Project report on

HIGH ENERGY PLANETARY MILLING OF Fe, Cr & Ni POWDER

Submitted by

Abhimanyu Vinay Rajput
&
Prasanta Kumar Bhuyan

Under the guidance of
Dr. Debasis Chaira

Department of Metallurgical and Materials Engineering

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CERTIFICATE

This is to certify that the thesis entitled, "***High-energy planetary milling of Fe, Cr and Ni powder***" submitted by **PRASANTA KUMAR BHUYAN (107MM015) and ABHIMANYU VINAY RAJPUT (107MM022)** in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

Dr. Debasis Chaira, Assistant Professor
Department of Metallurgical and Materials Engineering
National Institute of Technology Rourkela-769008

Table of contents

Sl. No.	Content	Page No.
1.	Abstract	7
2.	Introduction	8
3.	Objective	9
4.	Plan of work	9
5.	Literature review	10
6.	Experimental details	12
7.	Results and Discussion	14
8.	Conclusion	23
9.	Future scope of work	24
10.	Reference	25

List of Figures

Figure 1: The figure shows different elemental and compound phases present after successive hours of milling for the composition of Fe-18Cr-8Ni.

Figure 2: The figure shows different elemental and compound phases present after successive hours of milling for the composition of Fe-20Cr-10Ni.

Figure 3: Representative SEM micrographs of Fe-18Cr-8Ni powder milled for (a) 5 (b) 10 (c) 20 and (d) 30 hours

Figure 4: EDS spectra of Fe-18Cr-8Ni alloy after 30 hours of milling.

Figure 5: Representative SEM micrographs of Fe-20Cr-10Ni powder milled for (a) 5 (b) 10 (c) 20 and (d) 30 hours

Figure 6: EDS spectra of Fe-20Cr-10Ni alloy after 30 hours of milling.

Figure 7: Particle size distribution of Fe-18Cr-8Ni after 30 hours of milling.

Figure 8: Particle size distribution of Fe-20Cr-10Ni after 30 hours of milling.

Abstract

Stainless steel powder is widely used in offshore applications as it has excellent corrosion resistance property. In the present study, high-energy planetary milling of elemental Fe, Cr and Ni powder was carried out for 30 hours to prepare nanostructured stainless steel powder. In one set of experiment Cr: Ni weight ratio was 18:8 (rest Fe) whereas in another set the ratio was 20:10 (rest Fe). Milling was carried out in Toluene at a speed of 300 rpm for 30 hours. The extent of alloying, along with the structural and morphological changes of the occurring in the powder form of nano-material was analyzed and studied using X-ray diffractometer, Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS).

1. Introduction

Stainless steels, as the most widely applied materials, have been a subject of studies for many years. Many processing methods have been applied to improve their structure and properties. It is expected that further improvement of stainless steels can be achieved by refinement of their structure, down to a nano-crystalline range. Stainless steel powder is widely used in offshore applications as it has excellent corrosion resistance property. Typical applications of stainless steel powder are-

- Sintered Metallic Filters
- Anti-Corrosive Paintings
- Thermal Spray Coatings
- Consolidated Products By HIP

Typical stainless steel components used in offshore applications are-valve body, elbow raiser and mixer house. A range of components are available for applications with oil and gas, power generation and general engineering sectors.

In recent years a number of methods for refining the structure of metals and alloys by severe plastic deformation have been developed like hydrostatic extrusion, equal channel angular pressing, and high pressure torsion. Ball milling is also regarded as an effective method for obtaining nanocrystalline alloys.

Mechanical alloying (MA), which is done via the process of ball milling, is a well-established route for producing non-equilibrium structures.

The phase transitions during mechanical alloying and also after subsequent annealing in Fe–Cr–Ni alloy system in which two different elements namely Nickel, as a notable austenite (γ) forming element, and Chromium, as a ferrite (α) forming element, which are involved have been previously studied by M.H. Enayati, M.R. Bafandeh et al. [1]

In this work, two kinds of alloy compositions, Fe–18Cr–8Ni, and Fe–20Cr–10Ni (wt. %) were chosen for the study. Attempts were made to compare the variations in the stoichiometrically different compounds with the increasing time period of milling. X-Ray Diffraction, SEM & Particle-Size analyses were carried out for the comparison of the same.

2. Objective

The present work aims at:

- Preparation of nano-sized Stainless Steel powder of the compositions, Fe–18Cr–8Ni, and Fe–20Cr–10Ni (wt. %).
- Study of the variation in particle size with milling of the two different alloy compositions.
- Characterization of the prepared powder by using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS) study.
- Analysis of the results and establishment of suitable mixture ratio for the best properties.

3. Plan of work

a. Preparation of nano-sized Stainless Steel powder of alloy compositions, Fe–18Cr–8Ni, and Fe–20Cr–10Ni (wt. %), of varying size.

b. Particle size analysis of the prepared samples.

c. SEM, EDAX and XRD study of prepared samples.

4. Literature review

4.1 Nanomaterials

A nanomaterial consist of multiphase solid material with either one of the phases having one, two or three dimensions less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material [2]. Nanomaterials include a number of different types of porous media, colloids, and gels. However, nanomaterials are considered to be a solid combination of a bulk matrix and nano-dimensional phase(s) with varying properties due to their dissimilarities in structure and chemistry [3]. Hence, nanomaterials unique properties differentiate it from its component materials. For the impact of its varied properties a limit on size has been proposed. Size limits are for catalytic activity (size < 5 nm), for making a hard magnetic material soft (size < 20 nm), for refractive index changes (size < 50 nm), and even for achieving super-paramagnetism mechanical strengthening or restricting matrix dislocation movement (size < 100 nm) [4].

Nanomaterials differentiate themselves from conventional composite materials on grounds of very high surface to volume ratio of the reinforcing phase or/and very high aspect ratio. Fibres, sheets or particles can act as the reinforcing material. Another differentiating factor between nanomaterials and conventional composite materials is the interfacial area between the matrix and the reinforcement phase(s), which is of a higher order magnitude. The matrix material properties are significantly affected in the vicinity of the reinforcement as macro scale properties vary due to relatively small amount of nano-scale reinforcement. The reason for this is because of the high surface area contributed by the reinforcement phase. Addition of carbon improves the thermal and electrical conductivity in nanomaterials being an example. Properties like heat resistance, optical properties, strength, stiffness and resistance to damage and wear can be enhanced by different nano-particulates. The nano- reinforcement is dispersed into the matrix during processing. The *mass fraction* of the nano- particles introduced is very low (in the order of 0.5% to 5%) due to low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers like nanometer- diameter cylinders or nanometer-thin platelets.

4.2 Mechanical Milling

Mechanical Milling (MM) is usually carried out using a ball mill. A ball mill, (a type of grinder) is a cylindrical device used in grinding or mixing materials like ceramic raw materials ores, paints and chemicals. Ball mills rotate around a horizontal axis and the drums of the ball mill are partially filled with the material to be ground plus the grinding medium. Different materials that are used as media include ceramic balls, flint pebbles and stainless steel balls. An internal cascading effect reduces the material to a fine powder [5]. Industrial ball mills generally operate continuously, by taking the fed at one end and discharging at the other end. Large to medium-sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion). High-quality ball mills are potentially expensive and can grind mixture particles to as small as 5 nm, enormously increasing surface area and reaction rates. The grinding works on principle of critical speed. The critical speed can be understood as that speed after which the steel balls (which are responsible for the grinding of particles) start rotating along the direction of the cylindrical device, thus causing no further grinding.

Ball mills are used extensively in the Mechanical alloying process [6] in which they are not only used for grinding but for cold welding as well with the purpose of producing alloys from powders.

There are many types of grinding media suitable for use in a ball mill, each material having its own specific properties and advantages. Common in some applications are stainless steels balls. While usually very effective due to their high density and low contamination of the material being processed, stainless steel balls are unsuitable for some applications, including:

a) Black powder and other flammable materials require brass, non-sparking lead, bronze or antimony grinding media.

b) Contamination by iron of sensitive substances such as ceramic raw materials. In this application flint grinding or ceramic media is used. Ceramic media are also very corrosive resistant materials.

High density alumina media (90–95% alumina) are widely used in ceramic industry to grind frits, glazes, clay bodies, and other ingredients. These are more expensive than silica or silex media but are more efficient [7].

5. Experimental Details

5.1 Materials used

1. Fe–18Cr–8Ni (wt %).
2. Fe–20Cr–10Ni (wt %).
3. Steel ball -

5.2 Chemical used

Toluene ($C_6H_5CH_3$) - Wet milling

5.3 Milling Parameters

Milling time - 30 hours
Mill speed - 300 rpm
Ball to powder weight ratio-7:1

5.4 X-ray Diffraction

X-ray diffraction of the milled samples was carried out in a Philips X-pert PRO high-resolution X-ray diffractometer. The phase evolution at different stages of milling was studied by using Cu-Kα (λ=1.54059**Å**) radiation. The data was analyzed for phase's present, crystallite size and lattice micro strain.

5.5 SEM Study

Microstructural characterization of the milled powder was carried out by using JEOL JSM-6480 LV scanning electron microscope. The microstructural refinement of the powder samples and surface morphology of the sintered specimen were investigated at different magnifications, for example, 500X and 1000X.

The images obtained from the SEM can give an idea of the micro structural changes in the nano-material with varying milling times. SEM images were taken for specimen 1 at two different magnifications and two different locations on the slide for each magnification. The accelerating voltage used in each case was 20 kV. EDAX was also carried out to check for compositional changes in the nano-materials at different milling times.

6. Results and Discussion

6.1 X-ray diffraction Study (XRD)

Figure 1 and figure 2 shows the XRD patterns of Fe-18Cr-8Ni and Fe-20Cr-10Ni powder milled for various time periods. It is observed from both figures that there is a shift of peaks to lower Bragg's angle during milling, which indicated that alloying has occurred. It is also clear that the peaks are broad suggesting strain accumulation and grain refinement. It has been seen that after 20 hours of milling alloys of Fe-Cr and Fe-Ni have started to form.

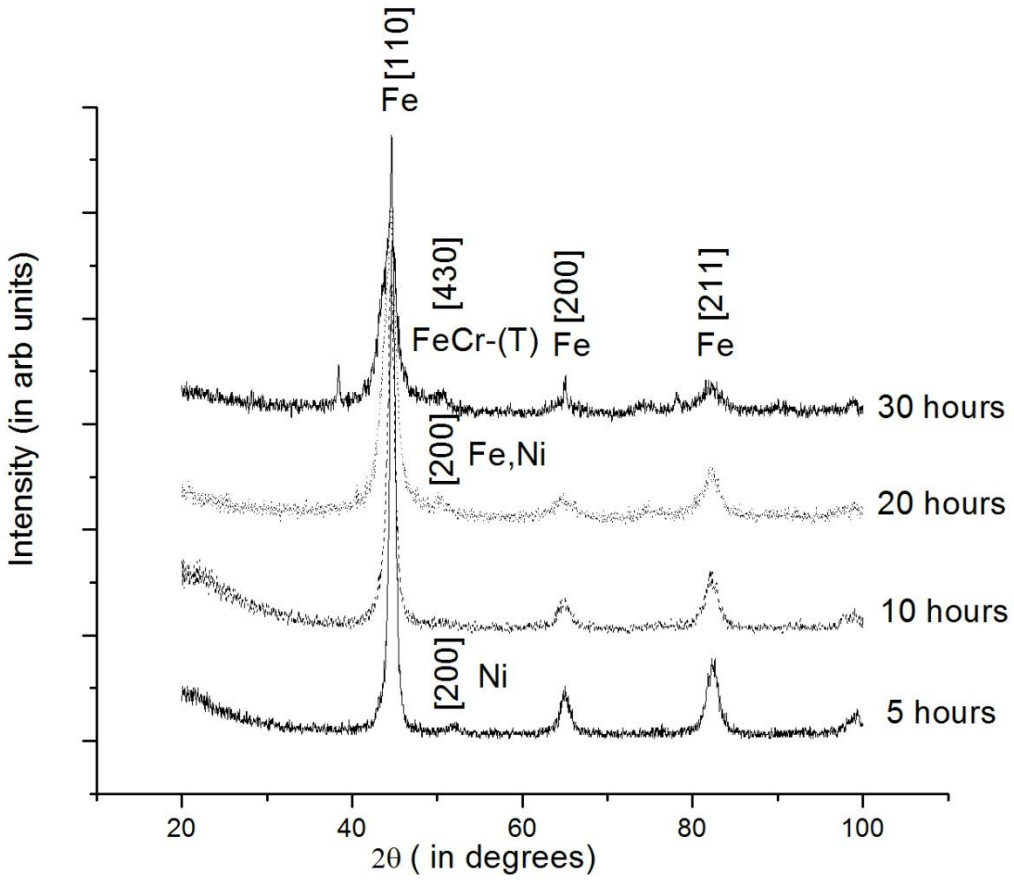


Figure 1: The following figure shows different elemental and compound phases present after successive hours of milling for the composition of Fe-18Cr-8Ni.

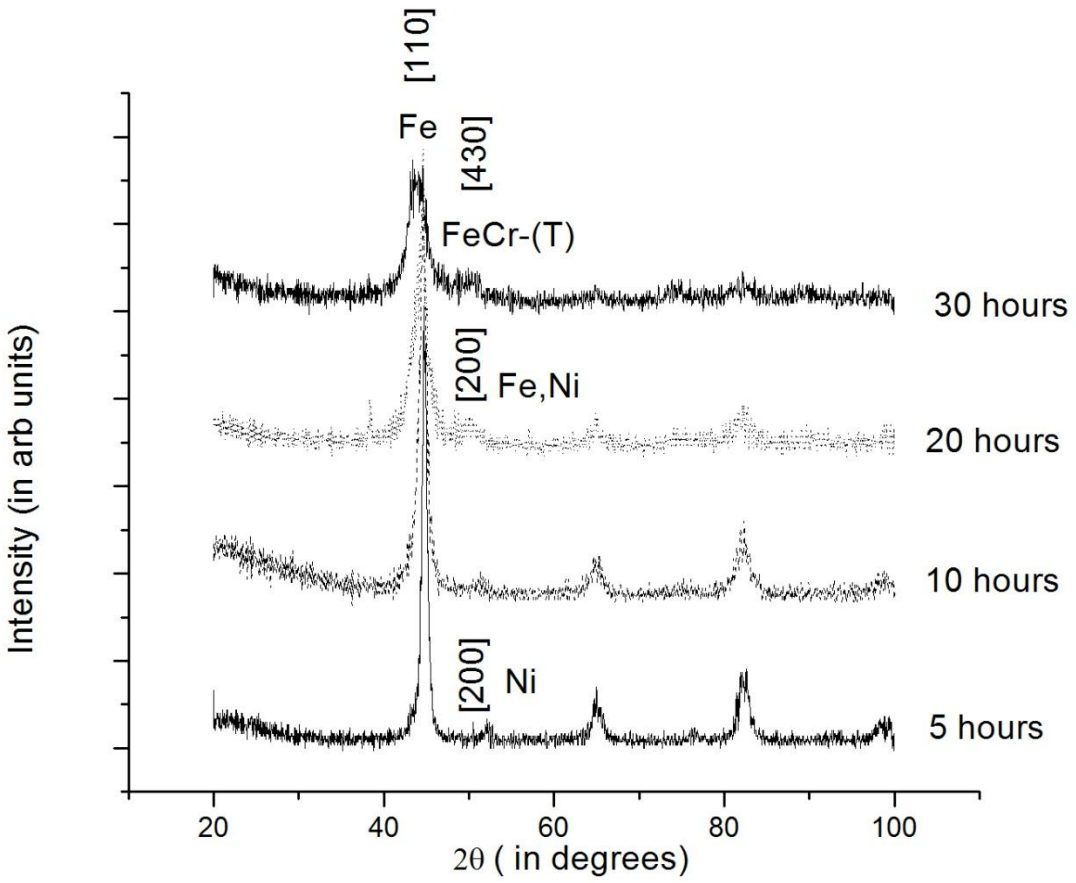


Figure 2: The following figure shows different elemental and compound phases present after successive hours of milling for the composition of Fe-20Cr-10Ni.

6.2 Crystal Size and Lattice Strain Determination

Some features of the activation process, particularly the crystal size, can be investigated by analyzing the X-ray diffraction pattern. For this purpose, milled powders were analyzed using X-ray diffraction (XRD) methods with Cu K_α radiation. The XRD peak broadening was used to measure the particle size and internal strain. The broadening due to small crystal size was evaluated through Scherrer formula

$$B_p(2\theta) = 0.9\lambda/D\cos\theta$$

where D is the average crystal size, $B_p(2\theta)$ the broadening of the diffraction line measured at full width half maximum intensity (FWHM), λ the wave length of the X-ray radiation and θ is the Bragg angle.

The strain broadening can be calculated as

$$B_s(2\theta) = 4\eta tan\theta$$

where $B_s(2\theta)$ is the broadening due to internal strains and η is the effective internal strains. The total broadening, $B_t(2\theta)$, due to both the crystal size and internal strains was assumed to be the linear addition of the two contributions.

From the slope and the intercept of the plot of $B_t\ cos\theta$ versus $sin\theta/\lambda$, the crystallite size and internal strain were calculated.

The decrease of the grain size and lattice strain to characterize the activation process has been determined from the X-ray diffraction patterns. Although the accumulation of lattice strain is a measure of defect formation, determining the defect structure was found to be more difficult [8].

Table 1

Phase	**2θ**	**FWHM (degree)**	**B (radian)**	**Crystal size t (nm)**	**Bcosθ/λ**	**Sinθ/λ**	**η**
Fe	44.622	0.1181	0.001031	310	0.000619	0.518638	-0.00087
Fe	64.9843	0.3936	0.003435		0.001881	0.485033	
Fe	84.0211	0.24	0.002094		0.001011	0.439296	

Table 1: Crystallite size and internal strain for the different phases of composition of Fe-18Cr-8Ni

Table 2

Phase	2θ	FWHM (degree)	B (radian)	Crystal size t (nm)	Bcosθ/λ	Sinθ/λ	η
Fe	82.225	2.092	0.018256		0.008932	0.444245	
Fe	74.83	2.093	0.018265	80	0.00942	0.463209	0.01125
Fe	43.606	2.325	0.020289		0.012233	0.519936	

Table 2: Crystallite size for the different phases of composition of Fe-20Cr-10Ni

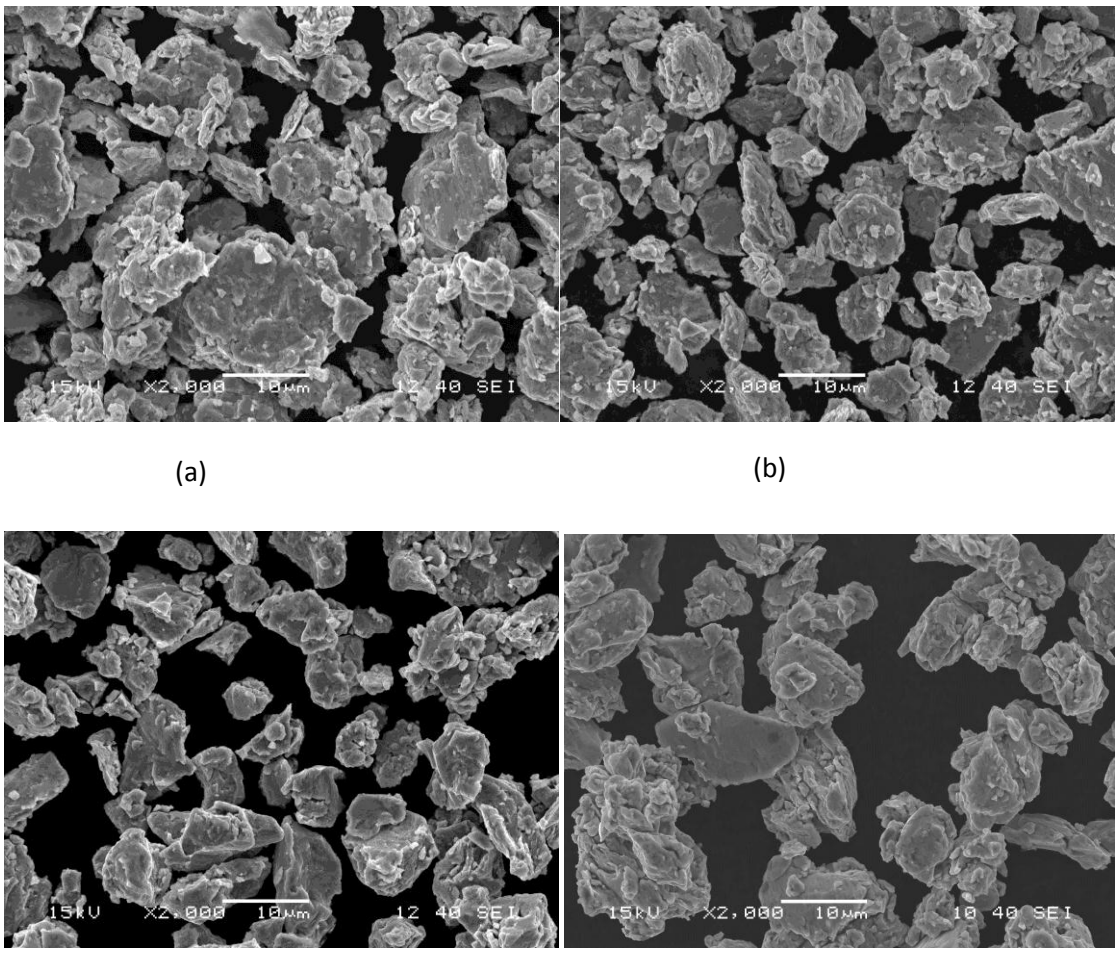
6.3 Scanning Electron Microscopy Study (SEM)

The scanning electron microscope provides images which give a relevant idea of the structural changes that nano-material undergoes due to the variation of milling times. The SEM images were taken for both the specimens at five different magnifications and five different locations on the slide for each magnification. The accelerating voltage used in for each case was 15 kV.

Figure 3 shows the SEM micrographs of Fe-18Cr-8Ni powder milled for different periods. It is evident from the figure that after 5 hours of milling the powders are flaky in nature and also there is an increase in size due to ductile nature of powders. But as milling progresses due to heavy plastic deformation during milling, strain hardening takes place which results in decrease in size of the particle. It is observed that after 30 hours of milling particle size is around 5 to 15 micrometer.

Figure 4 shows the EDS spectra of Fe-18Cr-8Ni after 30 hours of milling. The spectrum shows mainly the peaks of Fe, Cr, Ni and O_2. As milling was carried out in open atmosphere, some amount of oxidation has taken place. Table 1 shows the elemental composition of the alloy after 30 hours of milling.

Figure 5 shows the SEM micrographs of Fe-20Cr-10Ni powder milled for different periods. A similar trend is observed in the Fe-20Cr-10Ni powder as was in the Fe-18Cr-8Ni. With the progression of milling, decrease in size particle takes place due to heavy plastic deformation which is accompanied by strain hardening



(a) (b)

(c) (d)

Figure 3: Representative SEM micrographs of Fe-18Cr-8Ni powder milled for (a) 5 (b) 10 (c) 20 and (d) 30 hours

The specimen was subjected to EDAX analysis after milling them for 5 hours, 10 hours, 20 hours, and 30 hours.

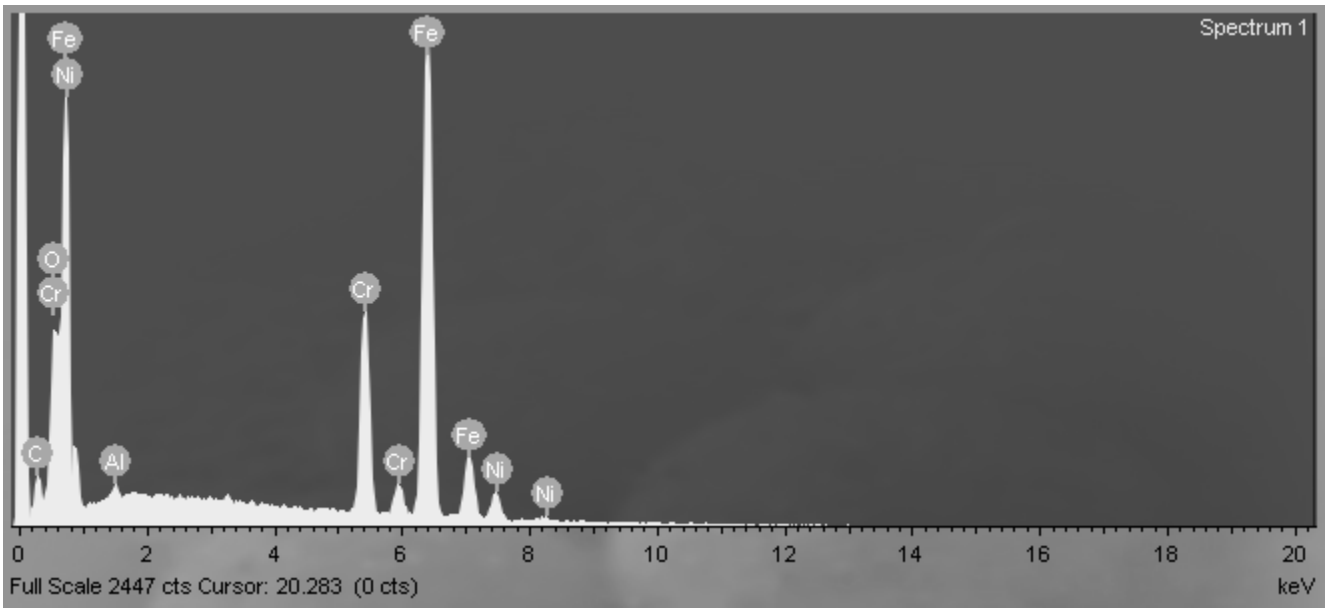


Figure 4: EDS spectra of Fe-18Cr-8Ni alloy after 30 hours of milling.

The result obtained has been shown below in tabular form.

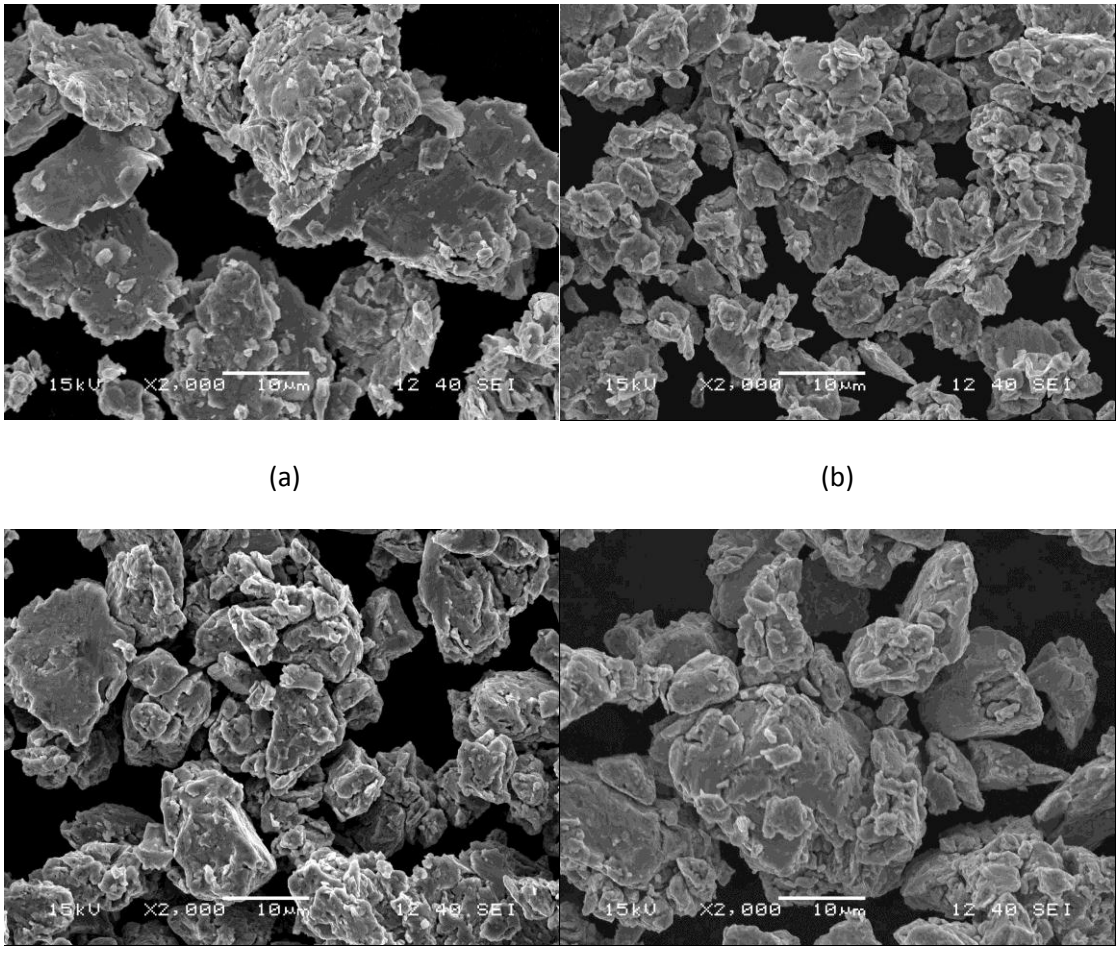
Table 3: Elemental composition of Fe-18Cr-8Ni alloy after 30 hours of milling obtained from EDS

Element	Weight% (Milling Time – 5 hours)	Weight% (Milling Time – 10 hours)	Weight% (Milling Time – 20 hours)	Weight% (Milling Time – 30 hours)
Cr K	16.72	18.70	17.19	15.74
Fe K	74.05	64.25	66.37	62.06
Ni K	5.81	6.06	6.49	6.33

Because proper mixing cannot be achieved in 5 hours the amount of Chromium and Nickel are found to be much lower than the initially added amount.

Specimen No.2 (Composition - Fe–20Cr–10Ni)

Initial composition of specimen number 2 used: Fe = 70.00, Cr = 20.00 & Ni = 10.00 in weight percentage (Fe-20Cr-10Ni).



(a) (b)

(c) (d)

Figure 5: Representative SEM micrographs of Fe-20Cr-10Ni powder milled for (a) 5 (b) 10 (c) 20 and (d) 30 hours

As can be clearly seen there is a drastic decrease in size of the particles with increased milling time. The agglomerated mass starts to break leading to smaller sizes.

The specimen was subjected to EDAX analysis after milling them for 5 hours, 10 hours, 20 hours, and 30 hours.

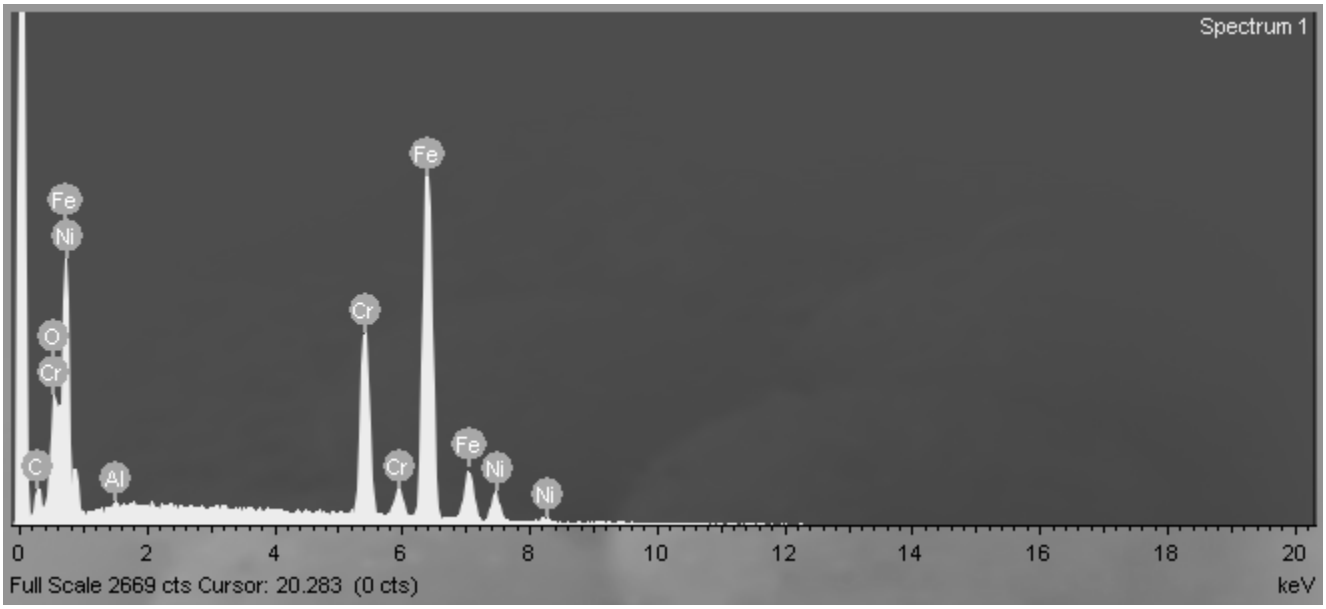


Figure 6: EDS spectra of Fe-20Cr-10Ni alloy after 30 hours of milling.

The result obtained has been shown below in tabular form.

Table 4: Elemental composition of Fe-18Cr-8Ni alloy after 30 hours of milling obtained from EDS

Element	Weight% (Milling Time – 5 hours)	Weight% (Milling Time – 10 hours)	Weight% (Milling Time – 20 hours)	Weight% (Milling Time – 30 hours)
Cr K	17.11	18.88	18.65	20.19
Fe K	60.01	62.38	60.98	62.33
Ni K	7.49	7.59	8.17	8.24

It can be inferred from the above graphs that with increase in milling time there is increased homogeneity as a result of which the amount of Chromium and Nickel detected are closer to the initial amount of Chromium and Nickel in the specimen.

Theoretically ball milling should ensure a homogenous composition even milling time is less but as can be seen from the above observations some amount of inhomogeneity exists even after the samples are milled for as long as 30 hours.

6.4 Particle Size Analysis

Figure 7 and figure 8 shows the particle size analysis of Fe-18Cr-8Ni and Fe-20Cr-10Ni milled for 30 hours. The graphs show that particle size distribution is bimodal distribution in both cases.

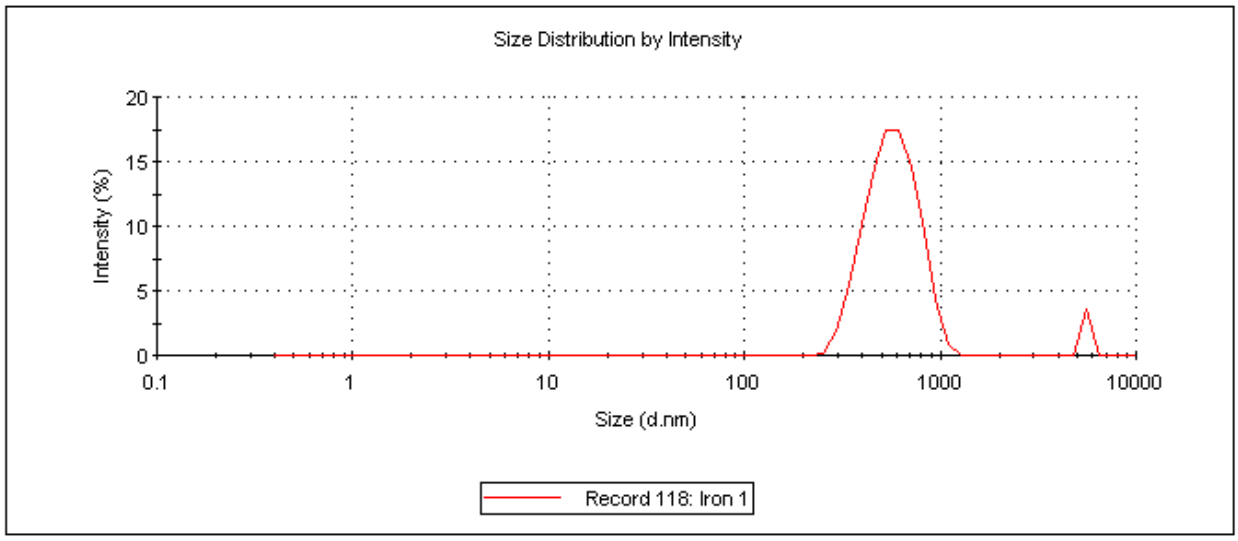


Figure 7: Particle size distribution of Fe-18Cr-8Ni after 30 hours of milling.

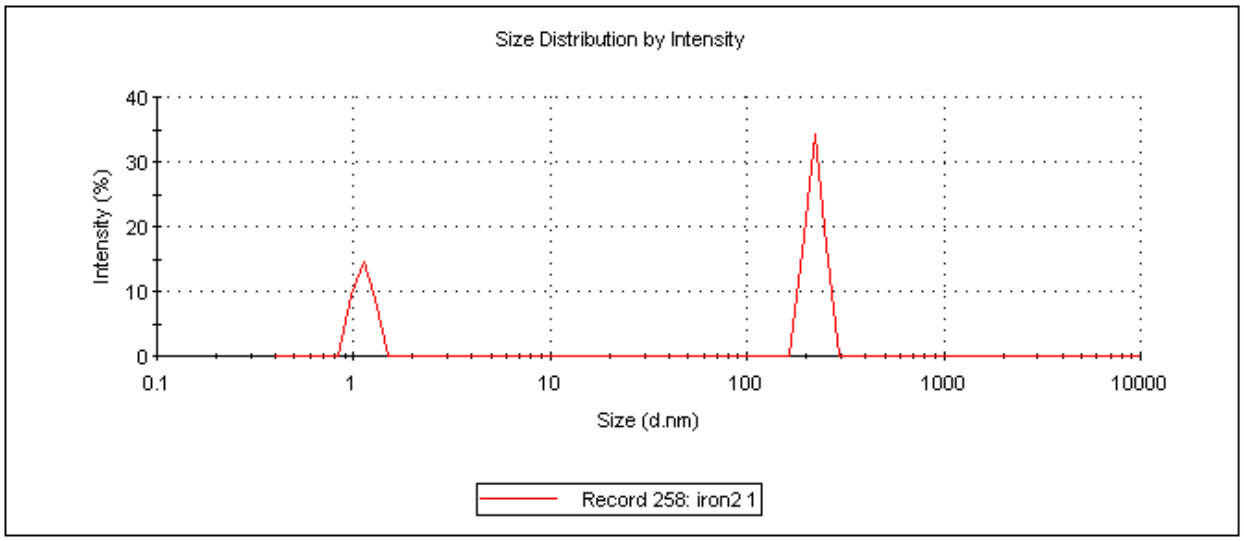


Figure 8: Particle size distribution of Fe-20Cr-10Ni after 30 hours of milling.

7. Conclusion

1) XRD study shows that alloys of Fe-Cr and Fe-Ni have started to form after 20 hours of milling. There is accumulation of internal strain and grain refinement after 30 hours of milling.
2) The SEM analysis shows that there is a definite decrease in the size of the particles with increase in milling time. Initially large flakes are formed but as milling progresses there is a reduction in size of the particles.
3) The homogeneity of the nano-materials increases with increase in milling time.
4) Although wet milling was carried out but oxidation of the powder could not be prevented.

8. Future Scope of Work

- Compaction of the powdered sample can be done using uniaxial hydraulic press at a desired pressure.
- Sintering of the prepared pellets in a controlled atmosphere at a decided temperature.
- Characterization of the sintered nanomaterials by using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD).
- Hardness testing of the sintered specimens using Vickers micro-hardness testing.
- Analysis of the results and establishment of suitable mixture ratio for the best properties.
- Stainless steel powder is widely used in offshore applications as it has excellent corrosion resistance property. Tests should be done for measuring property variations with the amount of chromium and nickel addition. Other mechanical properties like wear resistance can also be measured.
- If compaction can be done using advanced techniques like hot isostatic pressing there is further scope for improvement in mechanical properties due to the presence of porosity.

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