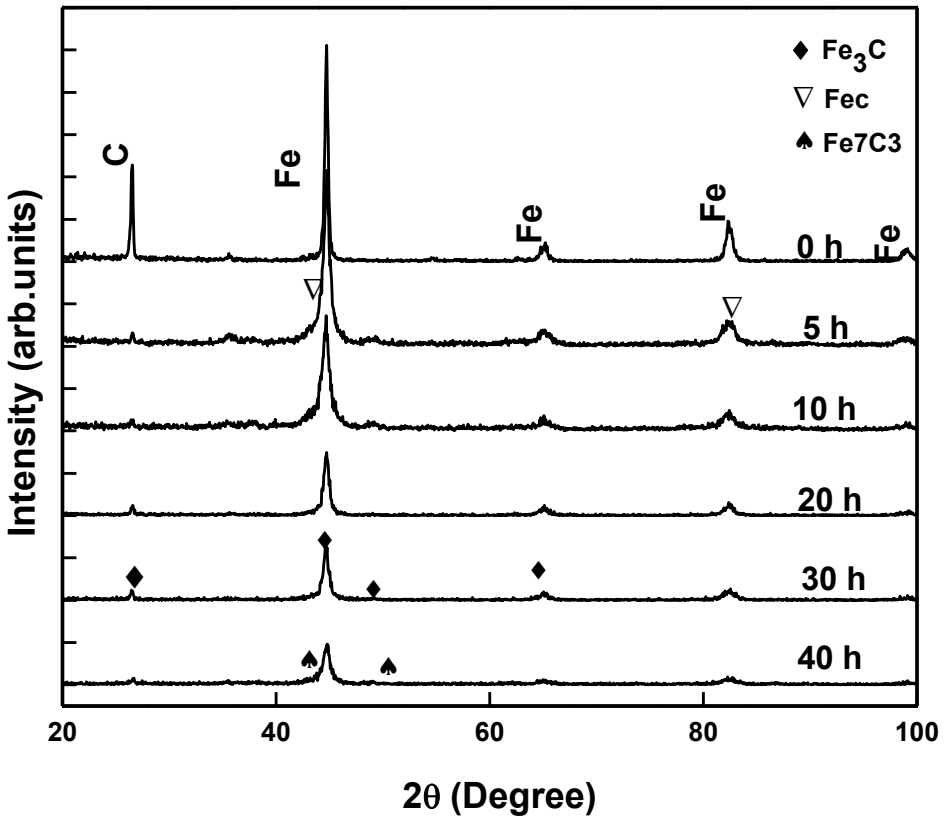

Figure 2 XRD spectra of powder of initial composition Fe-1 wt. %C Milled for 0, 5, 10, 20, 30, 40 h.

4.1.2. Scanning electron microscopy study

Figure 3 shows the SEM images of Fe-6.67 wt. % C milled for different time. As iron is ductile, during milling powder particles are cold welded together and become flakey at the initial milling period. But in later stage powder particle become strain hardened and brittle and size reduction takes place. It can be seen that initial powder is large (<50 μm) and agglomerated. After 40 h of milling powder size is around 5-10 μm.

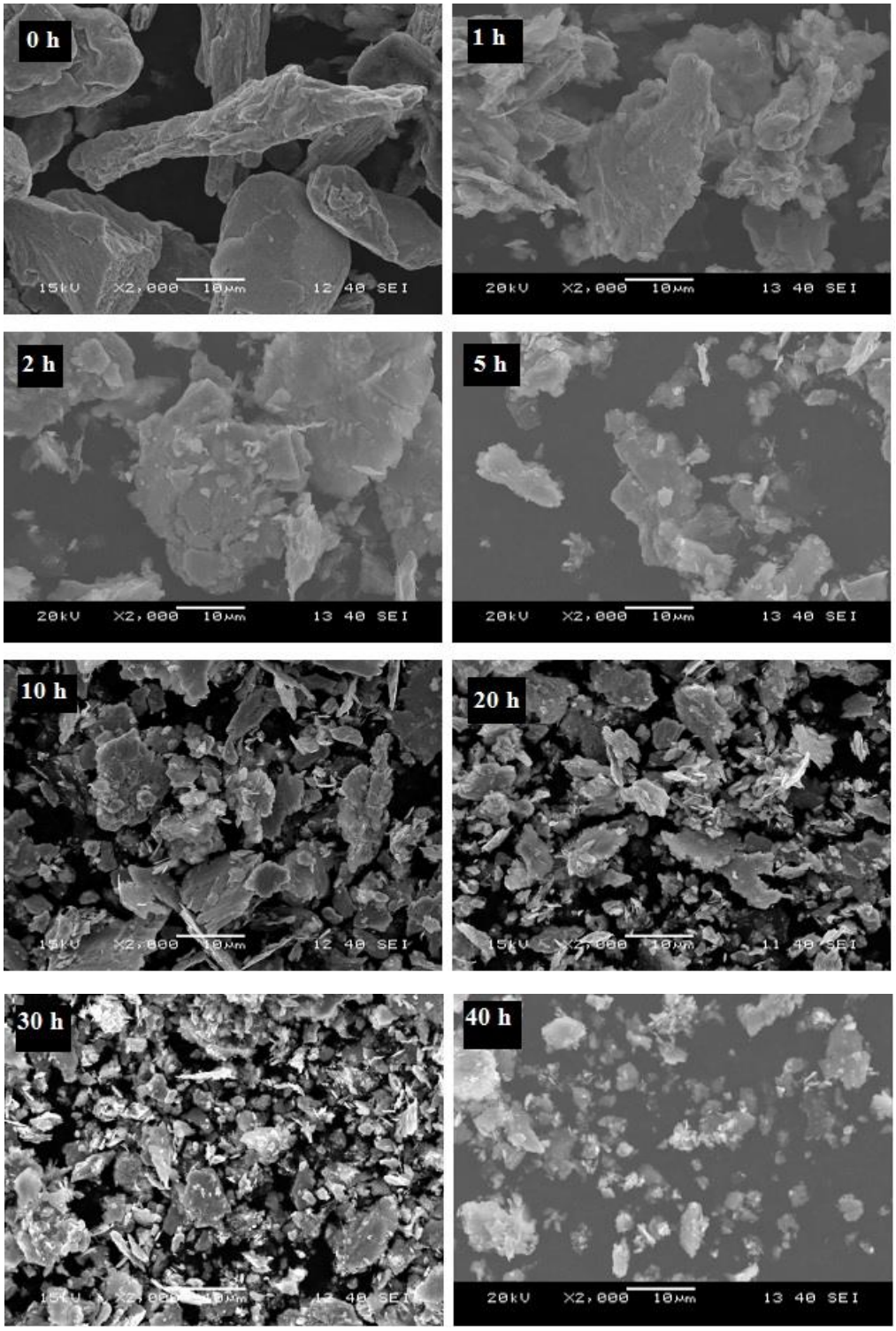

Figure 3 SEM images of milled powder of composition Fe-6.67 wt. %C at different milling time

4.1.3. Particle size measurement

Figure 4(a) and 4(b) show the particle size distribution of Fe-6.67 wt. %C and Fe-1 wt. %C milled for different time. It is seen that the particle size distribution curve shift to left side of the graph, indicates that particle size reduction takes place with milling time.

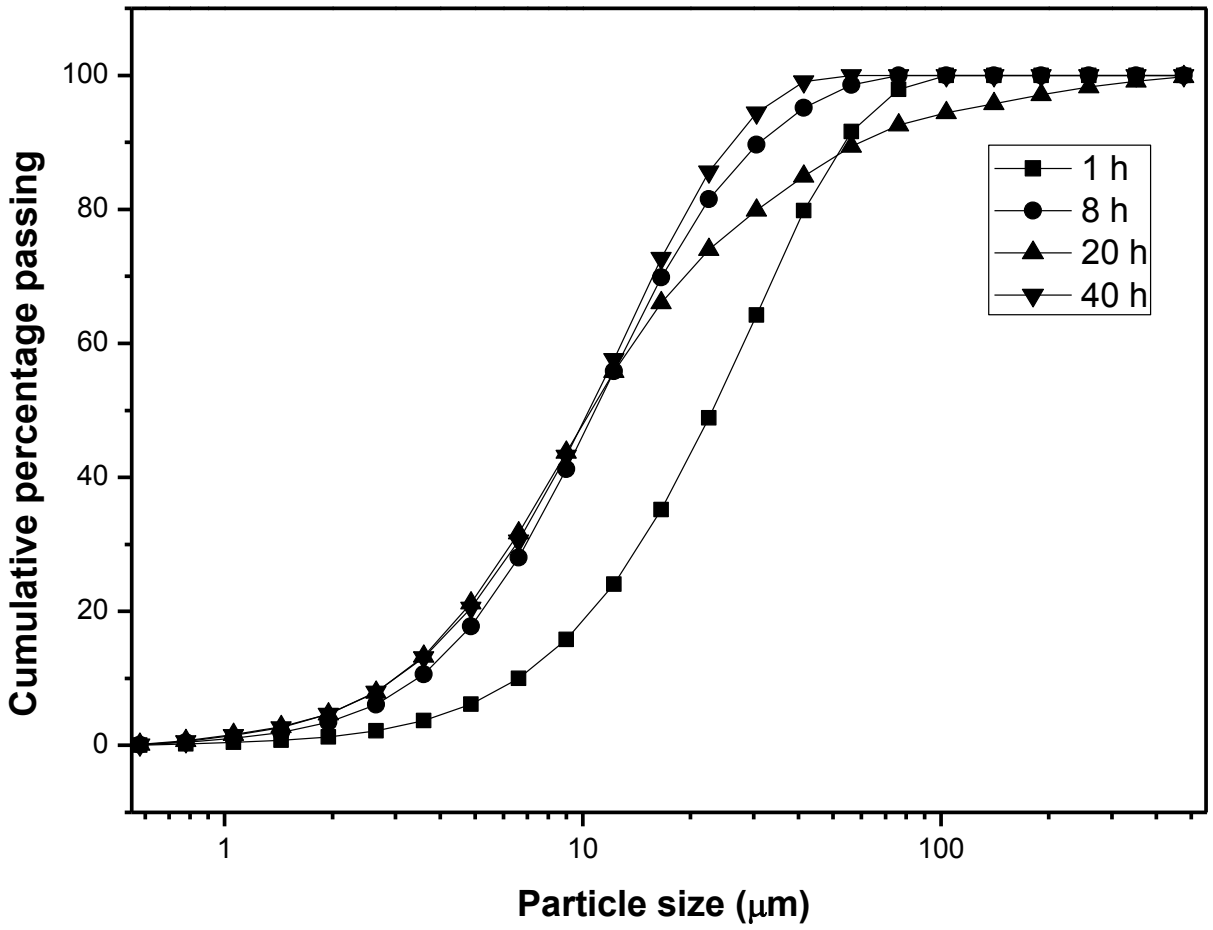

Figure 4(a) Particle size distribution of Fe-6.67 wt. %C

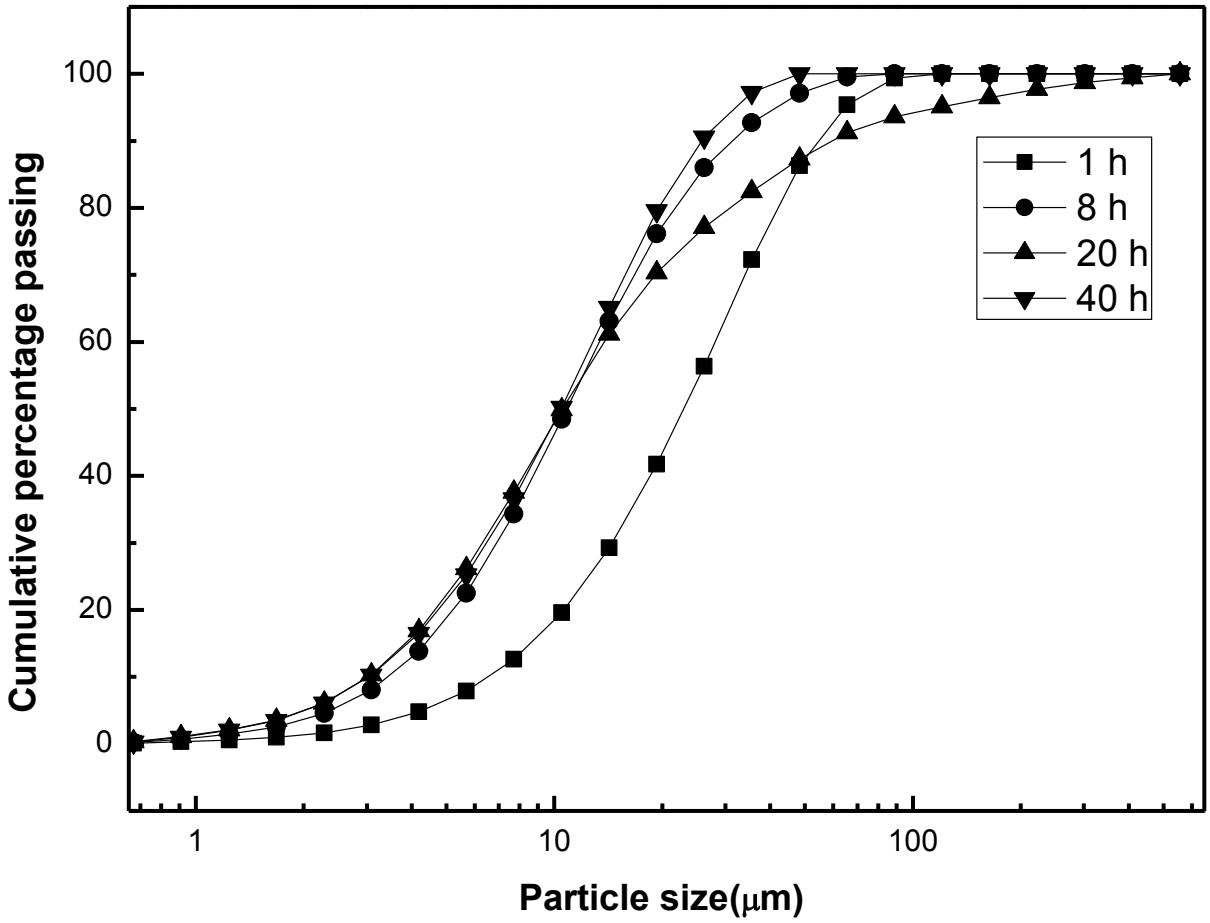

Figure 4(b) Particle size distribution of Fe-1 wt. %C

Figure 5 shows the variation of average particle size with milling time for Fe-6.67 wt. %C and Fe-1 wt. %C. It seems that initially (up to 10h) size reduction is very fast but in later stage size remains almost constant with milling. After 10 hours of milling the size remains almost constant for both cases. After 10 hours of grinding, it has reached its limit, called limit of comminution. The reason is that the rate of cold welding and fracture are almost equal. After 40 h of milling the average particle size are 10.47μm and 10.59 μm for Fe-6.67%C and Fe-1 wt. %C respectively

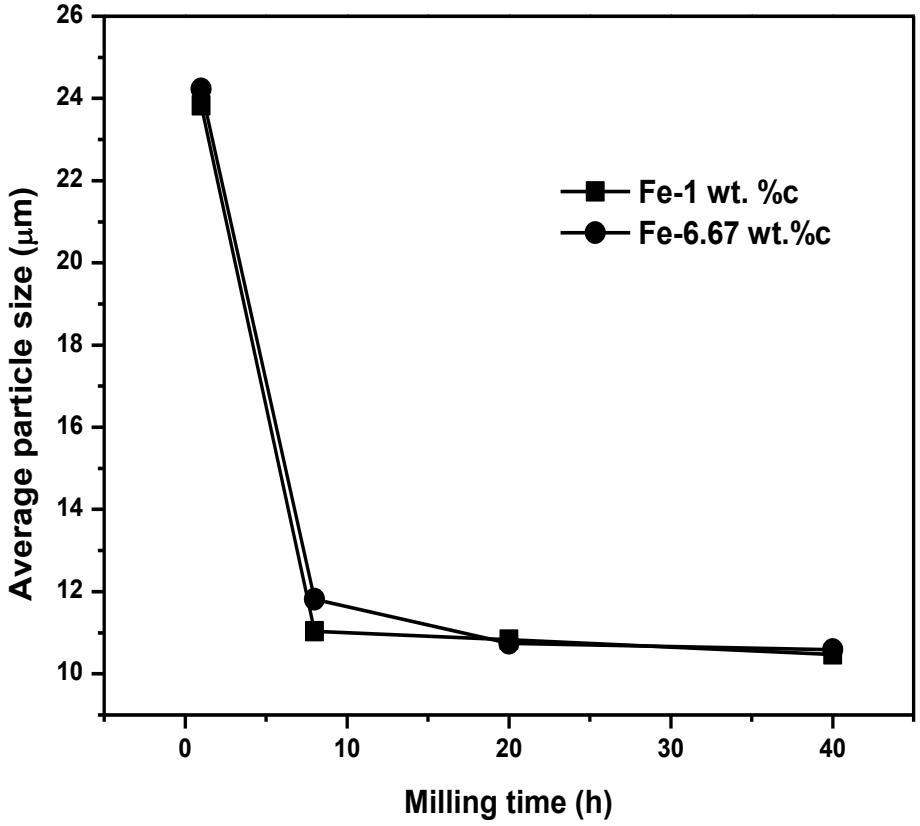

Figure 5 variation of average particle size with milling time for Fe-6.67 wt. %C and Fe-1 wt. %C

4.2 Consolidation of iron-iron carbide composite

The powders were compacted in cold uni-axial press and sintered in a tubular furnace at 1000, 1250ºC for 1.5 and 2h under argon atmosphere respectively. Finally the composites were characterized by different characterization techniques.

4.2.1 X-Ray diffraction study

Figure 6 (a) and (b) show the XRD spectra of Fe-6.67 wt. % C and Fe-1 wt. % C sintered at 1000ºC for 2 and 1.5 h. XRD spectra shows the presence of different iron carbides along with iron. It is also found that peak width decreases in both cases as compared to 40 hours milled powder after sintering. The reason is due to the relief of internal stress and grain growth after sintering. Milled powder contain large amount of stress and fine crystals due to the impact between powders and balls.

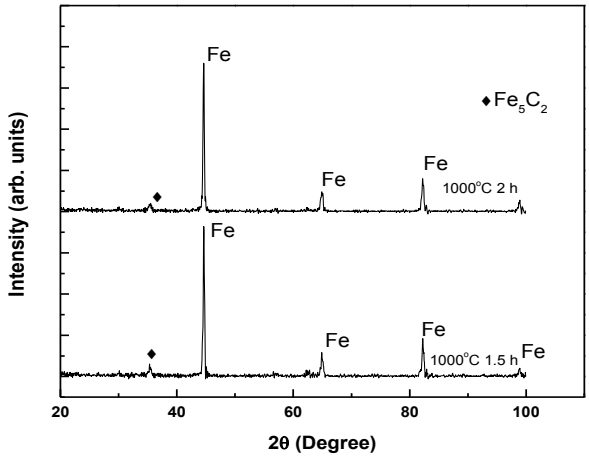

Figure 6 (a) XRD spectra of sintered pellets of composition Fe-1 wt. %C

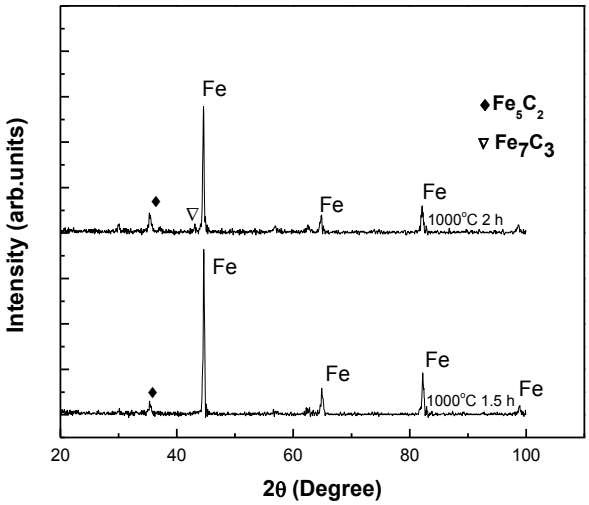

Figure 6 (b) XRD spectra of sintered pellets of composition Fe-6.67 wt. %C

4.2.2 Optical microscopy study

Figure 7 (a), 7 (b) & 7 (c) show the optical micrographs of 40 hours milled Fe-6.67 wt. %C and Fe-1 wt. % C powder sintered at 1000°C for 2 hours and 1.5 hours and 1250°C for 1.5 hours. It is seen from the micrographs that the dark areas are iron carbides and residual carbon, whereas yellow colored region is iron. It is also observed that the iron carbide and residual carbon amount increases with increasing carbon percentage in the sample. Fe-6.67 wt. % C sample shows higher black region representing more amount of iron carbides and residual carbon as compared to Fe-1 wt. % C.

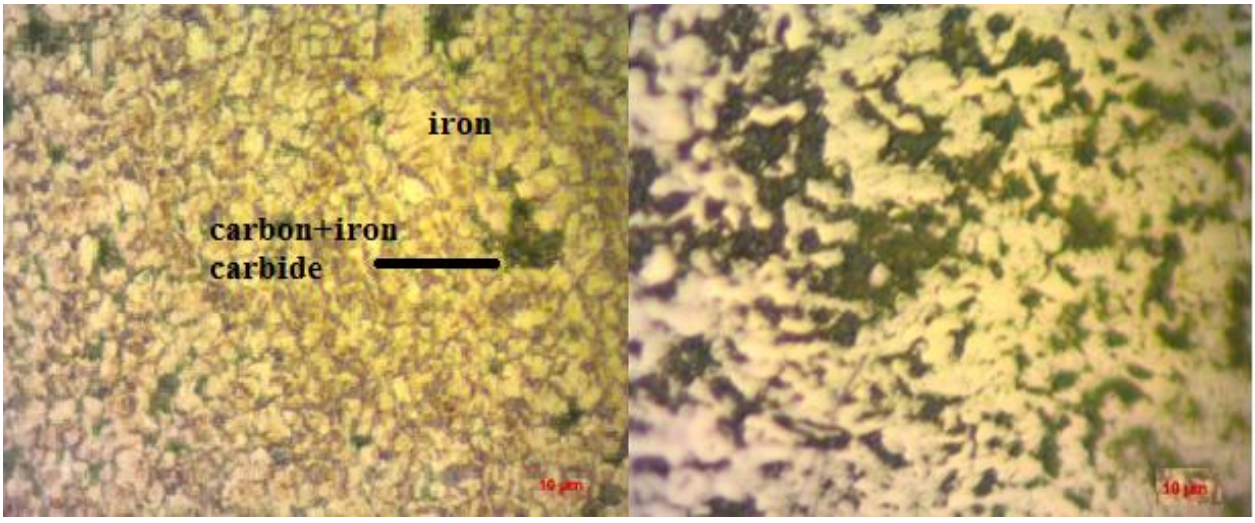

Figure 7 (a) Optical micrograph of composition Fe-1 wt. % C and Fe-6.67 wt. % C, sintered at 1000ºC for a soaking time of 2 h.

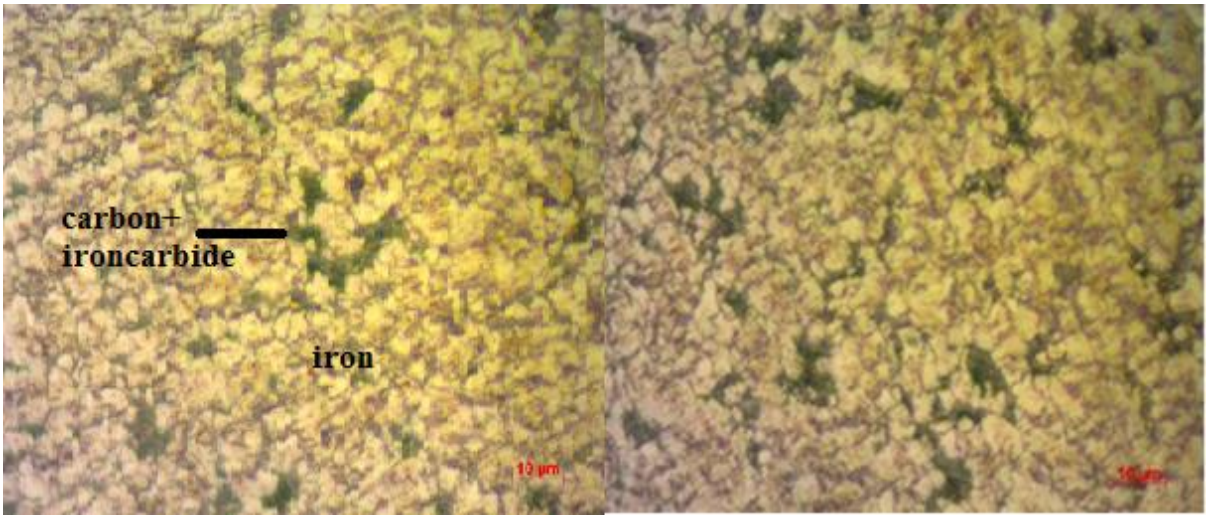

Figure 7 (b) Optical micrograph of composition Fe-1 wt. % C and Fe-6.67 wt. % C, sintered at 1000ºC for a soaking time of 1.5 h.

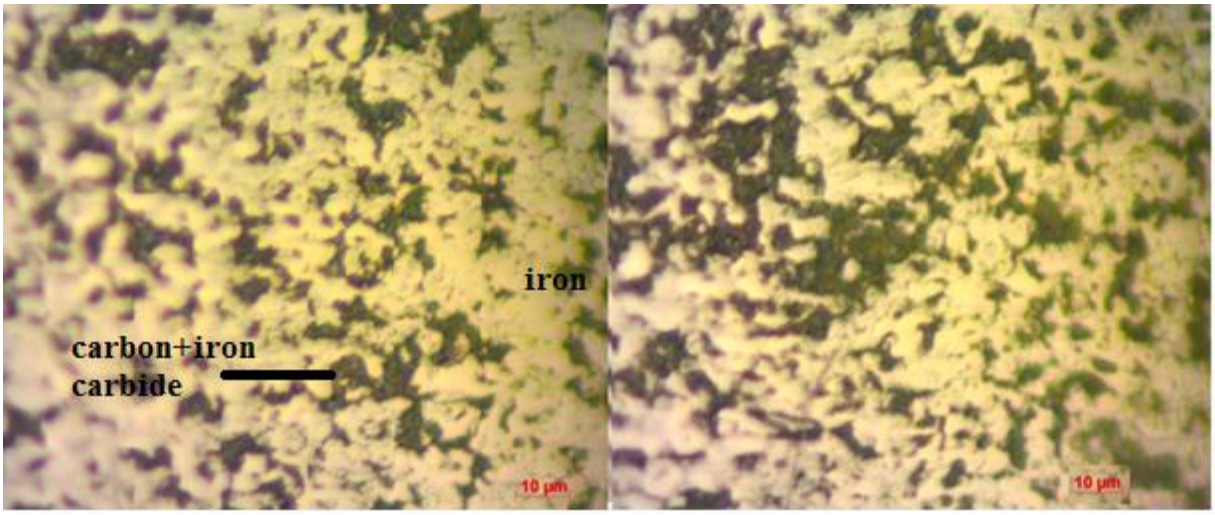

Figure 7 (c) Optical micrograph of composition Fe-1 wt. % C and Fe-6.67 wt. % C, sintered at 1250ºC for a soaking time of 1.5 h.

4.2.3 Density measurements

Figure 8 shows the variation of green density with milling time. It can be observed from the graph that green density decreases up to 10 h of milling and on further milling it increases. This is because as iron is a ductile material, at the initial stages of the milling the size of the particle increases and forms flake shape. Compaction of such powders results in high porosity and eventually density decreases. However, after 10 hours of milling particles become strain hardened and brittle. Milling of such powder results in size reduction of powders. Compaction of such powders results in less porosity and hence density increases. Hence, after 10 hours of milling green density increases continuously.

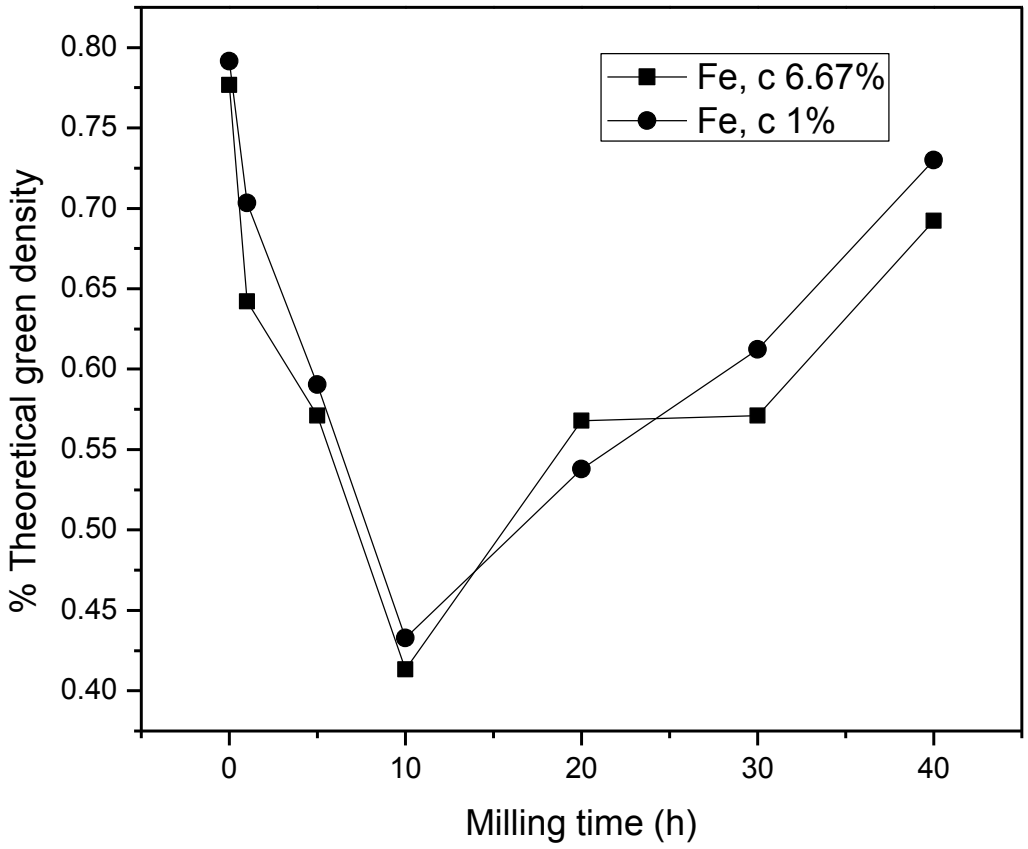

Figure 8 Variation of green density with milling time

4.2.4 Hardness study

Table 3 shows the variation of density and micro hardness for Fe-6.67 wt. % C and Fe- 1 wt. %C sintered for different times and temperatures. From the table is evident that both density and hardness value increases with increasing sintering temperature and time due to faster diffusion. As sintering temperature and time increases, bonding between particles improves and finally density and hardness increases.

Table 3 Relation between the sintered temperature, sintering time, %density and hardness of the pellets

Sample composition	Sintering temperature (°C)	Sintering time (h)	% sintered density	Vickers Micro hardness
Fe-6.67 wt. %C	1000	1.5	85.2	335
		2	89.08	379
	1250	1.5	95.06	836
Fe-1 wt. %C	1000	1.5	80.8	237
		2	85.71	301
	1250	1.5	90.7	780

4.2.5 Wear study

Figure 9 shows the variation of wear depth with sliding time for Fe-6.67 wt. % C and Fe-1 wt. % C composites sintered at 1000 and 1250^{o}C for 1.5 and 2 hours. From the graph it is found that wear depth is lower for Fe-6.67 wt. % C than Fe-1 wt. % C for the same sintering conditions. It is also found that wear depth decreases with increase in sintering temperature and sintering time. This is due to the fact that there is formation of more iron carbides in Fe-6.67 wt. % C than 1 wt. % C. As the temperature and time of sintering increases the hardness and density increases which results in more wear resistance and less wear depth. The residual graphite has a lubricating property which prevent the direct contact between the ball and the material which reduces the wear depth.

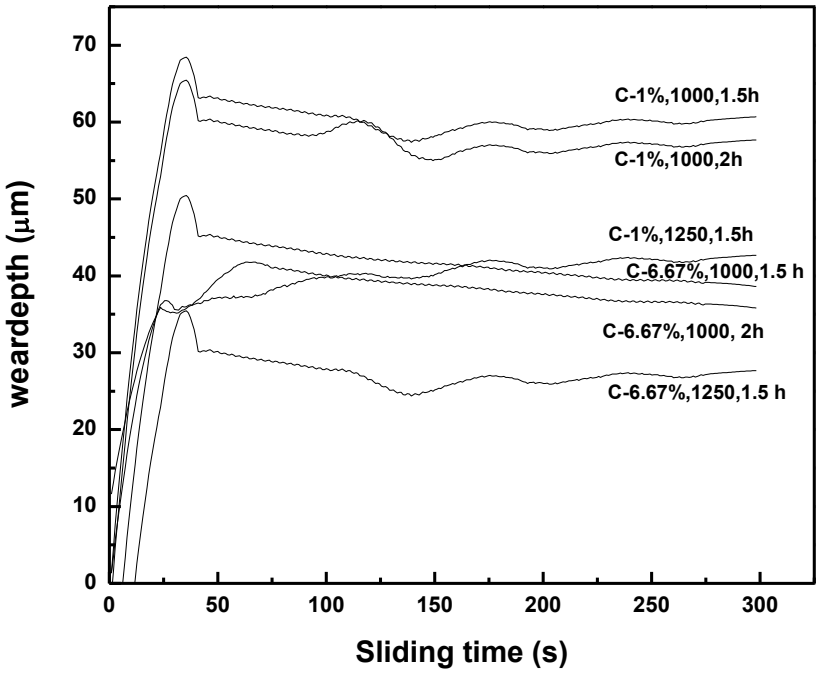

Figure 9 Variation of wear depth with sliding time for Fe-6.67 wt. % C and Fe-1 wt. % C sintered at 1000 and 1250°C for 1.5 and 2 hours

4.2.6. Surface profile study

Figure 10 shows the surface profile of Fe-6.67 wt. %C sintered at 1000°C for 2h. Surface profile was measured from surface to wear track and then surface. It can be seen from the profile the surface profile is smooth and a wear depth of about 75000A°.

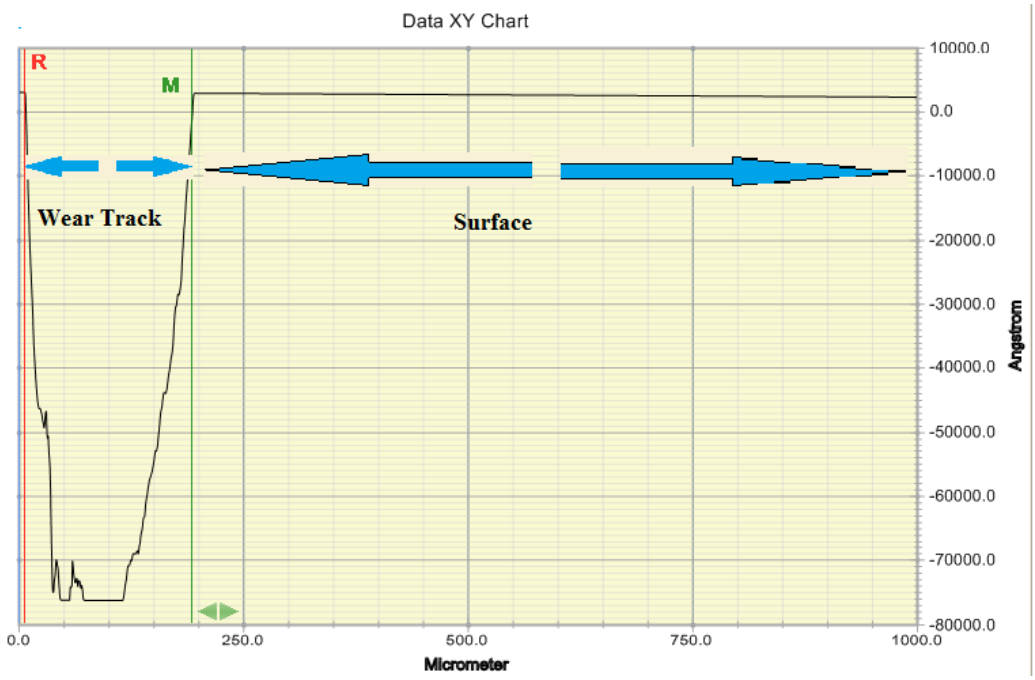

Figure 10 Surface profile of Fe-6.67 wt. % C sintered at 1000°C for 2h

5. Conclusions

1. Iron-iron carbide composite has been successfully synthesized by planetary milling followed by conventional sintering.
2. The effect of milling on the formation of iron carbide for a mixture of iron and graphite powder has been studied.
3. Initially, there is an increase in particle size due to flake formation as evident from SEM and particle size analysis. Further milling leads to strain hardening of powder and particle size decreases and remains constant after some time.
4. The XRD study shows that iron carbide has been formed by the milling of Fe and C.
5. Higher density, hardness and wear resistance are achieved for Fe-6.67 wt. %C than Fe- 1 wt. %C.

6. Future work

1. Consolidation of iron-iron carbide composite could be carried out using some advance consolidation techniques like hot pressing or spark plasma sintering (SPS) method to achieve high density and improved mechanical properties.
2. The interface of the iron-iron carbide composites can be studied by using transmission electron microscopy (TEM).

7. Reference

1. D William. Callister. “Material Science and Engineering” 7th edition, John Wiley and Sons, University of Utah, 2007, pp. 577-578.
2. C. Suryanarayana, Non equilibrium processing of materials, Pergamon materials,1999, Vol. 2, pp. 1-438
3. C. Suryanarayana, Mechanical alloying and milling, Progress in Materials, 2001, vol. 46, pp. 1-184
4. C. Suryanarayana, In: Powder metal technologies and applications. ASM Handbook, vol. 7. Materials Park, OH: ASM International, 1998. pp 80-90.
5. C. Suryanarayana. Recent developments in mechanical alloying. Adv. Mater. Sci. 2008. Vol. 18, pp. 203-218
6. C. Suryanarayana, Science and technology of mechanical alloying, progress in Materials Science, 2001, vol. 46, pp. 151–158
7. Arik, Halil, Turker, Mehmet: Production and characterization of in situ Fe–Fe_3C composite produced by mechanical alloying , Materials & Design, 2007, vol.7, pp. 31-40
8. S.J. Campbell, G.M. Wang, A. Calka, W.A. Kaczmarek, Ball milling of Fe_{75}–C_{25}: formation of Fe_3C and Fe_7C_3, Mater Sci Eng. A, A226–A228 (1997), pp. 75–79
9. D Chaira. Mishra, B.K. Sangal, S. Efficient synthesis and characterization of iron carbide powder by reaction milling. Powder Technology, 2009. Vol. 191, 149-154
10. Ghosh, B.Pradhan, S.K. Microstructure characterization of nanocrystalline Fe3C synthesized by high-energy ball milling. Journal of Alloys and Compounds. 2009. Vol. 477, pp 127-132
11. Y.Z Chen, A Herz, Y.J Li, C Borchers, P Choi, D Raabe, R Kirchheim, Nanocrystalline Fe–C alloys produced by ball milling of iron and graphite. ActaMaterialia. 2013, vol. 61, pp 3172-3185
12. F.C. Roblesh, Production and characterization of Fe-$C_{graphite}$ and Fe-$C_{fullerene}$ composites produced by different mechanical alloying techniques, Association of Metallurgical Engineers Serbia and Montenegro Scientific paper AME UDC669.15.18 (C60):621.7

13. R Nowosielski. W Pilarczyk, The Fe-C alloy obtained by mechanical alloying and sintering, journal of achievements in materials and manufacturing engineering2006, vol.18, pp 167-170
14. R.K Khatirkar, B.S Murty, Structural changes in iron powder during ball milling. Materials Chemistry and Physics 2010. Vol. 123, pp 247-253
15. Y Chen, J S Williams, High-energy ball milling induced non equilibrium phase transformations. Materials science and engineering 1997, pp 226-228.
16. G.M Wang, S.J Campbell. Ball milling of Fe-C. Nano structured materials, 1995. vol. 6, pp 389-392
17. Zuhailawati Hussain, Geok, Tan Chew, Projjal, Basu, Microstructure and hardness characterization of mechanically alloyed Fe – C elemental powder mixture. Materials and Design 2010, vol. 31, pp 2211-2215
18. H Hidaka, T Tsuchiyama, S Takaki, Relation between microstructure and hardness in Fe-c alloys with ultrafine grained structure, Scripta Materialia 2011, vol. 44, pp. 1503-1506