

École polytechnique de Louvain

Manufacturing of novel FeMnCoNiZn High entropy alloy via powder metallurgy

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Abstract

Research interest in high entropy alloys (HEAs) have significantly developed due to the broad possibilities in composition, microstructure and their remarkable properties. Some of these properties include high hardness, high strength and ductility, excellent corrosion and wear resistance. The design concept of this new family of alloys involves the combination of at least five major metallic elements, each of which has a varying atomic percentage, between 5% and 35%. Among the many systems of the HEA family, HEAs containing zinc have shown interesting results in their properties and an improved global performance. Despite their excellent properties, the manufacturing of HEAs brings some additional challenges in comparison to classic alloys based on one single element. Overall, the large difference in melting points and tendency of oxidation of the constitutive elements makes casting of HEAs more complex. Moreover, the high price of HEAs would benefit from a technology that would allow near-net shape products to eliminate costly material waste, thus increasing the overall efficiency of the manufacturing process. Hence other methods such as additive manufacturing or powder metallurgy are being considered for these materials. However, a major challenge in the manufacturing of these HEAs through powder metallurgy is the oxidation of the constitutive elements which diminishes the properties of the resulting alloy. This present Master thesis is focused on the production of a Zinc-based High entropy alloy - FeMnCoNiZn via powder metallurgy.

The aim of this study is to avoid oxidation during all stages of the production process. An equimolar FeMnCoNiZn HEA was produced starting from two types of raw powders: i) high purity elemental powders ii) Fe-95Mn - Iron Manganese pre-alloyed powder and Co, Ni, Zn high purity elemental powders. The microstructure was characterized before and after every processing step by SEM, EDX and XRD analysis. Micro-indentation tests were also performed on the sintered samples. The findings indicate that Mn is a critical element for oxidation pick up during the manufacturing process. Even though complete eradication of oxides particles was not achieved in the framework of this project, oxidation can be greatly reduced by the combined use of protective gases such as Ar and H₂ and sacrificial metal such as Titanium. Hence, an oxide-free HEA produced via powder metallurgy can be achieved providing that a fundamental understanding of the oxidation reactions occurring during the all process is available.

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Introduction

High Entropy alloys (HEAs) are a new class of alloys discovered by Yeh et al [1, 2] and have received extensive attention and further research over the years. Contrary to the design of most traditional alloy system which is usually based on one major constituent, HEAs are multi-component alloys consisting of at least five metallic elements, each element having a concentration near equimolar ratios. Exploration of different HEAs have over the years revealed the possibility of obtaining improved properties such as strength, oxidation resistance, work hardening ability, e.t.c, [3] and microstructures than is found with traditional alloys. HEAs enhance the formation of single phase solid solution and not intermetallic compounds during solidification.

The composition range of elements in any HEA is critical in determining the resulting phase, microstructure and stability at high temperature of the alloy. An example is the report by Zhang Y. et al [4]. where the effect of Aluminium content in HEA - $\text{CuCoNiCrAl}_x\text{Fe}$ was studied. Moreover, with the variety of metallic elements to be considered, there is yet few record on some elements such as Zinc.

Powder metallurgy is versatile, economical and a flexible way of producing HEAs with improved strength and microstructure. Although this process is energy efficient and environment-friendly, one major limitation to the high performance of alloys produced with this route is the oxidation of one or more of its constituents elements. Oxide layers are very brittle, thus when these engineering alloys are under stress, cracking of the oxide or plastic deformation of the oxide is prone to occur leading to a decreased performance [5].

This thesis thus focuses on the production of FeMnCoNiZn alloy via powder metallurgy and how the formation of Manganese oxide can be minimized during the process. Classified into four parts:

- Chapter one introduces the reader into the general concept of HEAs, powder metallurgy and the other subjects that are necessary to comprehend subsequent chapters.

- Chapter two contains detailed information on the material preparation and the different characterization techniques used to obtain the results.
- Chapter three details all the results obtained from the analysis of all samples.
- All results are discussed in chapter 4 and compared with literature.
- Finally, a conclusion summarizing all findings in this work is given.

Chapter 1

Theoretical Background

1.1 A brief history on High Entropy alloys

With evolving technology in today's world, new requirements have been on demand in various industries such as the aircraft or the high-speed manufacturing machinery industry, in order to constantly meet structural efficiency and safety. It has thus become crucial to develop new materials and continuously improve the properties of already existing materials. This has over the years led to the development of inter-metallic compounds, multicomponent alloys, and high-entropy alloys [6, 7].

From a trial-and-error process to an innovative knowledge-based research, existing metallic materials have been improved by alloying. With the publication of five journal articles by Jien-Wei Yeh and co-workers and another independent publication by Brian Cantor, high entropy alloys were birthed in 2004 and their investigation through extensive research and increased experimental studies has substantially accelerated over the years. This new alloy design approach has led to the production of alloys with simple structures, such as disordered face-centered-cubic solid solutions, and has also opened a path to the unexplored central region of the phase diagrams [8, 9].

1.2 Description of High-Entropy Alloy

High entropy alloys (HEAs), were initially referred to as alloys with a composition of at least five major metallic elements, in equimolar ratios [10].

However, the name 'high entropy' was given to these categories of alloy because it was believed that due to its high configurational entropy of mixing in comparison with traditional alloys, random solid solutions would prevail over intermetallic

compounds in these alloys [11].

Although there has been a lot of dispute as to the definition of high-entropy alloys, also referred to as multi-principal element alloys (MPEAs) or multi-component alloys (MCAs), this entropy concept led to the definition of HEAs in terms of configurational entropy of mixing [9]. Boltzmann expressed the entropy of a system as

$$\Delta S_{mix} = K \ln W \quad (1.2.1)$$

Where W is the thermodynamic probability or the number of possible ways of arranging the atoms and $K = 1.38 \times 10^{-23} J.K^{-1}$, the Boltzmann constant. For a system of n components, the ideal configurational entropy per mole is given as [12]:

$$\Delta S_{mix} = -R \sum_1^n x_i \ln x_i \quad (1.2.2)$$

Where R is the gas constant, and x_i is the atomic fraction of the i th element. For alloys of equal atomic fractions, $x_i = \frac{1}{n}$ and equation 1.2.2 reduces to:

$$\Delta S_{mix} = -R \ln \frac{1}{n} = R \ln n \quad (1.2.3)$$

Based on this ΔS_{mix} values, Yeh further divided all materials into four group [13]:

- Ultra-pure materials – having a value close to 0
- Low-entropy alloys – containing 1 or 2 principal elements and having $\Delta S_{mix} \leq 0.69R$
- Medium-entropy alloys - $0.69R \leq \Delta S_{mix} \leq 1.61R$ with two to four principal elements.
- High-entropy alloys - $\Delta S_{mix} \geq 1.61R$ with five or more principal elements.

The former definition does not take into account non-equiatomic HEAs, and with increasing number of HEAs, HEAs may also include minor elements for modification of the properties of the base HEA. Hence, it can be redefined as alloys encompassing principal elements with each having an atomic percentage of 5 – 35%. This is

expressed as

$$\begin{aligned}
n_{major} &\geq 5, \\
5at.\% \leq c_i &\leq 35at.\% \\
n_{minor} &\geq 0, \\
c_j &\leq 5at.\%
\end{aligned}
\tag{1.2.4}$$

with n_{major} and n_{minor} been the number of principal and secondary elements, c_i and c_j , the atomic percentages of the principal and secondary elements respectively.

The latter definition also does not take into account the fact that the entropy ΔS_{mix} , of an alloy can change with temperature [11]. From these two definitions, we can now refer to *HEA as an alloy with multi-principal elements having a mixing entropy $\Delta S_{mix} \geq 1.5$* , which increases the occurrence of a single-phase solid solution. It is however important to note that the above definitions are not a clear-cut definition of HEAs but just a guideline.

1.3 Core effects of HEAs

High entropy alloys have compositions that are completely different from traditional and conventional alloys. This exceptionality led Yeh in 2006 to propose the four core effects namely; high entropy effect, sluggish diffusion effect, lattice distortion effect and cocktail effect.

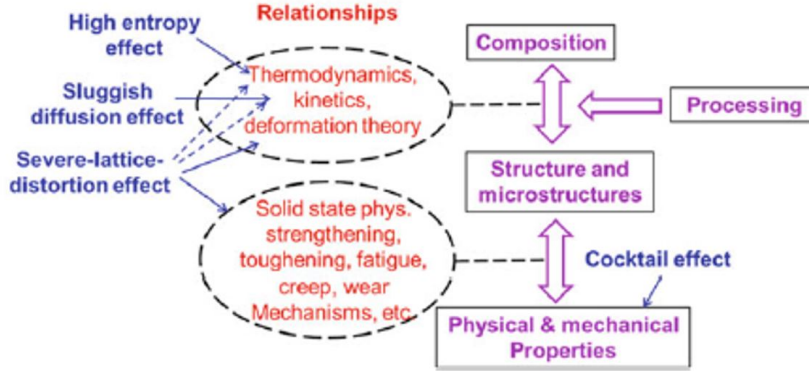


Figure 1.3.1: Areas influenced by the four core effects in the scheme of physical metallurgy [14].

They each explain the effect of thermodynamics, kinetics, microstructure and properties on HEAs as demonstrated in figure 1.3.1. These core effects are further explained below.

1.3.1 High Entropy Effect

High-entropy effect is one of the most important effect in HEAs, because it can enhance the formation of solid solution phases in the solid state of an alloy. Solid solution is the phase with the complete mixing or substantial mixing of all elements in the structure of FCC (face-centered cubic), BCC (body-centered cubic) or HCP (hexagonal closed-packed). Other phases that could possibly compete with the solid solution phase are the elemental phases and the intermetallic compounds. Elemental phase is the terminal solid solution based on one metal element, while intermetallic compound is a stoichiometric compound having precise superlattices. From a thermodynamic viewpoint, whether a reaction can occur in competition with others is determined by its Gibb's free energy of mixing which is expressed as [9, 14];

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad (1.3.1)$$

Where T is the absolute temperature, ΔH_{mix} is the enthalpy of mixing, which is a measure of the change in energy under constant temperature and pressure, ΔS_{mix} and is the entropy of mixing, which is a measure of the degree of randomness of a system at the atomic level. For the formation of solid solution phase, a medium negative ΔH_{mix} and highest ΔS_{mix} is required. Table 1.1 shows the comparisons of these parameters in all the possible phases.

Possible States	Elemental phases	Compounds	Solid Solutions
ΔH_{mix}	~ 0	Large negative	Medium negative
$-T \Delta S_{mix}$	~ 0	~ 0	$-RT \ln n$
ΔG_{mix}	~ 0	Large negative	Large negative

Table 1.1: Comparisons of ΔH_{mix} , ΔS_{mix} and ΔG_{mix} among elemental phases, compounds and solid solutions for n elements HEAs [15].

Although, we have other entropy effects such as vibrational, electronic randomness and magnetic dipole effect, configurational entropy dominates in disordered solid solutions. [15].

1.3.2 Severe lattice distortion effect

From Figure 1.3.2, we observe that pure metals have the similar type of atoms occupying their lattice sites, hence no form of distortion to the lattice is produced and conventional alloys experience slight distortion to their lattice due to the invasion of a minor amount of second atomic species [9].

In HEAs, the co-existence in high concentration of several atoms of different sizes

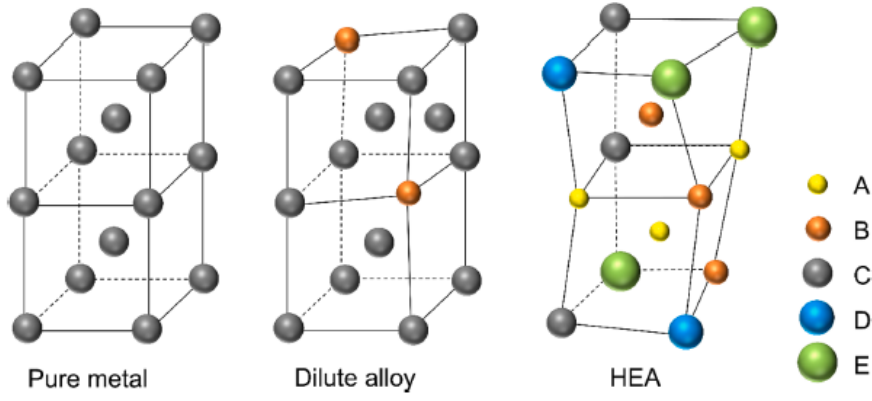


Figure 1.3.2: Diagram of lattice distortion in body-centered cubic pure metals, conventional dilute alloys and high-entropy alloys. A-E represents diverse element species in general [9].

in the lattice generates a severe distortion. Equation 1.3.2 shows the relationship between the lattice distortion for a multiple-element matrix and the variances in its atomic size δ

$$\delta = 100 \sqrt{\sum_{i=1}^{n'} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (1.3.2)$$

where $\bar{r} = \sum_{i=1}^{n'} c_i r_i$ and c_i and r_i represents the atomic percentage and atomic radius of the i th element respectively [14].

Besides the atomic size difference, bonding energy and crystal structure difference among constituent elements also causes lattice distortion. This distortion affects the properties of HEAs – increased hardness and strength via solution hardening, decreased electrical conductivity and thermal conductivity [15].

1.3.3 Sluggish Diffusion Effect

Generally, the creation of new phases requires harmonized diffusion of several kinds of atoms in order to achieve the partitioning of compositions. HEAs diffuse mainly through the vacancy mechanism, however, the rate at which atoms diffuse is in HEAs slower than that of other alloys due to lattice distortion. In a recent study by Yeh [16], where he studied the vacancy formation and compared the diffusion coefficients for the elements in pure metals, stainless steel and HEAs, the order of diffusion rates in three types of alloy system was discovered as shown below:

$$\text{HEAs} < \text{Stainless Steel} < \text{Pure metals}$$

Owing to the interaction between different atoms and the lattice distortion,

atoms need to overcome a potential energy barrier to migrate as they strive to maintain a site consistent with the lowest lattice potential energy. In the process, diffusion becomes challenging. This was reported by [17] after several experiments where he observed that the greater the number of elements, the slower the diffusion rate; hence the term ‘sluggish’. Sluggish diffusion affects all diffusion-controlled processes such as solidification, grain growth, recovery and recrystallization, phase transformation and creep resistance. This can in turn benefit the microstructure and property control for better performance [18].

1.3.4 Cocktail effect

Cocktail effect is not a hypothesis like the other core effects discussed, rather it is a composite effect that represents the results and enhanced properties that come from the interactions of various elements in the immense composition space of HEAs [11].

1.4 Properties of HEAs

The enormous range of composition possible with HEAs significantly increases the number of alloys to be characterized. When considering alloys in the same family, an addition or adjustment of one element can have a huge impact on the microstructure and properties. This microstructure and properties are very sensitive to the production method and post-process thermo-mechanical processing used.

1.4.1 High Hardness

With all elements having different atomic radius, there is an intense lattice distortion of the alloy. This impedes the movement of dislocation and thus leads to very high strength and hardness. From statistical data, HEAs exhibit hardness values ranging from 150 to 1200 HV [12]. Figure 1.4.1 shows the hardness values for 20 of the most studied HEAs in comparison with conventional alloys. This value greatly depends on the microstructure. HEAs with single phase FCC structures are very ductile but possess a low hardness value (100 – 200 HV) when compared with the BCC HEAs (>600 HV) and this mainly due to the presence of stronger second phases such as intermetallic phases [11].

1.4.2 Corrosion Properties

Due to high mixing entropy effect, HEAs form simple structures instead of complex intermetallic compounds and have thus shown excellent corrosion properties superior to that of conventional alloys particularly those consisting of Cr, Ni, Mo, Co Cu,

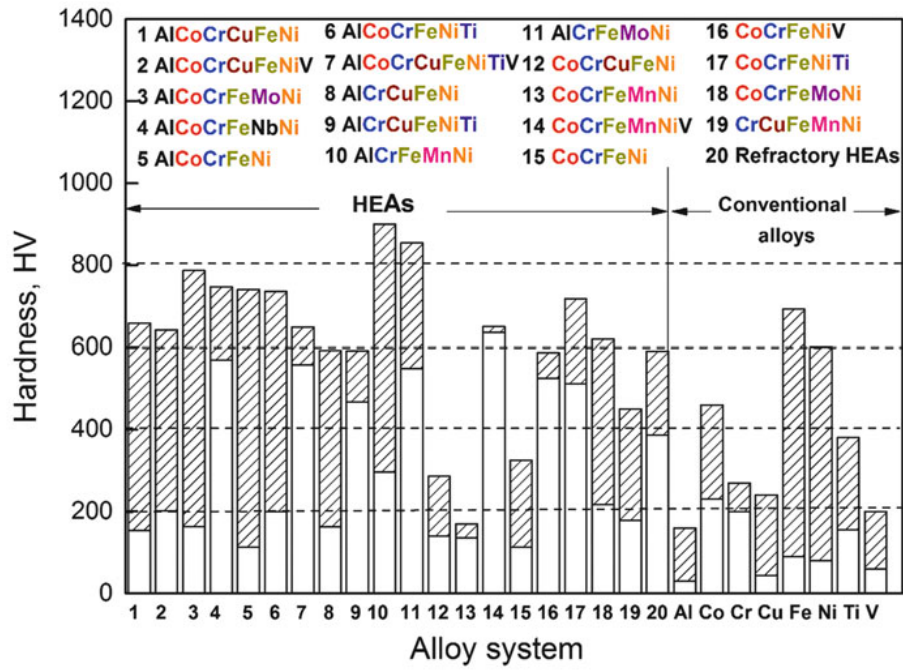


Figure 1.4.1: Hardness values of 20 most studied HEAs and some conventional alloys. The hatched region indicates the hardness range of individual alloy system [14]

or Ti. An example is $\text{Cu}_{0.5}\text{NiAlCoCrFeSi}$ HEA which exhibited better resistance than stainless steel in 1mol/L NaCl and 5mol/L H_2SO_4 solutions [19]. They are very relevant in chemical plants and marine application where anti-corrosive high strength materials are required. This property is also been utilized in their use as surface coatings [20].

1.5 HEAs containing Zinc

The element Zinc is rarely found in the formulaion of several HEAs, however in *alloys* containing this elements, interesting results have been observed.

Kai Wen et al. [21] studied the effect of age hardening on the properties of two Aluminium alloys - AlZnMgCu with high zinc content of 9.32 and 9.78 wt% respectively. Operating conditions and test results on the tensile properties at room temperature of these alloys is summarized in table 3.5. It was observed that alloy 1 with a higher zinc content had a slower decline in strength for the same holding time at 160°C.

AlFeTiCrZnCu HEA produced via mechanical alloying was sintered and subjected to Vicker's hardness [22]. This nanocrystalline equiatomic HEA had a Vicker's hardness and compressive strength of 9.50GPa and 2.19GPa respectively. The exceptional values reported was due to the presence of a greater fraction of nanocrys-

talline BCC phase. A wear study on this alloy also showed that AlFeTiCrZnCu HEA possess a greater wear resistance than the commercially used Nickel hard faced alloy.

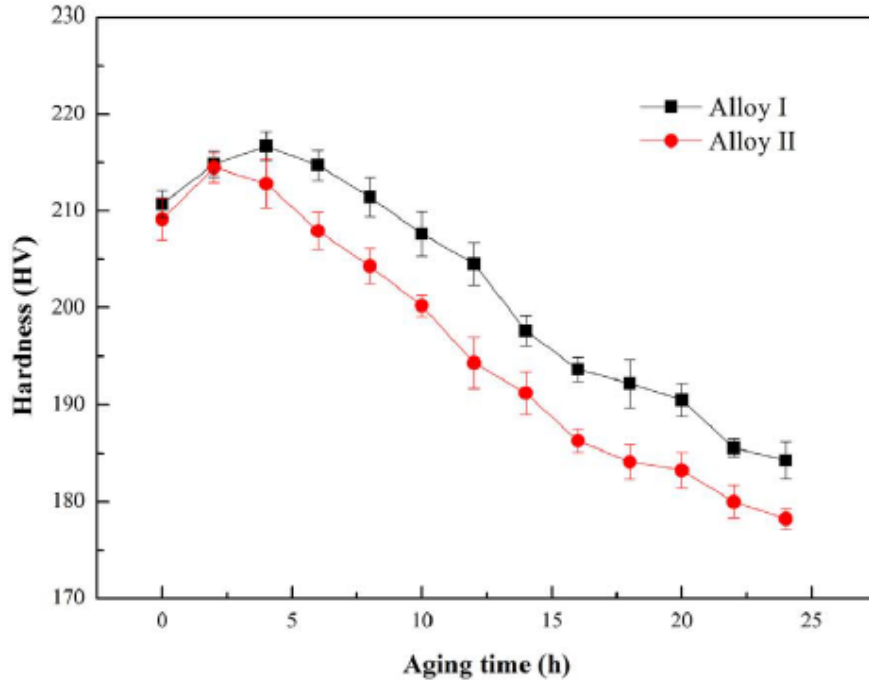


Figure 1.5.1: The hardness of two Aluminium alloys with high zinc content aged at 110°C for 8 hours and then held at 160°C

	Alloy 1	Alloy2
Aging temper.	110°C/8h + 160°C/6h	110°C/8h + 160°C/9h
UTS (MPa)	651	643
Yield Strength (MPa)	641	626
Elongation (%)	12.6	13.3
Hardness (HV)	214.7	198.3
Electrical conductivity ($MS.m^{-1}$)	20.4	21.1

Table 1.2: Mechanical properties and electrical conductivity of AlZnMgCu alloys.

Finally, Cardoso et al. [23] studied the mechanical behaviour of AlCrCuFeZn HEA, prepared via mechanical alloying and spark plasma sintering. The sintered sample exhibited a high hardness value of 627 HV which is attributed to the presence of a CuZn-enriched BCC phase. A similar result is also reported by [24, 25] on CuNiCoZnAlTi HEA. This is so because BCC structured alloys are generally harder than FCC alloys.

1.6 CALPHAD Based Method

Phase diagrams are fundamental tools to understand and predict phase transformation in metallic alloys following changes in temperature and composition. When properly constructed, it provides the various phase relations, an overview of the thermodynamic behaviour of a system and also the ultimate performance of the material. It is thus unique for a given material system. Phase Diagrams are developed purely via experimentation, which is an expensive and time-consuming process. While it is possible via experimentation for binary and ternary systems, it is almost impossible when a wide range of composition is been considered. With the use of various computational methods, such as quantum mechanics, molecular dynamics, meso-scale simulations and density functional theory (DFT) calculations, design process of alloys and many other materials can be significantly fast-tracked [14, 26].

CALPHAD, an acronym for CALculation of PHase Diagrams is a method with which multi-component phase diagram for materials and alloys design can be obtained. It allows predicting the phase diagram of higher-order system by extrapolating the results from its constituent lower-order system. Given that this method provides information about the phases present and their reaction temperatures, a micro-structural assessment can therefore be performed [27].

The phase equilibrium data for the lower-order systems – binaries and ternaries are collected and stored in a thermodynamic database. CALPHAD combines the use of this database and a computational software to give its prediction. The resulting as-extrapolated phase diagram is not always in complete agreement with the experimental phase diagram, but it still offers a close-ranged evaluation of what should be expected.

This approach was used in the study by Zhang et al. [28] where the thermodynamic database for the Al-Co-Cr-Fe-Ni system was developed using only the lower-order systems. There are various software packages for phase diagram calculation based on CALPHAD method, such as Pandat, Factsage and Thermocalc. In this report, Thermocalc software was used.

Ab initio molecular dynamics (AMID) is another effective way through which the phase stability of HEA system can be predicted. This approach is based on quantum mechanics and provides information on the preferred atomic bonding that may impact formation of disordered solid solution during solidification. It is used in predicting the structural, thermodynamic properties and diffusion constants at finite temperatures therefore complementing the information provided with CALPHAD [4].

1.7 Powder Metallurgy

Powder metallurgy is the art and science of manufacturing metallic components, either ferrous or nonferrous part of a wide variety of shapes via mixing of element or alloy powder. It is used in producing composite materials, and high performance components while offering compositional flexibility. Producing a component via this method can be grouped into four sequence of operations [5]:

- Powder production and characterization
- Compaction
- Sintering
- Finishing operations

1.7.1 Powder production and characterization

Powder is essentially the raw material involved in Powder metallurgy process, they can be that of pure elements, or pre-alloys. There are several methods to producing this powder, some of the commonly used methods are atomization, electrolysis and chemical decomposition of compounds. Crushing is also carried out as a preparatory step to reduce bulk materials into powders. These elemental powders and pre-alloys are mixed using mixers. The goal is to mix the powders for as long as it is necessary to achieve a thorough and homogeneous mix. In some cases, lubricants are added prior to mixing in order to minimize wear of the compaction tool [29].

1.7.2 Compaction

The goal at the stage is to produce a compact with adequate strength that will withstand subsequent handling. The powder mix is loaded into a die and pressure is applied using a hydraulic press, increasing the contact area between particles [5].

1.7.3 Sintering

Sintering of the compact is done in a furnace under a protective atmosphere in order to aid the bonding of particles. Upon heating to the sintering temperature, particles begin to fuse together leading to shrinkage and densification. Pores are gradually eliminated and a stage is attained when the density does not increase upon further heating [30]. This process ensures that the powders are sufficiently bonded into a coherent body with desired physical and mechanical properties. Figure 1.7.1 shows the evolution of the density of the compact as a function of time. Compacts of fine

powders densify faster than compacts of coarse powders.

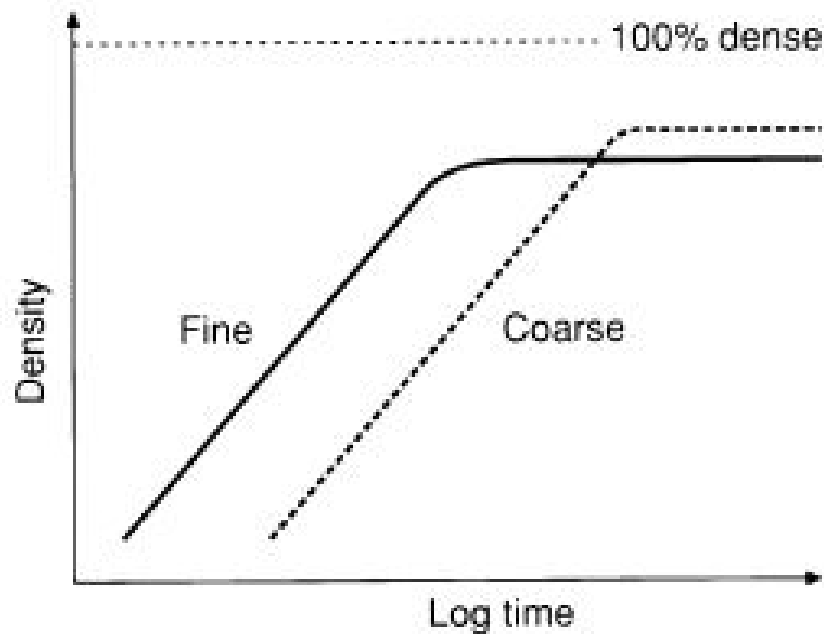


Figure 1.7.1: Schematic showing the evolution of density of the powder compact as a function of time [30]

1.7.4 Finishing operations

This includes plating, polishing, machining, e.t.c. It is usually done to improve surface finish and dimensional tolerance of the sintered part.

In summary, powder metallurgy is an excellent choice when the requirement for strength and high operating temperatures exceeds the capabilities of die casting alloys and other convectional manufacturing methods. It is simple in operation, energy efficient, effective in quality control and also produces less waste[31].

1.7.5 Limitation of Powder Metallurgy

In the use of powder metallurgy manufacturing technique, there are certain limitations related to the powder manufacturing, compaction and sintering steps. The ratio of surface area to volume of powder is generally large and increases with increasing fineness, thus contributing to their high reactivity with the atmosphere. Surface pollution such as oxidation and adsorption thus introduces contaminants to the powder.

A way to avoid this is to carry out the production and every other handling process under a protective atmosphere [31] and to also make use of pre-alloyed powders. If at any point which is usually the case, the metal powders are exposed

to air, they are covered with oxide layers. Internal oxidation is a process by which oxygen diffuses into an alloy and causes sub-surface precipitation of the oxides of one or more alloying elements [32]. All metals have different affinities for oxygen, for those with strong affinity such as Manganese and Chromium, getting rid of the oxide layer is a difficult process and they still have tendencies to acquire more at every step. It can be eliminated at high temperatures but would require proper understanding of the Ellingham diagram.

1.7.6 Ellingham Diagram

Ellingham diagram is a useful tool in exploring the probability that a chemical reaction would be favoured over the others in a material. Figure 1.7.2 is one of the common Ellingham diagrams – for metals reacting to form oxides. It is a plot of the Gibbs free energy against temperature that helps us understand the thermochemistry of oxidation. Majority of the oxides of everyday metals are thermodynamically stable at low temperature and would require high temperature to be decomposed [30]. When there is a reaction between a gas and a condensed phase that produces a condensed phase, we observe the lines slope upwards because entropy is reduced. However, when a solid reacts with a gas to produce an additional mole of gas, there is a huge increase in entropy causing a steep downward slope. This is the case for the reaction equation:



In the oxidation of solid carbon, the line is almost horizontal because there is a minor change in entropy. [33] A solid is reacting with a mole of gas to produce only a mole of gas.



1.7.7 Reduction of Metal Oxides

One of the main reasons the Ellingham diagram is extremely useful is because it helps in determining the ease with which a metallic oxide can be reduced to a metal. It gives information on the reaction that would occur before equilibrium is attained but not on the kinetics – how much time is required. The stability of the metal oxide as a function of temperature is dictated by the position of its line on the diagram. Moving from the upper region to the lower region, the reactivity of metals increases and their oxides become difficult to reduce [33]. Aluminium and Magnesium at the far bottom are thus highly stable and are exceptional reducing agents.

Consider a metal X that is to be obtained by reducing its metal oxide, XO_2 with a reducing agent Y,



The forward direction is highly favoured if YO_2 is more stable than XO_2 . In other words, the Gibbs's free energy of formation of YO_2 is more negative compared to that of XO_2 . Solid carbon for instance, would reduce Titanium dioxide at a temperature above 1620°C and also reduce other stable compounds like Manganese oxide and Silicon dioxide at temperatures of 1400°C and 1225°C . For a reducing agent to be highly effective, the reaction must possess a high negative value of ΔG° and the agent must be in contact with the metal oxide to be reduced. If the reducing agent is in solid form, having the reducing agent in a gaseous form is a quick way to achieve reduction [30].

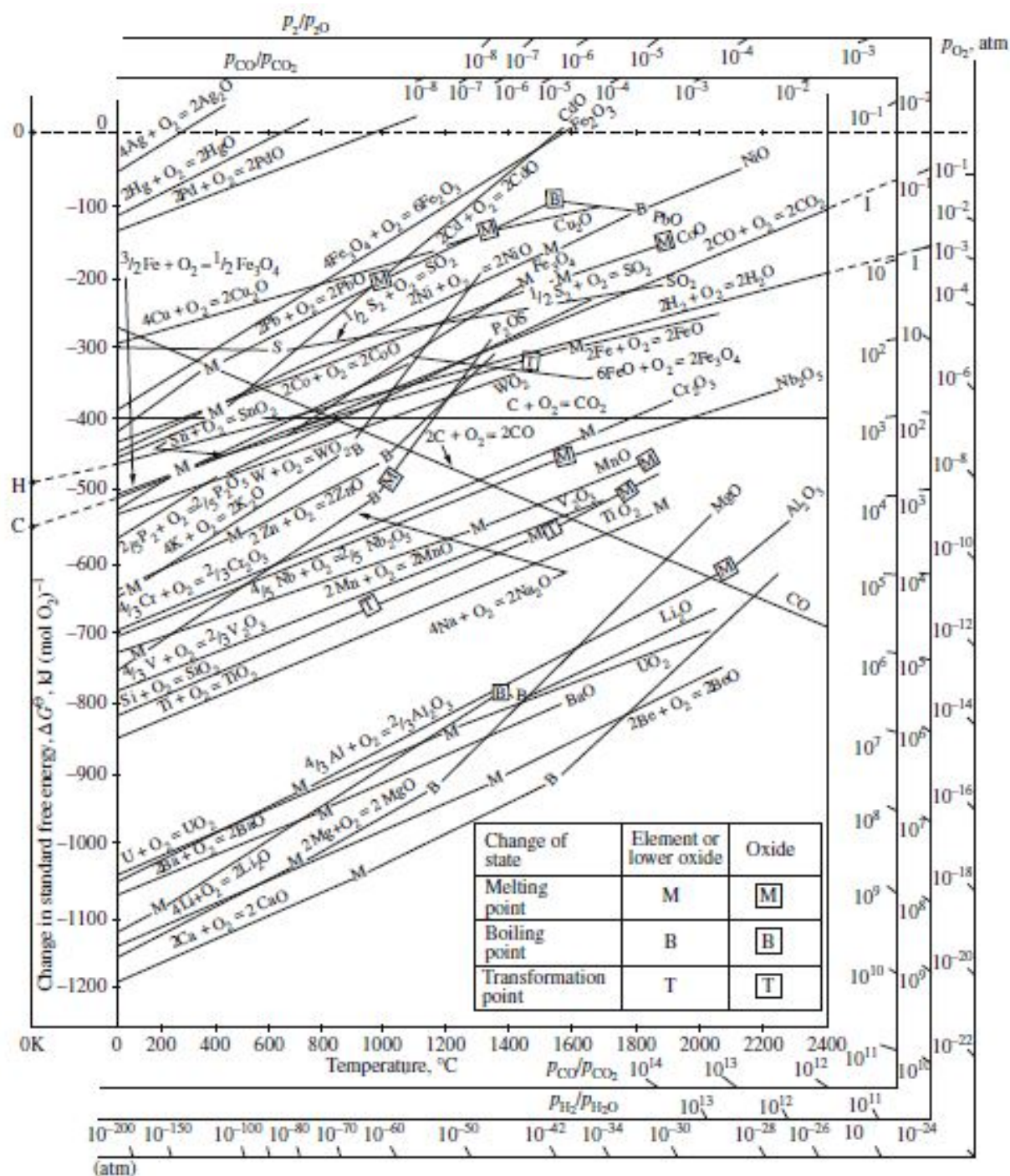


Figure 1.7.2: Ellingham Diagram for Oxides [33].

Chapter 2

Experimental Methods

In this section, details of preparation and processing of the FeMnCoNiZn sample is discussed. The different characterization methods used in analysing the microstructure and properties are explained. All equipment and experiments carried out in the framework of this thesis are at Institute of Mechanics, Materials and Civil Engineering (iMMC), UCLouvain except otherwise stated. The elements used were high purity of Fe, Mn, Co, Ni, Zn.

2.1 Sample Processing and Preparation

2.1.1 Pre thermal treatment

Case 1: In preparing 250g of FeMnCoNiZn, equal atomic proportion of each elements calculated using equation 2.1.1 and presented in table 2.1 was weighed and mixed for 48hours.

$$Weight(grams) = \frac{Atomic\ weight_i \times Total\ mass}{S.Atomic\ weight} \quad (2.1.1)$$

where $S.Atomic\ weight$ is the sum of the atomic weight of all elements.

Element	Fe	Mn	Co	Ni	Zn
Weight (g)	47.5238	46.7495	50.1447	49.9404	55.6416
Weight fraction	0.190	0.187	0.210	0.199	0.223

Table 2.1: Elemental calculation for 250g of FeMnCoNiZn Powder

Case 2: 200g of FeMnCoNiZn was prepared using Fe-95Mn weight fraction

of pre-alloyed powder. Table 2.3 shows the mass balance of the elements measured.

Element	Fe	Mn	Co	Ni	Zn
Weight (g)	39.3679	36.0507	40.1157	39.9524	44.5133
Weight fraction	0.197	0.180	0.201	0.199	0.223

Table 2.2: Elemental calculation for 200g of FeMnCoNiZn Powder

The resulting powder in both cases was compressed in small quantities using a compact die under uniaxial load of 50KN. The compressed powder was wrapped in a stainless steel sheet and encapsulated in a quartz capsule in order to prevent oxidation during heat treatment. All capsules from case 2 were filled with Argon – 5 %H₂ gas. Hydrogen as a reducing agent should contribute to the reduction of existing oxides that could be already present in the sample prior to heat treatment. For capsules from case 1, some were filled with Argon–5 %H₂ and in the others a piece of titanium was placed. The use of titanium in this step is in view of the fact that according to the ellingham diagram, it is a good reducing agent for Manganese oxide - MnO.

2.2 Thermal treatment

The electric furnace was pre-heated to 800°C, then the encapsulated samples were carefully placed directly into the furnace. Capsules from case 1 encapsulated in Argon–5 %H₂ gas were heat treated at 800°C for 3 days and 1000°C for 3 hours consecutively for homogenization. Other capsules from case 1 in which a piece of Titanium was placed were heat treated at 800°C for 5 days and 1000°C for 3 hours. They will be referred to as Case 1A and 1B respectively. Capsules of Case 2 was also subjected to heat treatment at 800°C for 3 days and 1000°C for 3 hours. All samples were quenched in water upon removal.

2.3 Post thermal treatment

Preparing the heat treated samples for characterization involved a number of steps discussed below:

2.3.1 Polishing

Samples were mounted into a Polyfast - conductive resin, making it easy to hold the specimen by hand while also protecting its edges during polishing. The sample was

held manually with a moderate pressure, while the polishing wheels on which the abrasive was placed was rotating at different speed. The samples were polished using a silicon carbide (SiC) abrasive paper, starting from coarse grit and progressively using finer grit sizes. The grit size used were 80, 320, 600, 800 and 1200. This was followed by a polishing step with diamond paste on finer abrasives of $6\mu m$ and $1\mu m$. At each step of the polishing, particles introduced from previous step was removed by cleaning the sample with ethanol. Finally, using a OP-S Non Dry colloidal silica suspension, a chemical polishing process was carried out. This step helps to reveal different phases and different crystallographic orientations of the sample when observed at the scanning electron microscope (SEM). The sample was placed in a ultrasound machine containing ethanol for 8 minutes: to get rid of gas or particles that might still be present in the sample.

2.3.2 Sintering

Sintering involves producing a component from powder compacts via elimination of the inherent porosity in the compacts by heating. The samples were milled into powder form for 20 minutes; 50g of the powder was used to produce powder compacts were produced under 4 tons of load. The sintering test was executed on a HP D10 SPS machine (at Belgian Ceramic Research Center - BCRC Mons.) in an argon atmosphere following the thermal cycle below:

- i Heating at $250^{\circ}\text{C}/\text{min}$ up until 750°C
- ii Heating at $50^{\circ}\text{C}/\text{min}$ from 750°C to 850°C
- iii Holding at 850°C for 2.5 min
- iv Cooling

A uniaxial pressure of 48MPa was applied on the compact and maintained for the entire duration of the sintering cycle. Figure 2.3.1 shows the evolution of the force and displacement with time. The blue line corresponds to the relative displacement of the sample during densification of the compact. During shrinkage of the powder compact, a upward displacement is observed, while a downward displacement happens during an expansion. The black curve represents the temperature as measured by the pyrometer at 5mm above the center of the sample's top face. The pressure applied on the compact is indicated by the red line on the curve. At 850°C , the density of the compact has attained a maximum and does not increase with further heating. The sintering curve for other samples are presented in Appendix A. The details of each sample after sintering is given in table

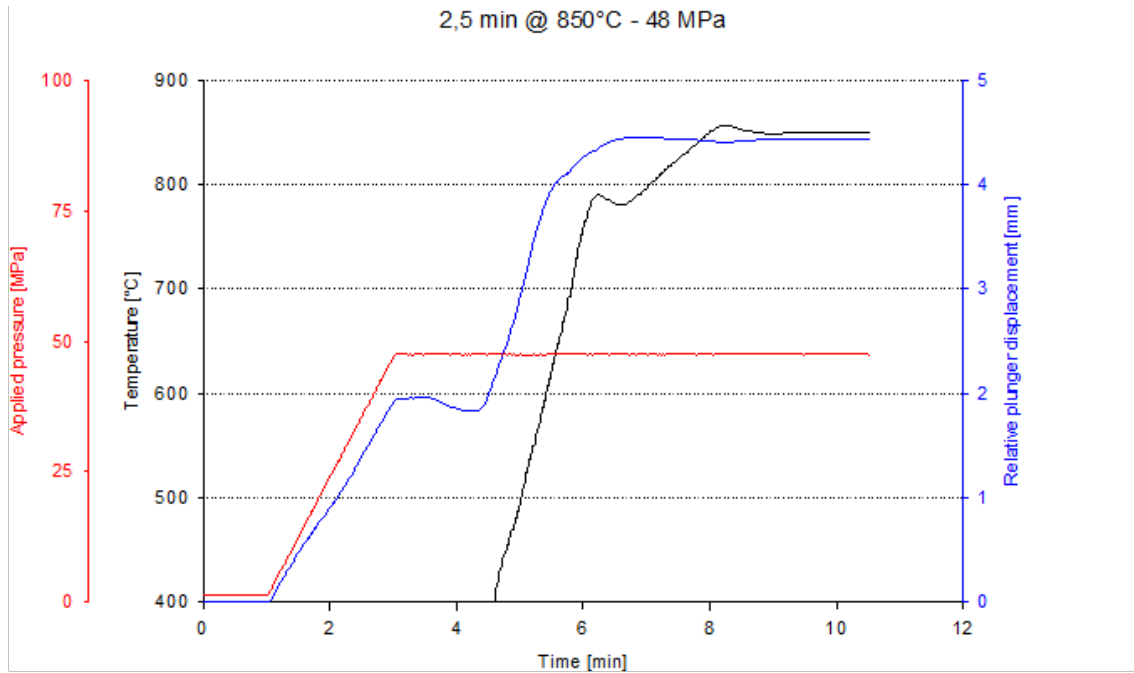


Figure 2.3.1: Evolution of temperature, applied pressure & piston displacement as a function of time

Sample	Case 1A	Case 1B	Case 2
Thickness (mm)	4.96	4.1	4.99
Diameter (mm)	40.07	40.01	40.03
Density (g/cm^3)	7.8	8.5	7.6

Table 2.3: Geometrical dimensions of all sintered samples

2.4 Sample analysis

The following techniques were used for analysing and characterization of the samples in the course of this project.

2.4.1 Inductively Coupled Plasma

Inductively coupled Plasma (ICP) was used to determine the composition of the sample including the presence of trace elements.

2.4.2 Optical Microscope

With the lenses/aperture in the optical microscope, magnified images of the sample were captured at magnification ranging from $50\mu m$ to $200\mu m$

2.4.3 Scanning Electron Microscope

Scanning Electron Microscope (SEM) was used to obtain finer details about the surface structure, grain size/shape, precipitates and defects in the samples in high resolution. Compared to the Optical microscope, The SEM provides a much higher magnification ($>100,000\times$) and greater depth of field compared to the optical microscope. The Back-scattered electrons detector (AsB) and the secondary electrons detector (SE2) were used in the SEM for characterization. The secondary electrons emerging from the surface of the sample (Figure 2.4.1) provides information on the topography of the sample's surface while the back-scattered electrons emerging from the broad region within the interaction volume provides relevant information on the crystallography, sample's composition and difference between phases. A high accelerating voltage of 15 & 20KV was used for imaging.

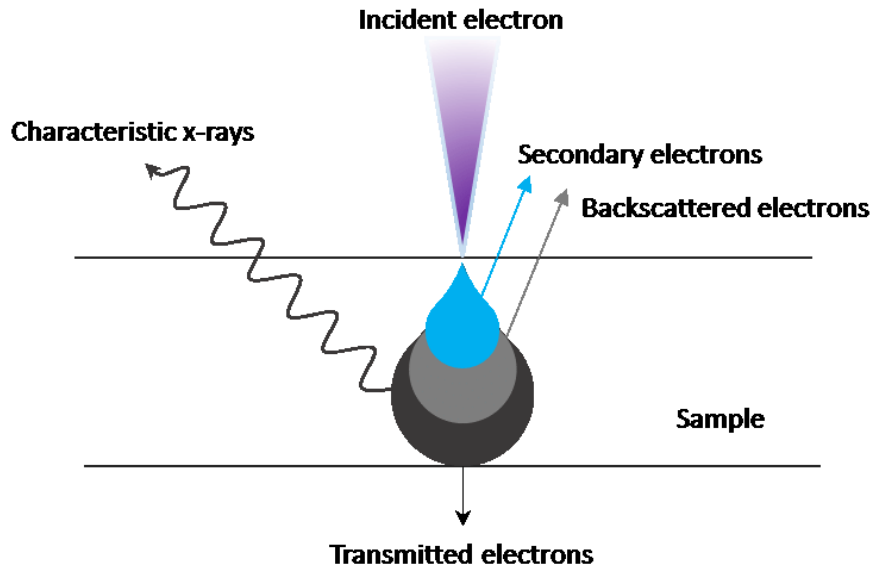


Figure 2.4.1: Schematic of various interactions between the electron beam and the sample [34]

2.4.4 Energy Dispersive X-Ray Spectroscopy

Energy dispersive X-Ray Spectroscopy (EDX) is a chemical micro-analysis technique that is used alongside the SEM. Here, an x-ray detector is used to collect the x-ray signal, measuring its energy and intensity distribution, and analyzing it to determine the elements present and their respective concentration in the analyzed region of the specimen. The intensity, corresponding to the number of times a particular voltage pulse is generated is plotted on the y-axis with a unit of counts per second (cps). Analysis was done on the heat treated alloy and cold rolled samples with an accelerating voltage of 15.0 kV. The resolution of the x-rays which can be defined as the maximum width of the interaction volume generated by the x-rays projected

up to the specimen surface, is dependent on the accelerating voltage and the atomic number of the specimen. A high accelerating voltage of 15 kV grants for high peak intensities and a total inclusion of x-ray peaks of heavy and light elements but it increases x-ray absorption and reduces the resolution obtainable.

2.4.5 Microstructural Analysis

After observing the samples at the SEM, two main variables to be determined are the average grain size and volume fraction of phases. These variables are computed using the ImageJ software. The grain size measurements involve drawing lines whose ends are touching the grain boundaries of a grain in the SEM image. The software computes the total length of the line. This step is carried out several times on different grains and images. At the end of the measurements, the length of the lines are summed up and divided by the number of counts. The result is the average grain size.

The volume fraction is obtained by calculating the amount of area occupied by a phase on the SEM images. Images with a sharp contrast difference are utilized in order to provide accurate results. This calculation is achieved with the ImageJ software. The threshold scale is adjusted carefully to capture only the phase of interest.

2.4.6 X-Ray Diffraction

XRD analysis is used to study the crystal structure - identify the crystalline phases present in the specimen and its chemical composition. An x-ray beam is directed at the sample, and as the sample and detector rotate, the intensity of the reflected X-ray is recorded. This XRD experiment was performed using a Cobalt anode of $k\text{-}\alpha$ values - 1.78897 & 1.79285, Voltage of 30KV, Current of 30mA. With a step size of 0.0198° , the 2θ angles were measured from 10° to 138° . Peaks of the XRD spectra were identified using the PDF-maint software.

2.4.7 Micro indentation Hardness Testing

The hardness of the sintered sample was obtained by carrying a micro indentation using the EMCOTEST Durascan Machine. The sample was mounted and polished, reflective enough to resolve the microscopic hardness impression. A precision diamond indenter at loads ranging from 50g to 500g was impressed into the material. The indenter is a pyramid with a square base shown in Figure 1.3.2, typical for a Vickers hardness measurement. With the test load, impression length and two diag-

onals measured the hardness value was calculated automatically using.

$$HV = 0.1891 \times \frac{F}{d^2} [N/mm^2] \quad (2.4.1)$$

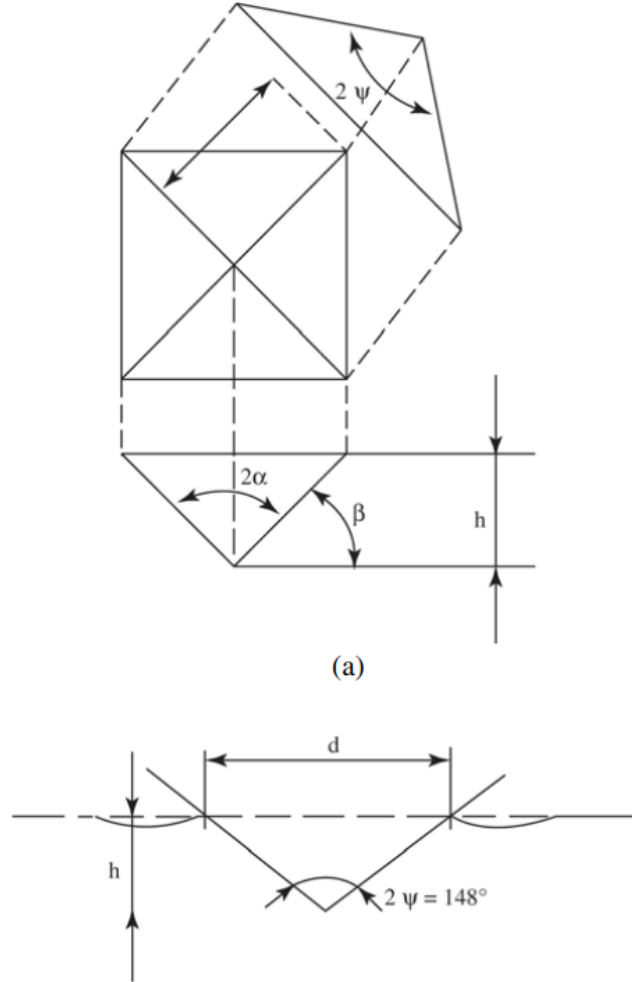


Figure 2.4.2: Vicker's Indenter [35].

2.4.8 X-Ray Fluorescence

X-ray fluorescence is a quantitative and quantitative elemental analysis used to determine the composition and concentration of various elements in a sample. Primary x-rays from a target tube directed towards the sample [36] leads to the emission of fluorescent x-rays characteristic of each element present in the sample. It is a non-destructive, rapid and reliable test. All XRF analysis in this report was conducted at the Belgian Ceramic Research Center (BCRC) Mons.

In summary, Figure 2.4.3 shows a schematic of all process

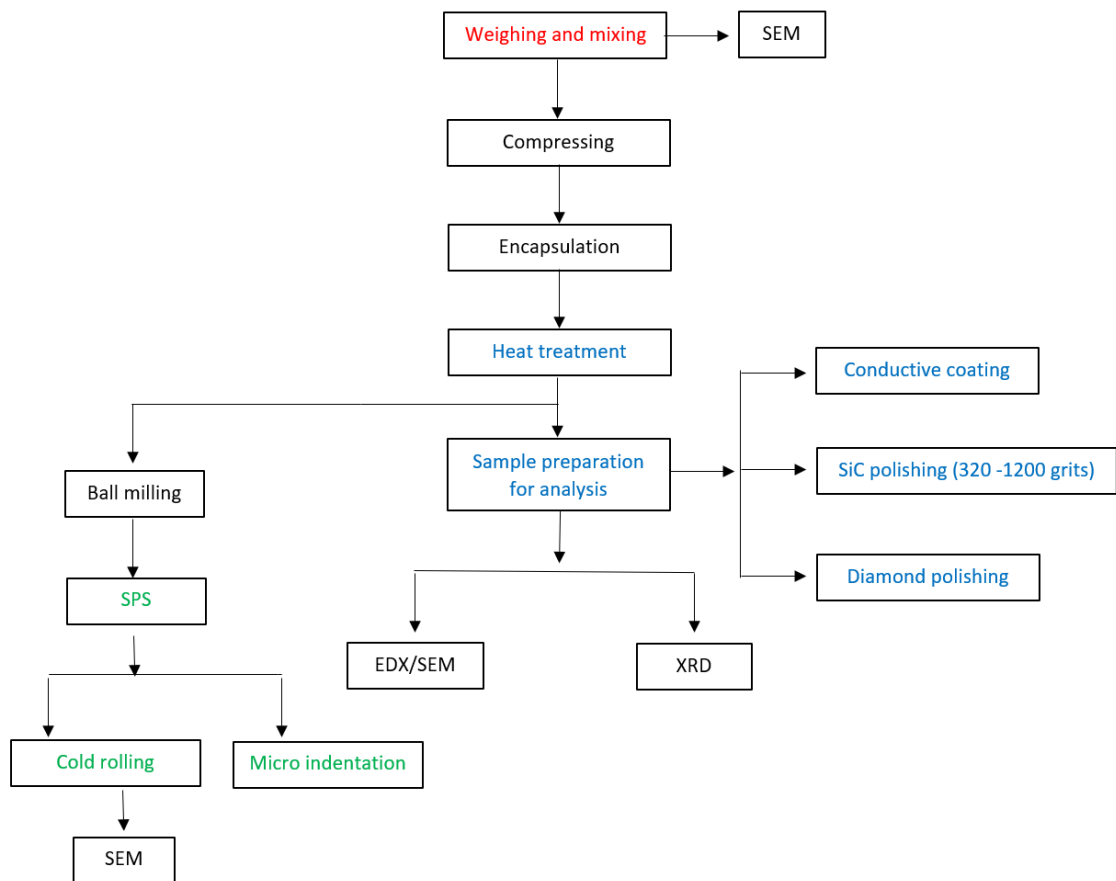


Figure 2.4.3: Schematic diagram of all process step.

Chapter 3

Results

All results from various analysis are presented in this chapter. The powder, heat-treated, sintered, and cold rolled samples were analyzed using the SEM, ICP, XRF and XRD.

3.1 Powder Characterization

3.1.1 FeMnCoNiZn elemental powder - Case 1

The FeMnCoNiZn powder after been mixed and compressed, was analyzed using Inductively Coupled Plasma (ICP). The average composition of major elements as measured by the ICP on three different samples is given in Table 3.1.

Figure 3.1.1 shows the micrographs of the powder carried out using the scanning electron microscope (SEM). At this stage, the powder is not homogeneous as there were large composition variation at several points. The EDX spectrum (although, its measurements is less efficient for lighter elements) of the powder revealed the presence of Manganese oxides.

At-%	Fe	Mn	Co	Ni	Zn
ICP result	19.0 ± 0.3	17.9 ± 0.5	19.9 ± 0.1	19.4 ± 0.1	22.9 ± 0.4

Table 3.1: ICP measurement of the composition of the mixed FeMnCoNiZn sample - Case 1.

X-ray diffracton (XRD), used to identify the crystalline phases was carried out on FeMnCoNiZn powder. Computing the diffraction peaks shows the presence of a FCC phase as predicted by Thermocalc. The spectrum acquired is shown in Figure 3.1.2; the analysis reveals a distinct main peak at 52° which corresponds to

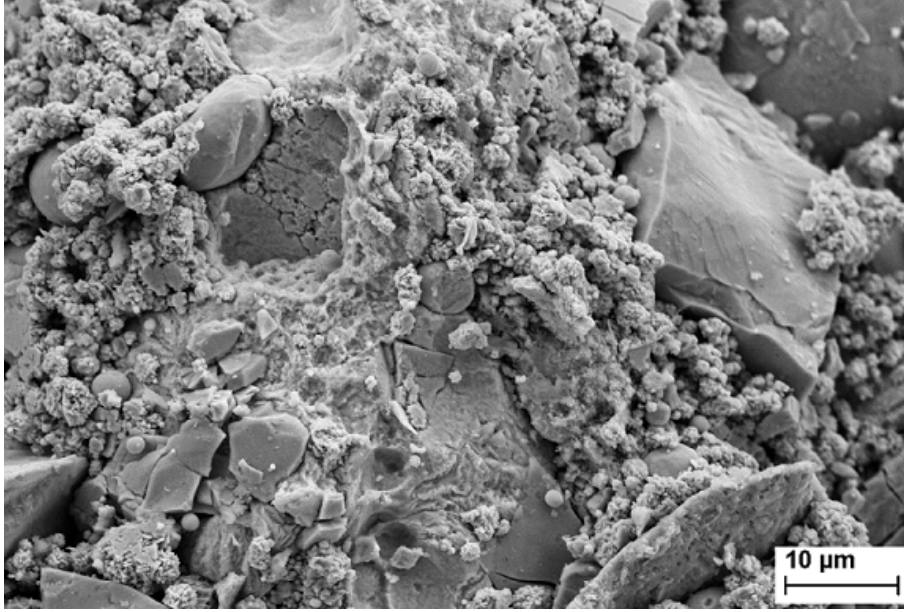


Figure 3.1.1: SEM image of the FeMnCoNiZn powder after mixing

Manganese oxide Mn_5O_8 . Smaller peaks of Hausmannite Mn_3O_4 and zinc oxide ZnO have also been identified.

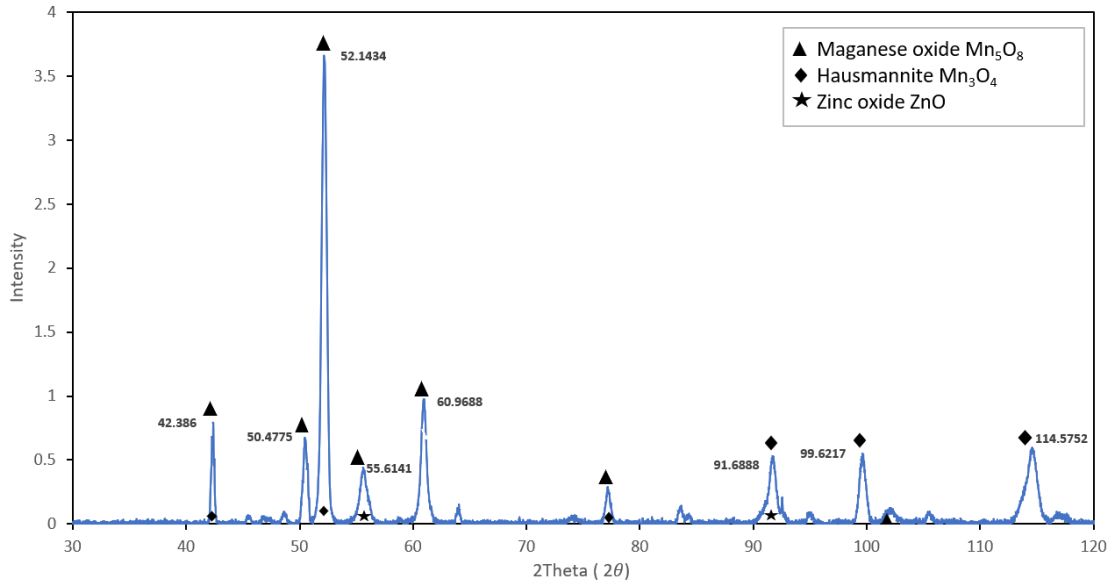


Figure 3.1.2: X-Ray diffraction pattern of the FeMnCoNiZn powder

3.2 CALPHAD - Thermo-Calc Prediction

The thermodynamic computations of the phases present at different temperatures as carried out using the TCHEA2 database in the Thermo-Calc software is shown in Figure 3.2.1. The simulation predicts the presence and stability of FCC structure in FeMnCoNiZn alloy between 825K to 1300K. This calculations were done without

considering the presence of oxides or impurities during the process. The solidus temperature is 1498K.

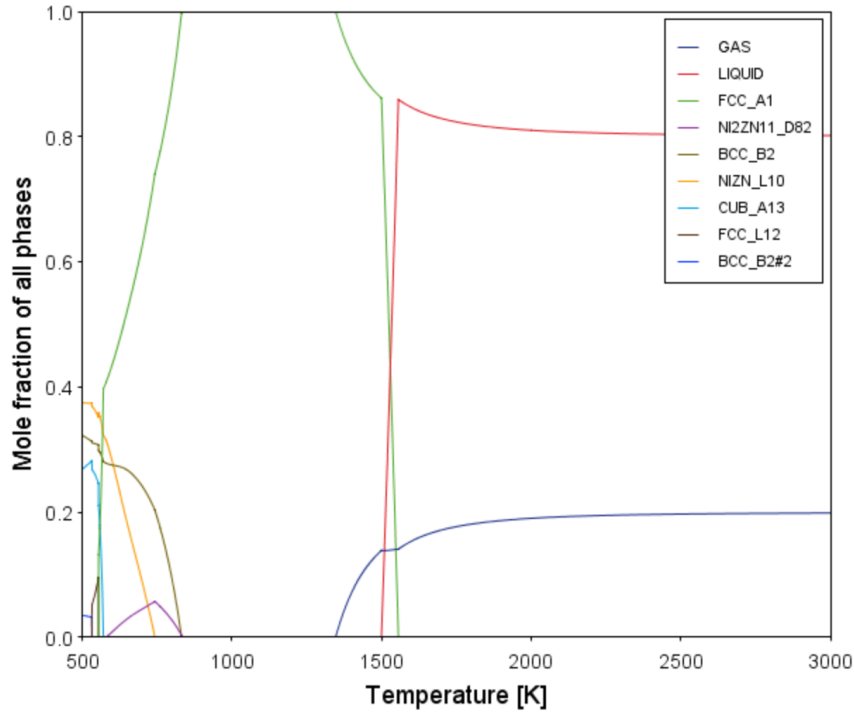


Figure 3.2.1: Calculated phase diagram of FeMnCoNiZn alloy using TCHEA2 database in the Thermo-Calc software

3.3 Heat treated Sample

In this section, the analysis done using SEM, EDX, XRD and XRF are presented.

Case 1A

The heat treated sample is observed in the scanning electron microscope (SEM), and images of its microstructure shows the presence of a homogeneous structure with a single phase as seen in Figure 3.3.1a. The presence of porosities located in the black region is also observed. With a high and low magnification at the SEM, dark precipitates alongside the matrix of some grains, is observed. This is indicated in Figure 3.3.1b. The average grain size of the powder after heat treatment is calculated to be $14.6\mu\text{m}$.

Using the EDX analysis, the composition of different zones both in the matrix and precipitates were carried out. The measurement of the five principal elements in the matrix varied from 12.38 to 31.52 atomic percent(%); Table 3.2 presents the average of chemical the composition alongside the standard deviation of the matrix

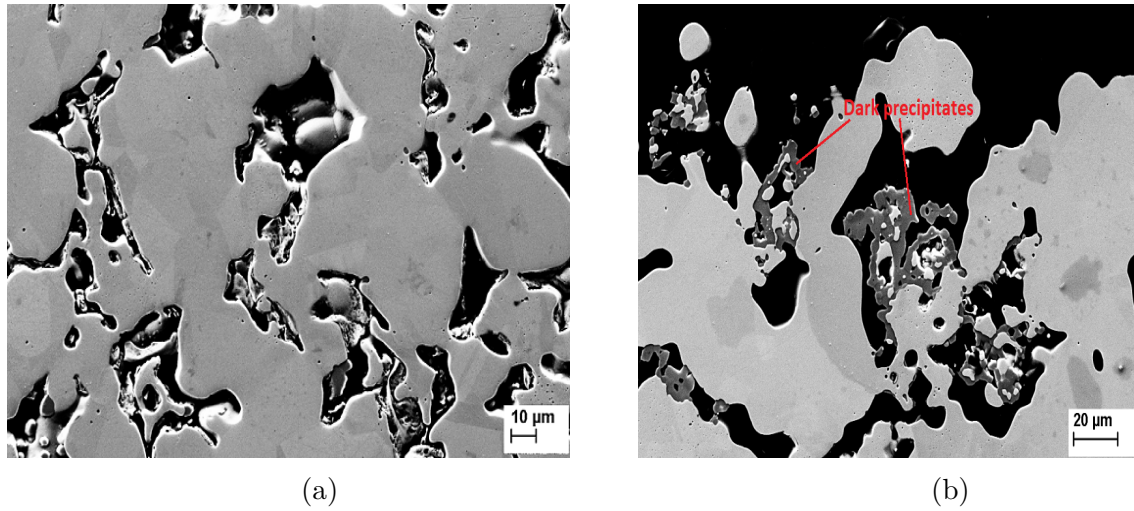


Figure 3.3.1: SEM images of the Heat treated FeMnCoNiZn alloy - Case 1A

measured at 6 different points. This chemical composition shows a nearly even distribution of the principal elements in the matrix.

At-%	Fe	Mn	Co	Ni	Zn
Comp.	24 ± 5	16 ± 2	20 ± 4	19 ± 1	19 ± 2

Table 3.2: Average chemical composition (at.%) measured by SEM-EDX of the Matrix of the Heat-Treated FeMnCoNiZn alloy - Case 1A.

XRD analysis on this heat treated sample was conducted to identify the crystalline phases. Figure 3.3.2 is the spectrum obtained showing five major peaks whose 2θ values are identified on the graph. The main peak located at 50° is identified as Iron Manganese Fe_3Mn_7 that covers a peak of Manganese oxide at 52° . Smaller peaks of Fe_3Mn_7 and MnFe_2O_4 are also identified.

Case 1B

Figure 3.3.3 is a low magnification SEM image that reveals the presence of several twins which are attributed to Face-Centered Cubic(FCC) structures. Their average size of the FCC grains is approximately $31\mu\text{m}$. Qualitative elemental mapping performed by the EDX shows the distribution of elements in a specific observed regions. This is shown in Figure 3.3.4. The composition here is not homogeneous. The concentration of Manganese in the dark precipitates in the region highlighted in green is relatively high compared to all other elements. This region is also rich in oxide impurities. The average composition as measured in this region is presented in Table 3.3.

XRF analysis on this sample was carried out at the BCRC Mons. The concentration of the five principal elements (wt.%) is presented in Table 3.4. The obtained

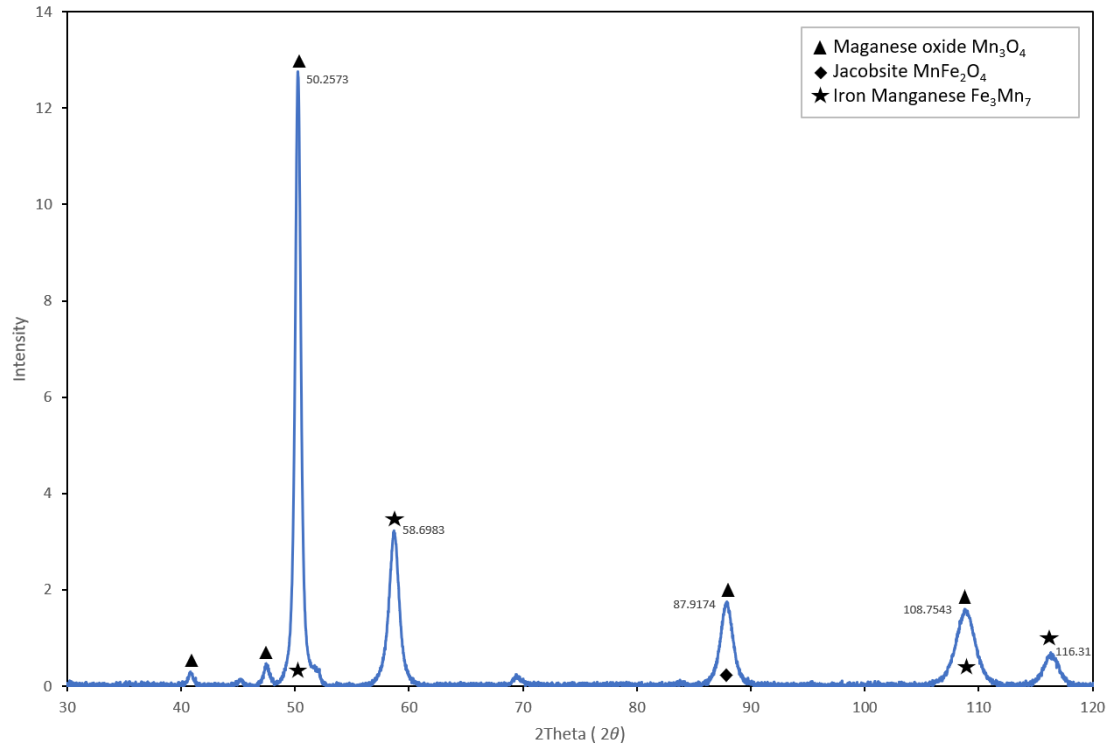


Figure 3.3.2: XRD diffraction pattern of the heat treated FeMnCoNiZn alloy - Case 1A



Figure 3.3.3: SEM Image showing the presence of twins in FeMnCoNiZn alloy after heat treatment - Case 1B

composition is close to the expected equi-atomic values. In the XRD pattern of this sample shown in Figure 3.3.5, the major peak is identified as Iron manganese Fe_3Mn_7 and Manganese Oxide Mn_2O_3 at 49.8° and 50.1° respectively, smaller peaks of Mn_2O_3 and FeTi are observed. This results correlates to the EDX anal-

At-%	Fe	Mn	Co	Ni	Zn	O
Comp.	0.8 ± 0.02	44.9 ± 0.04	0.2 ± 0.1	0.3 ± 0.3	0.12 ± 0.14	53.7 ± 0.3

Table 3.3: Average chemical composition (at.%) measured by SEM-EDX of dark precipitates in the green box in Figure 3.3 of Heat-Treated FeMnCoNiZn alloy - Case 1B.

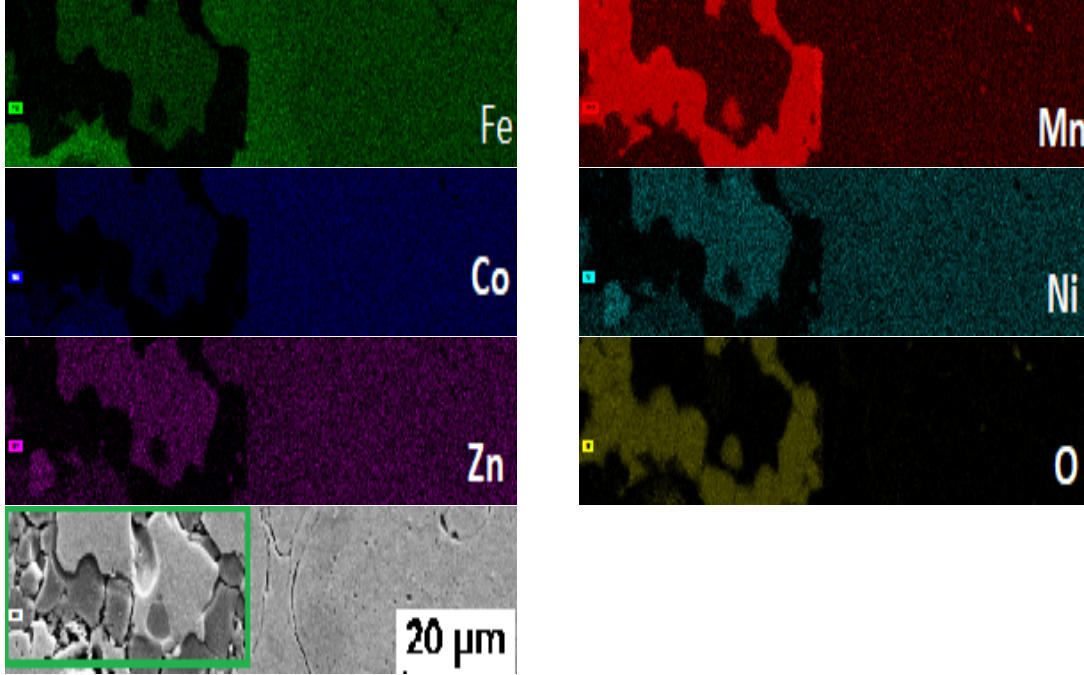


Figure 3.3.4: EDX maps showing the elemental distribution of Fe, Mn, Co, Ni, Zn and O in the corresponding SEM image - Case 1B.

ysis, according to table 3.3 the ratio of manganese and oxide is close to Mn_2O_3 composition.

Element	Fe	Mn	Co	Ni	Zn
Conc.- (wt.%)	19.9 ± 0.5	19.4 ± 0.4	19.1 ± 0.4	21.0 ± 0.5	20.6 ± 0.5

Table 3.4: Average chemical concentration of FeMnCoNiZn alloy measured by XRF - Case 1B

Case 2

Precipitates of oxides similar to that of Case 1 is observed on the surface of this sample. Figure 3.3.6 is an image of this observation. The grain size varied from $30\mu\text{m}$ to $57\mu\text{m}$. With the EDX, the composition of the sample was measured at 8 different points on the matrix and precipitates. The average composition measured

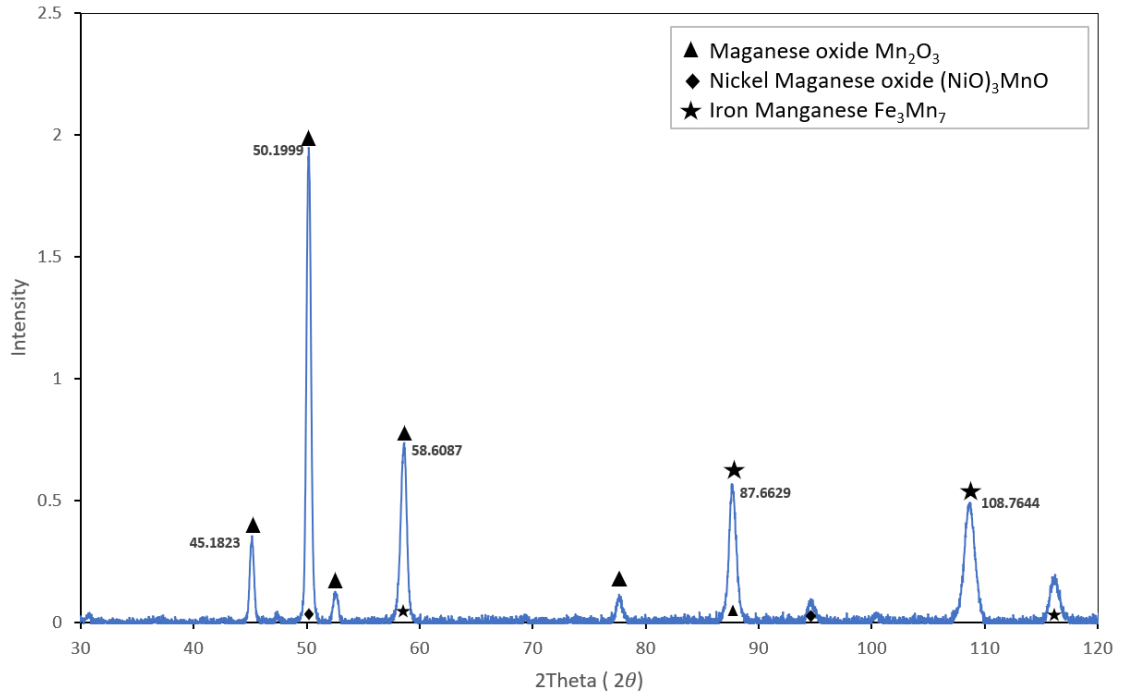


Figure 3.3.5: XRD diffraction pattern of the heat treated FeMnCoNiZn alloy - Case 1B

at the precipitates and standard deviation is presented in table 3.5

Element	Fe	Mn	Co	Ni	Zn	O
Comp. (at.%)	0.9 ± 1.6	44.5 ± 4.9	0.8 ± 1.2	1.0 ± 1.1	0.6 ± 0.6	52.1 ± 0.7

Table 3.5: Average chemical composition (at.%) of dark precipitates in the green box (in Figure 3.3.4) of Heat-Treated FeMnCoNiZn alloy - Case 2

XRF analysis on this sample was carried out at the BCRC Mons. The concentration (%) of the five principal elements is presented in Table 3.6. The obtained composition is close to the expected equi-atomic values.

Element	Fe	Mn	Co	Ni	Zn
Conc.- (wt.%)	19.1 ± 0.4	19.1 ± 0.4	19.2 ± 0.6	20.8 ± 0.5	21.4 ± 0.5

Table 3.6: Average chemical concentration of FeMnCoNiZn alloy measured by XRF - Case 2

3.4 Sintered Samples

Case 1A

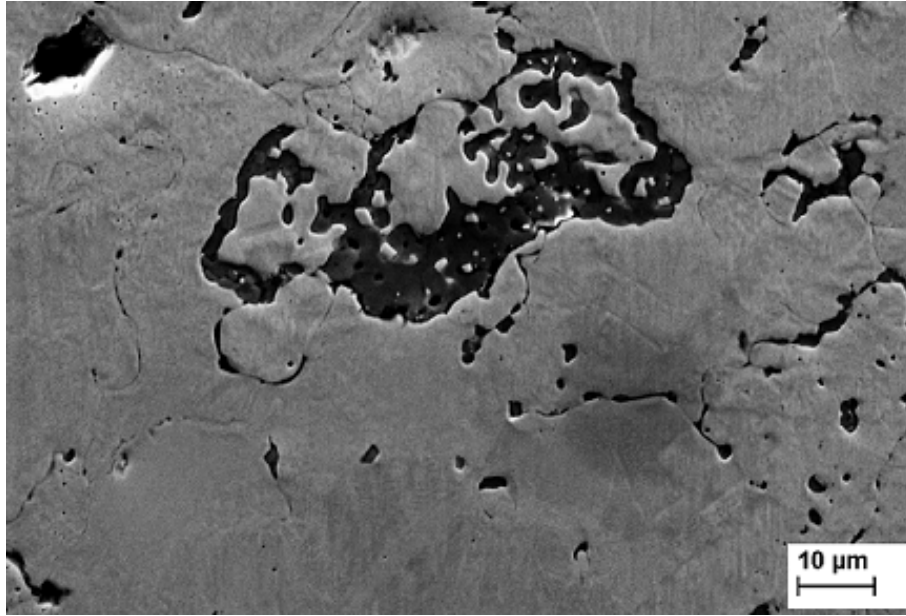


Figure 3.3.6: Microstructure of the FeMnCoNiZn alloy prepared with FeMn prealloy - Case 2

The heat treated alloy was subjected to milling followed by a sintering procedure, The microstructure of the sintered alloy is shown in Figure 3.4.1. The average grain size is also estimated to be 19μm. Figure 3.4.2 shows the EDX composition map for the five principal elements: Fe,Mn,Co,Ni and Zn. A closer view at these maps shows that Fe is rich in certain regions while the concentration of Zn and Co are simultaneously depleted in these areas.

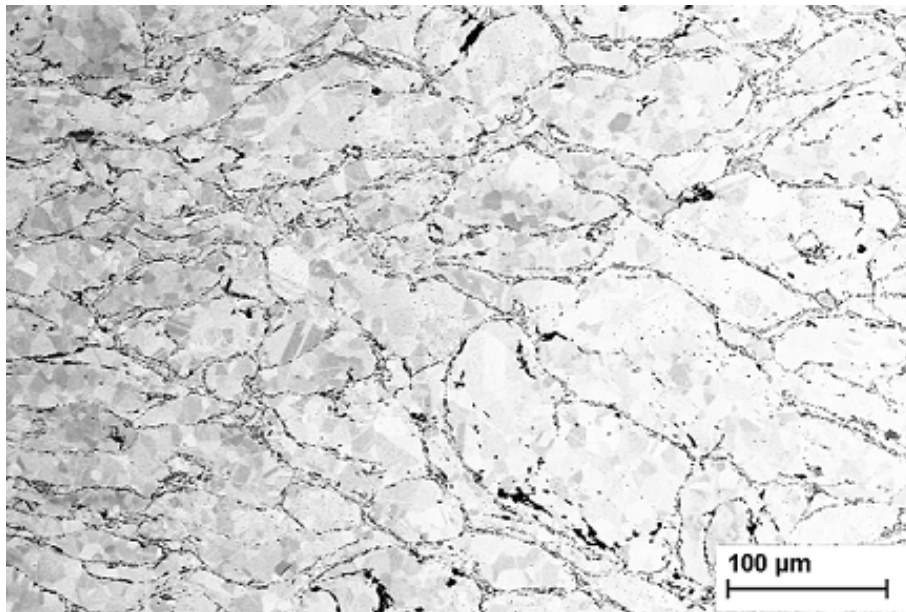


Figure 3.4.1: Microstructure of FeMnCoNiZn alloy after sintering - Case 1A

Case 1B

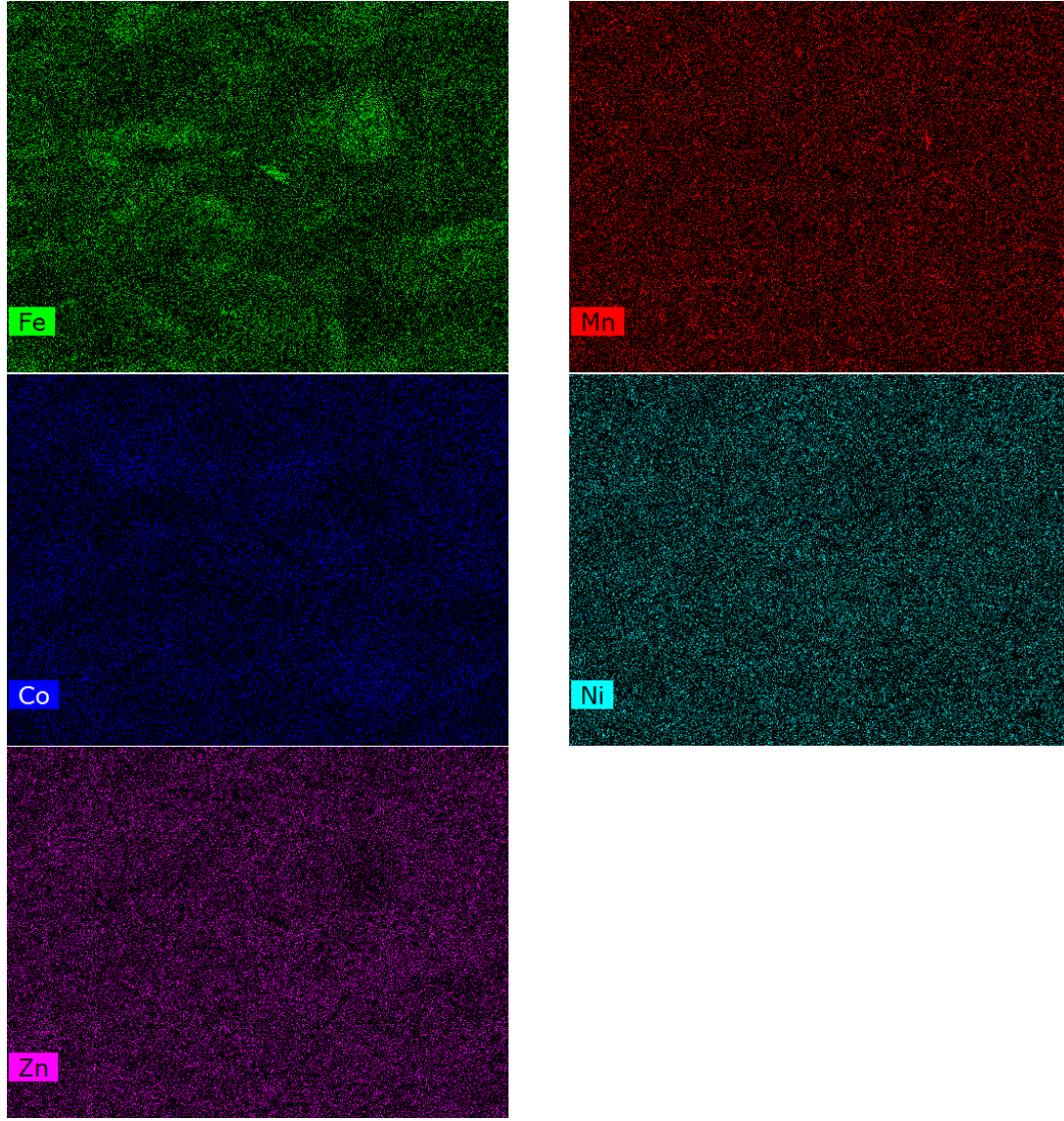


Figure 3.4.2: EDX maps of the principal elements in the sintered sample - Case 1A.

After sintering, the observed microstructure is shown in Figure 3.4.3. The average grain size is $37.6\mu\text{m}$. From EDX analysis, we observe a visible dark region within the matrix containing a higher amount of Iron varying between 32-48 at%. Figure 3.4.5 shows a low magnification SEM image of the sintered sample with its corresponding elemental EDX map for the five principal elements and oxygen in Figure 3.4.4.

Case 2

The observed microstructure is shown in Figure 3.4.6. The average grain size is $38\mu\text{m}$. The average composition of the sample in at.% along with the standard deviation measured at 6 different points by the EDX is shown in table 3.8. The principal elements have a near-even distribution over the matrix

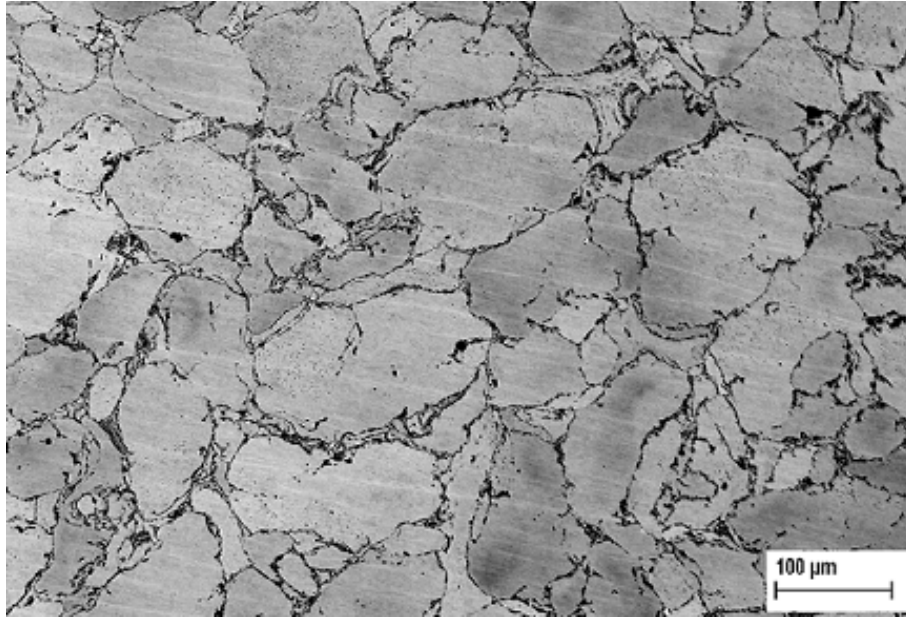


Figure 3.4.3: SEM Image of Sintered FeMnCoNiZn alloy - Case 1B

Element	Fe	Mn	Co	Ni	Zn
Comp.	18.9 ± 5.3	19.1 ± 1.3	23.9 ± 4.1	18.9 ± 1.0	18.9 ± 0.9

Table 3.7: Average chemical composition (at-%) measured by SEM-EDX of the Sintered FeMnCoNiZn alloy - Case 2

3.4.1 Hardness Measurement

Micro indentation provides a way to access the mechanical properties of the alloy FeMnCoNiZn. Results were obtained for all samples. *The hardness measurement in case 1B and case 2 were carried out on the InnovaTest hardness machine at BCRC Mons.*

Case 1A

With a load of 50g, the average of the Hardness measurements at nine different points along the diameter of the sample, on the sintered samples was 175 ± 6.71 HV. These points have diagonals between 23.7 and 22.4 denoting measurement on more than one grain. An example of the result obtained is given in Figure 3.4.7a. For a point with diagonal of 18, as shown in Figure 3.4.7b the hardness value was 264 HV.

Case 1B

With a load of 50g The average of the hardness measurements measured at five different points was 207.53 ± 8.8 HV.

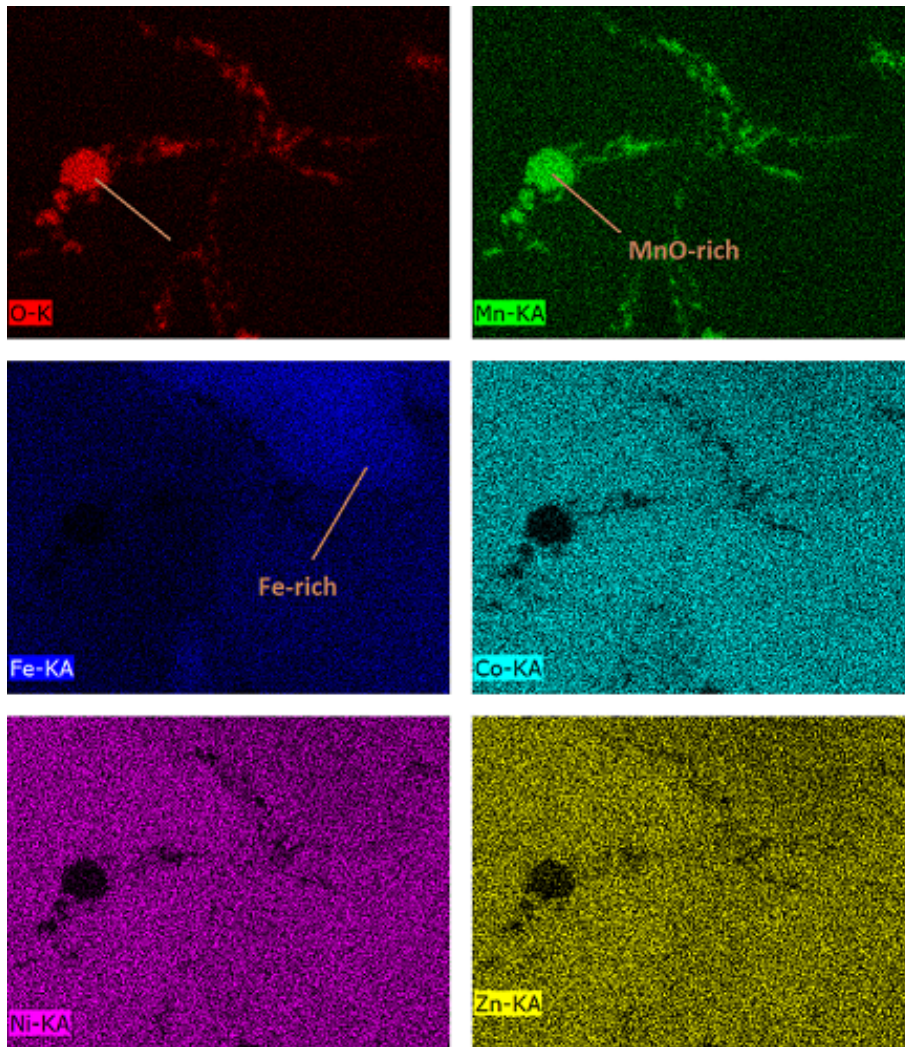


Figure 3.4.4: EDX map of sintered FeMnCoNiZn alloy - Case 1B

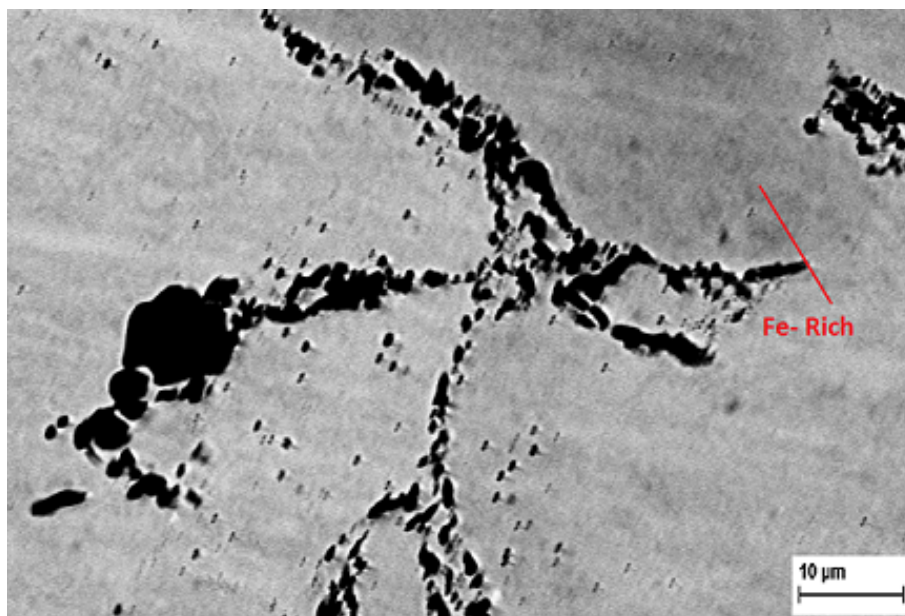


Figure 3.4.5: SEM Image of Sintered FeMnCoNiZn alloy - Case 1B. Corresponding EDX map in Figure 3.4.4

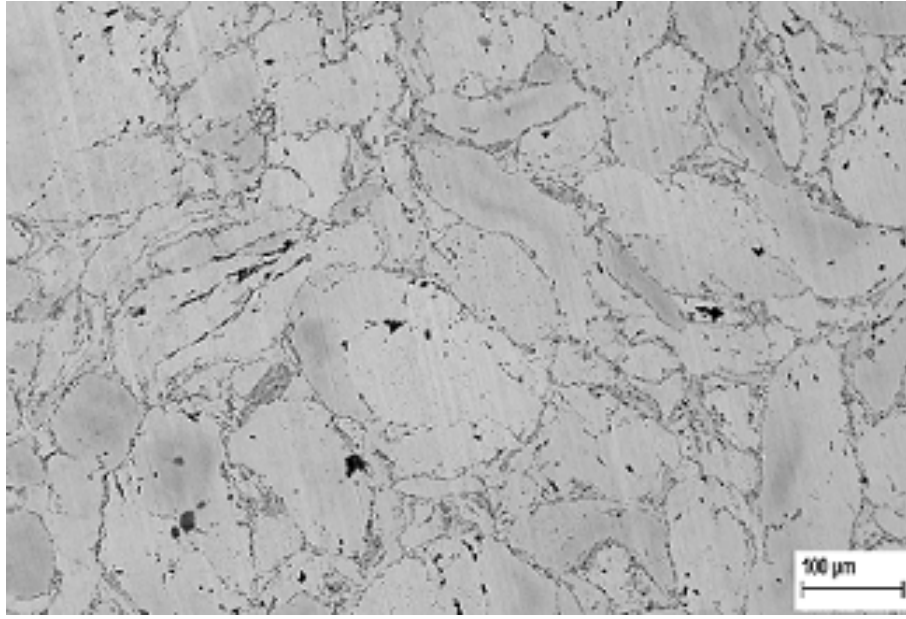


Figure 3.4.6: SEM Image of Sintered FeMnCoNiZn alloy - Case 2.

Case 2

The average hardness of six measurements at different points with a 50g load is 206.50 ± 4.03 HV.

In summary, the hardness report on all sample is shown in table . Images of all other measurements and the charts of average measurements are in Appendix B

Sample	Case 1A	Case 1B	Case 2
Average Hardness (HV)	175 ± 6.7	207.5 ± 8.8	206.5 ± 4.0

Table 3.8: Summary of hardness values measured on all sintered samples.

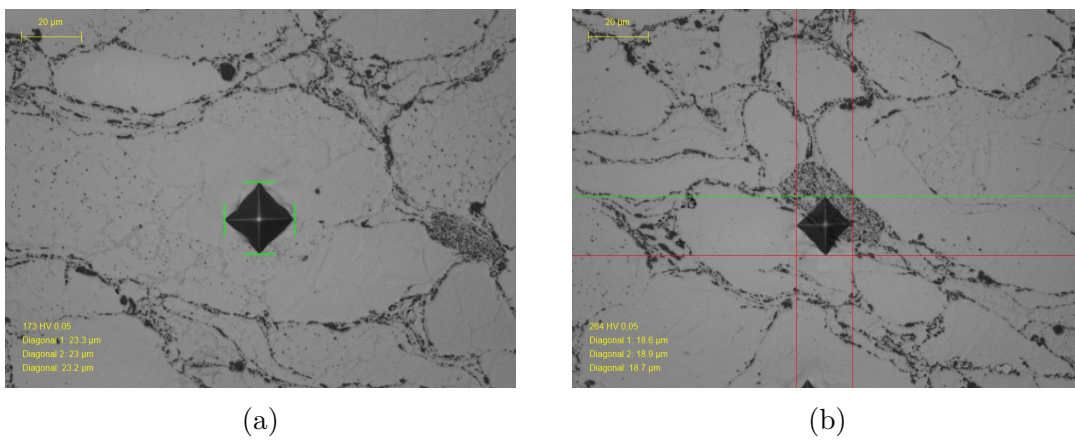


Figure 3.4.7: Example of the Hardness result obtained on sintered sample

3.4.2 Cold rolling

Case 1A The sintered sample was subjected to cold rolling, and after 5 cycles, the sample fractured. A fraction of the sample at the fractured region is then analysed using the SEM. The corresponding high magnification image showing its microstructure is presented in Figure 3.4.8. Fracture is observed along grain boundaries which corresponds to the site of precipitation of Mn-rich oxides. This could indicate that these regions are preferential paths for crack initiation and propagation.

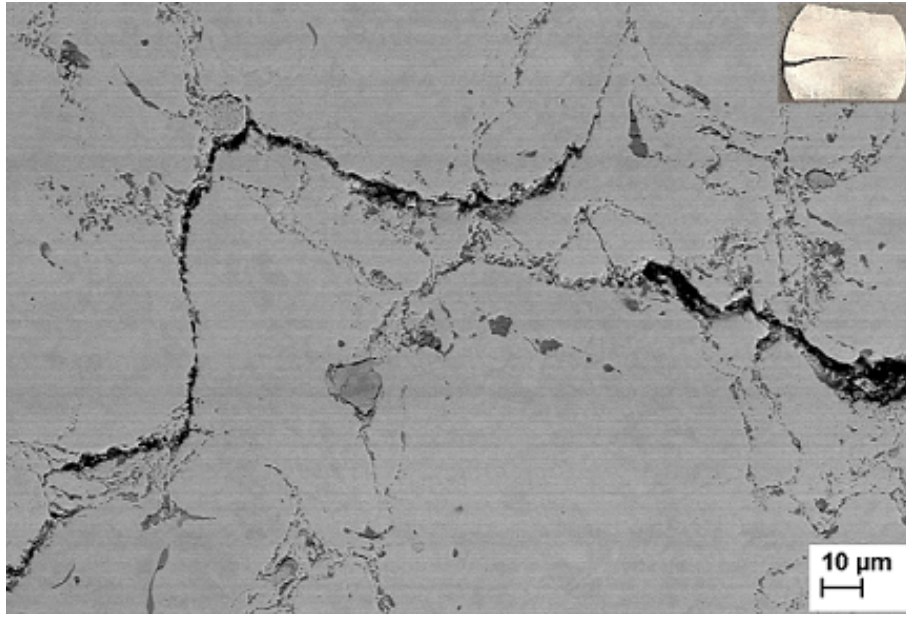


Figure 3.4.8: Microstructure of the cold rolled sample showing the fracture along grain boundaries. An insert of the cold rolled sample after fracture is shown.

3.5 Oxide quantification of Heat Treated alloy.

The SEM images were treated to determine the volume fraction of oxides present. Figure 3.5.1, 3.5.2 and 3.5.3 are the SEM images used to quantify the volume fraction of oxides present in Case 1A, 1B and 2 respectively. Table 3.9 is a summary of the results obtained.

Sample	Case 1A	Case 1B	Case 2
a	15.74	17.9	12.85
b	16.21	16.4	8.33
c	18.54	13.6	5.0
d	14.9		
<i>Avg. $\pm$ SD</i>	16.3 ± 1.6	15.9 ± 2.2	8.7 ± 3.9

Table 3.9: Volume fraction of oxides (%) for all heat treated FeMnCoNiZn alloy produced. Corresponding SEM images is shown in Figure 3.5.1, 3.5.2 and 3.5.3.

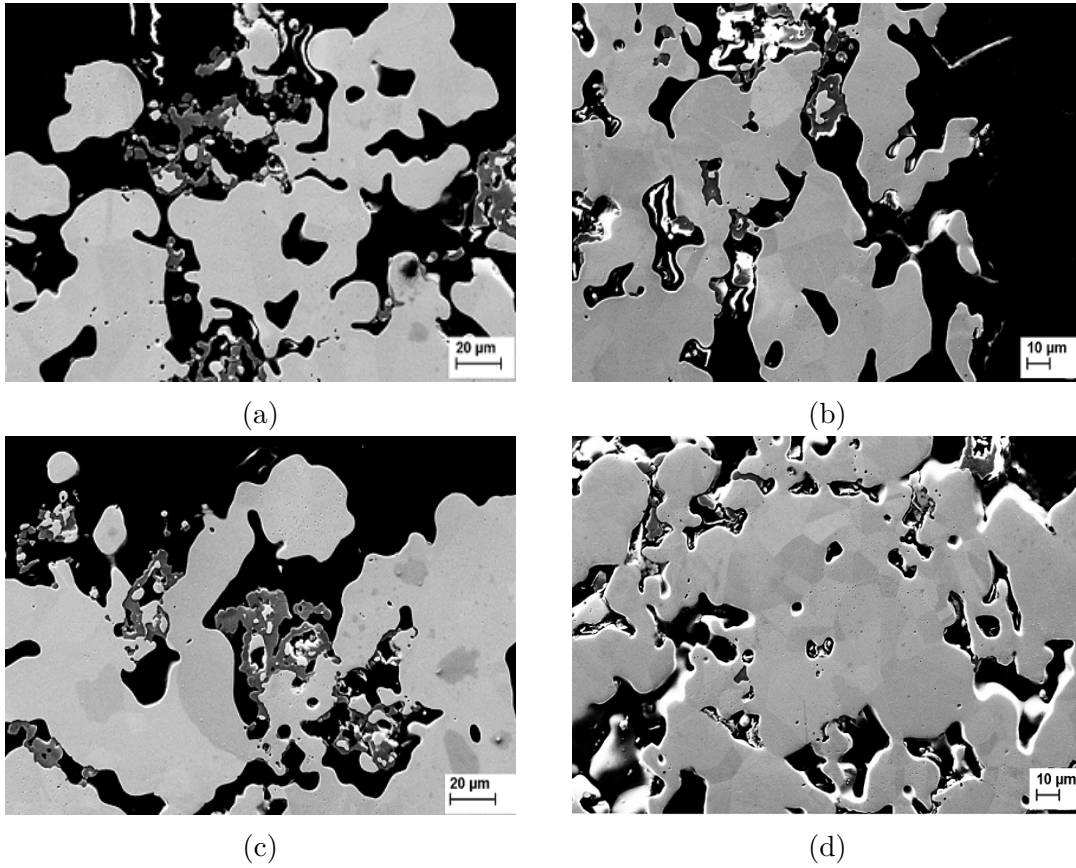
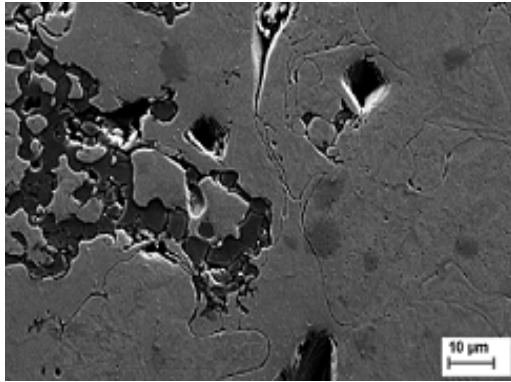
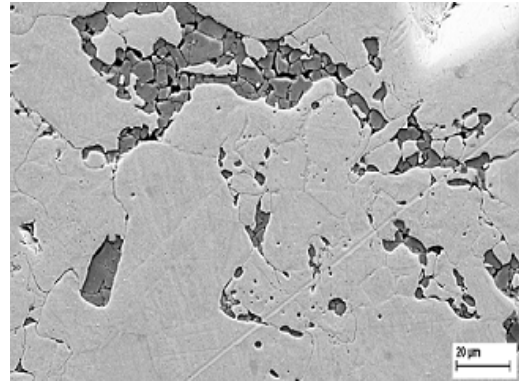


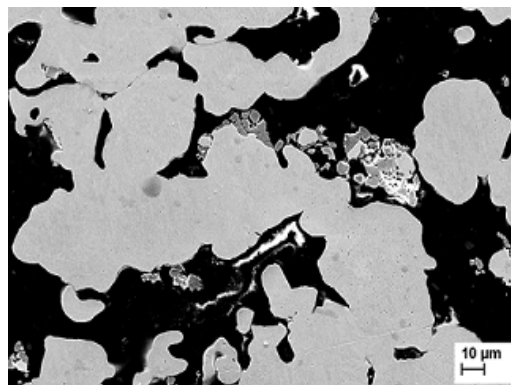
Figure 3.5.1: SEM micrograph of the Heat treated alloy used for oxide quantification - Case 1A



(a)

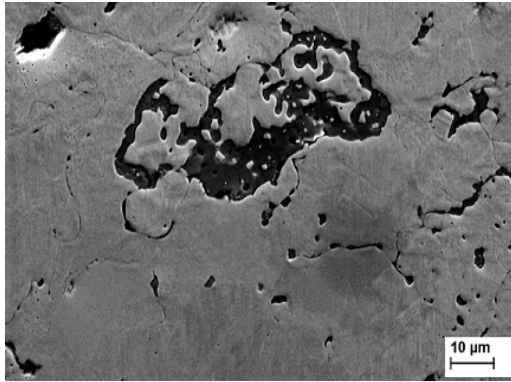


(b)

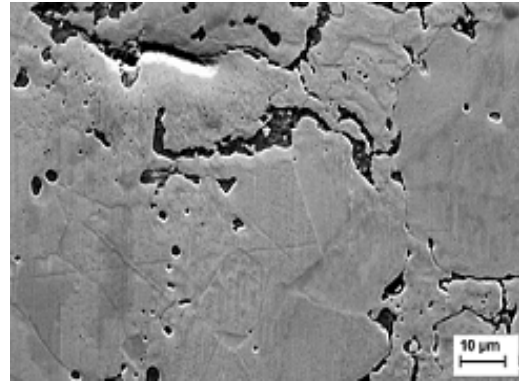


(c)

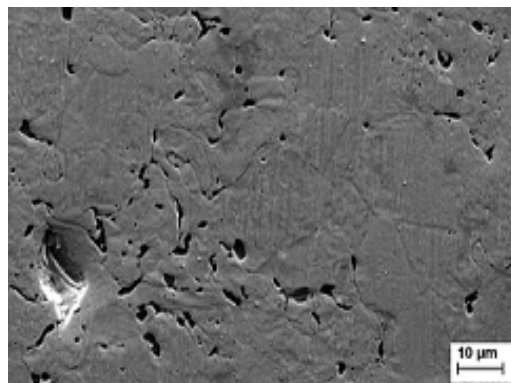
Figure 3.5.2: SEM micrograph of the Heat treated alloy used for oxide quantification - Case 1B



(a)



(b)



(c)

Figure 3.5.3: SEM micrograph of the Heat treated alloy used for oxide quantification - Case 2

Chapter 4

Dicussion

In this chapter, results is discussed and comparison is made with literature.

4.1 Composition of FeMnCoNiZn alloy

The average composition as measured by the ICP in 3.1, revealed a close equiatomic composition of 19Fe-18Mn-20Co-20Ni-23Zn. The ICP results obtained were in good agreement with results obtained from the EDX measurements. The slight variation in both results can be attributed to the fact that the SEM-EDX measurement take into account only a small volume of material - therefore it is a local measurement while the ICP is a global characterization that gives the averaged analysis on the total mass of each sample.

In addition elements like zinc is prone to evaporation and could evaporate from the bulk sample during heat treatment. Heterogeneities of the material such as shown in Figure 4.1.1 could also affect the measure. The EDX analysis reveals in an appreciable amount the presence of oxides.

4.2 Microstructure of FeMnCoNiZn alloy

Case 1

Phases such as intermetallic compounds mentioned in section 1.3.1 were not observed in FeMnCoNiZn alloy. The alloy formed a single phase FCC structure with no intermediate phases. This structure is in agreement with Thermocalc prediction. In the XRD spectrum of the heat treated samples, the major peaks observed in both cases corresponds to Manganese oxide - Mn_3O_4 and Mn_2O_3 . The existence of these two manganese oxides is very frequent out of the possible four oxides which can be thermodynamically formed according to Manganese-Oxygen phase diagram. In

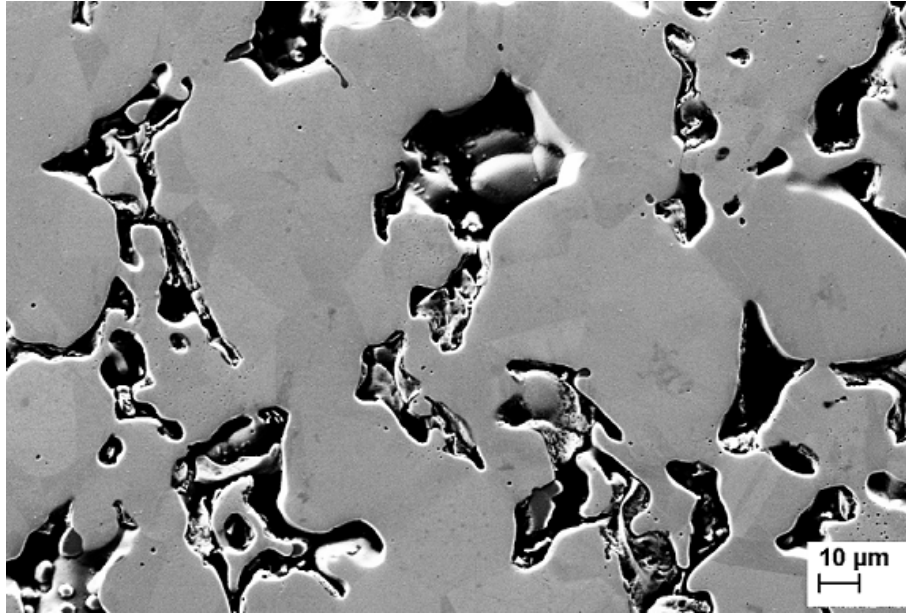


Figure 4.1.1: SEM Image of FeMnCoNiZn alloy.

Figure 3.3.2 and 3.3.5 the peaks observed are located at almost the same 2θ value. Since it is known that the starting powder are the same in this case, the slight variation might be due to the presence of impurities. Porosities were found in large amounts on the surface of both samples. The results from the EDX analysis showed that phase containing a large amount of Iron was present within the matrix. This is confirmed with the presence of peaks corresponding to Iron Manganese Fe_3Mn_7 in the XRD spectrum. Specifically in Case 1B, where an increased grain size is observed, this can be attributed to longer heat treatment time.

Case 2

Although the XRD analysis was not performed on this heat treated alloy due to time constraint, the EDX results in 3.5 provides facts that a Mn-rich phase is present in the sample. The values are not taken into account because of the measurement limit of the EDX.

4.3 Oxide quantification of heat treated alloys

On the heat treated samples, precipitates of oxides are evident even at a higher magnification as shown in Figure 4.3.1. The EDX maps presented in Figure 3.3.4 show enrichment of Manganese-rich precipitates in certain regions.

As discussed in section 1.7.5, one of the limitation attributed to powder metallurgy is the ease with which elemental powders react with the atmosphere, Manganese with strong affinity for oxygen requires better handling to get rid of the oxide layer. Using the ellingham diagram, Titanium is a good reducing agent for

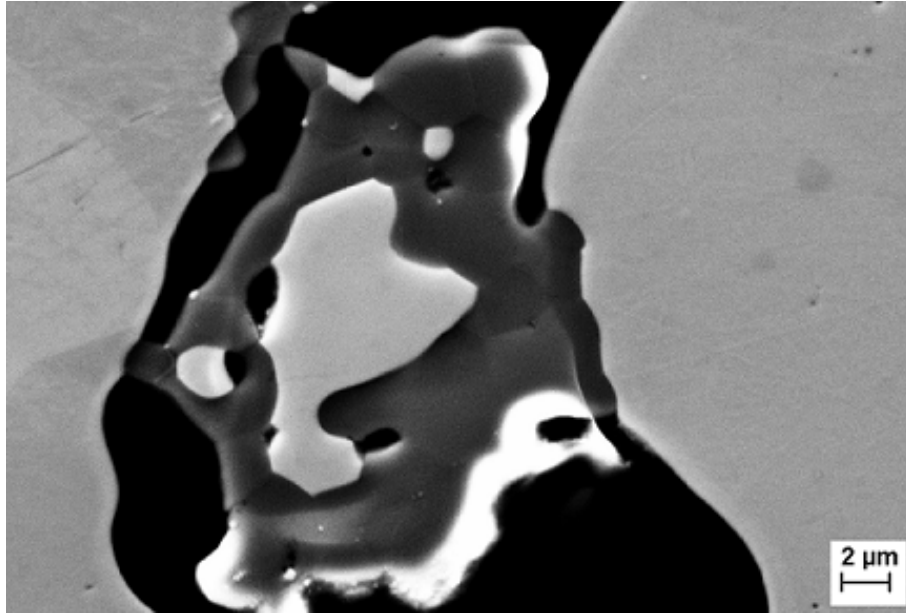
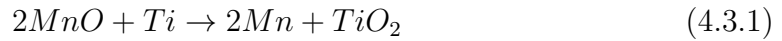


Figure 4.3.1: High magnification image revealing the matrix of FeMnCoNiZn surrounded by precipitates.

Manganese Oxide.



Quantifying the the oxides present in all cases helps to determine the effectiveness of the approach. From the results obtained in table 3.9, it can be seen that the use of titanium is effective as it reduced the amount of Manganese oxide phase by a value of 20%. This affirms that the presence reducing atmosphere is beneficial to the powder metallurgy production process. However the driving force for this reaction has a low negative value of ΔG° , $-20Kcal$; which implies that the reduction reaction would not proceed rapidly at a temperature of $800^\circ C$. This therefore explains the miniature variance observed.

As stated in section 1.7.5, another approach to minimizing the presence of oxide is the use of pre-alloyed powder. In this study, results obtained are in correlation with literature as discussed in 1.7.5. A 50% decrease in the oxides present is observed. This is a positive advancement.

If prealloyed powder are then used in the manufacturing of an alloy and all process steps are executed under a protective atmosphere, producing an alloy free of oxide impurities is highly achievable. Further progress in this area would also require that a more quantitative and promising approach to oxide quantification is adopted. JMatPro (Java-based Materials Properties) is a software for materials property simulation that can be used to calculate the equilibrium fraction of

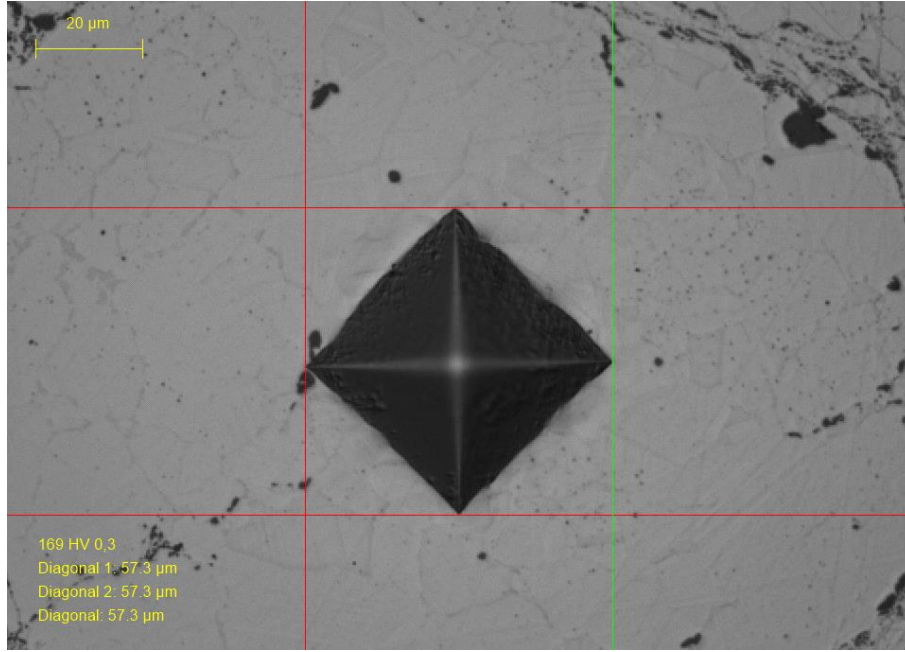


Figure 4.4.1: SEM image showing a Vicker's indent applied Sintered sample 1A

a precipitate after different heat treatments. Another reliable technique is *Matrix dissolution* done chemically or electrolytically to extract precipitates and analyse it using the XRD, TEM or EDX without matrix interference. This technique was utilized by Junfang Lu *et al.* and Hegetschweiler A *et al.* in a study on the selective dissolution of steel to extract and study Titanium carbon-nitride (TiCN) [37, 38].

4.4 Mechanical Behaviour

4.4.1 Hardness Properties

All the samples were sintered under the same conditions and showed different Vicker's hardness value.

Recall that in Case 1A, the average grain size of the sintered sample is about $19\mu\text{m}$, hence if the indentation of the vicker's hardness is larger than the average grain size, as shown in Figure 4.4.1, the hardness value would be impacted due to the presence of impurities and porosities along the grain boundaries. However, a hardness value of 264HV is obtained as shown in Figure 4.4.2 in a region with substantial oxide particles. This can be attributed to the fact that these particles can act as strengthner in the FCC matrix.

In Case 1B with a large grain size of $37.6\mu\text{m}$, the hardness value of 207.53 HV is obtained, when the indentation of the vicker's hardness is smaller than the average grain size. This is therefore an improvement to that obtained in Case 1A. The

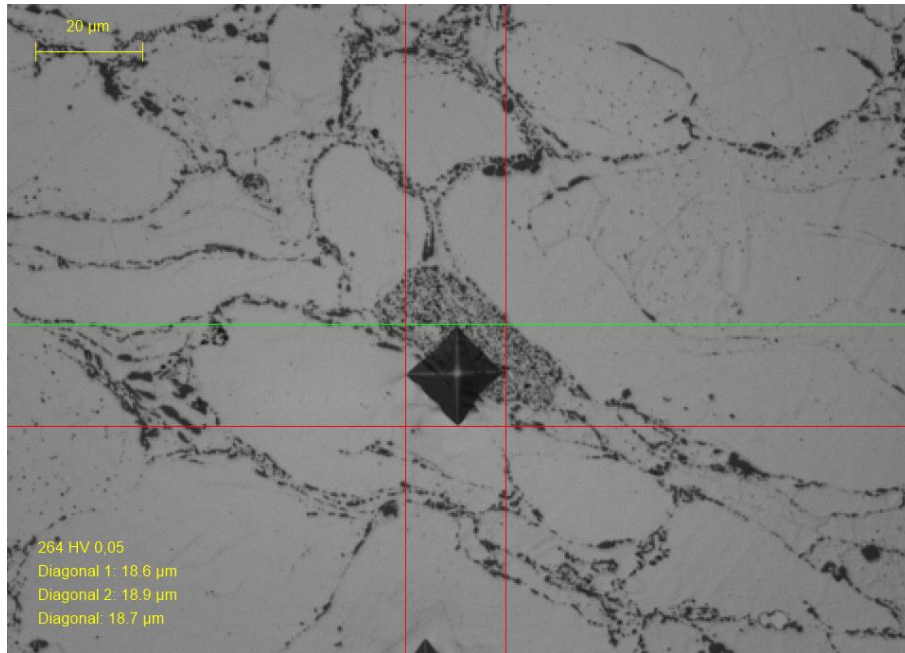


Figure 4.4.2: SEM image showing a Vicker's indent applied on an FCC grain in Sintered sample 1A

hardness measurements in this Case was done at the BCRC Mons, therefore there could be a slight difference with the machines used and this could be a contributing factor to the improved hardness obtained. However, as discussed in Chapter 1, HEAs with a single phase FCC structures posses a hardness value within the range of 100-200 HV [11].

In Case 2 - where the alloy was prepared with pre-alloyed Fe-95Mn powder and elemental powder of the remaining principal elements, a improved hardness value of 206.5 HV is obtained. Based on the relationship between hardness and yield strength, it thus implies that the resulting yield strength of the alloy would be in the range of 610 MPa. Based on the result in Case 1A and Case 2, we can therefore presume that for the hardness properties, the effect of Titanium as a reducing is almost equivalent to the effect obtained when a pre-alloyed powder is used. However, with the improved reduction in oxide associated with the use of pre-alloyed powder, an improved ductility is expected. As reported in Chapter 1, Kai Wen *et al.* [21] obtained a hardness value of 214.7 HV and 198.3 HV for Al alloys with high zinc content which a close correlation is obtained in this study.

Kai Wen observed the influence of a slight increase in the percentage of zinc in AlFeTiCrZnCu alloy. For a 0.005% increase in zinc, an increase in hardness and yield strength by a factor of 0.2. In this work a similar hardness value in the range of ~ 210 HV is obtained. Although Cardoso *et al.* [23] observed high hardness value of 661 HV on a sintered sample of AlCrCuFeZn HEA, this is owing to the fact that a high fraction of BCC phase is obtained and the precipitation of a second

phase within the FCC grains occurred during sintering. This is also the reason for the high hardness and yield strength obtained in CuNiCoZnAlTi alloy as reported by Varalakshmi *et al.* [25]

4.4.2 Oxidation effect on Mechanical properties

The preferential path of fracture along the grain boundaries corresponding to Mn-rich oxides shown in Figure 4.4.3 can be associated to the fact that growth stresses are generated by oxidation process and their response to compression can be the disintegrating of the oxide from the alloy substrate. On an industrial scale, it becomes imperative that this is avoided totally owing to the fact that cracking can expose a fresh part of the alloy to the oxidizing environment. This effect is comparable to the precipitation of Cr_{23}C_6 at the grain boundaries of stainless steels [39] that to a great extent reduces the mechanical properties and oxidation resistance of 316 stainless steel.

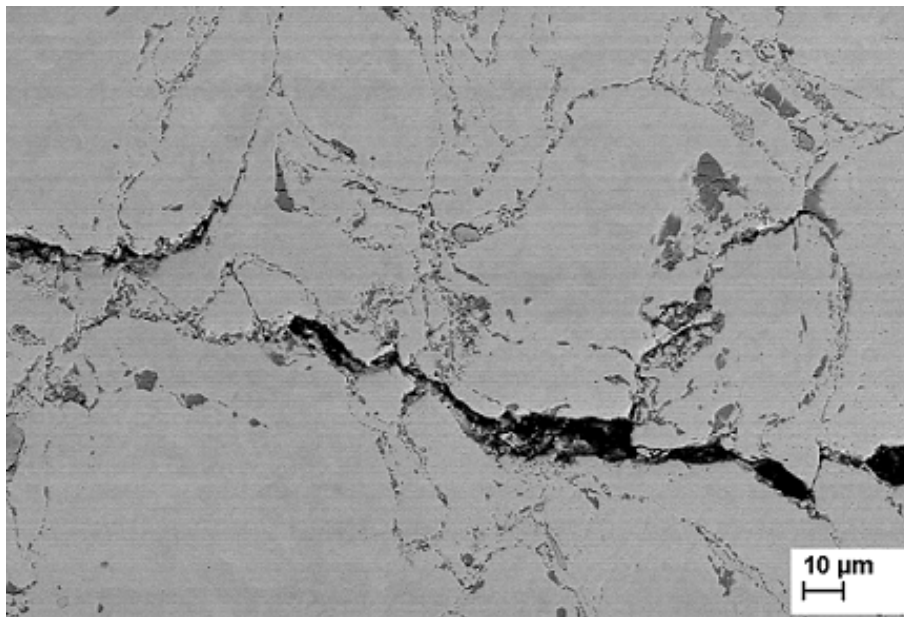


Figure 4.4.3: SEM Image showing the crack initiation of the cold rolled sample

Chapter 5

Conclusion

This study has presented the production and characterization of FeMnCoNiZn alloy via powder metallurgy. One major challenge of this work was to reduce the amount of oxidation during the production cycle. The equimolar FeMnCoNiZn alloy was produced via two methods:

- from high purity elemental powders,
- from pre-alloyed Fe-95Mn - Iron Manganese powder and Co, Ni, Zn high purity elemental powders.

The aim was to investigate if the use of alternative raw material such as pre-alloyed powder and different processing conditions could have an impact on the oxidation of the sample during heat treatment and sintering.

The microstructure of the resulting FeMnCoNiZn alloy was examined. A single phase FCC solid solution was observed. However, around 18 vol.% of oxide phase was present in the sample after the production process. Manganese having a high affinity for oxygen was the major oxide phase present. Three different approaches were attempted to minimize the formation of the oxide phase:

- Use of inert and reducing gas phases such as $Ar - H_2$ gas mix during the heat treatment,
- Use of sacrificial metal such as Ti , which will be oxidized in place of Mn during heat treatment, Use of pre-alloyed Fe95Mn powder.

The oxide phase in each of the resulting alloy was quantified.

A slight improvement observed with the use of Titanium can be attributed to its less negative ΔG° value for the spontaneity of the reaction. With the use of Fe-

95Mn - Iron Manganese pre-alloyed powder in the preparation of FeMnCoNiZn, and a $Ar - H_2$ gas reducing atmosphere, there was further reduction in Manganese oxide phase, this showed that the use of pre-alloy contributes significantly to producing a alloy with excellent properties. With reduction in the oxides, the samples showed an increase in their hardness values.

This results can be improved by performing all production steps - from the powder manufacturing stage to the sintering in a protective atmosphere, in order to reduce the risk of oxidation. This process is attainable in the industry and components with improved microstructure (cumulating in property improvements) and very close final dimensions can be produced at reduced costs.

Bibliography

- [1] J-W Yeh et al. “Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes”. In: *Advanced Engineering Materials* 6.5 (2004), pp. 299–303.
- [2] Brain Cantor et al. “Microstructural development in equiatomic multicomponent alloys”. In: *Materials Science and Engineering: A* 375 (2004), pp. 213–218.
- [3] B Cantor. “Multicomponent high-entropy Cantor alloys”. In: *Progress in Materials Science* (2020).
- [4] Yong Zhang et al. “Microstructures and properties of high-entropy alloys”. In: *Progress in materials science* 61 (2014), pp. 1–93.
- [5] PC Angelo and Ramayyar Subramanian. *Powder metallurgy: science, technology and applications*. PHI Learning Pvt. Ltd., 2008.
- [6] Piyush Sharma, VK Dwivedi, and Shashi Prakash Dwivedi. “Development of high entropy alloys: A review”. In: *Materials Today: Proceedings* (2021).
- [7] Bingbing Zhang et al. “Effects of Cu and Zn on microstructures and mechanical behavior of the medium-entropy aluminum alloy”. In: *Journal of Alloys and Compounds* 820 (2020).
- [8] Krishanu Biswas et al. “High entropy alloys: Key issues under passionate debate”. In: *Scripta Materialia* 188 (2020), pp. 54–58.
- [9] Weidong Li et al. “Mechanical behavior of high-entropy alloys”. In: *Progress in Materials Science* (2021).
- [10] ON Senkov et al. “Accelerated exploration of multi-principal element alloys for structural applications”. In: *Calphad* 50 (2015), pp. 32–48.
- [11] Daniel B Miracle and Oleg N Senkov. “A critical review of high entropy alloys and related concepts”. In: *Acta Materialia* 122 (2017), pp. 448–511.
- [12] Zezhou Li et al. “Mechanical properties of high-entropy alloys with emphasis on face-centered cubic alloys”. In: *Progress in Materials Science* 102 (2019), pp. 296–345.

- [13] Yong Zhang. *High-Entropy Materials*. Springer, 2019.
- [14] C Zhang et al. “High-Entropy alloys: fundamentals and applications”. In: (2016).
- [15] Bhagevatula Satyanarayana Murty et al. *High-entropy alloys*. Elsevier, 2019.
- [16] YEH Jien-Wei. “Recent progress in high entropy alloys”. In: *Ann. Chim. Sci. Mat* 31.6 (2006), pp. 633–648.
- [17] K-Y Tsai, M-H Tsai, and J-W Yeh. “Sluggish diffusion in Co–Cr–Fe–Mn–Ni high-entropy alloys”. In: *Acta Materialia* 61.13 (2013), pp. 4887–4897.
- [18] Jien-Wei Yeh. “Alloy design strategies and future trends in high-entropy alloys”. In: *Jom* 65.12 (2013), pp. 1759–1771.
- [19] Xiang Yin and Shuqiong Xu. “Properties and preparation of high entropy alloys”. In: *MATEC web of conferences*. Vol. 142. EDP Sciences. 2018.
- [20] Yunzhu Shi, Bin Yang, and Peter K Liaw. “Corrosion-resistant high-entropy alloys: A review”. In: *Metals* 7.2 (2017), p. 43.
- [21] Kai Wen et al. “Aging behavior and fatigue crack propagation of high Zn-containing Al-Zn-Mg-Cu alloys with zinc variation”. In: *Progress in Natural Science: Materials International* 27.2 (2017), pp. 217–227.
- [22] S Varalakshmi et al. “Hot consolidation and mechanical properties of nanocrystalline equiatomic AlFeTiCrZnCu high entropy alloy after mechanical alloying”. In: *Journal of materials science* 45.19 (2010), pp. 5158–5163.
- [23] Kátia Regina Cardoso et al. “Mechanical alloying and spark plasma sintering of AlCrCuFeZn high entropy alloy”. In: *Materials Science and Technology* 36.17 (2020), pp. 1861–1869.
- [24] S Varalakshmi, M Kamaraj, and BS Murty. “Processing and properties of nanocrystalline CuNiCoZnAlTi high entropy alloys by mechanical alloying”. In: *Materials Science and Engineering: A* 527.4-5 (2010), pp. 1027–1030.
- [25] S Varalakshmi, M Kamaraj, and BS Murty. “Formation and stability of equiatomic and nonequiatomic nanocrystalline CuNiCoZnAlTi high-entropy alloys by mechanical alloying”. In: *Metallurgical and Materials Transactions A* 41.10 (2010), pp. 2703–2709.
- [26] Fan Zhang et al. “An understanding of high entropy alloys from phase diagram calculations”. In: *Calphad* 45 (2014), pp. 1–10.
- [27] Rainer Schmid-Fetzer. “Phase diagrams: the beginning of wisdom”. In: *Journal of Phase Equilibria and Diffusion* 35.6 (2014), pp. 735–760.
- [28] AJ Zaddach et al. “Mechanical properties and stacking fault energies of NiFe–CrCoMn high-entropy alloy”. In: *Jom* 65.12 (2013), pp. 1780–1789.

- [29] A Panda et al. “Advantages and effectiveness of the powder metallurgy in manufacturing technologies”. In: *Metalurgija* 57.4 (2018), pp. 353–356.
- [30] James Evans and Lutgard De Jonghe. *The Production and Processing of Inorganic Materials*. Springer, 2016.
- [31] Isaac Chang and Yuyuan Zhao. *Advances in powder metallurgy: properties, processing and applications*. Elsevier, 2013.
- [32] Neil Birks, Gerald H Meier, and Frederick S Pettit. *Introduction to the high temperature oxidation of metals*. Cambridge university press, 2006.
- [33] MIT. *Ellingham Diagrams*. Last accessed 01 July 2021. 2017. URL: https://web.mit.edu/2.813/www/readings/Ellingham_diagrams.pdf.
- [34] Barimar Prabhava Sai Narayana. “A Study of Electronic Structure and Thermal Stability of Engineered SOI Material”. PhD thesis. Trinity College Dublin, 2018.
- [35] Adonias Ribeiro Franco Jr et al. “The use of a Vickers indenter in depth sensing indentation for measuring elastic modulus and Vickers hardness”. In: *Materials Research* 7 (2004), pp. 483–491.
- [36] AD Karathanasis, BF Hajek, et al. “Elemental analysis by X-ray fluorescence spectroscopy”. In: *Methods of soil analysis. Part 3* (1996), pp. 161–223.
- [37] Junfang Lu et al. “Matrix dissolution techniques applied to extract and quantify precipitates from a microalloyed steel”. In: *Metallurgical and Materials Transactions A* 42.7 (2011), pp. 1767–1784.
- [38] Andreas Hegetschweiler, Thorsten Staudt, and Tobias Kraus. “An improved method for the matrix dissolution extraction of nanoparticles from microalloyed steel”. In: *Journal of Materials Science* 54.7 (2019), pp. 5813–5824.
- [39] Thomas Sourmail. “Precipitation in creep resistant austenitic stainless steels”. In: *Materials science and technology* 17.1 (2001), pp. 1–14.

Appendix A

Sintering Curves

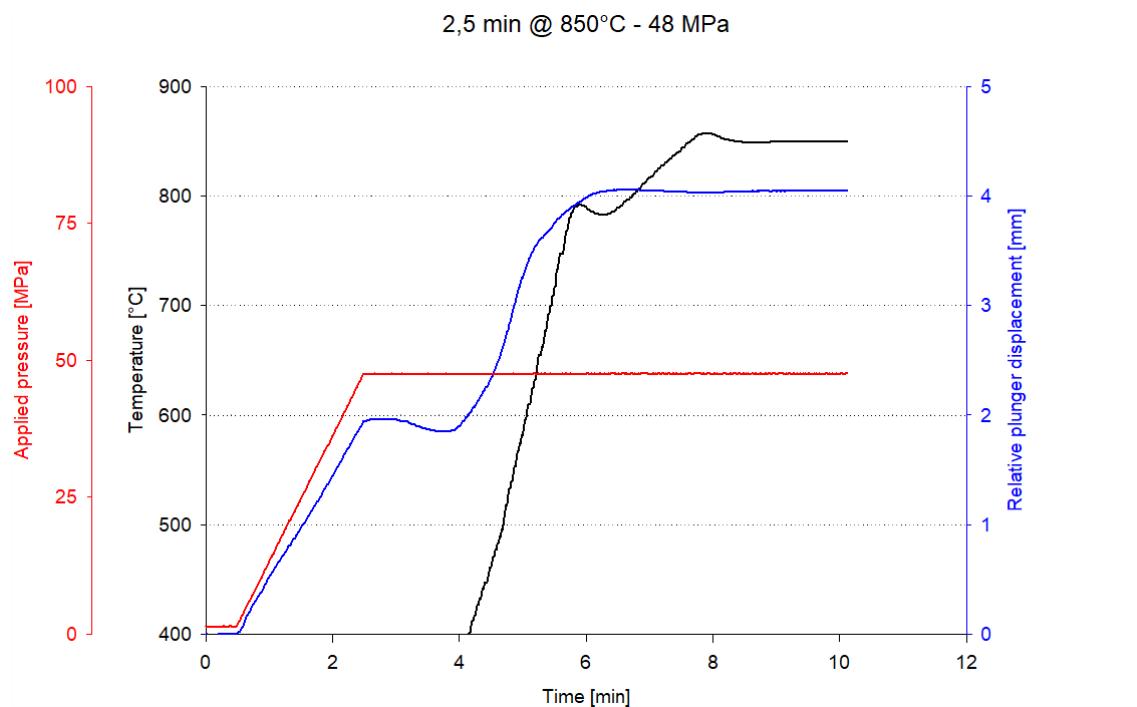


Figure A.0.1: Sintering diagram showing the evolution of temperature, applied pressure & piston displacement as a function of time - Case 1B

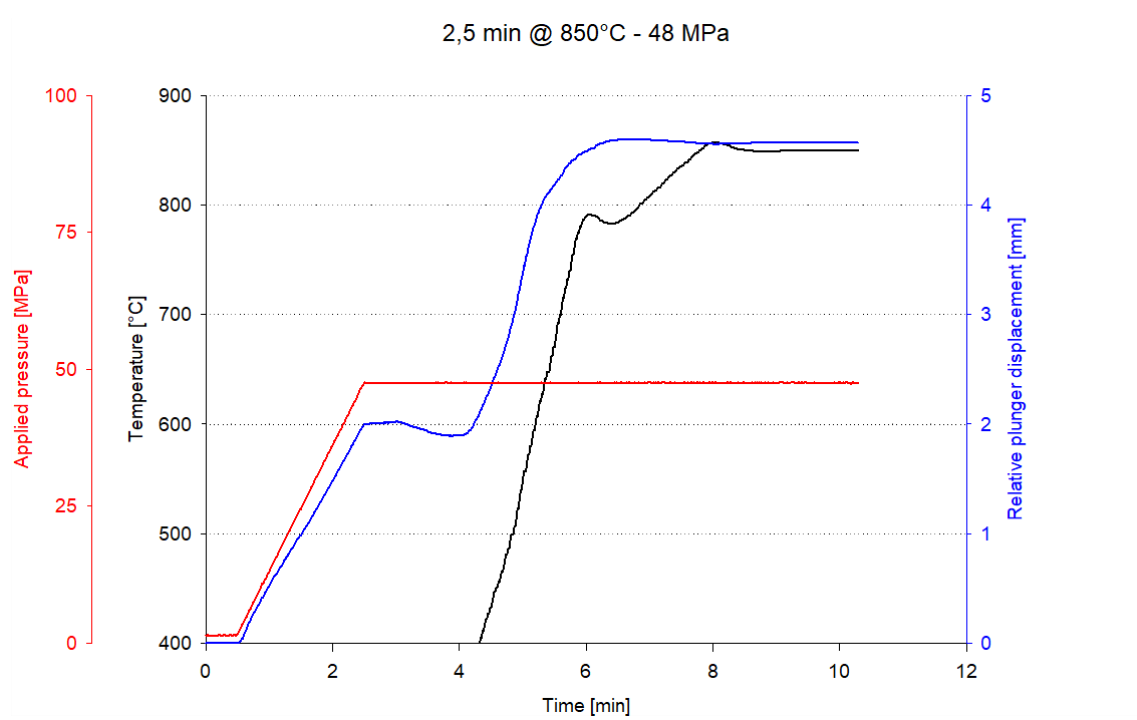


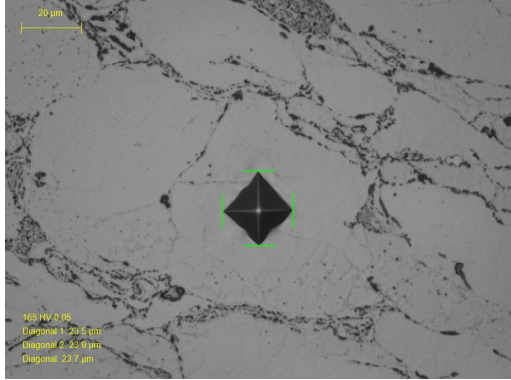
Figure A.0.2: Sintering diagram of the showing the evolution of temperature, applied pressure & piston displacement as a function of time - Case 2

Appendix B

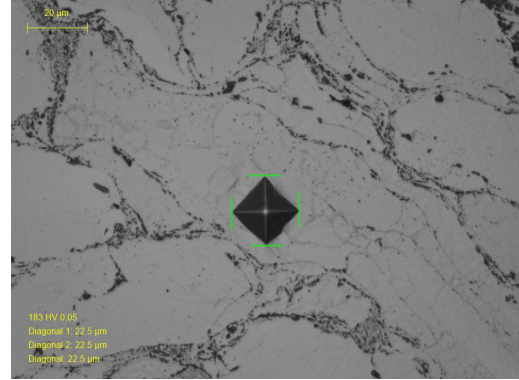
Hardness Test

Diagonal 1 (μm)	Diagonal 2 (μm)	Hardness (HV)
23.346	22.992	173
22.995	23.529	171
23.525	23.882	165
23.170	22.833	175
22.487	22.479	183
22.821	22.464	181
23.523	22.992	171
22.473	22.462	184
	Average	175

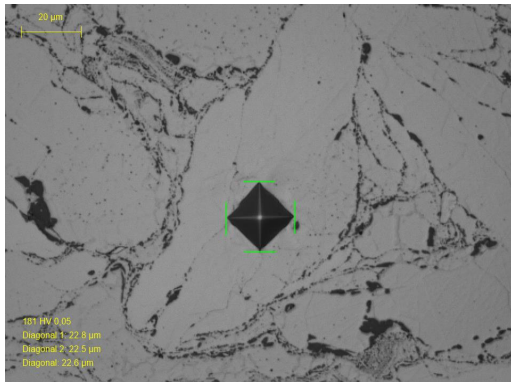
Table B.1: Chart for the the different hardness measurements obtained on a sintered sample - Case 1A.



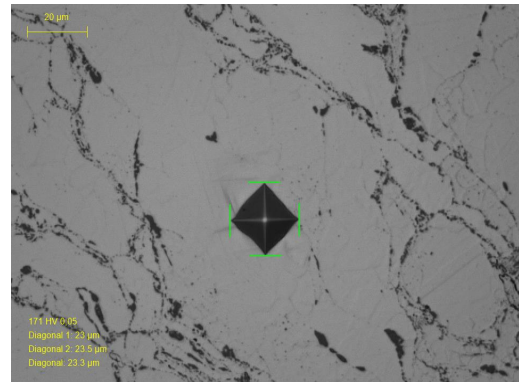
(a)



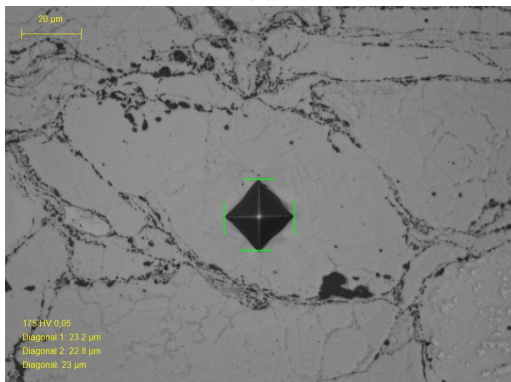
(b)



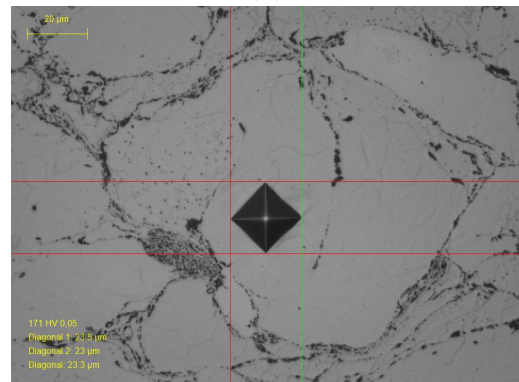
(c)



(d)



(e)



(f)

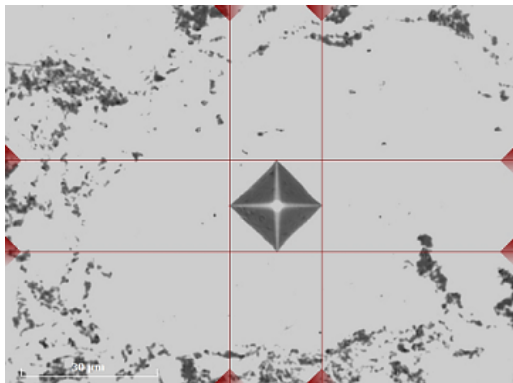
Figure B.0.1: Images of the hardness result obtained on sintered sample - Case 1A

Diagonal 1 (μm)	Diagonal 2 (μm)	Hardness (HV)
20.3	20.4	224
21.5	21.1	204.34
21.5	21.5	200.22
20.6	21.5	208.6
21.5	21.5	200.21
	Average	207.53

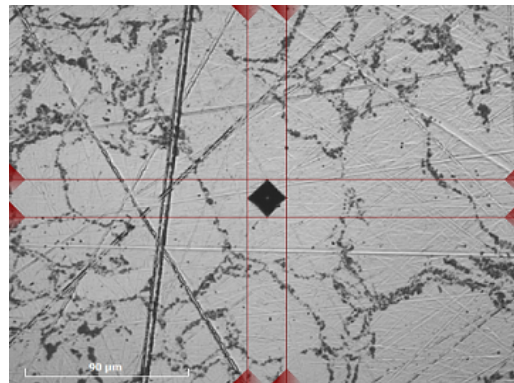
Table B.2: Chart for the the different hardness measurements obtained on a sintered sample - Case 1B.

Diagonal 1 (μm)	Diagonal 2 (μm)	Hardness (HV)
21.3	21.3	204.34
21.1	21.3	206.47
20.9	21.5	206.38
20.9	21.1	210.79
21.5	21.5	200.21
20.9	21.1	210.82
	Average	206.5

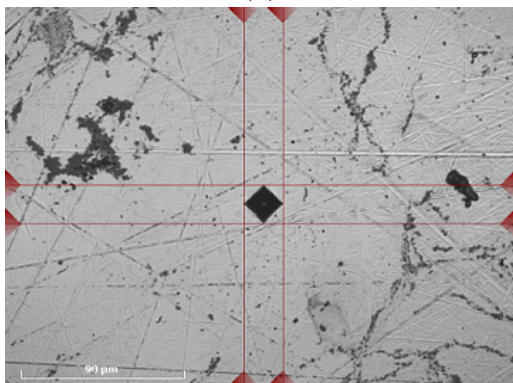
Table B.3: Chart for the the different hardness measurements obtained on a sintered sample - Case 2.



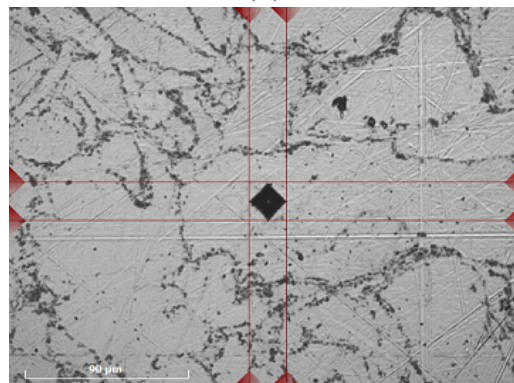
(a)



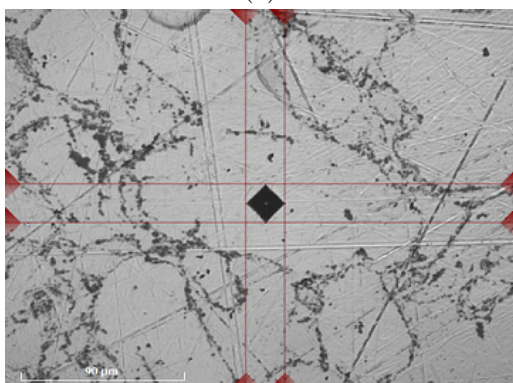
(b)



(c)

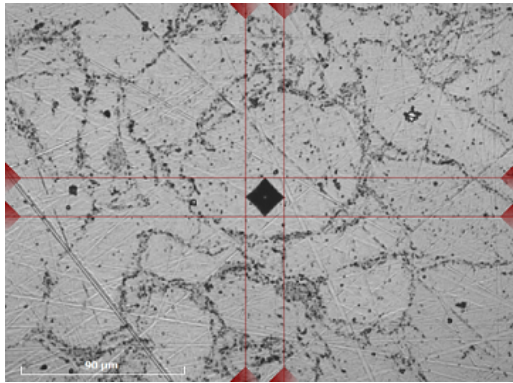


(d)

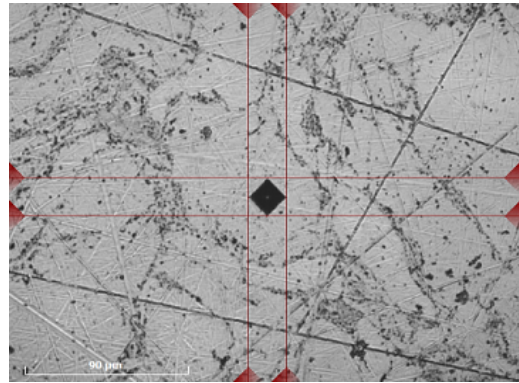


(e)

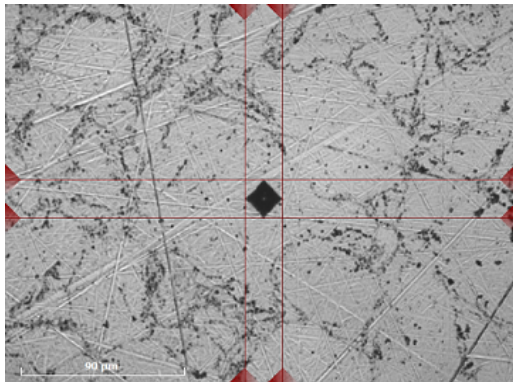
Figure B.0.2: Images of the hardness result obtained on sintered sample - Case 1B



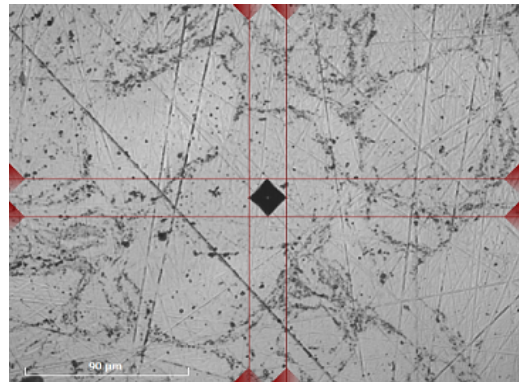
(a)



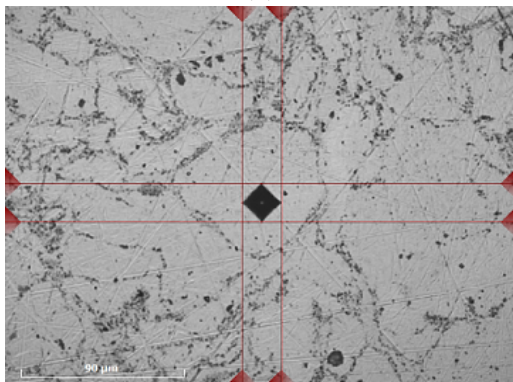
(b)



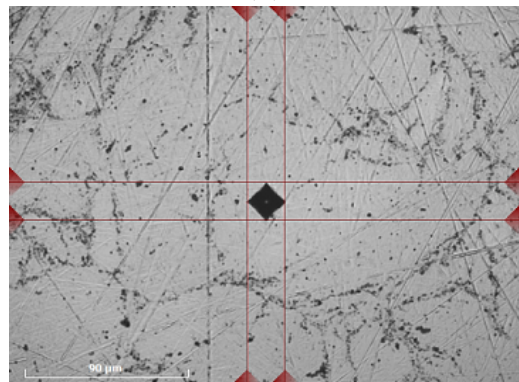
(c)



(d)



(e)



(f)

Figure B.0.3: Images of the hardness result obtained on sintered sample - Case 1B

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