

**ANTAL KERPELY DOCTORAL SCHOOL OF  
MATERIALS SCIENCE & TECHNOLOGY**



**IMPROVING THE HARDNESS AND WEAR RESISTANCE OF  
CAST IRON SURFACE BY LASER MELT BEAM INJECTION  
METHOD (LMI) WITH MECHANICAL ALLOYED POWDER**

A PhD dissertation submitted in the defence process for the degree of  
Doctor of Philosophy in the subject of Material Science and Technology

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## **Abstract**

In current work, the laser melt injection process (LMI) is applied for cast iron to increase surface hardness and abrasive wear resistant, using 85 wt% iron coated NbC and 15 wt% Si powders after mechanical alloying (MA) process for different period time (5, 15, 30, 60, 120 and 240 min) and investigate the effect of MA time on the microstructure and the hardness values of the reinforcing powder. The effect of the MA on the physical and mechanochemical properties of iron coated NbC+Si powders, and the microstructure of the cast iron samples treated by LMI was studied and investigated using scanning electron microscopy (SEM) and energy dispersive spectrum (EDS), X-ray diffraction (XRD). The particles size, morphology, and structural changes were characterised using laser particle size analysis (LPSA), while the hardness values measured by the Vickers hardness, while the wear resistant measure by dry sliding friction ball-on-disc wear tester Taylor Hobson.

The results show that the binding alloy and the hard phase were fine distributed in the hard layer and strong metallurgical bonds were formed between cast iron and the reinforcing particles. Due to the mutual diffusion of alloying elements, the hardness of cast iron specimens increased by 3 times and the wear resistant increased by 4.6 -7.3 times.

## **1. Introduction**

Many engineering materials used for applications in which hardness and wear resistance is the primary requirement are multiphase materials. A particular group of multiphase materials is especially relevant to tribological applications: materials composed of a metallic matrix reinforced by dispersion of hard particles often applied to tool steel, cast irons, cobalt-based alloys, hard metal and some metallic matrix composite. As a result, the preparation of the wear-resistant materials, especially the hard facing coating, is an essential topic in the tribological field. Hardfacing coating methods which use high energy density sources such as the electric arc and laser have been widely applied commercially to enhance the wear and corrosion resistance, is well known that the wear behaviour is not an intrinsic property of the material, but it depends on the overall conditions of the tribological system: loading conditions, hardness, dimensions, shape, and roughness of the counter-body, siding speed and environment. Nevertheless, designing and selection of materials are an essential step when submitted to a given set of conditions. Increasing attention is present to metal matrix composites consisting of hard and brittle carbide particles embedded in a sturdy metal binder.

Typical applications are Laser melt injection process, as protective coatings and in rapid tooling and laser-assisted mould repair. Laser powder deposition is a widely used process in fast tooling applications and as a coating technique.

## 1.1 Objectives

The primary objective of the current work is to improve the mechanical properties (hardness and wear resistance) of cast iron surface by the laser melt injection method with a reinforcement powder of iron coated niobium carbide and silicon prepared by mechanical alloying which is a solid-state process that has been successful in producing nanocomposite and nanostructure compounds by mechanochemical reactions. The goal of the mechanical alloying is to improve the initial surface properties and structure of iron coated NbC and Si using green chemistry to produce desired characteristics for laser melt beam injection.

In this work, mixtures of iron coated NbC and Si powders corresponding to nominal contents 85 wt% of iron coated NbC and 15 wt% of Si prepared by MA, and apply this powders on the LMI process to treat the surfaces of cast iron specimens, and study the following points:

1. To investigate the effect of mechanical alloying time on the microstructure of iron coated NbC+Si powder and what possible phases can be generated during the mechanical alloying process for different milling periods.
2. To study the effect of mechanical alloying time on the specific surface area of iron coated NbC+Si powder particles and the dissolving rate of the powder components in the liquid iron matrix during the LMI process.
3. To investigate the effect of mechanical alloying time on the wettability and diffusivity of iron coated NbC+Si powder in the liquid iron matrix during the LMI process.
4. To study the effect of the different mechanical alloying time for iron coated NbC+Si powder which used as a reinforcement powder in the LMI process, on the hardness and wear resistant values of the cast iron samples.

## 2 EXPERIMENTAL SECTIONS

### 2.1 Samples preparation

#### 2.1.1 Grinding of iron coated NbC and Si powder by a planetary ball mill

The initial powder size of iron coated NbC (1-1.2 mm), and Si (2.5-5 mm) was reduced by milling in a planetary ball mill for a few micrometers ( $\leq 63 \mu\text{m}$ ). The aim was to be the feed powder of mechanical alloying process by a stirred media mill smaller than  $63 \mu\text{m}$ . The container of the mill was made from iron, filled with steel balls. The grinding ball size was 40 mm, and three of them was in the grinding chamber. After the first grinding stage, the mill

product was sieved at 63  $\mu\text{m}$ , the fine size fraction was collected, and the coarse fraction was fed into the mill again and ground until reaching finer size than 63  $\mu\text{m}$  (quantitatively ground).

### 2.1.2 Preparation of Cast Iron samples

The samples cast iron was prepared by cutting the rod of cast iron by cutting machine, the size of the samples  $30 \times 35 \times 5$  mm and thickness 5 mm. The chemical composition of the cast iron used in this study for laboratory experiments is 69.42 wt% Fe, 28.41 wt% C, 1.44 wt% Si and 0.73 wt% Cu.

### 2.2 Mechanical Alloying process (MA)

The previously prepared (grinded and sieved) iron coated NbC and silicon samples were mechanically alloyed in a batch stirred media mill with a grinding chamber volume of 530  $\text{cm}^3$ . The milling chamber was equipped with a water jacket cooling in order to control the temperature of the milling chamber. During the mechanical alloying experiments, the temperature of the milling chamber was constant  $30 \pm 2$   $^\circ\text{C}$ . The stirrer consisted of perforated triangular shaped disc rotors fixed on a drive shaft. The consumed electric power during the experiments was measured by microcomputer controlled digital energy meter Carlo Gavazzi WM1-DIN for the characterization of the specific grinding energy. The energy meter recorded the electric work in cumulated form; in this way, the grinding work could be calculated as the difference between the initial and the final values. The mechanical milling experiments were executed in a stirred media mill using different milling times: 5, 15, 30, 60, 120 and 240 minutes. The circumferential speed (tip speed) of the rotor in the stirred ball mill was  $10.56 \text{ ms}^{-1}$ . The weight of the feed material is as follows: iron coated NbC 24.6 g, and Si 4.35 g, furthermore, to avoid the several problems that arise in a dry mode milling, such as aggregation, agglomeration, sticking on the liners and the milling media, the isopropanol was added as liquid media in 147.36 g for one batch. The media filling ratio was 70% during MA.

**Table 1. Mechanical alloying conditions of iron coated NbC+Si powder**

| Milling time<br>min | Grinding work<br>Wh | Specific grinding energy<br>kJ/kg | Temperature of the<br>suspension ( $^\circ\text{C}$ ) |
|---------------------|---------------------|-----------------------------------|---|
| 5                   | 21                  | 725                               | 28.6  |
| 15                  | 52                  | 1796                              | 31.1  |
| 30                  | 94                  | 3247                              | 27.0  |
| 60                  | 198                 | 6839                              | 32.6  |
| 120                 | 406                 | 14024                             | 32.4  |
| 240                 | 990                 | 34197                             | 31.8  |

Milling media was sintered zirconium silicate beads with, the size range of 1.0-1.2 mm, its specific weight was  $4.1 \text{ kg l}^{-1}$ , and microhardness was 1000 HV. After the end of each work

phase, all the operating data and details (grinding work, temperature, visual observation of the suspension) are noticed as shown in Table 1.

## 2.3 Laser Melt beam Injection process

### 2.3.1 First part of LMI experiment

LMI experiments are performed on two parts, part one to select the appropriate experimental conditions (laser energy, powder feed rate and laser spot width) which corresponds to the powder type and sample type (cast iron), where different laser energies are applied ranging 2000-2700 W, different powder feed rate 250-500 mm/min and different powder type: iron coated NbC, iron coated NbC+Si without MA and iron coated NbC+Si after MA. Applying high laser power 2700 W leads to the melting and deformation the surface of a sample, where the temperature is controlled by the energy of the laser (see Fig. 1), and resultant lower hardness values, therefore, these values will not be taken into consideration. The final experimental conditions are selected depending on the experiment result that achieves the highest hardness value.

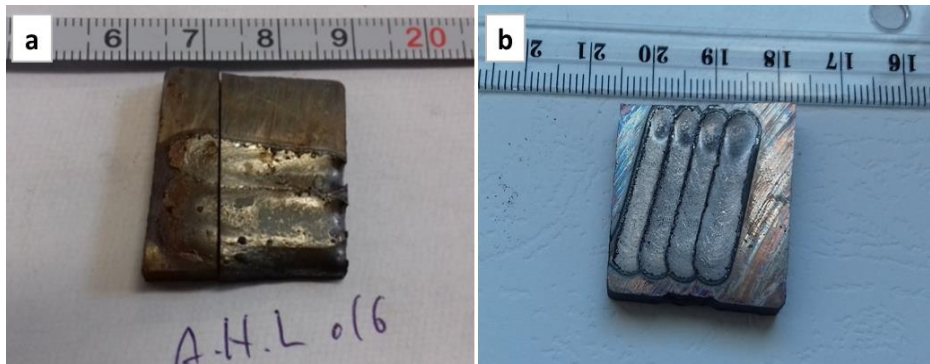


Figure 1. Cast iron samples after LMI process (a) Laser energy 2700 W (b) Laser energy 2500 W

### 2.3.2 Second part of LMI experiment

In this part, the effect of powder type which used in the LMI process on hardness and wear resistant values was studied, the cast iron sample  $30 \times 35 \times 5$  mm was used for reinforcing by iron coated Niobium carbide-Silicon powder, placed the powder in a container of the laser melt beam injection device. The distance between the sample and the nozzle must be 17mm, switch on the device and start the process. The process was carried out under the argon gas to avoid oxidation of samples. Depending on the results of LMI experiments in part one, the LMI conditions which will be applied in the second part of experiments is 2500 W laser energy, 500 mm/min feed rate, with using iron coated niobium carbide-silicon powders

without mechanical alloying and after the mechanical alloying process for a different period time (5, 15, 30, 60, 120 and 240 min). The details of each experiment are tabulated, as shown in Table 2.

**Table 2. Experimental conditions**

| Coating powder                                     | Power of laser W | Moving speed mm/min. | Coating depth mm | Coating width mm |
|--|------------------|----------------------|------------------|------------------|
| <i>NbC 85 wt% + Si 15 wt%</i>                      | 2500             | 500                  | 1                | 3                |
| <i>NbC 85 wt% + Si 15 wt%<br/>After MA 5 min</i>   | 2500             | 500                  | 1                | 3                |
| <i>NbC 85 wt% + Si 15 wt%<br/>After MA 15 min</i>  | 2500             | 500                  | 1                | 3                |
| <i>NbC 85 wt% + Si 15 wt%<br/>After MA 30 min</i>  | 2500             | 500                  | 1                | 3                |
| <i>NbC 85 wt% + Si 15 wt%<br/>After MA 60 min</i>  | 2500             | 500                  | 1                | 3                |
| <i>NbC 85 wt% + Si 15 wt%<br/>After MA 120 min</i> | 2500             | 500                  | 1                | 3                |
| <i>NbC 85 wt% + Si 15 wt%<br/>After MA 240 min</i> | 2500             | 500                  | 1                | 3                |

## 2.4 Brazing experiments

The spreading property of iron coated NbC+Si powder was examined by the sessile drop method for the nickel foil with the cast iron specimen. Where the surface of the cast iron substrate (10x15 mm) and the nickel foil (10x15 mm) was cleaned by sodium hydroxide (NaOH) solution, after that, washed by distilled water and then by alcohol (C<sub>2</sub>H<sub>5</sub>OH). The cast iron specimens covered by a layer of iron coated NbC+Si powder (without or after mechanical alloying), then nickel alloy foil placed on the top of the iron coated NbC+Si powder layer, after that, the specimens placed in the vacuum furnace ( $1 \cdot 10^{-4}$  mbar), then the furnace heated up to temperature 1100 °C, which is the molten temperature of nickel foil, the sample was kept at 1100°C for 10 minutes after 10 minutes reduce the furnace temperature gradually, when the temperature inside the furnace reaches 300 °C, the furnace chamber is filled with nitrogen gas to avoid oxidation the samples and then continue to reduce the furnace temperature till reached room temperature.

## 3 RESULTS AND DISCUSSION

### 3.1. Mechanical alloying process

#### 3.1.1. Material fineness

A significant fluctuation can be observed in the particle size distribution of the iron coated NbC+Si powder after the mechanical alloying process.

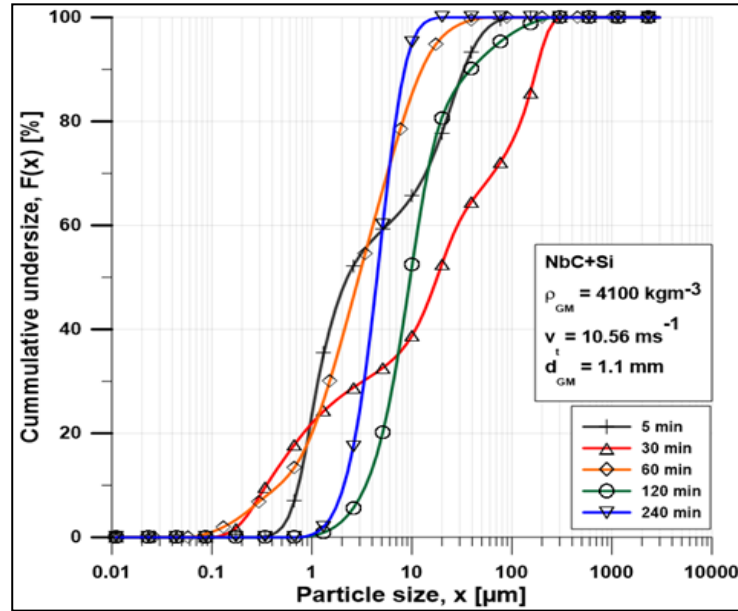


Figure 2. Cumulative particle size distribution curves of the MA (iron coated NbC+Si) powder

Figure 2 shows the cumulative particle size distribution curves of the mechanically alloyed iron coated NbC+Si particles. Remarkable coarsening of the particles appears at 30 min residence time, probably due to the aggregation and/or agglomeration and/or mechanical alloying of the particles. After this, the iron coated NbC+Si ground material became finer, coarser and then, finer again. There is no significant shift in particle size, either progressive or regressive, was observed. However, this shift was to be expected as in the case of brittle materials in general, but when the grinding kinetics was investigated, the non-brittle behaviour of the materials was found to be the cause behind this behaviour which results in more deformation and structural changing than particle size reduction.

In Figure 3, the geometric (outer) specific surface area is plotted as a function of milling time. A sudden decrease in specific surface area was noticed after 60 min milling time in the stirred media mill. According to the kinetic consideration in the milling procedure, it can be divided into three main stages. In the first stage, the specific surface area rises linearly with the milling time (the so-called Rittinger section) with the maximum specific surface area reached  $56500 \text{ cm}^2\text{cm}^{-3}$  at 60 min milling time. In the second stage, the slope of the specific surface area decreases (section of aggregation), while in the third stage, the specific surface

area decreases drastically with the milling time (which can be explained by the phenomenon of agglomeration, where the bonding force between the particles become stronger than in the agglomeration phenomenon.) down to  $16000 \text{ cm}^2\text{cm}^{-3}$ . However, from the cumulative undersize curves, no tendency can be observed; the specific surface are calculated from it shows the general trend that was to be expected with brittle materials.

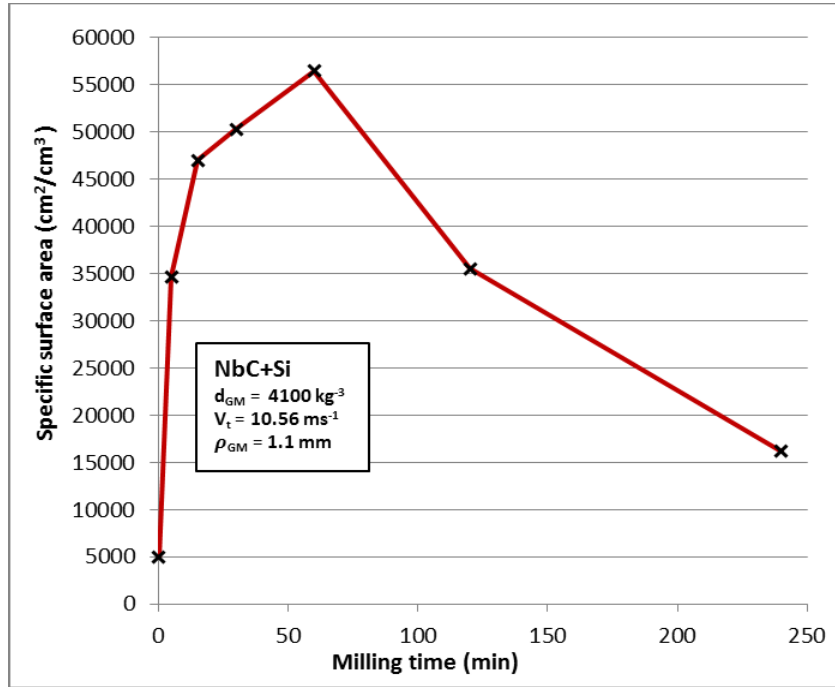
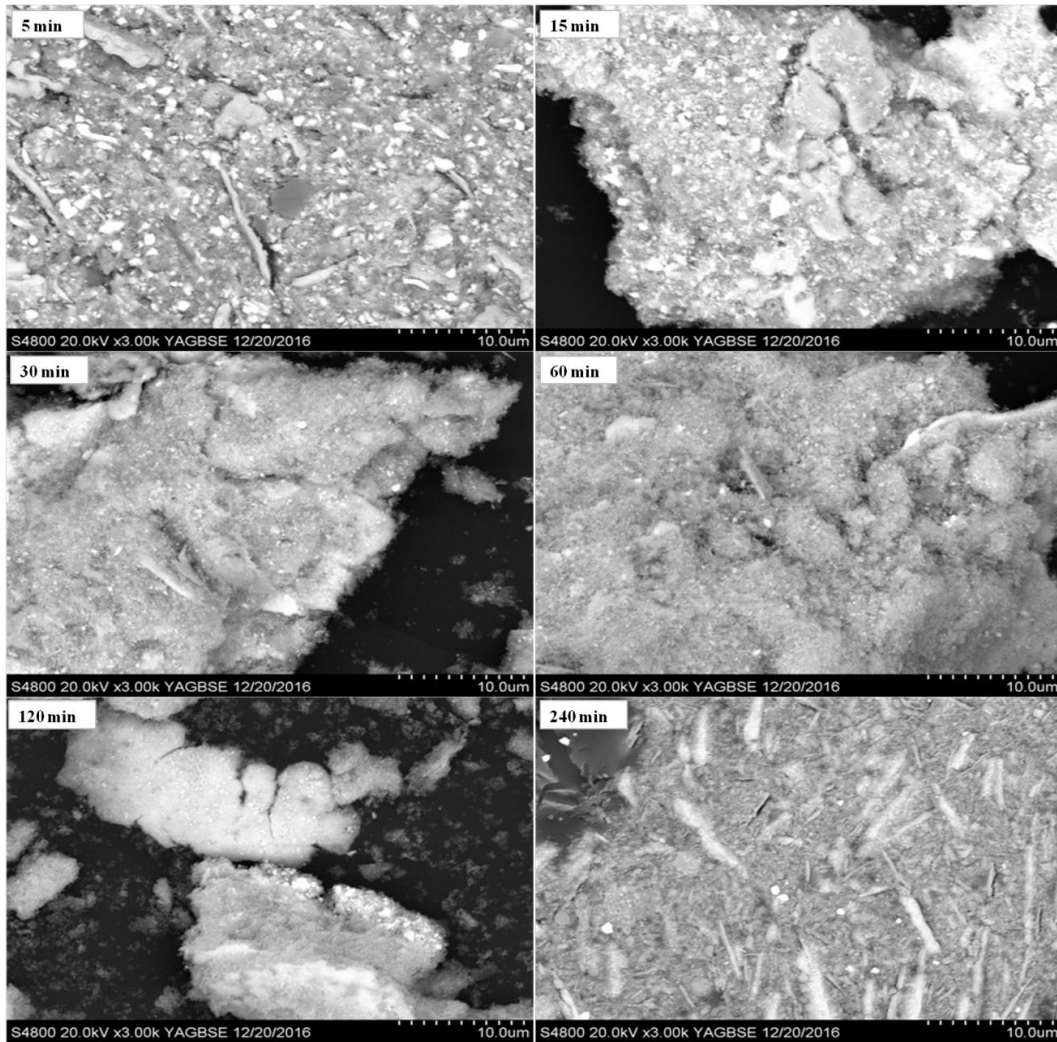


Figure 3. Diagram of a specific surface area as a function of milling time

### 3.1.2. Microstructure

The samples for SEM analysis are prepared by taking a small amount of iron coated NbC+Si powder after each milling process 5, 15, 30, 60, 120, 240 min, then the powder is placed in the resin mould, after the resin dried, the particles of powder were on the upper surface of the sample and ready for SEM investigation. From the SEM images in Figure 4, it can be seen the effect of milling for different periods of time (5-240 min) on the variation of the particles size of iron coated NbC+Si powder. At the beginning (for 5 min) milling time the particle size starts to decrease, then the agglomeration stage can be noticed at more extended milling time (240 min). It is not possible to distinguish particles of NbC from Si, which indicates that they have reached the nanometer size (see Figure 4).

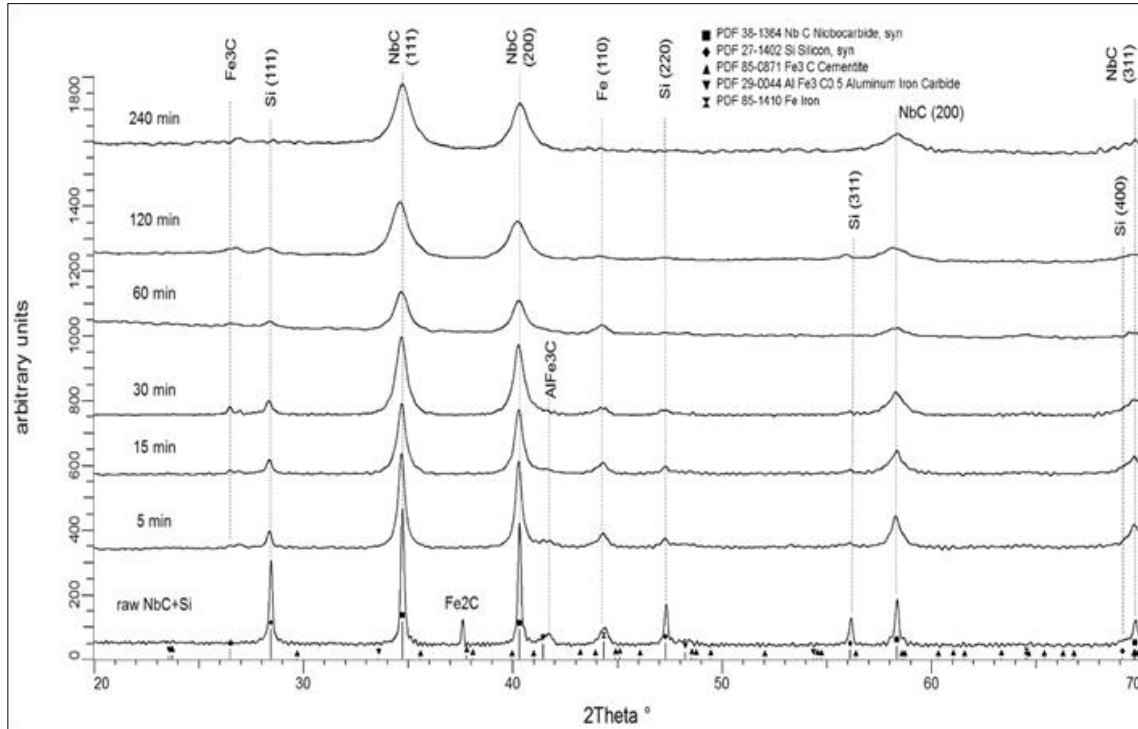




**Figure 4. SEM images of the iron coated NbC+Si powder after MA for (5 - 240 min.) milling time**

### **3.1.3 Phase composition-Structural evolutions**

Figure 5 shows the XRD spectra of the iron coated NbC+Si milled powders as a function of milling time. As can be seen from the patterns, in the initial powders mixture, sharp diffraction peaks related to NbC, Si and Fe are evident. Also, minor phases such as Al-Fe-carbide and Fe-carbides are observed. By the milling initiation, due to the development of nano-sized structure and the introduction of the high level of micro-strain, the sharp peaks are considerably broadened. By further milling, the peaks of the initial materials gradually vanish.



**Figure 5. XRD patterns of NbC+Si powder after MA for different milling time**

The further analysis of the XRD patterns indicates that increasing the milling time has a significant effect on the transformation of different phases in the powders. The peak broadening caused by crystallite size reduction is observed for each phase, with the Si being significantly reduced already in the 5 min stage. After 240 min of milling, it was seen that the diffraction peak of silicon is disappeared, and this is lead that the Si changed to an amorphous phase. While the XRD peaks have revealed that the NbC (111) and NbC (200) phase powder mixtures exhibit a series of changes during the milling, compared to the starting material, NbC phase demonstrates a lower and broaden diffraction peaks, where observe the net height and net area increasing with the milling time until reach to the maximum value at 30 min of milling time, after that tend to the drop until reach the minimum value at 60 min, after that going to increase after 120 min of milling time.

The more extended milling time 240 min leads to a remarkable broadening of NbC diffraction peaks and a decrease in the intensity of Si and Fe diffraction peaks. The peaks of Si and Fe disappear after 120 min of milling indicating the formation of a solid solution (or secondary solid solution) of Si, C and Fe phase in NbC phase. It is well known that high velocity stirred media milling supply input of high energy to the powder system. During this process, a large number of flaws, including dislocations and new grain boundary are generated rendering the diffusion between different components facile and in the occurrence of a solid solution of Si and Fe phase in NbC phase.

## 3.2 Laser melt beam injection process analysis

### 3.2.1 LMI experiments

The original cast iron (ADI) substrate which used in the experiments of the laser melt beam injection process has a surface hardness of 300-450 HV<sub>0.05</sub>. After the LMI process, the samples are cut into halves and preparing for hardness test, as shown in Figure 6.

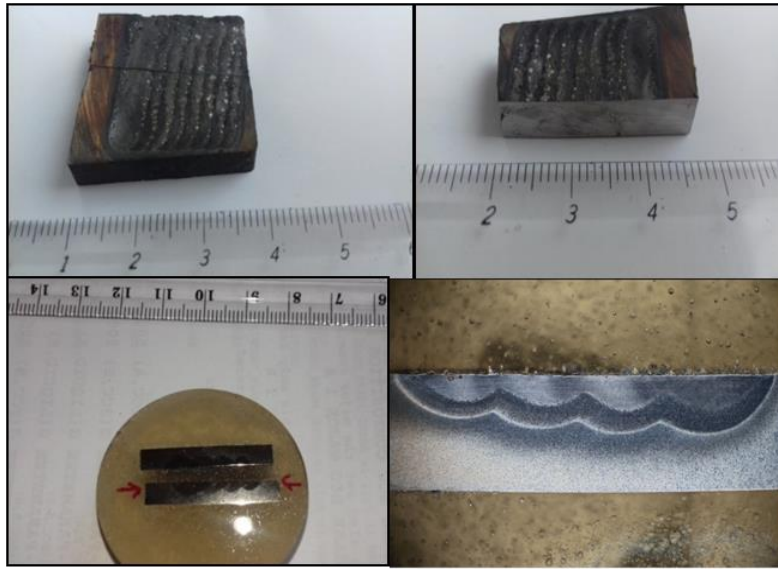


Figure 6. Cast Iron samples after laser melt beam injection process

### 3.2.2 SEM analysis of LMI experiments part 2

In this part of the LMI experiment, the effect of powder type on the microstructure and hardness values was studied, where from SEM images in Figure 7 for LMI experiment which used iron coated NbC powder only without Si, observe the niobium particles <math><10 \mu\text{m}</math>, uniform spread in the molten iron matrix approximately. Also, find the carbon particles aggregating on the border of the heat affected zone of the laser, in the form of arcs. It should be noted to the previous studies shows that homogeneous nucleation of NbC can be as the Nb and C atoms in the molten pool meeting. During the LMI process and because of the high-temperature gradient and rapid cooling, a certain amount of Nb particles remain un-melted, and it acted as the substrate of NbC nucleation.

The in-situ NbC particles owing to its high melting point, it precipitated out from the molten pool firstly, and the atoms of Al, Fe, and Si were squeezed into the interface between the NbC particles and the liquid phase.

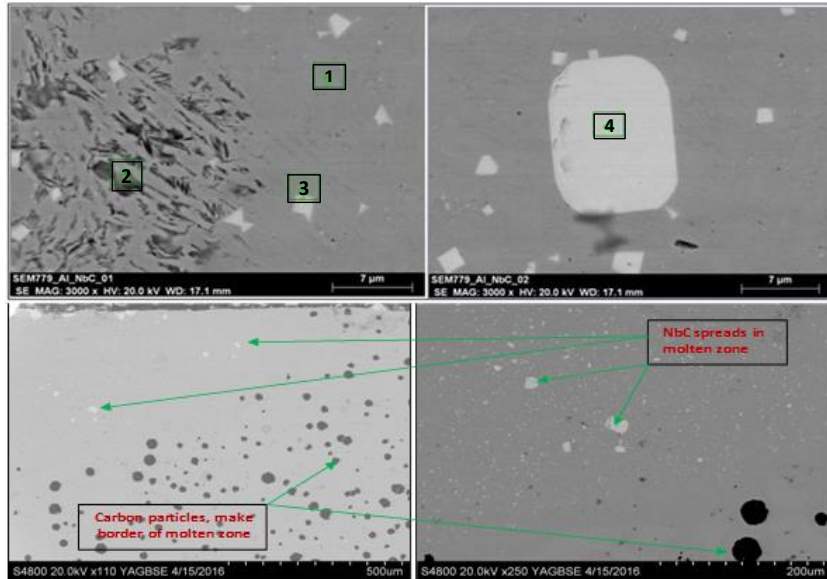


Figure 7. SEM images of the cross-section of exp. No. 1 iron coated NbC powder only

### 3.2.3 LMI experiment using (NbC+Si) powder without the MA process

From SEM images of the experiment which used 85 wt% iron coated niobium carbide with 15 wt% silicon powder without MA, can observe effect of addition silicon on the microstructure of the cross-section of cast iron sample after LMI process, the addition of silicon was improved the diffusivity of niobium particles in the melt iron matrix and promoted particles refinement and form a homogeneous and fine microstructure, with remaining a very few niobium particles which size  $\leq 20 \mu\text{m}$ , as shown in the Figure 8.

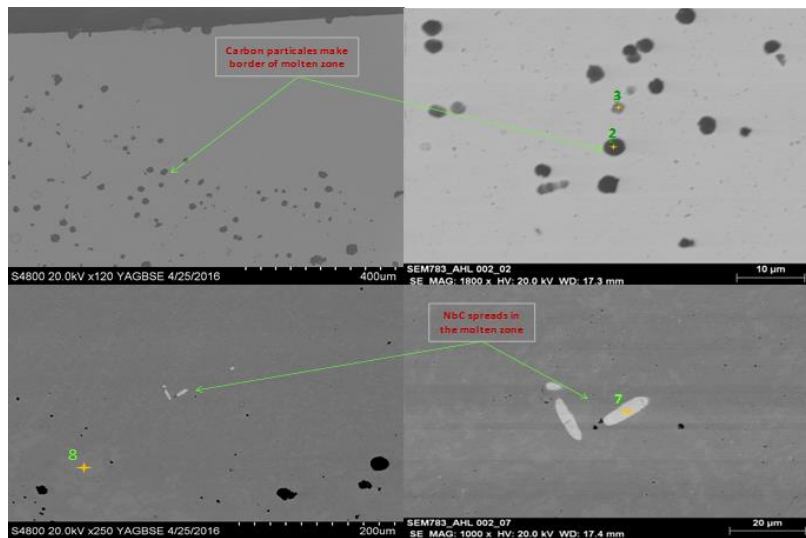
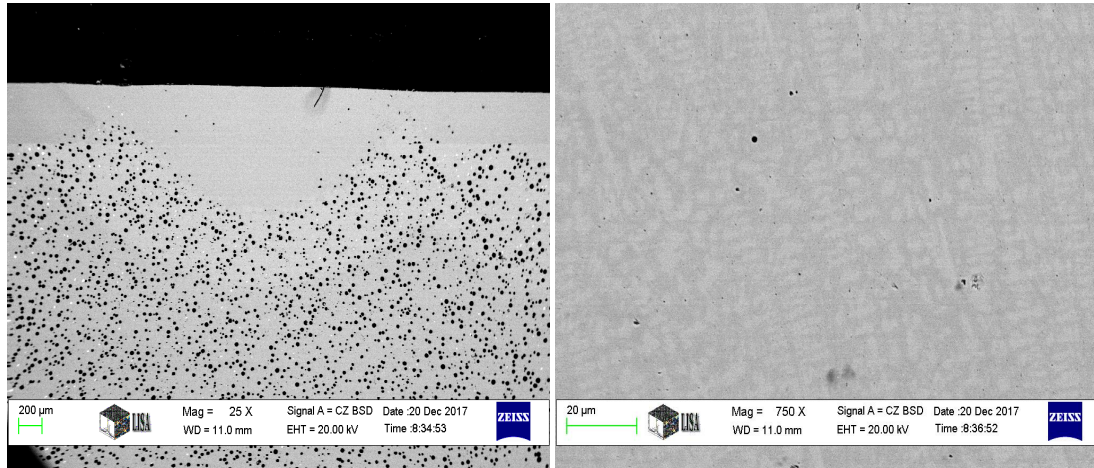


Figure 8. SEM images of the cross-section of the cast iron sample of exp. (NbC 85 wt%. with Si 15 wt%, without MA, laser energy 2500W, moving speed 500 mm/min)

### 3.2.4 LMI experiment using 5 min. MA powder



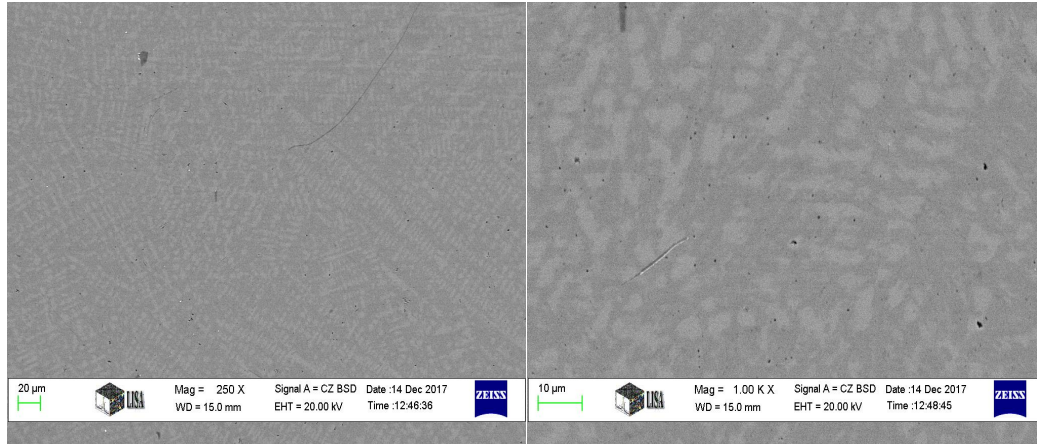
**Figure 9. SEM images of the cross-section of the cast iron coating sample of exp. (NbC 85 wt%+ Si 15 wt%., after MA 5 min, 2500W laser energy, moving speed 500 mm/min)**

From SEM scan images of Figure 9 of the experiment which used iron coated niobium carbide 85 wt% with silicon 15wt% powder after MA for 5 min, can observe effect of mechanical alloying on the components of reinforcing powder, where it dissolved homogeneously manner in the iron matrix, also observed that the eutectic microstructure (similar ledeburite microstructure) was formed during the terminal stages of solidification, due to the high temperature (2173-2375 K) was generated during the LMI process, following its rapid cooling rate after the LMI process.

### 3.2.5 LMI experiment using 240 min. MA powder

From SEM images of Figure 10 for experiments which use iron coated NbC+Si powder that mechanical alloyed for 240 min, observed that the significant difference in the microstructure of the cross-section of cast iron after LMI process, due to the action of mechanical alloying on the components of reinforcing powder for a longer time, where it dissolved manner in the iron matrix homogeneously and there no agglomeration areas for the niobium particles due to the new phases was generated.

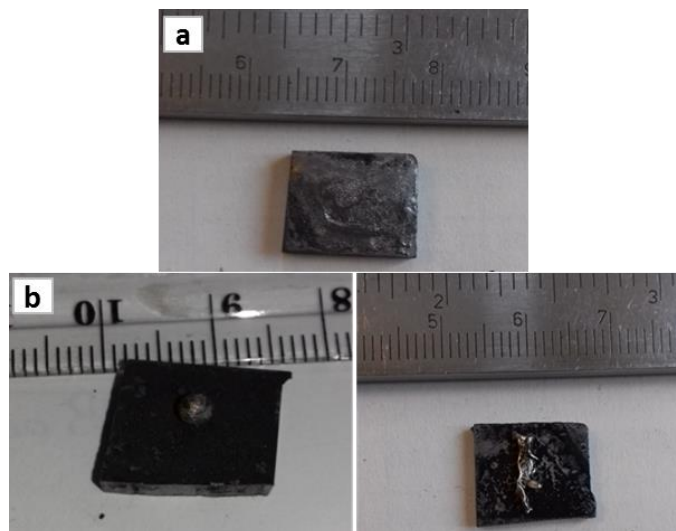
From previous Figs. 7 - 10, can realize the effect of MA on the microstructure of cross-section of the cast iron samples after LMI process, with comparison with a diagram of the specific surface area as a function of the MA time at Figure 3, where observed some particles of niobium agglomerates in the small gatherings due to the effect of mechanical alloying time which increase the specific surface area and surface energy of niobium particles and reduce the wettability in the iron matrix. This is effect increasing with MA time on the agglomerates of the niobium particles in the small gatherings and increasing the area of the agglomerate with increasing of MA time for 30 min and 120 min.



**Figure 10. SEM images of cast iron coating (NbC 85 wt%+ Si 15 wt%, after MA 240 min, 2500w laser energy, moving speed 500 mm/min)**

### 3.3 Brazing results

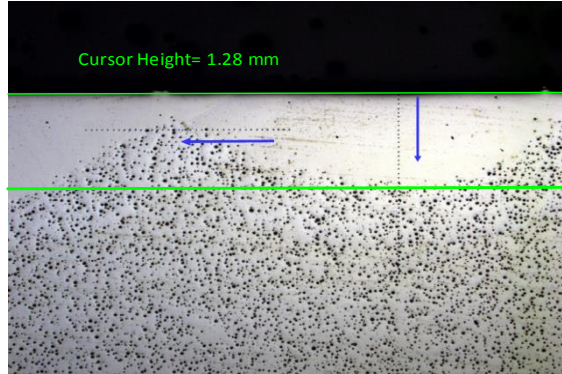
From the brazed cast iron samples, observed that the poor spreading results between cast iron substrates and nickel foil when using iron coated NbC+Si powder after the mechanical alloying process, as shown in Figures 11. The probable reason that the mechanical alloying process for iron coated NbC+Si powder, causes reduce the spreading property of the melted metal due to the effect of mechanical alloying time and milling energy for increases the specific surface area and surface energy of powder particles and reduce the wettability.



**Figure 11. Cast iron sample after the brazing process (a). (Ni alloy foil+ NbC+Si) powder without MA (b). Ni alloy foil+ NbC+Si) powder after MA**

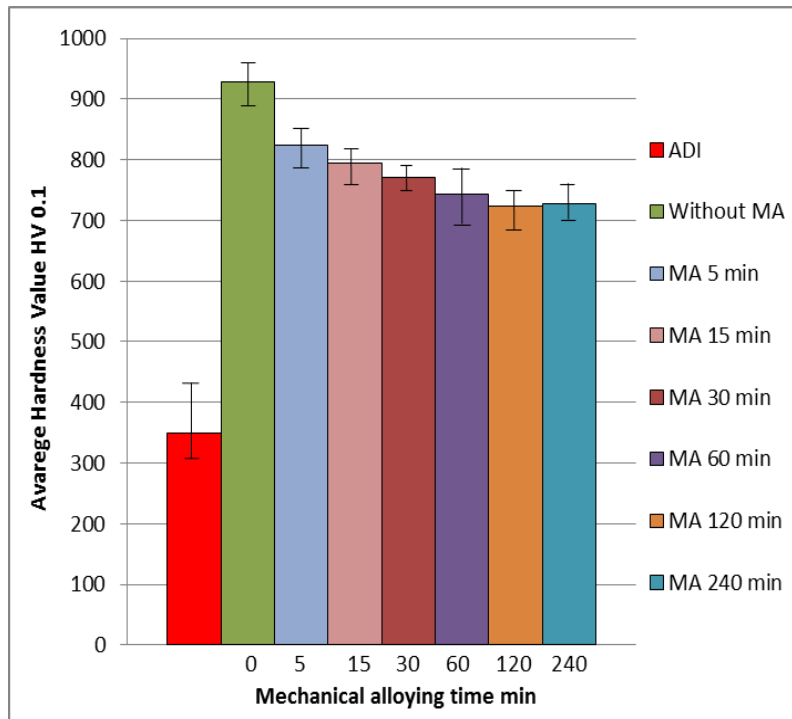
### 3.4 Hardness investigation

Vickers hardness investigation was done on samples after the LMI process at horizontal and vertical direction using a raster pattern, as shown in Figure 12.



**Figure 12. Hardness test after the LMI process at horizontal and vertical direction**

From the average hardness value diagrams Figure 13, observe the difference between the average of hardness values of experiments, from maximum value 928 HV<sub>0.1</sub> to minimum value 777 HV<sub>0.1</sub>, depending on the type of powder used in the laser coating and the laser properties (amount of laser energy, moving speed), the different reinforcing powder compositions have resulted in different microhardness values, since the hardness of the reinforcing powder iron coated NbC+Si without MA, is higher than the reinforcing powder iron coated NbC+Si after MA.



**Figure 13. Diagram of the average hardness value of experiments**

The probable reason that the change in the observed microstructure of the powder iron coated NbC+Si after mechanical alloying caused effect on the characteristic of diffusivity and solubility of powder components, where from previous SEM images observe that the niobium carbide tends to agglomeration in small areas and not on a regular basis in the matrix of iron. Here it was noted that the mechanical alloying causes agglomeration to niobium carbide particles and prevent their spread on a regular basis relatively within melt iron matrix, which creates regions free from niobium carbide, and that causes low hardness in this regions.

Due to the mechanical alloying, the size of the NbC particles decreases to the nanometers size, which helps increase the solubility of the NbC precipitates in the melted iron matrix, therefore limiting their ability to prevent grain growth. As noted previously, it acts as an inhibitor for grain growth when it was in the micrometre size.

### 3.5 Wear resistant investigation

Wear resistance properties are characterized using the mass loss of the specimen and by observing the wear scars and debris. This approximation was valid, where the groove area which generated by dry sliding of Al<sub>2</sub>O<sub>3</sub> ball on the surface of the sample is calculated with the depth of the groove, depending on this two parameters it's possible to measure the wear resistant value, where the lower value of depth and groove area means high wear resistance. The mass variation of the Al<sub>2</sub>O<sub>3</sub> ball is not measured.

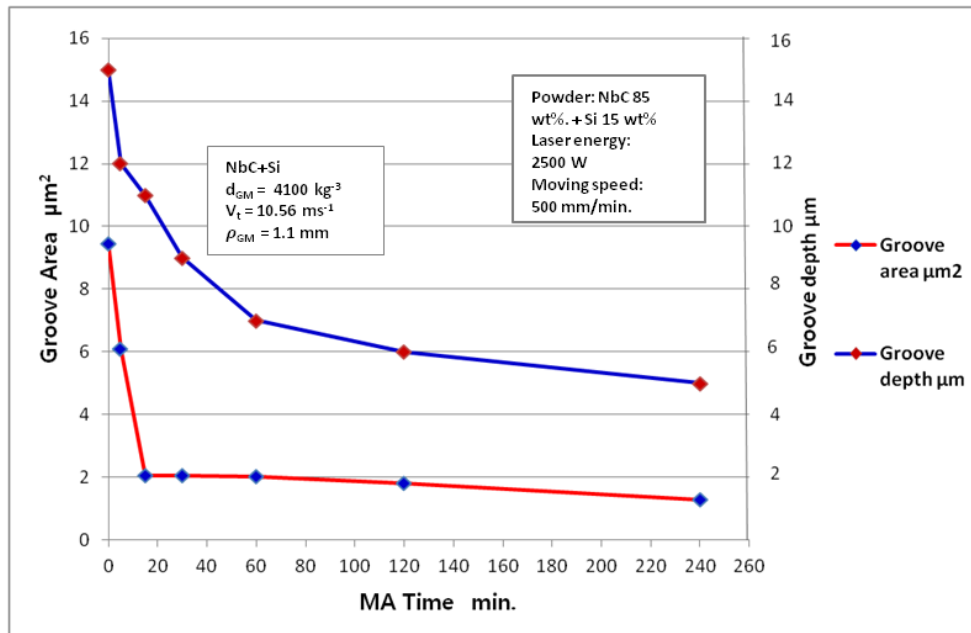


Figure 14. The groove area and depth values of the dry sliding Al<sub>2</sub>O<sub>3</sub> ball on the cast iron substrate after the LMI process as a function of MA time



The dry sliding wear test results in Figure 14, indicate that the wear resistance of the cast iron specimens which have been processed by the laser melt beam injection process with iron coated NbC+Si powder is about 4.6-7.3 times higher than that of the raw cast iron specimen. The new microstructure of cast iron after the laser melt beam injection process becomes more uniform and finer when using iron coated NbC+Si powder after MA than used iron coated NbC+Si powder without MA. The novel microstructure characteristics ensure the LMI process to provide excellent wear resistance, especially the specimens which used iron coated NbC+Si powder after MA for 240 min, and accordingly, wear and friction was abridged because of grain refinement, this explains the different behaviour of the microhardness with MA time of reinforcement powder.

### Conclusions & Claims

1. Based on the scanning electron microscopy images, I established that the addition of 15 wt% of silicon powder to the 85 wt% iron coated niobium carbide powder, which was used as reinforcement powder in the laser melt beam injection process (LMI), improves the diffusivity of niobium carbide particles in the melted iron matrix and promotes particle refinement and form an fine microstructure, and changed the form of niobium particles from the polygon grains (Figure A/a) to longitudinal grains (Figure A/b), which would be under the size of 20  $\mu\text{m}$ , if at all they remain dispersed in the iron matrix.

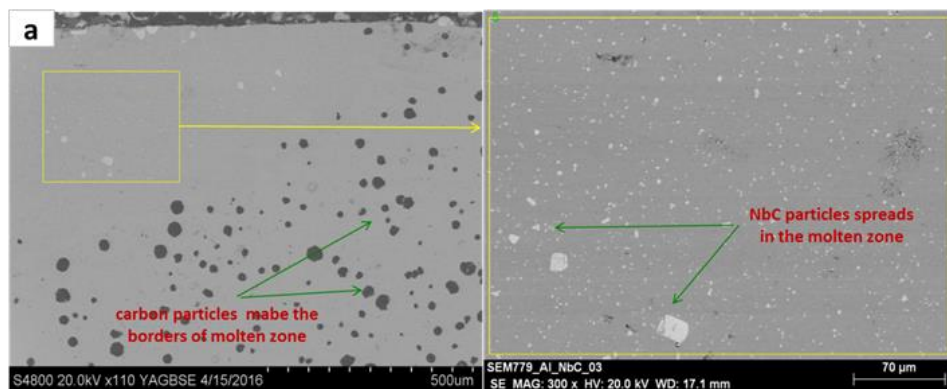
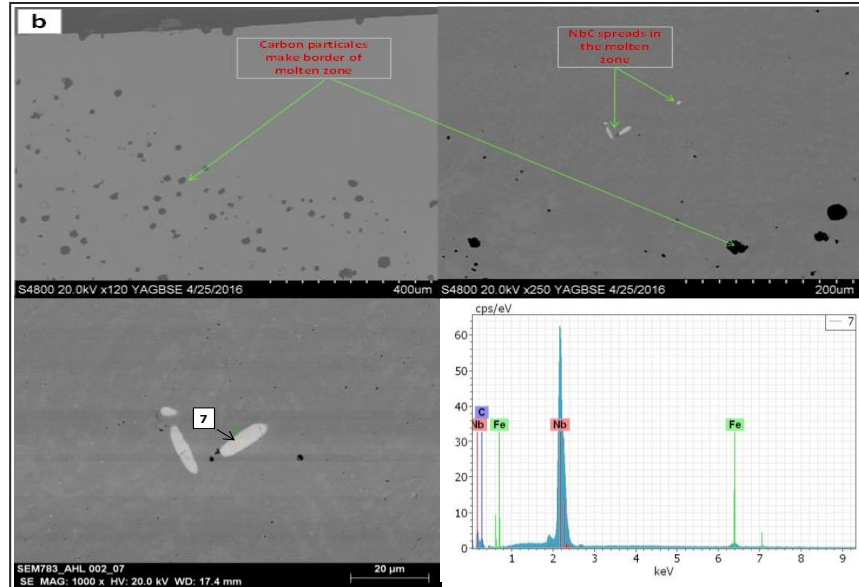
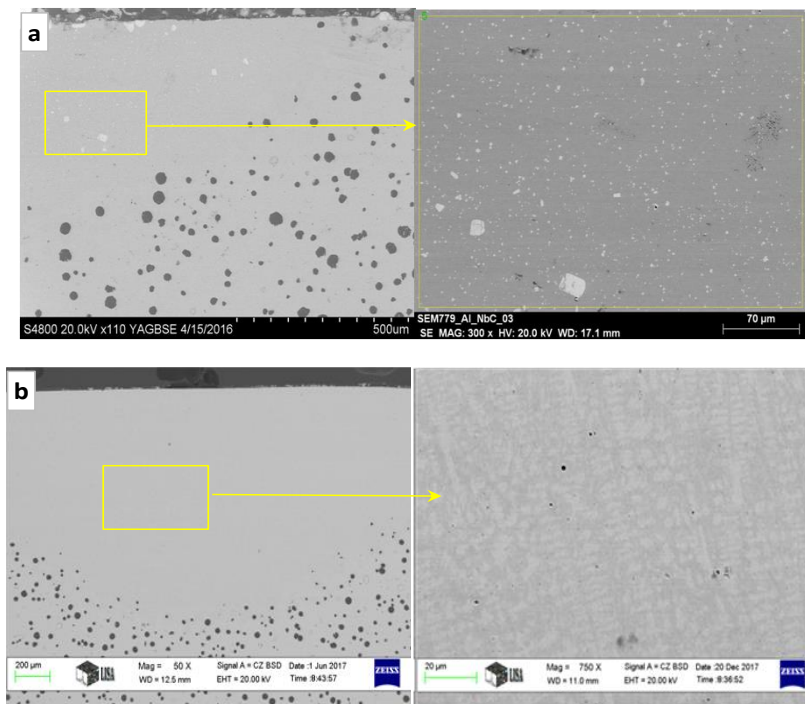


Figure A. SEM of a cross-section of cast iron samples after laser melt beam injection process (a) iron coated NbC powder



**Figure A. SEM and EDS image of a cross-section of cast iron samples after laser melt beam injection process (b) iron coated NbC+Si powder**

2. I established that mechanical alloying (MA) of the iron coated NbC 85 wt% + Si 15 wt% powder from 5 min to 240 min improved the solubility of the powder components in the liquid iron matrix during the laser melt beam injection (LMI) process, as shown in Figure B.

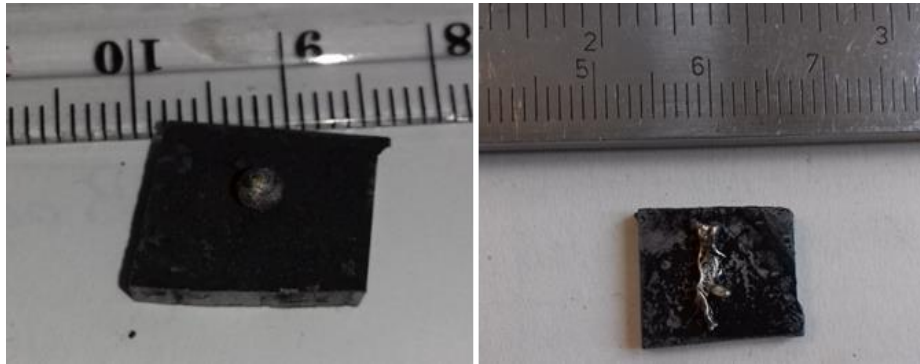


**Figure B. SEM images for the cross-section of cast iron samples after the LMI process (a) Iron coated NbC+Si powder without MA (b) Iron coated NbC+Si powder after MA for 240 min.**

**3.** I determined that the mechanical alloying process for iron coated NbC+Si powder causes reduce the spreading property of the melted metal due to mechanical alloying time and milling energy increasing the specific surface area and surface energy of powder particles and reducing the wettability, see Figures C and D.



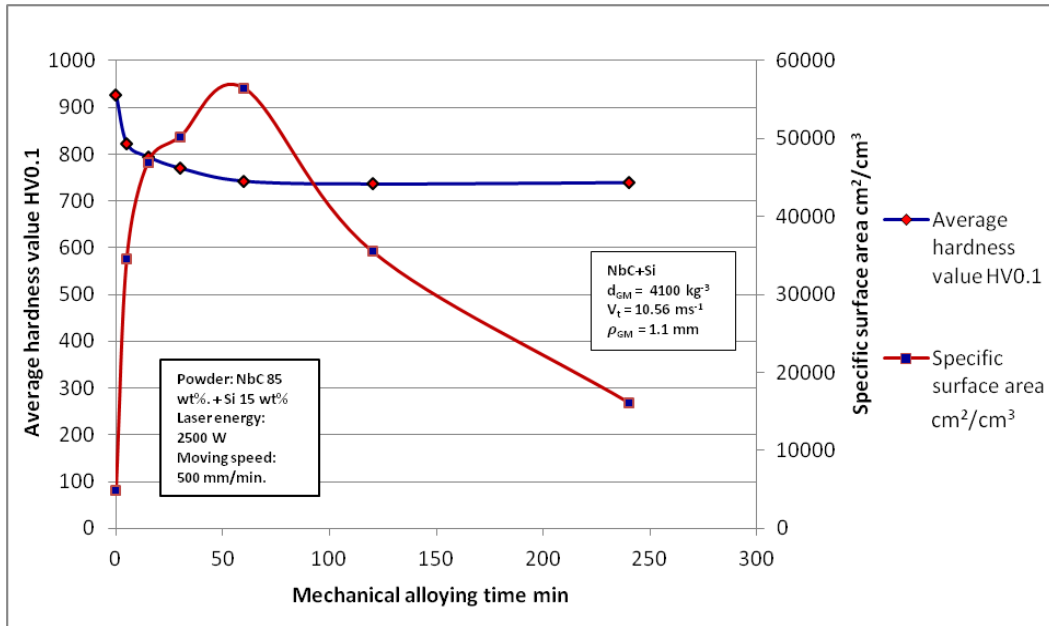
**Figure C. Cast iron sample after the brazing process (Ni alloy foil+ iron coated NbC+Si powder without MA)**



**Figure D. Cast iron samples after the brazing process (Ni alloy foil + iron coated NbC+Si powder after MA)**

**4.** I established that the increase in the mechanical alloying (MA) time and specific milling energy of iron coated NbC 85 wt% + Si 15 wt% powder, which used as reinforcing powder in the laser melt beam injection (LMI) process, caused the hardness values of the cross-section of cast iron treated by LMI process to decrease, from a maximum 928 HV<sub>0.1</sub> to a minimum 777 HV<sub>0.1</sub>, as shown in the Figure E. The probable reason is that due to mechanical alloying, the size of the NbC particles decreases to the nanocrystalline size, increasing the specific surface area, which helps increase the solubility of the NbC precipitates in the melted iron matrix, therefore limiting their ability to prevent grain growth. As noted previously, it acts as an inhibitor for grain growth when it was in the micrometre size. One more reason for decreases in the microhardness, as reported earlier, is that during high-energy milling (MA),

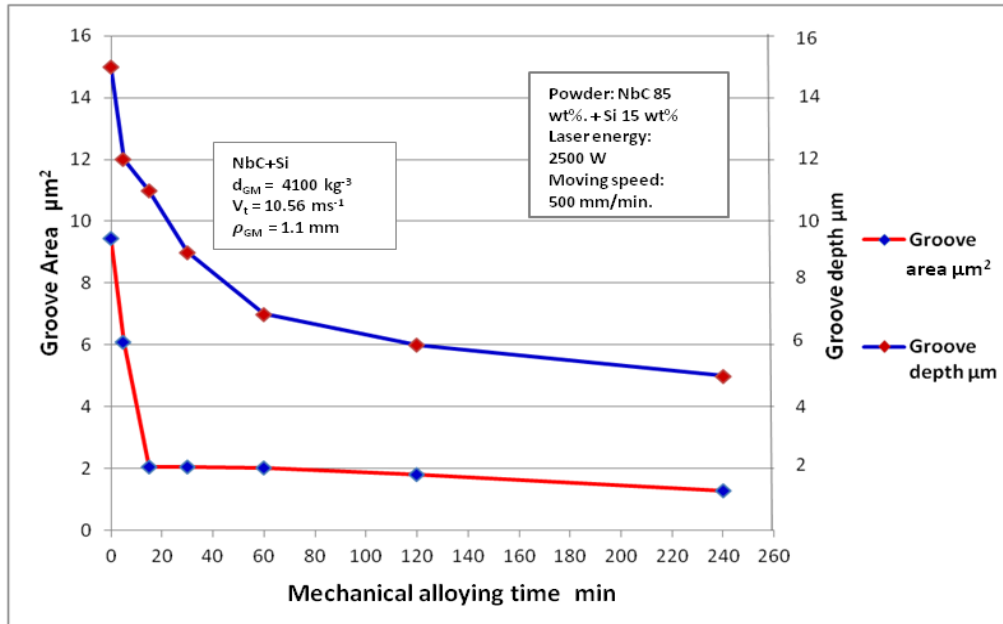
the powders experience large mechanical deformation. Therefore, the products of MA can be compounds, composites, amorphous phases, nanocrystalline materials and metastable and/or supersaturated solid solutions. The same was observed from XRD patterns of iron coated NbC+Si powder, where the Si, Fe and Fe<sub>2</sub>C peaks disappeared after 240 min of the MA process, which has an effect on the diffusivity of Nb in the Fe and precipitation hardening. Hard and brittle Fe<sub>3</sub>C and Nb<sub>4</sub>C<sub>3</sub> precipitates disperse in the NbC matrix and have a significant impact on the microhardness.



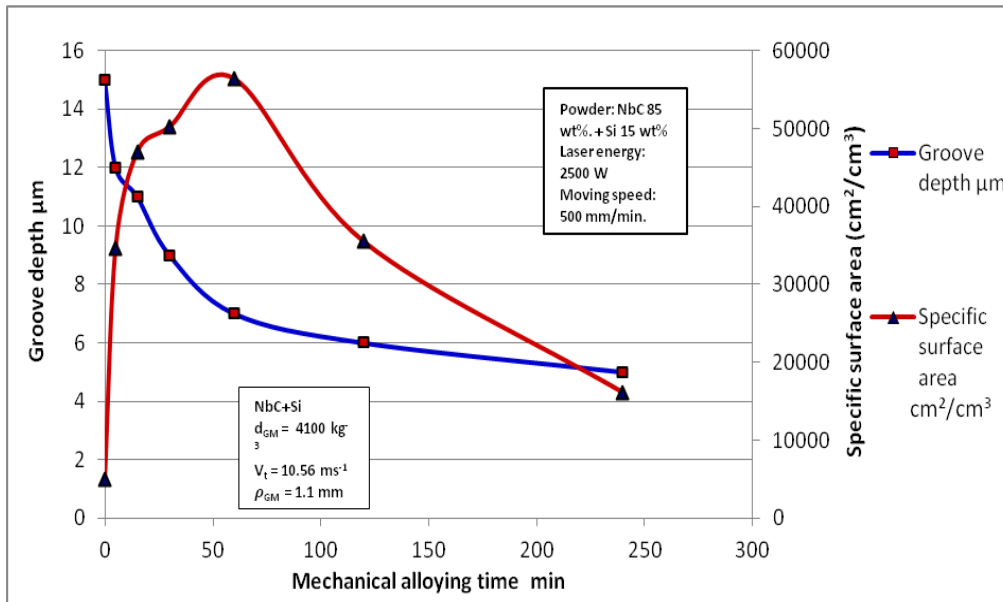
**Figure E. Average hardness values of cast iron samples after the LMI process as a function of MA time and specific surface area of iron coated NbC+Si powder**

5. I established that the wear resistance values of the cross section of the cast iron that was treated by the laser melt beam injection (LMI) process increases with increasing in mechanical alloying (MA) time of the iron coated NbC 85 wt% + Si 15 wt% powder, as shown in Figure F, which shows the results of the groove area and/or groove depth values after dry sliding wear resistance tests, where the groove area decrease from 9.458  $\mu\text{m}$  to 1.289  $\mu\text{m}$ . The new microstructure of cast iron surface after the LMI process became more uniform and finer when using mechanically alloyed iron coated NbC+Si powder than when using iron coated NbC+Si powder without MA, especially the specimens which used iron coated NbC+Si powder after MA for 240 min as shown in Figure G. The novel microstructure characteristics ensure the laser melt beam injection process has excellent wear resistance. The microstructure features can also determine the wear behaviours, and accordingly, wear and friction were reduced because of grain refinement. This explains the different behaviour of the microhardness with

MA time of the reinforcement powder. Consequently the effect of microstructure features of iron coated NbC+Si powder on the LMI process is obvious, and the wear resistance has been improved and confirmed under dry the sliding wear test.



**Figure F.** The groove area & depth values of the dry sliding Al<sub>2</sub>O<sub>3</sub> ball on the cast iron substrate after the LMI process as a function of MA time



**Figure G.** The groove area & depth values of the dry sliding Al<sub>2</sub>O<sub>3</sub> ball on the cast iron substrate after the LMI process as a function of MA time and specific surface area of iron coated NbC+Si powder

**Publications related to this thesis work**

## 1. Scientific publication

1. Al-Azzawi Ali, Peter Baumli: Methods of composite coating: a review, *Materials Science and Engineering*, University of Miskolc HU ISSN 2063-6792, 40 (1) (2015) 26-32.
2. Al-Azzawi Ali, Peter Baumli, Gábor Mucsi: Mechanical Alloying and Milling. Conference paper: MultiScience-XXIX. microCAD International Multidisciplinary Scientific Conference. DOI: 10.26649/musci.2015.017.
3. H. Al-Azzawi, J. Sytchev, P. Baumli: Increasing the surface hardness of a Cast Iron Surface by Electrodeposition of Boron from Molten Salts, *Arch. Metall. Mater.* 62 (2017), 2B, 1015-1018
4. Al-Azzawi, Peter Baumli: Coating of 1.4404 stainless steel by a combination of brazing and nitriding. *J. Metallurgical and Materials Engineering.* 24(3) (2018) 209-218.
5. Ali Al-Azzawi, Ferenc Kristály, Ádám Rácz, Peter Baumli and Gábor Mucsi: Mechanical alloying of NbC and Si in a stirred media mill, (accepted manuscript DOI: 10.2298/JMMB181124016A, *Journal of Mining and Metallurgy Section B: Metallurgy*).

## 2. Oral and Poster Presentations

1. Ali Al-Azzawi, George Kaptay, Gabor Mucsi: Preparation of nano- and microparticles with high mechanical properties, EUROMAT 2015, Warsaw, Poland, September 20 – 24, 2015, poster.
2. Ali Al-Azzawi, Jaroslav Sytchev, Peter Baumli: Surface Hardening of Steels, 14th International Symposium on Novel and Nano Materials (ISNNM-2016), 2016 Júl. 3-júl 8, poster.
3. Mechanical alloying of NbC and Si in a stirred media mill, A. Al-Azzawi, P. Baumli, F. Kristály A. Rácz, G. Mucsi. 9th International Conference on Mechanochemistry and Mechanical Alloying (INCOME 2017), September 3-7, 2017, Kosice, Slovakia, poster.
4. Al-Azzawi Ali, Peter Baumli, Gábor Mucsi: Mechanical alloying and milling, MicroCAD Miskolc, 2015 április 9-10, Oral presentation, SESSIONS B: Applied materials.
5. Ali H. Hasan Al-Azzawi, Sytchev Jaroslav, Péter Baumli: Modification of a Cast Iron Surface by Electrodeposition of Boron from Molten Salts, MicroCAD 2016 április, conference, Miskolc.
6. Al-Azzawi Ali, Peter Baumli, Gábor Mucsi: Preliminary grinding experiments of Niobium carbide and silicon, MicroCAD Miskolc, 2017 April 20-21.
7. Al-Azzawi Ali, Peter Baumli: Coating of 1.4404 stainless steel by a combination of brazing and nitriding, (ISCAME 2018) October 11-12, Debrecen, poster.