

PRODUCTION AND CHARACTERIZATION OF CaNi
COMPOUNDS FOR METAL HYDRIDE BATTERIES

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COMPOUNDS FOR METAL HYDRIDE BATTERIES**

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ABSTRACT

PRODUCTION AND CHARACTERIZATION OF $\text{CaNi}_{5-x}\text{M}_x$ COMPOUNDS FOR METAL HYDRIDE BATTERIES

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Ni - MH batteries have superior properties which are long cycle life, low maintenance, high power, light weight, good thermal performance and configurable design. Hydrogen storage alloys play a dominant role in power service life of a Ni - MH battery and determining the electrochemical properties of the battery. LaNi_5 , belonging to the CaCu_5 crystal structure type, satisfy many of the properties. The most important property of LaNi_5 is fast hydrogen kinetics. Recently, CaNi_5 , belonging to same crystal type, has taken some attention due to its low cost, higher hydrogen storage capacity, good kinetic properties. However, the main restriction of its use is its very low cycle life.

The aim of the study is to obtain a more stable structure providing higher cycle life by the addition of different alloying elements. In this study, the effect of sixteen alloying elements (Mn, Sm, Sn, Al, Y, Cu, Si, Zn, Cr, Mg, Fe, Dy, V, Ti, Hf and Er) on cycle life was investigated. Sm, Y, Dy, Ti, Hf and Er were added for replacement of Ca and Mn, Sn, Al, Cu, Si, Zn, Cr, Mg, Fe and V were added for replacement of Ni. Alloys were produced by vacuum casting and heat treating followed by ball milling. The cells assembled, using the produced active materials as anode, which were cycled for charging and discharging. As a result, replacement of Ca with Hf, Ti, Dy and Er, and replacement of Ni with Si and Mn were observed to show better cycle durability rather than pure CaNi_5 .

Keywords: Ni-MH batteries, hydrogen storage materials, CaNi_5

ÖZ

METAL HİDRÜR BATARYALAR İÇİN $\text{CaNi}_{5-x}\text{M}_x$ ESASLI BİLEŞİKLERİN ÜRETİMİ VE KARAKTERİZASYONU

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Ni - MH bataryalar, uzun çevrim ömrü, az bakım gerektirmesi, yüksek güç, hafif olması, yüksek termal performans gibi üstün özelliklere sahiptir. Ni - MH bataryaların kullanım ömrü ve bataryanın elektrokimyasal özelliklerinin tespiti açısından hidrojen depolayan alaşımlar baskın bir rol oynamaktadır. LaNi_5 , CaCu_5 kristal yapı grubuna bağlı olup, belirtilen bütün özellikleri karşılamaktadır. LaNi_5 ' in en önemli özelliği ise hızlı hidrojen kinetiğidir. CaNi_5 aynı kristal yapı grubuna bağlı olup az maliyet, yüksek hidrojen depolama kapasitesi ve yüksek kinetik özellikleri ile dikkatleri üzerine çekmiştir. Ancak, bu iyi özelliklerinin yanı sıra düşük çevrim ömrü CaNi_5 kullanılmasını sınırlandırmaktadır.

Bu çalışmanın amacı, alaşım elementleri ekleyerek yüksek çevrim ömrü sağlayan daha kararlı bileşiklerin elde edilmesidir. Yapılan bu çalışmada, 16 farklı alaşım

elementinin (Mn, Sm, Sn, Al, Y, Cu, Si, Zn, Cr, Mg, Fe, Dy, V, Ti, Hf ve Er) çevrim ömrü üzerindeki etkileri incelenmiştir.

Sm, Y, Dy, Ti, Hf ve Er elementleri Ca ile yer deęiřtirmesi için ve Mn, Sn, Al, Cu, Si, Zn, Cr, Mg, Fe ve V Ni ile yer deęiřtirmesi için eklenmiştir. Alařımlar vakumlu döküm, ısıl işlem ve toplu öğütme proseslerinden sırasıyla geçerek üretilmiştir. Üretilen aktif madde oluşturulan hücrenin anot malzemesi olarak kullanılmıştır. Üretilen elektrotlar çevrim ömrünün belirlenmesi için řarj – deřarj edilmiştir. Sonuç olarak, Ca elementinin Hf, Ti, Dy ve Er elementleri ile ve Si ve Mn elementlerinin Ni ile yer deęiřtirmesi ile saf CaNi_5 bileřiğinden daha iyi çevrim ömrü kararlılıęı gözlenmiştir.

Anahtar kelimeler: Ni-MH bataryalar, hidrojen depolama malzemeleri, CaNi_5

*Dedicated to my beloved Fatih Pişkin
and
my family*

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CHAPTER 1

INTRODUCTION

1.1 Batteries

Battery is a device containing active materials that converts, store chemical energy into electrical energy. During this conversion there are occurrence of basic reactions; oxidation and reduction reactions. There is transferring of electrons during these reactions from one material to another to produce direct current electricity [1].

Ni – MH (Nickel – Metal Hydride) batteries have become popular by considering the advantages of its properties which are long cycle life, good thermal performance, light weight and better hydrogen storage properties with respect to other energy sources [2].

1.2 Components of Cells and Batteries

Unit of battery can be referred as cell. Battery involves one or more electrochemical cells. These cells can be connected each other either in series or in parallel or in any combination, according to desired output voltage and capacity. The cell has three major components; anode, cathode and electrolyte [3]. The anode is the electrode where the oxidation reaction takes place during discharging and electrons are fed out of the cell into the external circuit. The cathode is the electrode where the reduction reaction takes place and electrons from the external circuit turn to cell. There is

another component which is ionic conductor for the battery. This ionic conductor is electrolyte providing medium to complete electrical circuit for ion transfer between anode and cathode [1].

1.3 Primary and Secondary (Rechargeable) Batteries

Batteries can be classified as primary and secondary batteries. Primary batteries cannot be recharged whereas secondary batteries can.

Primary batteries can convert chemical energy into electrical energy for one time. In primary cells, reactions are irreversible and they include only fixed amount of active material discharging only once a time. Although primary cells can be used for one time, they have some advantages. These are good shelf life, high energy density at low to moderate discharge rates and ease of use. These kinds of batteries are convenient, usually inexpensive and lightweight source for several applications [4].

Secondary batteries are rechargeable batteries. After completion of discharging of cell, externally applied electrical energy forces a reversal of the electrochemical process. In consequence, stored energy can be used for another time. These reactions can be repeated for several times due to the characteristics of batteries. This property is an fundamental advantage for the usage of secondary batteries [3]. There are two main application groups for the usage of secondary batteries; in first group secondary batteries are connected to the electricity and charged by a prime energy source. Standby Power Sources (UPS), hybrid electric vehicles and stationary energy storage (SES) systems are some examples for this group. There is another group for the secondary batteries which are used or discharged as primary batteries, but recharged after using. Therefore, portable consumer products, power tools, electric vehicles can be some examples for this group of secondary batteries.

There are commonly four main groups for the secondary batteries; nickel cadmium batteries, lithium – ion batteries, lead acid batteries and Ni – MH batteries. There are some good marks for the Ni – MH batteries over than the other type of secondary batteries. These can be summarized as being rechargeable, safety, non – hazardous and having good cycle life.

The nickel – hydrogen battery cell is a rechargeable electrochemical cell which has extended service life. Ni – MH batteries are one of the most widely used secondary batteries due to its properties such as flexible cell sizes, safe operation, flexible packaging, maintenance free, excellent thermal properties, simple and inexpensive charging and environmentally and recyclable materials of production of it [5].

CHAPTER 2

NICKEL METAL HYDRIDE BATTERIES

2.1 Nickel – Metal Hydride Batteries

There is a force for the improvement in the technology of Ni – MH batteries due to technical and environmental needs. Especially, better energy performance and environmental properties of Ni – MH batteries over than nickel cadmium batteries make Ni – MH batteries valuable [2]. Possibility of increasing in capacity accelerates development of Ni – MH batteries in the early 1900s. There is a usage of Ni – MH batteries in portable consumer electronics and automotive batteries. Best application of Ni – MH batteries is for electric vehicle (EV) and hybrid electric vehicle (HEV) [5]. General Motors, Honda EV Plus, Ford Ranger EV and Vectrix scooter are used Ni – MH technology. Also, Hybrid vehicles such as the Toyota Prius, Honda Insight, Ford Escape Hybrid, Chevrolet Malibu Hybrid, and Honda Civic Hybrid also use them. From all of these companies, Toyota Prius is the first mass – produced and it presents from 1997 to our time. Hybrid sales of this company is 4 million worldwide since 1997 [6]. Although there are several advantages of Ni – MH batteries, there are some drawbacks of Ni – MH batteries when they are compared with other secondary batteries. The performance of a Ni – MH batteries is measured in the terms of capacity, cycle life and charge – discharge properties. These properties need to be improved for the widely usage of these batteries. Because, charge-discharge cycles of Ni – MH batteries is almost 1000 cycles whereas Ni – Cd batteries have almost 2000 cycles. This charge – discharge properties depend on electrode characteristics and manufacturing method. This is the main issue which needs to be improved in Ni –

MH batteries [2]. Hydrogen storage alloys have unique ability to reversibly absorb hydrogen and release significant amount of hydrogen electrochemically which effect performance of the battery [7].

2.2 Hydrogen Storage Alloys – AB₅

Design of the hydrogen storage alloys depends on three main aspects which are alloy composition, bulk and surface structure. Hydrogen storage alloys has significant role on the service life of Ni – MH batteries and their properties affect the electrochemical properties. The generalized preparation route for the production of hydrogen storage alloys is composed of rapid solidification and pulverization processes [7]. Mechanical alloying is the process to mill the powders and has several advantages for preparing hydrogen storage alloys. These advantages can be summarized as easy and controlled synthesis of powders, simple and inexpensive method operating at room temperature [8]. There is also another way to produce hydrogen storage alloys which is experienced in this study is vacuum casting of the materials followed by milling into powders to use for hydrogen storage alloys.

Hydrogen storage alloys can be classified basically into six groups. These groups are; AB₅, AB₃, A₂B₇, AB₂, AB and Mg – type alloys. Hydrogen storage capacity had to be studied for technology of mobile application. Their thermodynamic and kinetic properties, activation and deactivation, poisoning effects and storage capacity are the important parameters for the usage as hydrogen storage alloys [9].

For energy storage and transmission, hydrogen is a promising medium. There are several methods to store hydrogen which are liquid storage, glass microspheres or metal hydrides. In metal hydrides, hydrogen storage is much higher rather than the other methods [9]. Reaction of hydrogen is reversible with metal followed reaction:



For selecting materials for hydrogen storage, reaction kinetics of hydrogen adsorption and desorption in metal- hydrogen system is an essential parameter. Moreover, this property of kinetics depends upon the material that is used. Also, these properties are affected by alloy composition and crystal structure of the material [10]. According to these properties related with kinetics and thermodynamics, LaNi₅ has controllable reaction rate rather than Mg - based alloys which is extremely sluggish [11].

There is another essential factor for hydrogen storage materials which is storage criteria. For usage of hydrides as energy storage, there are some requirements have to be satisfied. Mainly, hydrides must be able to store large quantities of hydrogen, quickly formed and decomposed, safety, satisfied reaction kinetic, resistance to poisoning from contaminants and low cost. To satisfy all these requirements, different hydrides have been investigated for energy storage which are expressed in this section.

The AB₅ compounds have more hydrogen storage properties because nickel atoms have critical roles which are positioned in the crystallographic plane that governs the hydrogenation behavior. In AB₅ compounds, the most popular and commercial used compound is LaNi₅ belongs to CaCu₅ crystal structure [12], Figure 2.1.

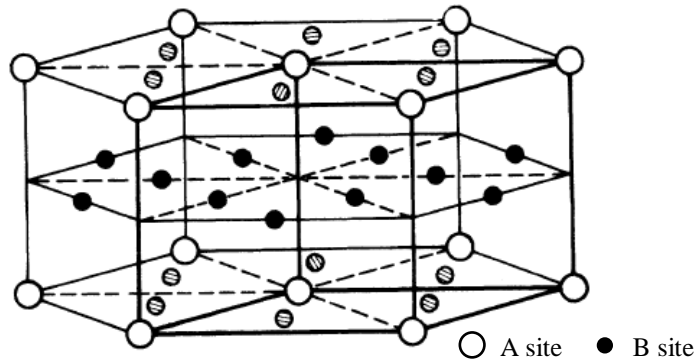


Figure 2.1. Hexagonal symmetry of AB_5 structure which defines the positional parameters of A and B site atoms [12] .

This crystal type, AB_5 has the ability of absorbing large quantities of hydrogen at ambient temperatures and pressure and great potential as hydrogen storage media. The known compound for AB_5 – type compounds are $CaNi_5$, $LaNi_5$, YNi_5 and $ThNi_5$ [12]. AB_5 compounds have attractive properties such as forming hydrides with equilibrium pressures of a few atmospheres at temperatures up to 100°C , tolerance to gaseous impurities and easy activation in the initial cycle. However, almost all compounds belongs to AB_5 group include Ni element which makes the cost higher [13]. $LaNi_5$ has taken the most attention intermetallic in AB_5 group and has a characteristic property that La has a strong affinity for hydrogen whereas Ni absorbs little or no hydrogen [14]. In the usage of this compound, there is another important reaction which takes place on surface is surface segregation process. La element diffuses to surface and bonds with O element which is impurity in hydrogen gas to form its oxides. During this reaction, Ni is not stable as $LaNi_5$, it is present in the form of Ni or Ni-rich particles. This cause continuous formation of fresh Ni particles [11]. This mechanism is also affected by activation and deactivation mechanism. Because of higher cost of compound, some substitution of Ni and La has been

studied. Moreover, promising compound CaNi_5 has been studied to take the place of LaNi_5 belonging the same crystal structure, CaCu_5 .

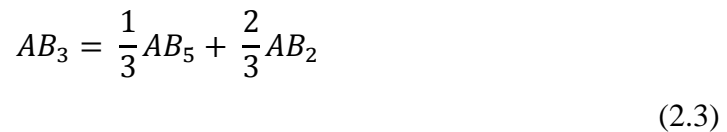
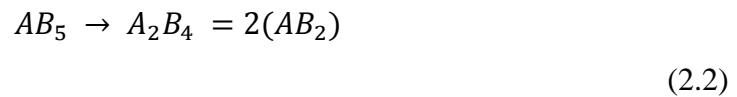
In the group of AB compounds, there is one most studied compound which is FeTi. AB compounds store hydrogen at the lowest cost. There are two stable intermetallics formed in the Fe – Ti alloy system is FeTi and Fe_2Ti . However, Fe_2Ti does not absorb adequate amount of hydrogen [15]. FeTi belongs to the CsCl crystal structure. Decomposed hydride formation is easier by the reaction with hydrogen of FeTi [16]. There is a need for activation of FeTi before the reaction with hydrogen [17, 18]. There is also occurrence of surface segregation as in LaNi_5 . During this process Ti atoms move surface layer and Fe atoms appear in the deeper layers as catalyst in the dissociation of hydrogen molecules. This hydrogen activation process is needed due to formation of Fe atoms in the vicinity of the surface [9]. There is difference with AB_5 compounds which is reaction kinetics are controlled by heat transfer [11]. There is also drawback of AB compounds such as reaction kinetics are severely affected by the presence of contaminants especially O_2 and H_2O . Effect of these contaminants is losing of FeTi starts and this reaction is not a reversible reaction. Another AB compound rather than FeTi is TiCo [19]. This alloy has better properties such as easy activation and shows better resistance to impurities. However, equilibrium dissociation pressure is too low. There are studies to improve this pressure by addition of manganese [9]. Other typical AB compounds are ZrNi [20-22] and ZrCo [23, 24]. In these intermetallics, Zr element reacts with larger amount of hydrogen and absorbs small amount of hydrogen that is not enough for the hydrogen storage applications.

AB_2 – type compounds have higher storage capacities and resistance to impurities and this makes these intermetallic compounds important in hydrogen storage alloys. AB_2 – type compounds form two kind of structures which are cubic C15 [25] and hexagonal C14 structure [26]. According to their crystal structure, Laves phases,

there is occurrence of different interstitial sites and as a consequence, by the increasing volume of unit cell, hydrogen absorption increases without changing structure. [9] In AB₂ –type alloys, there are different Zr – based alloys with the formula ZrB₂ where B equals to V, Cr, Mn, Fe Co or Mo. Hydrogen absorption properties decreases by increasing in 3d occupation[27].

Mg and Mg – based alloys have been investigated as a hydrogen storage alloys because of their high storage capacity up to 7.6 wt.% in case of pure MgH₂ [28]. This is the first important criteria for the hydrogen storage alloys and the second one is Mg – based alloys are inexpensive. The main drawback for Mg – based hydrides is the high sorption temperature of > 200°C, whereas 80°C is required for more applications. Also, there is poor reaction kinetics and occurred hydride is too stable for most practical applications [9].

There is relationship between the structures of intermetallics such as AB₅, AB₂ and A₂B₇. All of these compounds can be derived from AB₅ structure. These intermetallics are related with each other and can be derived formulas below, the first formula shows how AB₂ – type alloys form. The other formulas show forming of other structures is obtained by combining AB₅ and AB₂ units [29] .



In the literature, when these structures are compared, it is resulted that maximum hydrogen can be absorbed by the AB_3 , A_2B_7 , AB_5 and AB_2 – type alloys, are $ErCo_3H_{5.5}$, $Ce_2Ni_7H_6$, AB_5H_6 , AB_2H_4 , $AB_3H_{4.7}$ structures, respectively [13, 30, 31].

From the literature, one can see that each alloy has some good as well as bad properties. Therefore, it can be said that there is no certain hydrogen storage alloy to satisfy all requirements. These properties are summarized and compared in Table 2.1. All these information shows that there is a need for improvement of properties of hydrogen storage alloy. Alloying additions to A and B – site is good way to try to obtain all requirements.

Table 2.1 Summary and comparison of hydrogen storage alloys [9].

Alloy type	Quantity of hydrogen absorbed	
	H / M	wt. %
AB_5	1.0 up to 1.5	1.4% to max 1.9%
AB	1.0	1.8% max.
AB_2	From 1.0 up to 2.0	From 1.5% to 2.0%
Mg - compounds	1.3 up to 2.0	From 3.5% up to 6.7%
$AB_3 + A_2B_7$	Max of 1.4 for AB_3 . Max of 0.67 for A_2B_7 .	1.6% max.

2.3 $CaNi_5$ as Hydrogen Storage Alloys

$CaNi_5$ is promising compound belonging to the same crystal structure as $LaNi_5$ has the potential to replace this compound due to its low cost, higher hydrogen storage capacity, good kinetic properties. $CaNi_5$ alloys are low cost hydride electrode materials, therefore it is studied as an anode material [32]. However, the main

restriction of its use is its very low cycle life. Therefore, lower cycle life has to be improved. CaNi_5 is the member of AB_5 – type alloys which has $P6/mmm$ space group. Figure 2.2 shows the crystal structure of CaNi_5 unit cell.

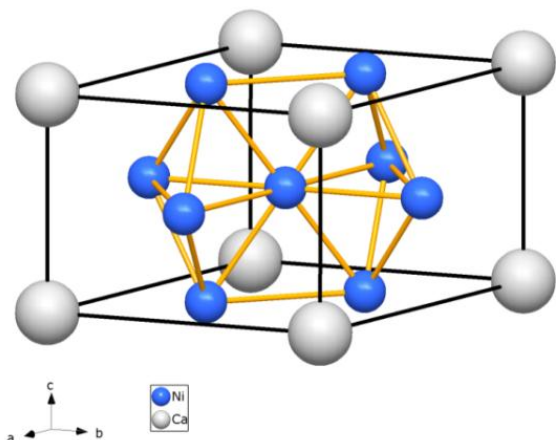
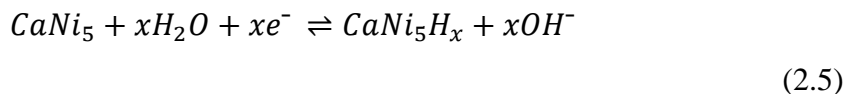
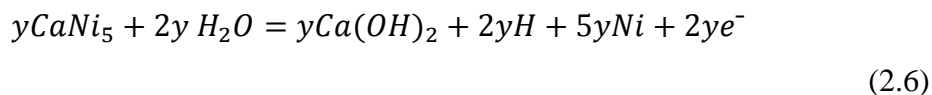


Figure 2.2 Unit cell of CaNi_5 structure.

Ca element is too sensitive and has less resistant to H_2O and O_2 . Therefore, not only during preparations but also during electrochemical tests, Ca element can be exposed to corrosion. There are some reactions which occur during charging and discharging. The CaNi_5 -type hydride electrodes can be charged and discharged reversibly [32];



There is another reaction which is irreversible capacity loss caused by electrochemical corrosion of Ca in the electrolyte during discharging [32];



Therefore, the discharge capacity can be calculated by the equation which is given below;

$$C = xF/3.6W_{CaNi_5} + 2yF/3.6W_{CaNi_5} \text{ (mA h g}^{-1}\text{)} \quad (2.7)$$

where F , W_{CaNi_5} , x and y are Faraday constant and molecular weight of $CaNi_5$, respectively.

The problem for the usage of $CaNi_5$ in practical applications and possible ways to overcome in lower cycle life are only slightly studies in literature. These discussions can be summarized; exact composition of $CaNi_5$ formed at low temperatures, there is a surface segregation effect which is similar as $LaNi_5$ and discussed in the section 2.2 and there is a problem about activation of $CaNi_5$ [33]. These drawbacks of $CaNi_5$ make it the subject of research, from production to electrochemical testing. In literature, it is generally synthesized by mechanical alloying of Ca and Ni powder followed by isothermal annealing [34]. The importance of alloying is to obtain the same crystal structure after addition of alloying elements as crystal structure of $CaNi_5$.

There are limited studies about substitution of Ca and Ni element by alloying elements in $CaNi_5$. In the study of Li and Suda [35], effects of alloying elements which are replaced by Ca and Ni were investigated. In that study, La – substitution replacing Ca atom showed improvements on the cycle life of the battery due to better anti – corrosive nature of La than that of Ca in alkaline solution. However, it is also stated that increasing amount of La element in the structure can cause decreasing of the durability [35]. Similar effects are also observed by the substitution of Ti and Zr. It was observed that Al substitution makes no difference on microstructure and phase structure of $CaNi_5$. Al alloying causes oxidation problems on the surface of $CaNi_5$.

Due to the difficulties of controlling the calcium vaporization, there was remaining phase of Ca_2Ni_7 .

Mg substitution improves the durability due to the formation of $\text{Mg}(\text{OH})_2$ which has higher chemical stability. Substitution of Mg element, it cause decrease in the atomic volume and little changes in lattice volume. Co substitution cause decreasing in cycle durability because of poor affinity between Ca and Co elements. [35].

Also Jensen and Bjerrum [36] have studied effects of different alloying element. They showed effect and changes on the chemical and electrochemical properties. In this study, substitution of Ni was done by common B metals such as Al, Cr, Mn, Fe, Co Cu Zn and Mg. It was observed that there is an occurrence of different three groups according to their behavior in formation of CaNi_5 crystal structure. Cu and Zn replace Ni completely in CaNi_5 compound. Cr, Mn, Fe and Co elements have poor affinity to form binary intermetallics, hence there is formation of different phases rather than AB_5 – type alloys. Moreover, Al, Sn and Mg elements are studied and it was observed that they form binary intermetallics in the form of other compounds except AB_5 stoichiometry.

Moreover, Ovshinsky and Young [37] studied on electrochemically stabilized CaNi_5 alloys and electrodes and showed results in US Patent. In their study, the alloy material includes at least one alloying element protects the active material from degradation during electrochemical process. This protection is provided by preventing dissolution of Ca in electrolyte. In their study, they used misch metal, rare earth elements, zirconium and mixture of Zr with Ti or V and Si, Al, Ge, Sn, In, Cu, Zn and Co were used as alloying elements. The electrochemical results of their study can be summarized as; unalloyed compound, CaNi_5 , lost its half capacity in the third cycle whereas alloyed compound with Mg and Zr almost does not lose its capacity till the twelfth cycle. Also, alloyed compound with Mg, Zr and Si with a specific

calculated amount shows almost the same electrochemical properties and loses 20% of its capacity till twelfth cycle. All of these results showed to us, alloyed compounds showed improvement in the cyclic durability compared with unalloyed compound, CaNi_5 and alloying elements have effects to prevent degradation of CaNi_5 in the electrolyte.

From the literature, as understood the main problem of CaNi_5 is lower cycle life and cyclic stability. Results of searching in literature showed that the main mechanism is the degradation of CaNi_5 . This degradation process is resulted in the formation of Ca(OH)_2 [35]. For understanding this mechanism, effects of alloying was studied using an ab initio pseudo potential method. In this method, formation energies of the CaNi_5 compounds having different alloying elements were calculated for the understanding of the effect of the alloying element on the stability of the compound. It was found that, lower formation energy, compared to the pure compound, increases the stability which could improve the cyclic durability of CaNi_5 to be used as an anode in Ni-MH batteries. In addition, in order to investigate effects of alloying on Ca diffusion in CaNi_5 , activation energies of Ca diffusion for different alloys were calculated by Nudged Elastic Band method (NEB) method [38].

NEB method is used to find reaction pathways when both the initial and final states are known. Alloying models were selected for the calculation of activation energy by this method. In the selection of alloying elements, decrease in the formation energy of the system and distance between Ni atoms were effective. Thus, decreasing of system energy showed that the possibility of formation of more stable structure. Moreover, by the decreasing of distances between Ni atoms, diffusion activation energy of Ca atom in crystal structure can be difficult. Therefore, activation energy of alloying models of Dy, Er, Gd, Hf, La, Sm, Ti, Y and Zr by the replacement of Ca atom and Al, Fe, Hf, P, Si, Sn, Ti, V and Zr by the replacement of Ni element were calculated.

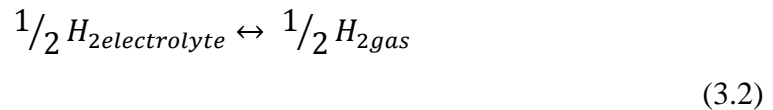
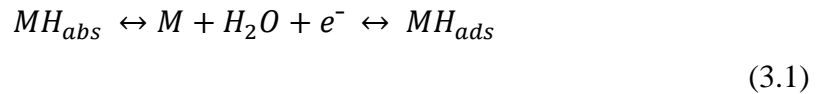
Thus, elements were selected which the changes in activation energy is higher to prevent the degradation of CaNi_5 by difficult diffusion of Ca atom.

CHAPTER 3

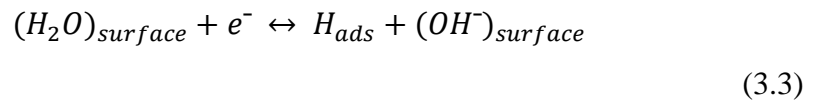
ELECTROCHEMICAL PRINCIPLES AND REACTIONS

3.1 Electrochemical Principles and Reactions

The electrode is a metal electrolyte interface where the electrochemical reaction occurring on the metal surface in the electrolyte. Charge transfer through the electrode occurs by electrochemical reaction [39]. Thermodynamics of electrodes of intermetallics were explained and the reactions that occur during charge transfer reaction on the MH electrode / electrolyte surface is given below equation;



Reactions that occur on the surface can be summarized by Max Volmer reaction and the steps of charge transfer reactions [2] are shown in Figure 3.1 to make the understanding easier;



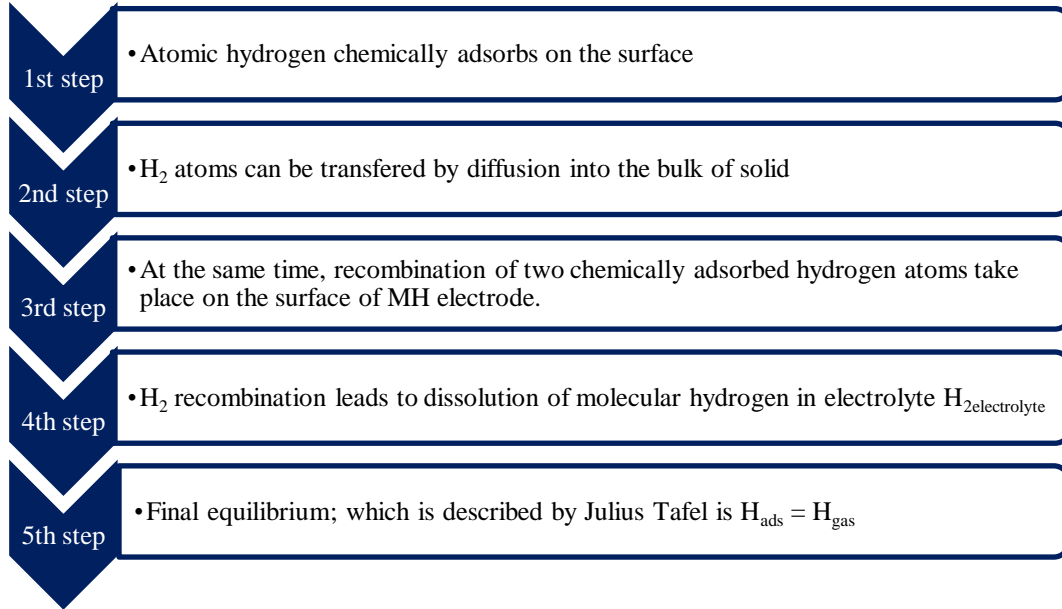
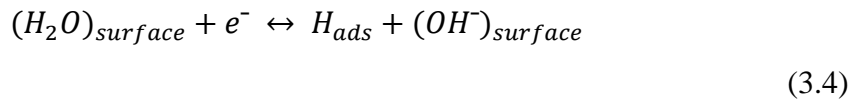


Figure 3.1 Schematic illustration of charge transfer reaction on the MH electrode/electrolyte surfaces in steps.

Diffusion rate of hydrogen depends on charge transformation between the bulk of solid and bulk of electrolyte. Adsorbed hydrogen atoms specify the chemical potential for surface hydrogen. For the formation of alloy / metal hydrogenation chemical potential differences between the surface and solid bulk is the primary element. This hydrogenation can be described by some reactions which are [2];



Electrochemical hydrogenation is an important process and its steps are basically summarized on below. Corrosion reactions can be observed during electrochemical

hydrogenation. Steps of hydrogenation is summarized in Figure 3.2 [7]. Charge transformation during electrochemical reactions occurs on the surface of metal hydride electrode with electrolyte is shown in Figure 3.3[2].

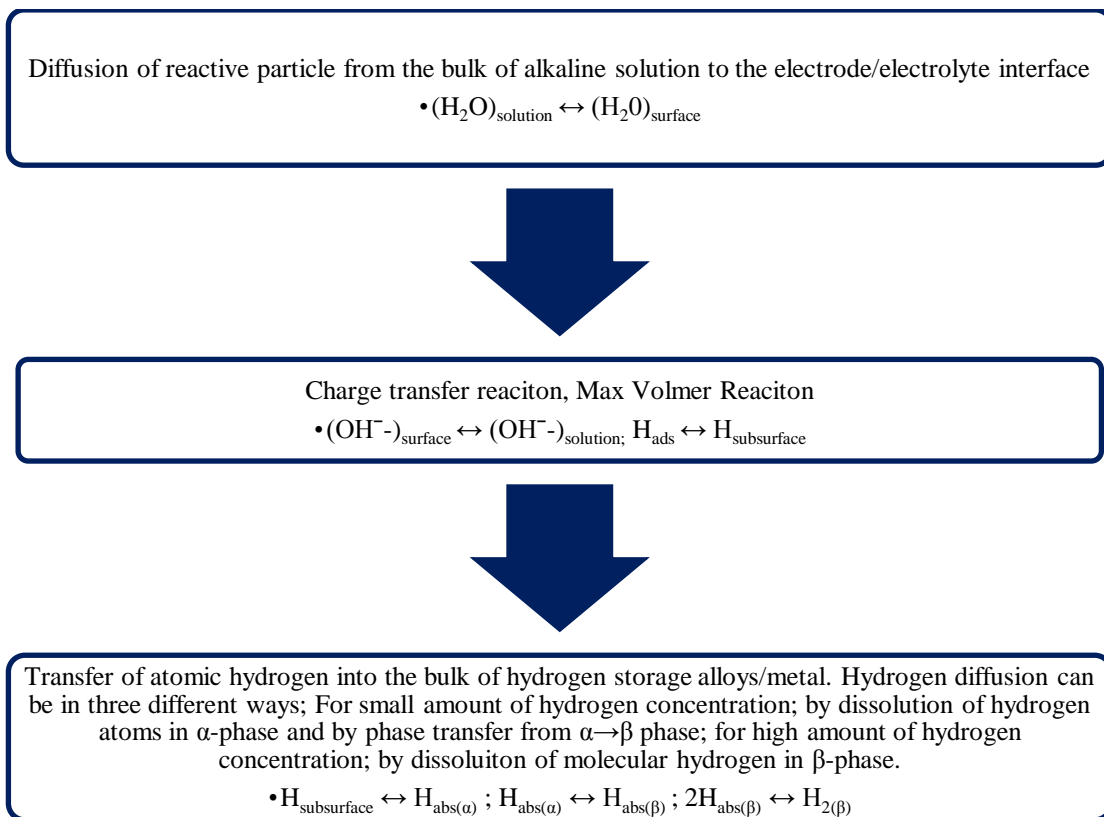


Figure 3.2 Electrocatalytic activity of MH electrode.

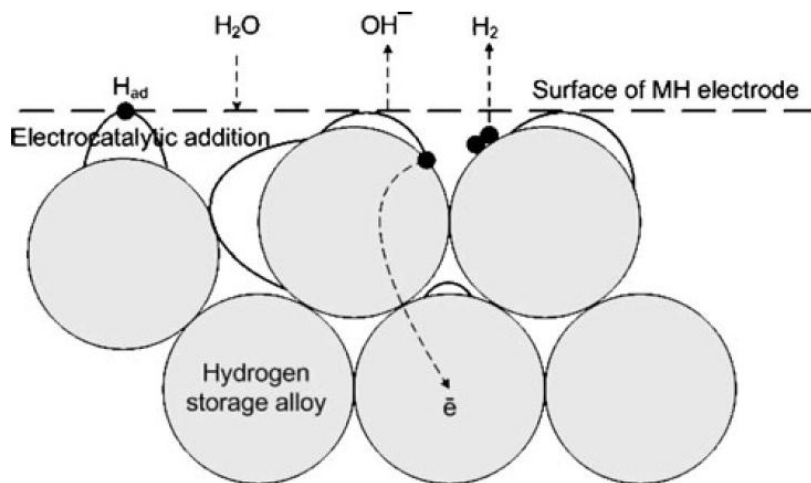


Figure 3.3. Charge transfer reaction on the surface of MH electrode with electrocatalytic addition [7].

During this charge – discharge transfer reactions there are changes on the content of the hydrogen. This change can be shown and hydrogen storage can be understood better in Figure 3.4[8].

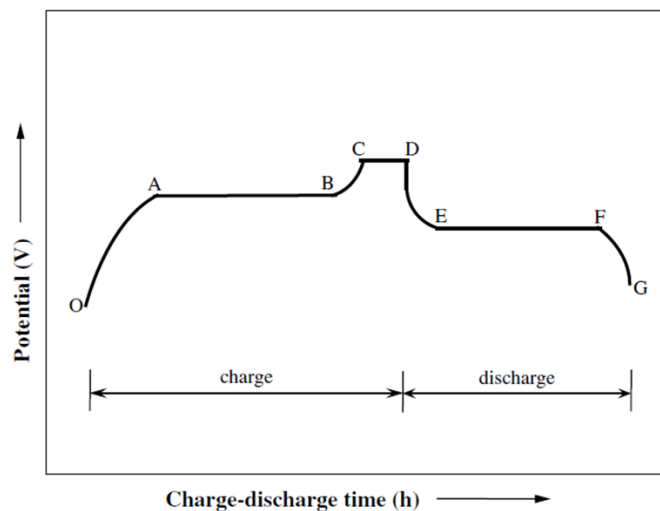


Figure 3.4. Schematic illustration of a charge-discharge curve for a hydrogen storage alloy [7].

According to the Figure 3.4, hydrogen content increases between the points A and B, then increasing of the content of hydrogen stops and improvement in hydrogen evaluation take place between the point C and D. After all these reactions, discharging starts and continues from the point D till G. Therefore, it can be noted that charge transfer and hydrogen diffusion are the two most important factors for the evaluating electrochemical properties of a hydrogen storage alloys [40].

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Specimen Preparation

Experimental procedure was progressed according to the steps shown in the Figure 4.1.

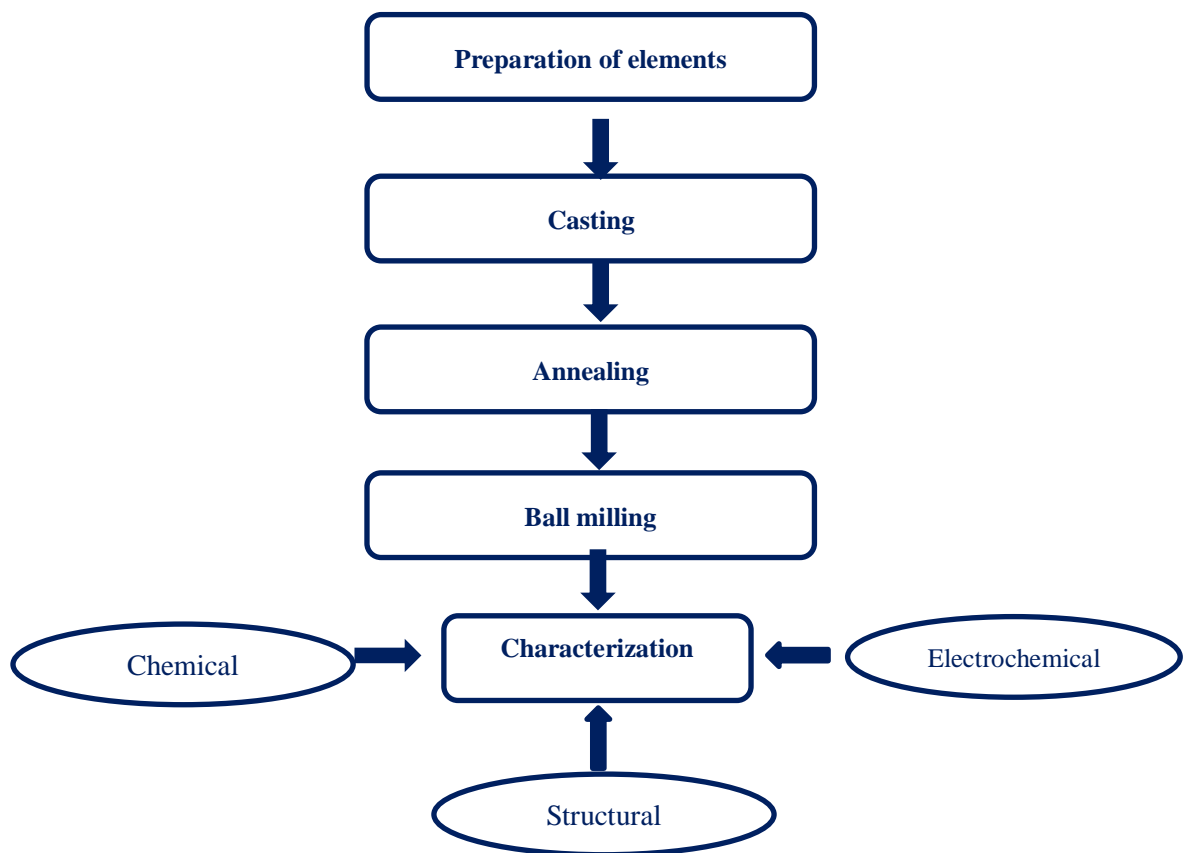


Figure 4.1 Experimental procedure.

Sixteen alloying elements (Mn, Sm, Sn, Al, Y, Cu, Si, Zn, Cr, Mg, Fe, Dy, V, Ti, Hf and Er) were added in system by the calculation of replacement of either one Ni or Ca atom in the system. Therefore, all alloying elements were added by 2 % at. in to the system. Sm, Y, Dy, Ti, Hf and Er were added for replacement of Ca and Mn, Sn, Al, Cu, Si, Zn, Cr, Mg, Fe and V were added for replacement of Ni. Selected alloying elements were put in ceramic crucible and cast by vacuum casting method by mini-casting unit (Indutherm, MC-15 Mini Casting System). Cast alloys were annealed to homogenize and characterized for structural and electrochemical analysis.

Precursors were 2 – 6 mm in diameter particles of calcium with ≤ 98.5 purity from Merck and nickel particles with ≤ 99.99 purity from Alfa Aesar. The characteristic property of Ca element is easier oxidation. Therefore, Ca element was kept in glove box to eliminate oxidation of Ca. During alloying studies, Mn, Sm, Sn, Al, Y, Cu, Si Zn, Cr, Mg Fe, Dy, V, Ti, Hf and Er were investigated to improve the cycle life of CaNi_5 by searching effects of alloying elements on structural and electrochemical properties.

4.1.1 Casting of CaNi_5 Compound

The alloys were prepared by vacuum casting by mini-casting unit (Indutherm, MC-15 Mini Casting System) in ceramic crucible. The raw materials and selected alloying elements were cast in desired composition. The important parameters during casting are heating regime, time and atmosphere in casting unit. Before casting, casting unit was swept by Ar for four times to remove oxygen from the chamber. Ca has lower melting point and boiling point of Ca element is closer to the melting point of Ni element as shown in phase diagram of CaNi_5 , Figure 4.2. To prevent the occurrence of unwanted phases during casting and obtain stoichiometric ratio between Ca and Ni element, heating regime is too important.

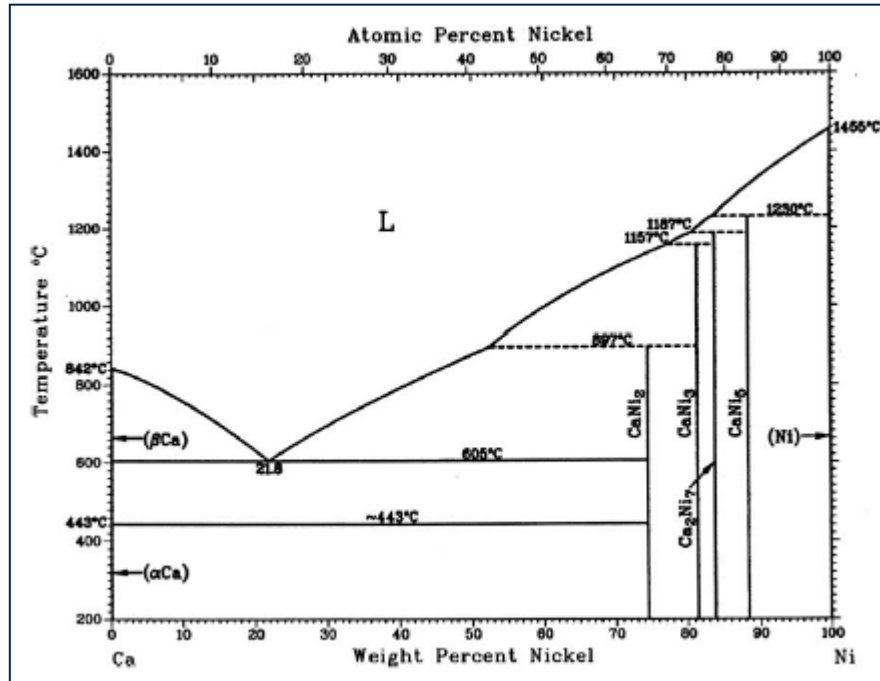


Figure 4.2 Phase diagram of Ca – Ni.

Then, time is an important issue to eliminate overheating and damaging crucible during casting. Mixture of selected alloying element and Ni element kept at approximately 700°C for 30-45 sec for melting of Ca, then temperature was heated up to the temperature below 1500°C for 30-45 sec. Finally, mixture was heated at 1500°C for 10 sec. Casting was carried out approximately between 70-100 sec depending on alloying element, and then cast into the copper mold under argon atmosphere.

4.1.2 Annealing of the Alloy

Ca is prone to oxidation under room conditions. Therefore, it is also important not to oxidize Ca during annealing. Annealing process gives a more homogeneous chemical structure, this result with better expected electrochemical properties. The factors that

essential are annealing time, atmosphere and temperature. Annealing process was carried under Ar atmosphere, Ar and H atmosphere and vacuum. When the process was carried under vacuum and Ar and H atmosphere, unwanted phases cannot be eliminated from the structure. Therefore, all experiments were carried under Ar atmosphere which has given better results. Longer annealing time was not helpful to eliminate unwanted phases, on the contrary it causes formation of another phases. Studied annealing temperatures were chosen 650°C, 850°C and 950°C. Best results were obtained when the temperature was 850°C. Unwanted phases could not be eliminated at lower temperatures and increasing in temperature result with increasing in the amount of Ni element. Therefore, optimum conditions were decided to carry under Ar atmosphere for 4 hours at 850°C after all experiments at different conditions.

4.1.3 Ball Milling of Alloy Powder

After homogenization, produced product was pulverized with ball mill for 6 hours in tungsten carbide (WC) jar. The ball to the powder mass ratio was 10:1. All studies showed that if the rotation speed is higher than 200 rpm/min, there is occurrence of other Ca – Ni phases. The reason is to use ball mill is not for alloying, but to obtain finer particle size. Therefore, 200 rpm/min was chosen to mill the products. The other effective parameter is to obtain narrow size distribution. To obtain this distribution, ball milling was studied in dry and wet medium for 2, 6 and 10 hours.

4.2 Cell Construction

The electrochemical properties, charge – discharge characteristics, cycle life discharge capacities and open circuit potential were performed on a Solartron potentiostat at room temperature in a 6M KOH electrolyte solution using two

electrode cells. Before these measurements, anode and cathode active materials had to be prepared as an electrode.

There are factors take an important role in the construction of a cell to specify mechanical properties of components and transportation of ions between both active materials and active materials and electrolyte in electrochemical systems. These are;

1. Binders used in both anode and cathode electrode
2. Additives to improve connectivity in both anode and cathode electrode
3. Co additive into the cathode
4. Composition of electrolyte
5. Separator material

4.2.1 Binders

In the preparation of negative electrodes, binders have an important impact on the capacity, cycle life and internal resistance of the batteries. Each binder has different physical properties, thus the properties affected and results obtained are different, too. For this reason, choice of binders is an important issue for preparation of electrodes.

During studies, 5 different binders were tried to form electrode from produced active anode material. These binders are; polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), poly(acrylic acid) (PAA), polyvinylalcohol (PVA), carboxymethylcellulose (CMC) and Coathylene.

The first test was PVDF which was mostly used in lithium ion batteries. PVDF was dissolved in N – Methyl – 2 – pyrrolione (NMP) and then mixed with active material to obtain paste. Therefore, it could be assumed that there is a thin film surrounds the active material. Obtained paste to form battery plaque was rolled up nickel expanded metal provided by DEXMET Company with a 3Ni5 – 060 code which has 0.076 mm

nominal original thickness, 0.127 mm strand width and 1.52 mm long way of the diamond. Then, all prepared electrodes were dried in vacuum drying oven. PVDF showed worse results, in Ni – MH batteries using aqueous electrolytes, compared with lithium batteries using aprotic organic electrolytes. Internal resistance increased due to the formation of thin films around the particles and Van der Waals bonds. Moreover, mechanical durability of electrodes was not sufficient to use in electrochemical tests.

PTFE, another common binder, was used as liquid dispersion with 60.4% bulk ratio provided by Dupont, a code number PTFE TE 3875. This binder was added into the anode mixture to obtain 3 wt% solid PTFE. Manual mixing of active material and PTFE powders with particle size between 50-500nm was not successful. Then, Mixer Mill, Retsch MM400, was used to mix the powders and binders with 20 shakes per second for between 10 – 20 minutes. However, the mixture was not homogeneous because of coagulation of PTFE. Nevertheless obtained mixture was rolled up on nickel expanded metal and pressed under pressure of 4000 kg. Because of inhomogeneous mixture of powders and binder, mechanical properties were not sufficient.

PVA is used as separately and also with CMC by mixing different ratios in the preparation of anode electrodes. PVA is soluble in water and has tendency to form film around the particles and have much adhesion property. Better mechanical properties were obtained by adding higher amount of PVA, therefore it was not chosen as a binder to use in anode electrode. Because it forms strong bonds with active materials and covers the particles. Higher amount of PVA cause decay in the mechanical properties. This can cause breaking of electrodes and connection of anode and cathode which results as short circuits in the cell.

PAA is an anionic - type polymer. PAA loses its protons and charges as negative in neutral pH water and cause formation of polyelectrolyte. The reason of trying PAA as binder in anode electrode is to obtain different functional groups and have higher elasticity. Elasticity is important to prevent mechanical degradation which is caused by volume changes during charging – discharging processes. On the other hand, PAA loses this elasticity property by dissolving again in batteries. Also, due to its higher adhesion properties, there are difficulties during preparation of electrodes.

CMC is hydrocolloid that can be dissolved in water easier and shows different properties due to the differences in pH values. Studies of CMC, 5 different CMC were tried with viscosity values between 100 cps and 100000 cps and all solutions were prepared with 1%, 3% and 5% by weight ratio. Those solutions were used in preparation of anode and cathode and also they were tried together with other binders to obtain maximum performance. Those studies resulted in chosen of CMC with viscosity value between 1000 – 2500 cps to use in the preparation of cathode.

There is a usage of nano – sized binders in the batteries instead of binders which cause formation of thin film. The common binder is PTFE. However, there is a need of special mixers to mix with active material. There is another product of Dupont which can be used specially in alkali batteries, called as Coathylene which is actually nano – sized polyethylene powder of high purity with a property of electrochemically inactive.

Coathylene is a thermoplastic which has good mechanical, thermal and electrical properties. Tensile strength at break is 12 MPa, elongation at break is 470%, modulus of elasticity is 227 MPa, thermal conductivity at 20 °C is 0.35 W / mK and coefficient of linear expansion is at between 20 – 90 °C is $2.5 \times 10^{-4} \text{ K}^{-1}$. Volume resistance of Coathylene is higher than $10^{17} \text{ } \Omega\text{cm}$, surface resistance is $10^{14} \text{ } \Omega$ and dielectric constant is 2.4 at 10^6 Hz . All these properties make Coathylene best binder to use in

anode electrode. Coathylene was mixed with active material with 3% weight ratio by Mixer Mills. Prepared mixture was pressed under 4000 kg/cm^2 on to nickel expanded metal to obtain better mechanical properties.

4.2.2 Conductive additives

Conductive additives are used in both anode and cathode to improve conductivity between the particles. In batteries, carbon black and graphite are commonly used as conductivity additives; there are other additives for conductivity in Ni – MH batteries. In this study, Ni powder which is less than 325 mesh and carbon black acetylene provided from Alfa Aesar with 99.9% purity are used for cathode and anode electrode, respectively. Carbon has to have spherical and elliptical shapes and more linear and branched structure to make the conductivity higher. Electrical conductivity is an important parameter to obtain higher electrochemical properties in batteries.

4.2.3 Cobalt additive

In the preparation of cathode electrode, compounds including Co are used except that spherical NiOOH particles. Cobalt additives forms CoOOH during charging and forms thin film around the NiOOH particles, thus electrical conductivity has higher values. Cobalt significantly improves charge efficiency by lowering active material recharge voltage and by decreasing the rate of oxygen evolution at a given electrode voltage. Moreover, cobalt additive decreases the reversible potentials for the charge and discharge reactions of the active materials. On the other hand, cobalt additives have positive effects on cycle life by increasing expansion and performance of electrode.

4.2.4 Electrolyte

Concentration of electrolyte is an important issue in the performance and capacity of batteries. In Ni – MH batteries, generally potassium hydroxide solution is used as an electrolyte between 26% and 31 wt%. In the literature, it shows that electrodes operating with 35% to 40% electrolyte have given significantly lower cycle life. Also, electrodes containing 20% potassium hydroxide electrolyte cause problems supporting high discharge rates, possibly because of having insufficient ionic strength to support the required ionic current flow[41]. Ionic conductivity, activity coefficient and viscosity are the important parameters of KOH electrolyte solution affecting performance of Ni – MH batteries. Therefore, 6M of KOH electrolyte solution which equals to 30 wt.% was prepared to use in electrochemical tests.

4.2.5 Separator

Separator prevents the short circuit of the anode and cathode in the cell and holds the electrolyte and provides ionic transportation between the electrodes in the constructed cell. In the cell, during electrochemical reactions, there can be connection between anode and cathode. This can be resulted with short circuits in the cell. Thus, one important responsibility of separator is to prevent of connection between electrodes. For this reason, nonwoven and microporous separators are used, which act as a reservoir for the electrolyte and prevents the electrochemical contact of the anode and cathode electrode. In alkali batteries, use of nonwoven separators is common. In this kind of separators, electrolyte is absorbed at the surface of the fibers by separator and due to the higher pore volume; it allows faster and easier ionic transportation. Electrolyte absorption and wicking rate of the separator we have used is 100 g / m² and 40 mm / 10 min in 30% by weight electrolyte, respectively. PP separator, Celgard 3401, is produced especially for alkali batteries by Celgard company. This separator has thickness of 25 μm and 41% pore volume with 0.043 μm pore size.

In this study, nonwoven separator, FS 2213 E, is used provided by Freudenberg company. This separator has high homogeneity, reliable separation, minimized resistance, high pore volume, good thermal bonding. This separator has thickness of 90 μ m and weight of 30 g / m² and has 71% pore volume. It has maximum tensile strength at machine direction and cross direction is ≥ 50 N / 5 cm and ≥ 25 N / 5 cm, respectively.

4.2.6 Cell Construction

The anode was made by mixing and constructing a mixture of 95% of alloy powder produced, 3% of binder, Coathylene, and 2% of carbon black. The cathode was made by mixing 85% of nickeloxyhydroxide (NiOOH) with 10% of nickel powder and 5% of Co by weight ratio. CMC was added 2wt.% as a binder in cathode electrode. Anode and cathode powders were mixed by Mixer Mills and then electrolyte was used to obtain paste to roll up onto nickel expanded metal. 19mm diameter disks were obtained and dried in drying oven. This process was followed by placing of cathode – separator - anode into cell which is made of delrin material. Sealed cell is shown in Figure 4.3.



Figure 4.3 Sealed cell.

4.3 Electrochemical Measurements

Produced active material was used to form cell. For the electrochemical characterization of electrodes, potentiostat was used to carry out galvanostatic charge and discharge cycles. When the battery was produced, it was in totally discharged state. Therefore, electrochemical tests were started by charging. Characteristics of Ni – MH batteries is activation of anode materials storing hydrogen. Thus, it was expected to have increasing capacity in first few charges – discharge cycles. The electrodes were cycled by charging at 20 mA / g for 8 h and discharging 2 mA / g for 8 h down to 1 V.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Ball Milling of Powders

Produced active materials were pulverized in ball mill with a 10:1 ratio respect to ball to the powder ratio by weight. Different rotation speed, time and medium were tried to obtain finer particle size. When rotation speed is higher than 200 rpm / min for a long time, different Ca – Ni phases were observed rather than CaNi₅. Ball milling was totally 6 hours with 10 minutes break after each 30minutes.

5.2 Particle Size Measurement

Particle size is important because finer grain size means larger surface area. Larger surface area explains contact points between the electrolyte and active materials.

Particle size measurement of powders which were milled for 2 hours and 200 rpm / min are shown in Figure 5.1. As shown in Figure 5.1 average particle size is 22.96 μm . However, there are still particles which have particle size over 60 μm with a 10% volume. Also, SEM studies showed that there were other larger particles which have almost 150 μm grain size.

All these studies were carried out in dry medium. Therefore, methanol and ethanol were tried as different medium and then ethanol was chosen for milling of powders. Due to the oxidation of Ca, formation of different phases and reactivity of

compounds, methanol was not useful for the rest of experiments. Results of experiments of particle size measurement which were carried out for 2 hours in dry medium and ethanol are shown in Figure 5.1 and 5.2, respectively. Results for 10 hours in ethanol with a speed of 200 rpm / min are shown in Figure 5.3.

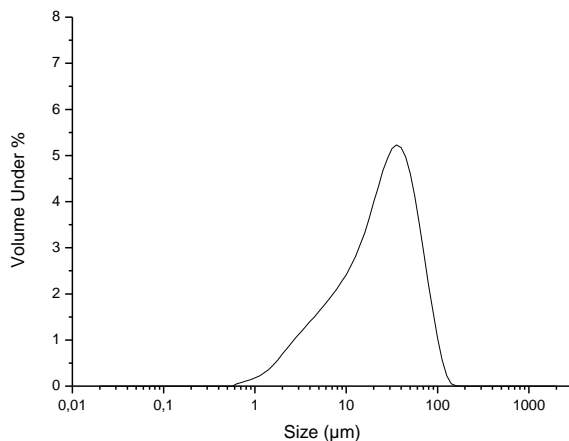


Figure 5.1 Particle size measurement of CaNi₅ powders for 2 hours at 200 rpm / min in dry medium.

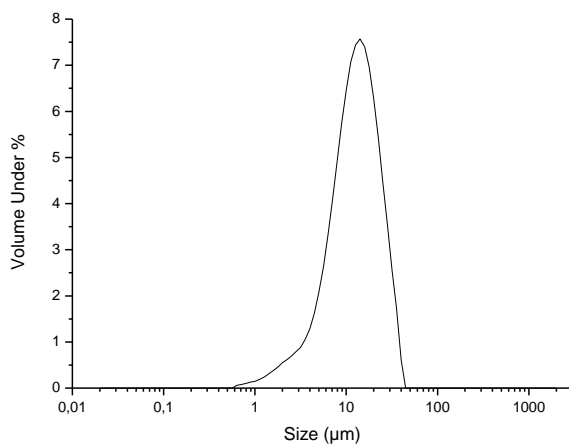


Figure 5.2 Particle size measurement of CaNi₅ powder for 2 hours at 200 rpm / min in ethanol.

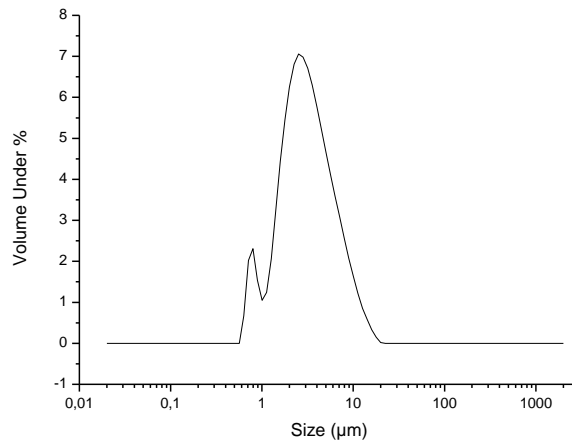


Figure 5.3 Particle size measurement of CaNi₅ powder for 10 hours at 200 rpm / min in ethanol.

When the milling time was increased from 2 hours to 10 hours, average particle size of powders was changes from 11.96 μm to 2.77 μm. when the medium was chosen as wet, finer grain size and narrow size distribution was obtained. However, there is bimodal particle size distribution where the milling time was 10 hours. Also, because of losing Ca element, metallic Ni element formation was observed when the time was increased up to 10 hours and this caused higher FWHM in the X – Ray Diffractometer (XRD) profile of the powders which may be due to internal stress as shown in Figure 5.4.

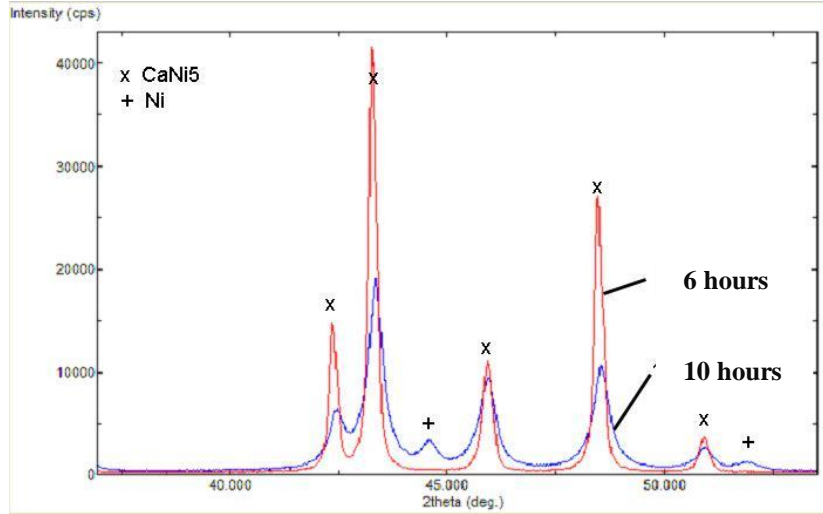


Figure 5.4 XRD spectrum of unalloyed CaNi_5 powders for 6 hours (blue) and 10 hours (red) in ethanol.

As result of all these experimental studies, powders were milled for 6 hours and obtained particles with $4 \mu\text{m}$ of average particles and including 10% of grains smaller than $1.5 \mu\text{m}$ and larger than $9 \mu\text{m}$ as shown in Figure 5.5. For the repeatability of the experiments, experiments were tried with all these fixed parameters for several times. All the results, including phase analysis and particle size measurements, gave the same results. Then, all experiments were carried out for 6 hours with 200 rpm / min in ethanol medium.

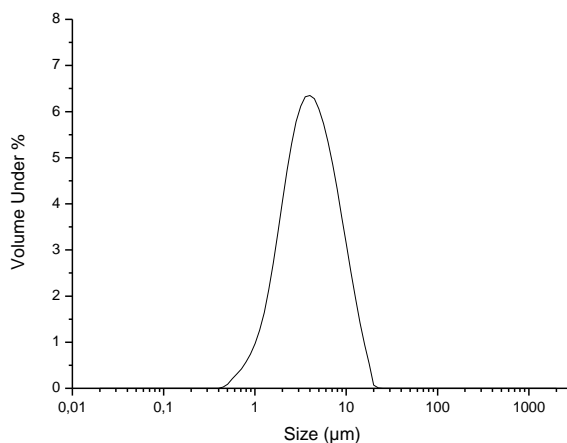


Figure 5.5 Particle size measurement of CaNi_5 powder for 6 hours at 200 rpm / min in ethanol.

5.3 Selection of Alloying Elements

Researching in literature and theoretical studies helped us to choose alloying elements for substitution in CaNi_5 crystal system. Calculated activation energy of alloying models is given in section 2.3. Not only activation energy of the system, but also formation energy of the system was studied by calculating of replacement of one Ca and/or Ni atom in the system. According to these calculation of formation energy, Figure 5.6 was tabulated. Decreasing in the formation energy means more stable structure. Therefore, theoretical studies result that replacement of Ca by alloying of rare earth elements make the structure more stable. On periodic table, these elements can be selected as La, Ce, Dy, Er, Gd, Sm, Th, Yb and Ac. Also, some transition elements such as Hf, Sc, Y and Zr make the formation energy of system lower. It was established that Al, Si, Ge and P have significant effect and Sn, Sc, Zn, Zr, Hf and Ti have local effect on the replacement of Ni element. After all these studies, Sm, Y, Dy, Ti, Hf and Er were selected for replacement of Ca and Mn, Sn, Al, Cu, Si, Zn, Cr, Mg, Fe and V were selected for replacement of Ni [38].

H																		% Change in the Formation Energy of CaNi ₅ with Alloying																		He																	
Li		Be		M														B		C		N		O		F		Ne																									
24,60				Alloying element														77,77																																			
-0,07				Ca														1,97																																			
5,74				Ni in														3,10																																			
		Mg		Ni out														Al		Si		P		S		Cl		Ar																									
34,94		10,44																10,54		26,60		40,03																															
30,33		-0,68																-21,49		-26,16		-29,03																															
31,71		1,18																-22,35		-30,24		-33,08																															
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr																			
57,33		0,00		-17,32		1,09		27,41		55,50		27,82		38,44		47,46		47,77		42,33		26,09				25,82																											
71,34		22,05		-8,67		-10,18		4,55		13,85		1,42		3,60		6,85		0,00		-1,42		-10,24				-19,48																											
67,22		21,42		-6,90		-10,51		0,73		12,21		3,03		3,25		5,74		0,00		0,87		-8,76				-21,92																											
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe																			
				-21,71		-17,55		8,74		39,31								35,35		37,11		24,75		16,78		15,04		21,77																									
				8,56		-4,02		4,52		16,81								-3,08		9,31		6,54		-0,33		-7,66		-8,47																									
				9,22		-2,19		4,37		14,01								-3,84		9,84		8,24		-2,15		-10,76		-14,33																									
Cs		Ba		Lan*		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rd																			
		25,74				-17,54		7,89		40,72										34,18		32,85				27,62		27,02																									
		56,14				-8,11		1,04		18,38										-2,75		7,57				11,92		12,56																									
		51,65				-6,97		-0,54		12,77										-4,39		5,89				9,49		7,29																									
Fr		Ra		Act*																																																	
						La		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu																			
						-17,76		-12,81				-16,89				-19,42				-21,92				-22,80				-23,38				-10,32																					
						13,12		23,36				17,69				13,18				8,68				5,85				3,07				7,11																					
						12,34		23,70				17,52				12,76				9,32				6,32				3,54				8,41																					
						Ac		Th		Pa		U																																									
						-9,53		-32,81																																													
						28,82		2,74																																													
						25,00		0,07																																													

Figure 5.6 Effect of alloying elements on formation energy of CaNi₅ on periodic table [38].

5.4 Quantitative Phase Analysis by Rietveld Refinement

All powders of CaNi₅ have scanned between 10 - 90° with 2θ angles by using XRD. XRD analyses were carried out by using the data provided from Pearson Crystal Structure Database and Maud Program to refine XRD spectrum. Rietveld method was used for the quantification of phases by using Maud Program. Besides, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were used to identify both microstructure and chemical analyses.

Results of XRD analyses are shown in Table 5.1. Some Rietveld analyses of samples are also shown in Figure 5.7, 5.8 and 5.9. After Rietveld analyses, theoretical and

practical results were compared for lattice parameters and results of goodness of fit (Rw%) were shown in Table 5.3. CaNi₅ was obtained with 99% purity without addition of alloying elements. Metallic Ni element was observed by addition of alloying elements with an increasing amount.

Table 5.1 Results of Rietveld analyses of produced alloys.

Sample	CaNi₅ (% wt.)	Ca₂Ni₇ (% wt.)	CaNi₃ (% wt.)	CaNi₂ (% wt.)	Ni (% wt.)	CaO (% wt.)	NiO (% wt.)
Unalloyed	98.80	-	-	-	0.95	0.25	-
Si	83.50	-	-	-	13.87	2.62	-
Sn	85.65	-	-	-	13.31	1.02	-
Al	66.11	11.76	-	-	21.75	2.18	-
Zn	77.28	-	-	-	22.19	0.51	-
Y	66.40	-	-	-	33.07	0.52	-
Sm	63.91	-	-	-	35.66	0.41	-
Mn	95.74	-	-	-	4.18	-	0.08
Cu	98.88	-	-	-	0.96	0.16	-
Cr	24.07	38.80	4.28	-	32.85	-	-
Mg	72.91	24.84	-	-	2.25	-	-
Fe	45.92	-	31.07	-	-	1.30	-
Dy	49.70	-	-	-	50.08	0.22	-
V	23.41	35.89	-	-	40.69	-	-
Ti	52.78	4.82	-	-	42.40	-	-
Hf	22.93	25.39	-	-	51.66	-	-
Er	36.76	-	-	-	63.24	-	-

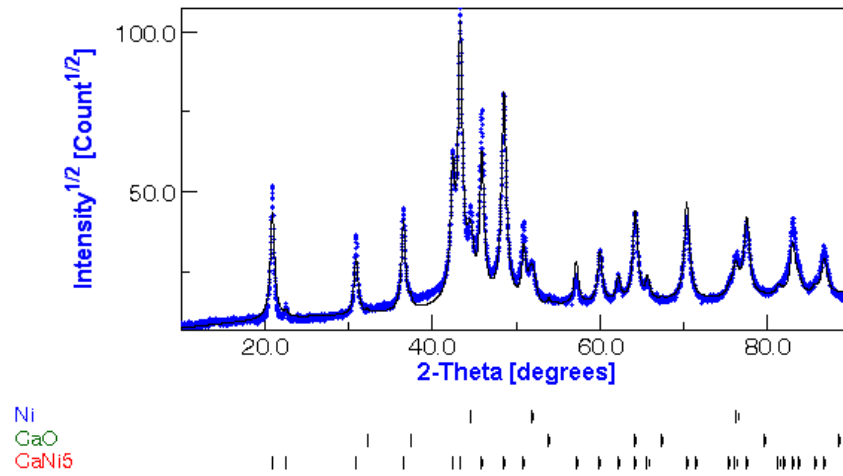


Figure 5.7 Rietveld analysis of unalloyed compound.

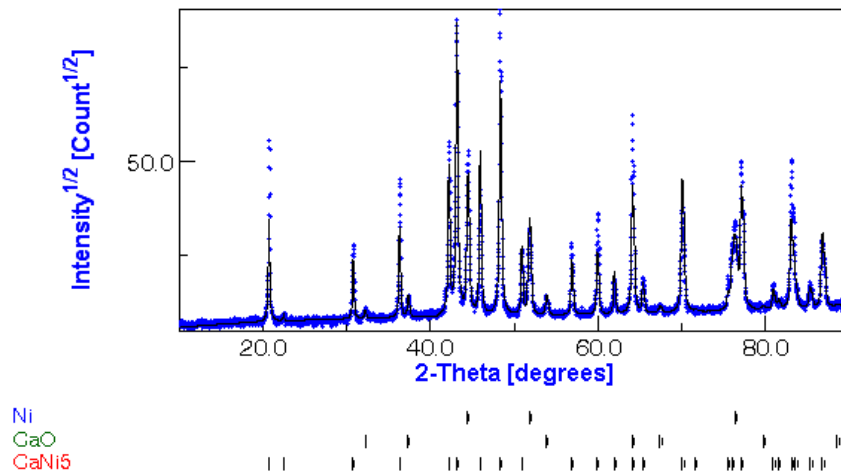


Figure 5.8 Rietveld analysis of Si - alloyed compound.

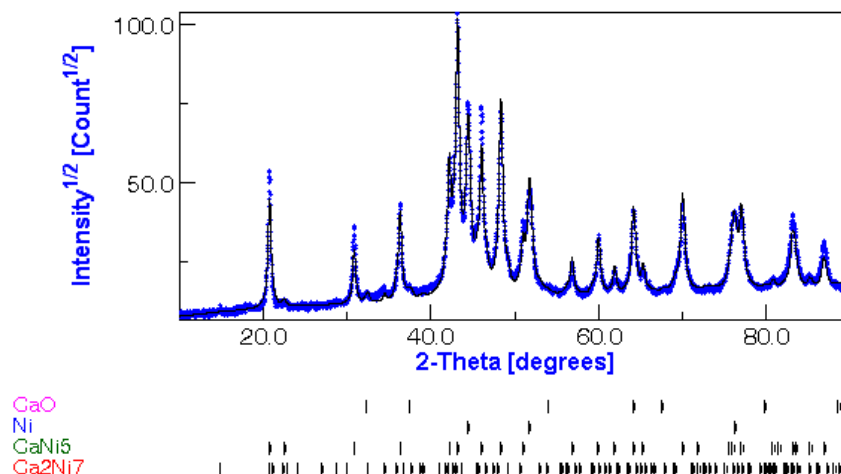


Figure 5.9 Rietveld analysis of Al - alloyed compound.

Lattice parameters are calculated as a result of Rietveld analyses and shown in Table 5.2. As seen on table, all alloyed compounds of CaNi_5 have a result expansion in a lattice parameter. c parameters have a variable tendency on the both positive and negative side.

Table 5.2 Lattice parameters of CaNi_5 phase in the compounds.

Sample	a (Å)	c (Å)	Rw%
Unalloyed	4.93	3.96	17.53
Si	4.94	3.95	19.18
Sn	4.98	3.97	17.27
Al	4.96	3.95	20.14
Zn	4.96	3.95	18.19
Y	4.94	3.95	18.91
Sm	4.95	3.95	21.72
Cu	4.95	3.95	15.16

Table 5.2 (continued)

Cr	4.95	3.94	11.37
Mg	4.93	3.97	14.77
Fe	4.95	3.94	15.89
V	4.95	3.94	12.33
Ti	4.94	3.96	14.81
Hf	4.92	3.98	18.24
Er	4.92	3.96	19.61
Mn	4.92	3.97	26.97

5.5 Structural Characterization

XRD analyses were done to understand phases including produced compounds. Therefore, XRD analyses are not enough to characterize the structure. SEM analyses were done to understand the microstructure and also particle size and EDS analyses were done to identify chemical composition. Microstructure of unalloyed compound is shown in Figure 5.10. and it is also observed that particle size under 10 μm as the particle size measurement in Figure 5.5. Chemical composition of EDS analyses of all compounds are shown in Table 5.3. According to the phase analysis, it was obtained less amount of Ca approximately by 0.33 at% in weight. This result expresses the existence of metallic Ni element. 83.5% CaNi_5 , 13.87% Ni and 2.62% CaO were calculated in Si – alloyed compound by Rietveld refinement. General microstructure of this compound is shown in Figure 5.11. Average particle size measurement was identified as 4 – 5 μm on SEM micrographs. Chemical analysis showed that Si element was replaced with Ni element and therefore the amount of Ni element decreased. EDS analyses were carried out by analyzing different points of the sample. All results showed that Si has uniform distribution in the compound.

Table 5.3 Chemical composition analyses of produced compounds by using EDS.

Alloying Element (M)	Ca at%	Ni at%	M at%
Unalloyed	16.33	83.67	-
Mn	15.33	82.65	2.02
Sm	13.39	84.03	2.58
Sn	14.45	83.06	2.49
Al	12.19	84.6	3.21
Y	14.58	83.46	1.96
Cu	15.12	81.26	3.62
Si	15.01	82.25	2.74
Zn	14.81	83.59	1.6
Cr	18.46	79.89	1.65
Mg	14.9	82.56	2.54
Fe	13.34	84.42	2.24
Dy	10.01	87.6	2.39
V	17.67	80.65	1.68
Ti	12.9	85.56	1.54
Hf	12.49	84.72	2.78
Er	5.34	91.83	2.83

Generally, when alloying element was used, there was increase in the amount of Ni element. Reason for this may be the time spending for melting all alloying additions and losing of Ca element during this time or thermodynamic balance of ternary phase diagram. This metallic Ni element is not problem for the battery due to using of Ni element as conductivity addition. Ni element has an important duty such as providing electrical conductivity and conductivity between the powder particles. General

microstructure of this compound is shown in Figure 5.12. Chemical analysis showed that Sn element was replaced with Ni element and therefore the amount of Ni element decreased. EDS analyses were carried out by analyzing different points of the sample. EDS results showed that distribution of Sn is 2.74% atomic in the alloy compound.

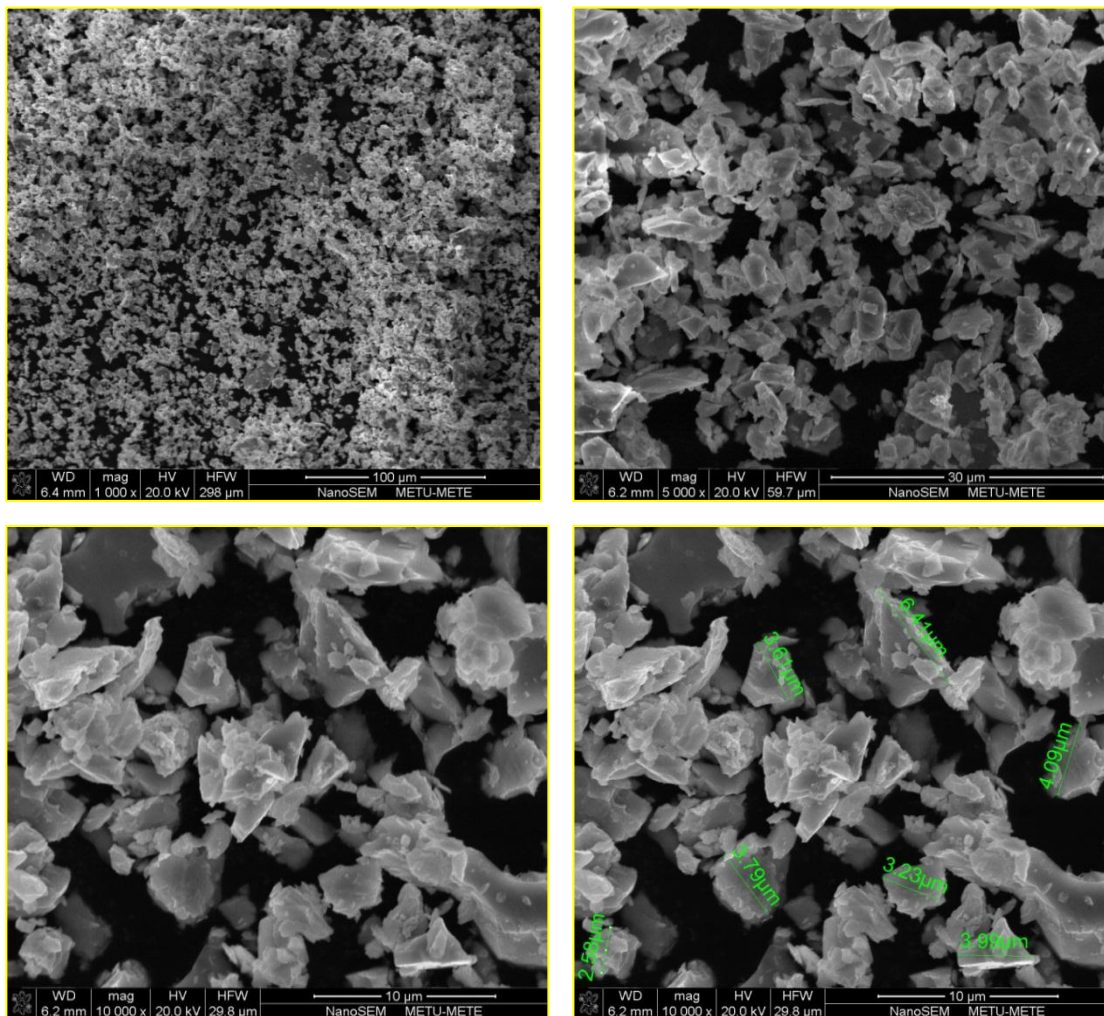


Figure 5.10 Microstructure of unalloyed compound at 1000x, 5000x and 10000x.

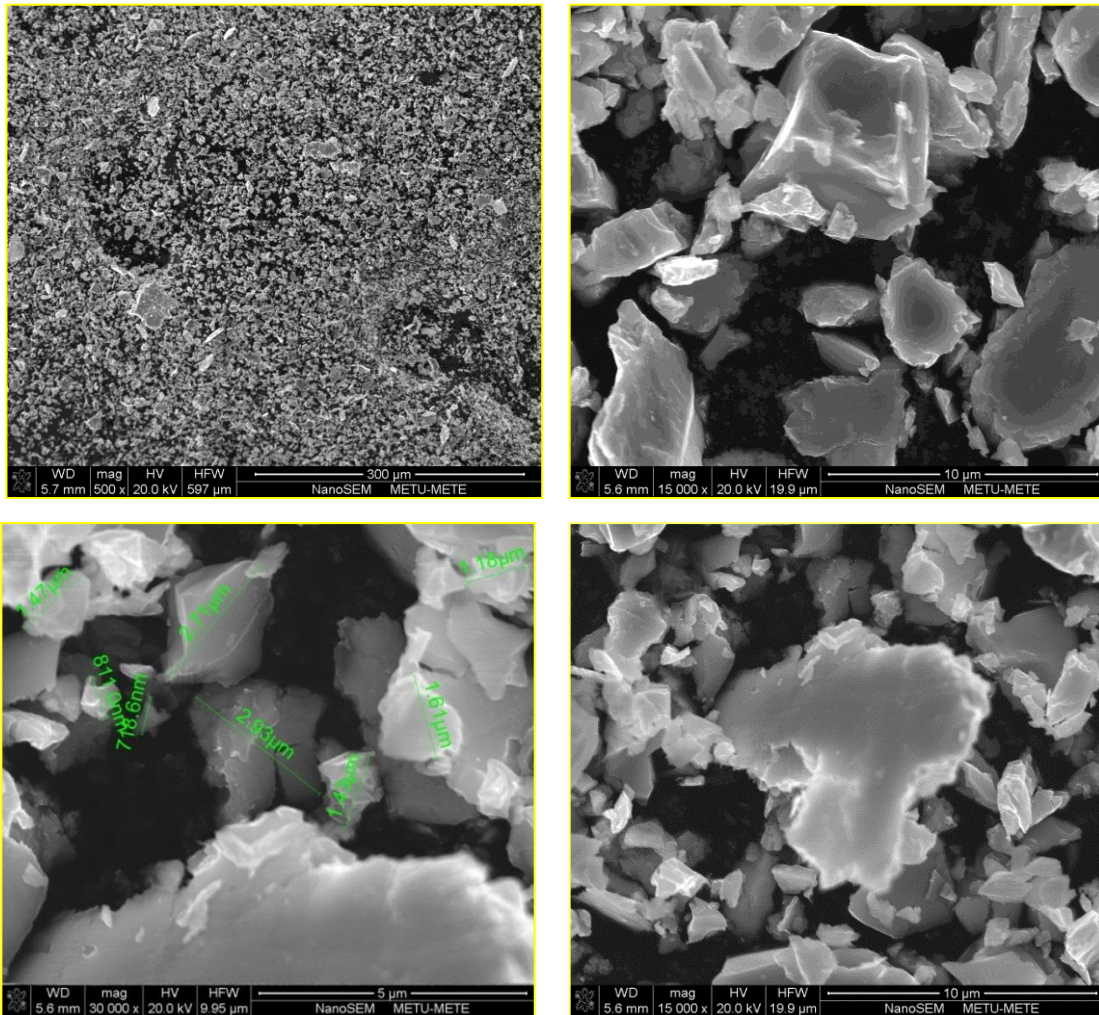


Figure 5.11 Microstructure of Si - allyled compound at 500x, 15000x and 30000x.

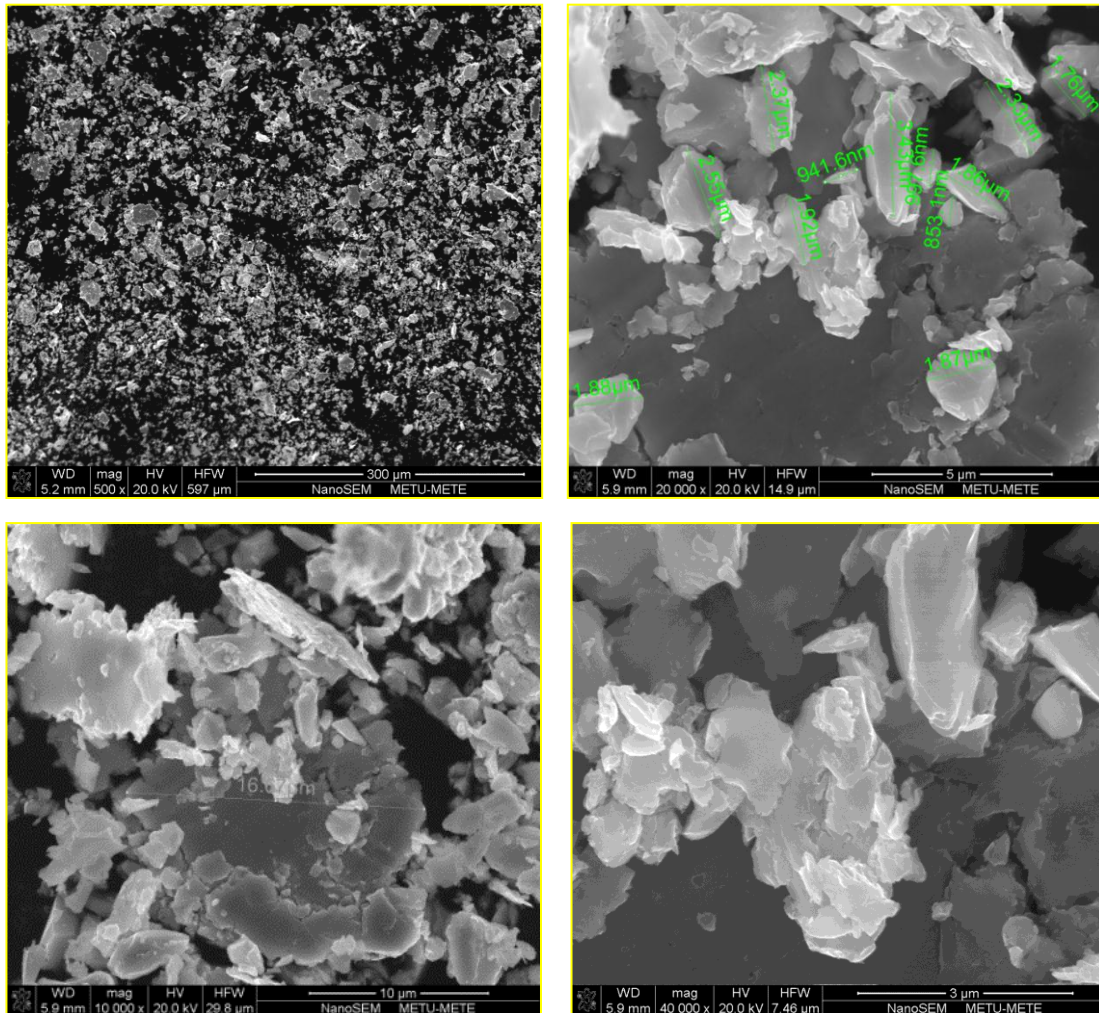


Figure 5.12 Microstructure of Sn - alloyed compound at 500x, 20000x and 40000x.

When the alloying element is used as Al, 66.11% CaNi_5 , 21.75% Ni, 11.76% Ca_2Ni_7 and 2.18% CaO was obtained. In the limited number of literature about CaNi_5 , it was found that when x equals to the number between 0.5 and 1 in the formula of $\text{CaNi}_{5-x}\text{M}_x$, Ca_2Ni_7 and CaNi_2 phases were observed [36]. Figure 5.13 shows microstructure of Al – alloyed compound. Chemical composition of Al element was found that as 3.21% at by EDS.

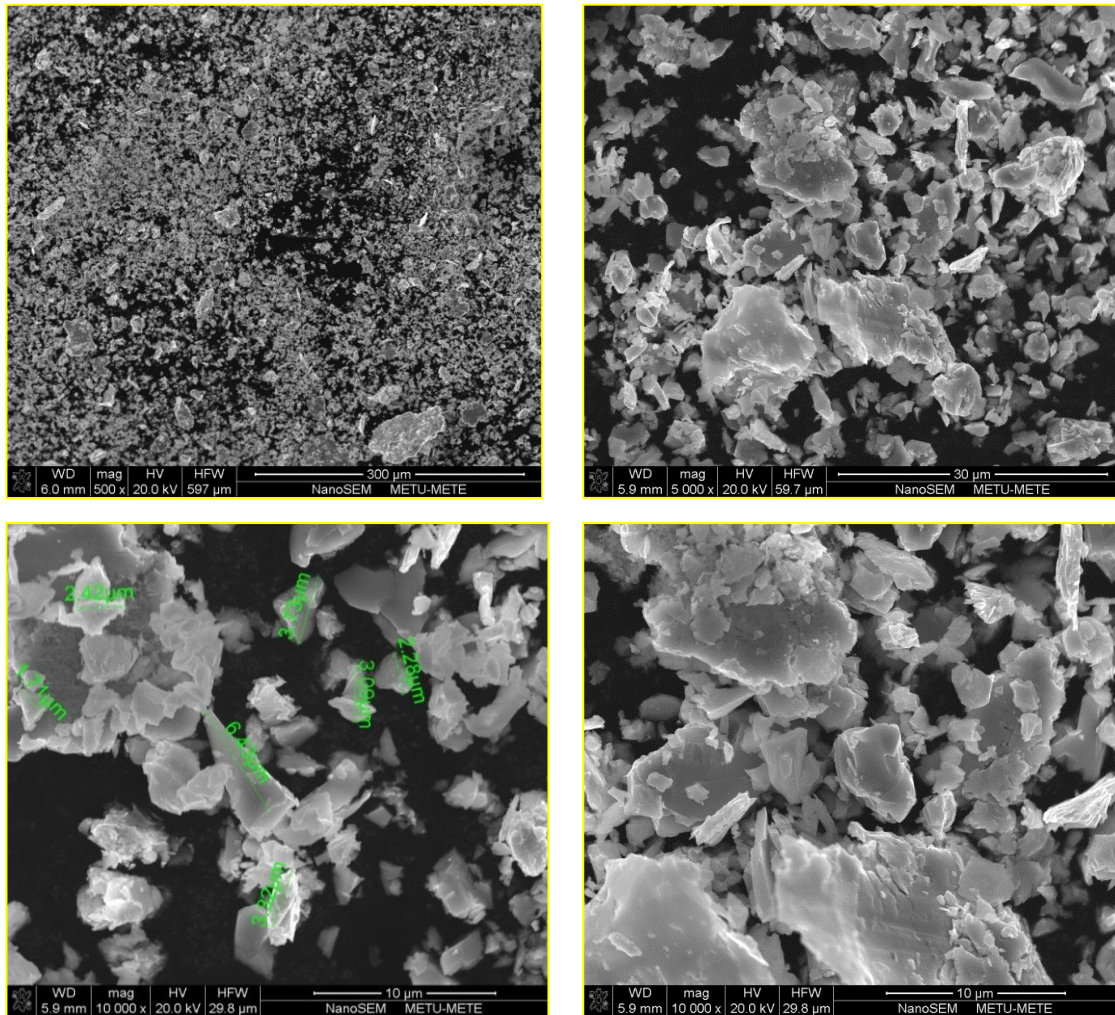


Figure 5.13 Microstructure of Al - alloyed compound at 500x, 5000x and 10000x.

77.28% CaNi_5 , 22.19% Ni and 0.51% CaO was obtained when Zn was used as alloying element. Microstructure of Zn – alloyed compound is shown in Figure 5.14.

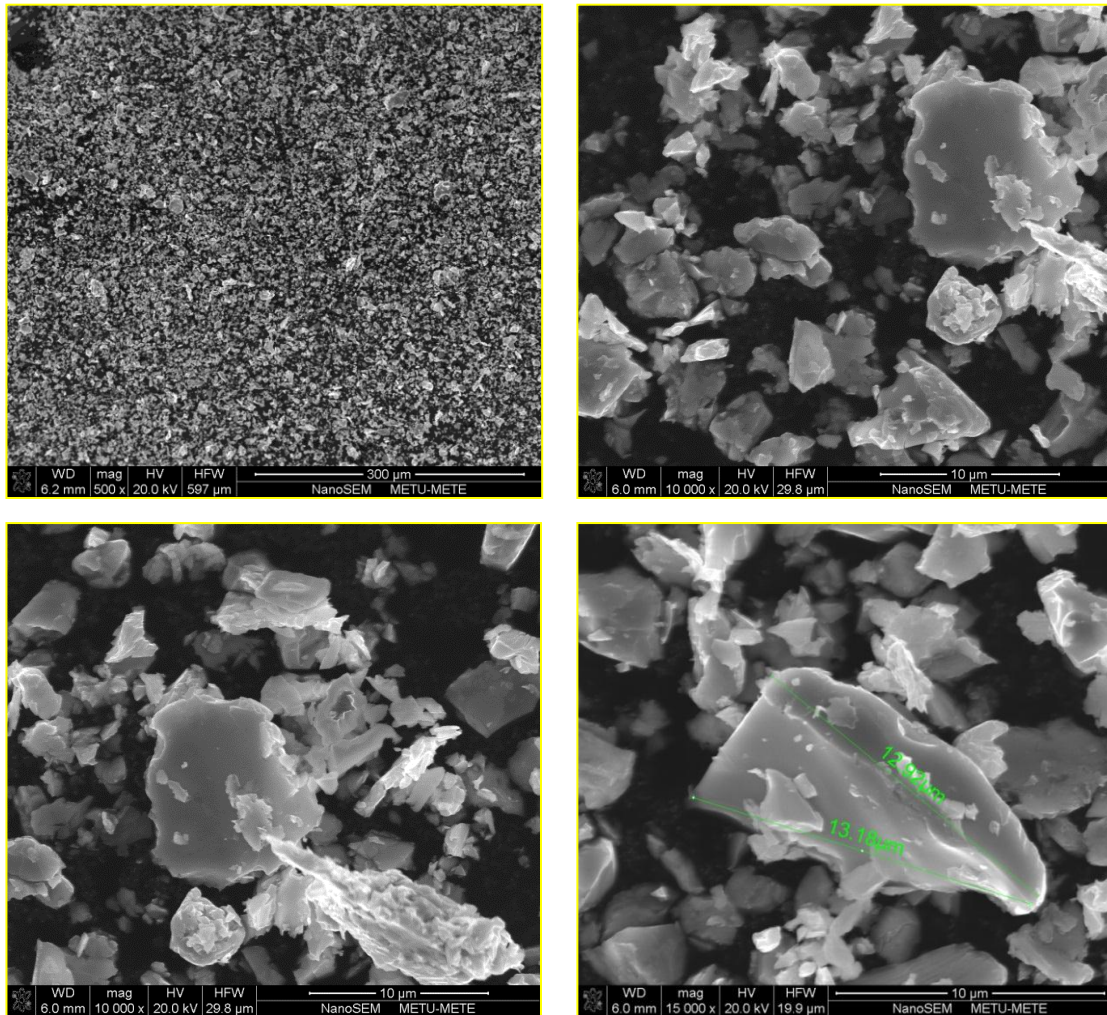


Figure 5.14 Microstructure of Zn - allyed compound at 500x, 10000x and 15000x.

Rietveld refinement results showed that Y – allyed compound and Sm – allyed compound included 66.40% and 63.91% CaNi_5 ; 33.07% and 35.66% Ni; 0.52% and 0.41% CaO, respectively. SEM micrographs of Y – allyed and Sm – allyed compounds are shown in Figure 5.15 and 5.16.

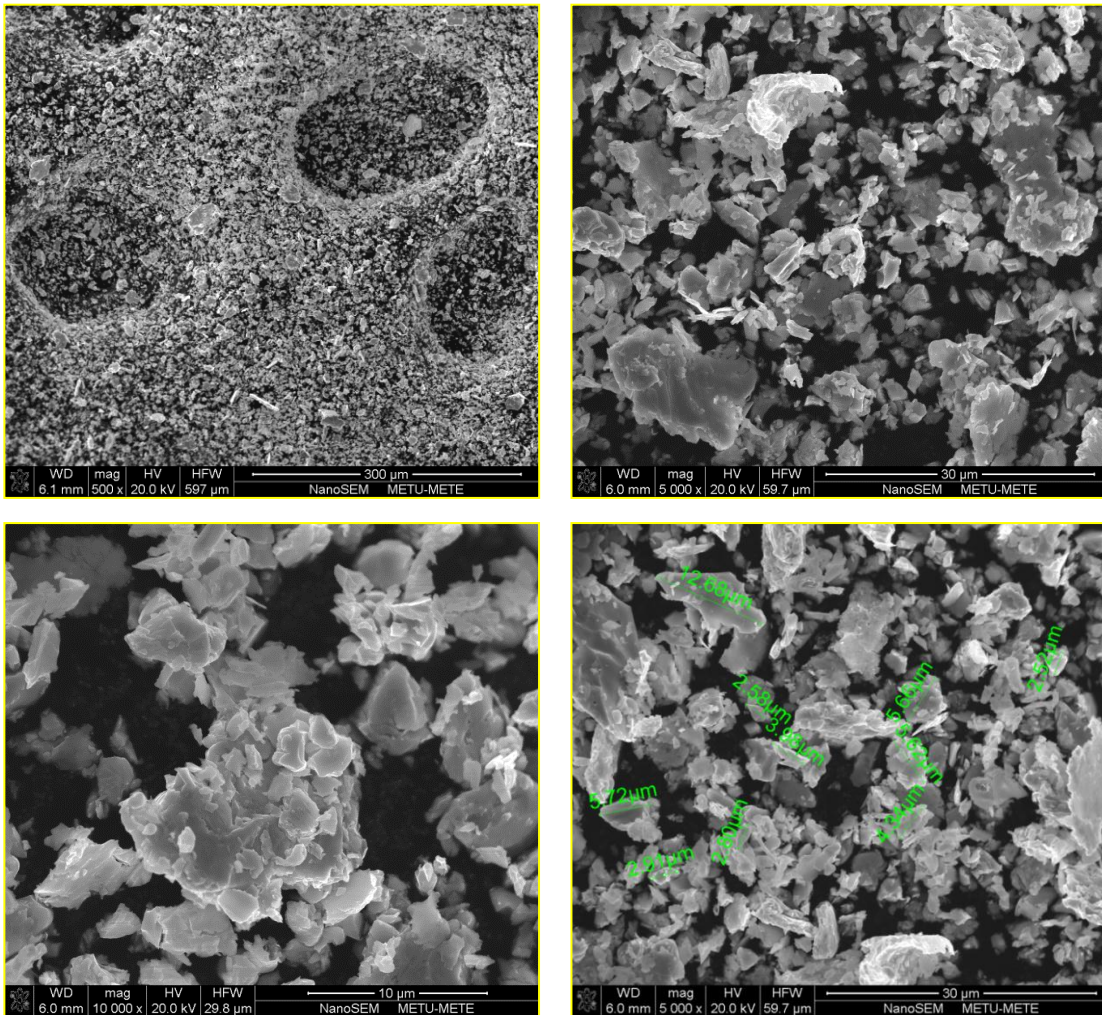


Figure 5.15 Microstructure of Y - alloyed compound at 500x, 5000x and 10000x.

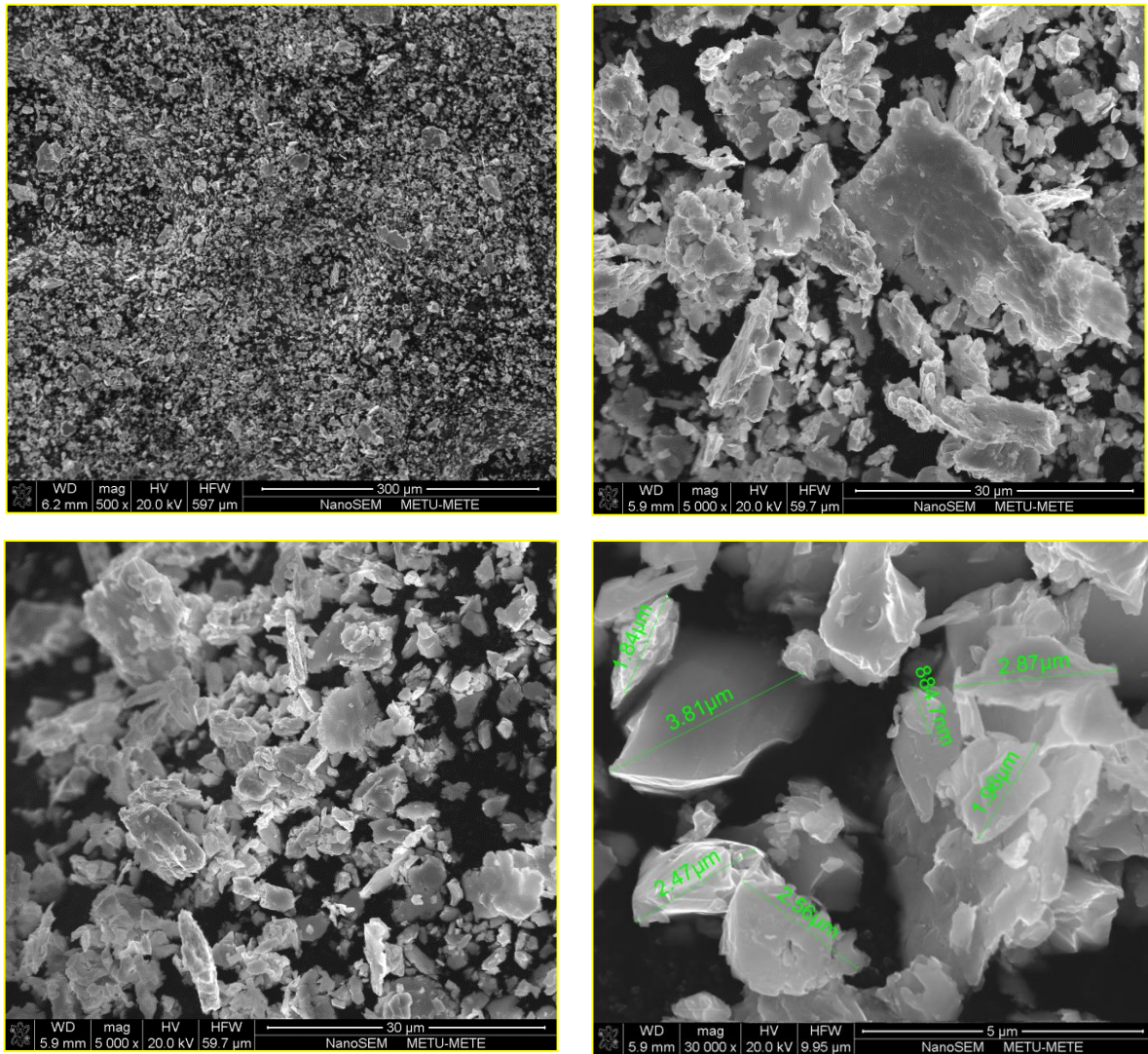


Figure 5.16 Microstructure of Sm - alloyed compound at 500x, 5000x and 10000x.

Other compounds which were produced with rest of other alloying elements are shown in Figure 5.17 – 5.26.

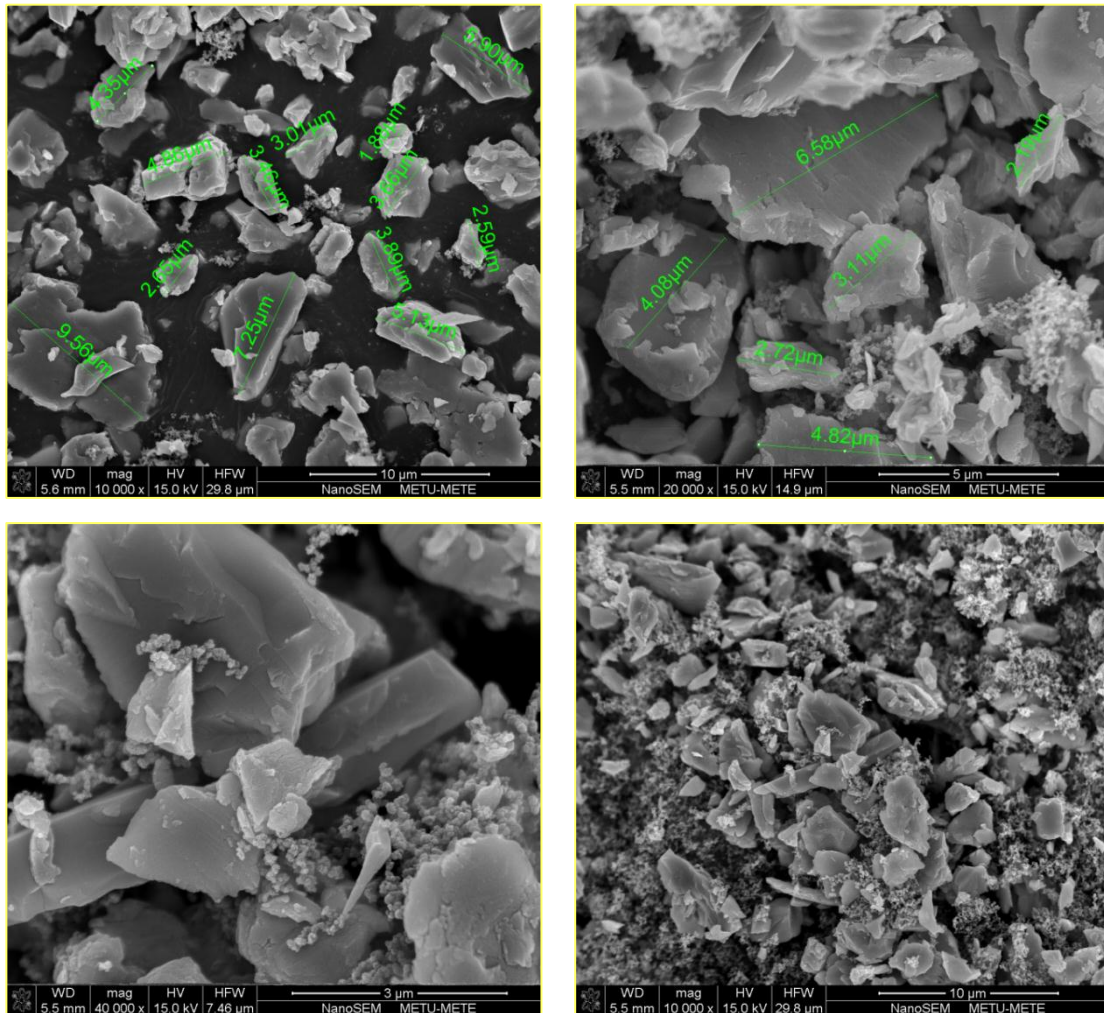


Figure 5.17 Microstructure of Mn - alloyed compound at 10000x, 20000x and 40000x.

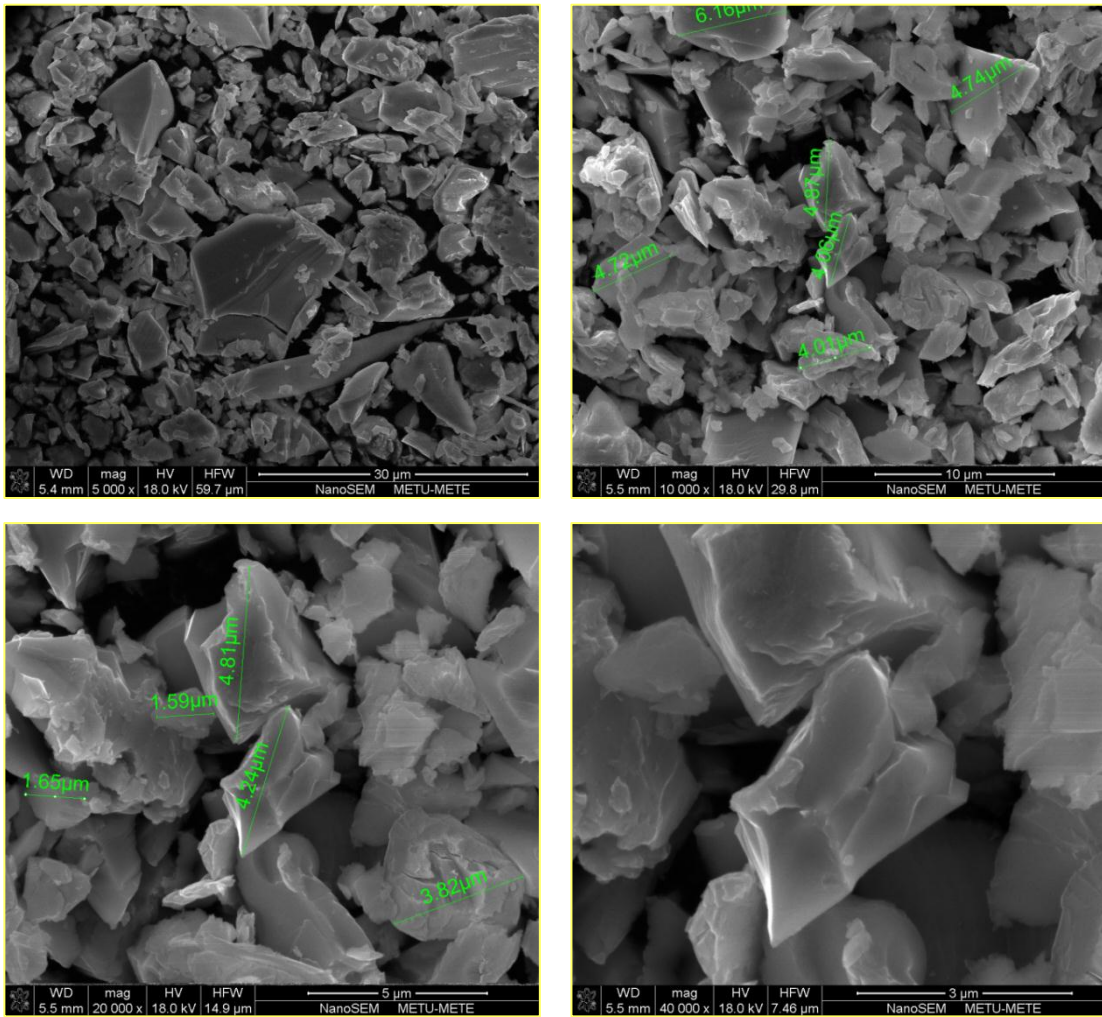


Figure 5.18 Microstructure of Cu - alloyed compound at 5000x, 1000x, 20000x and 40000x.

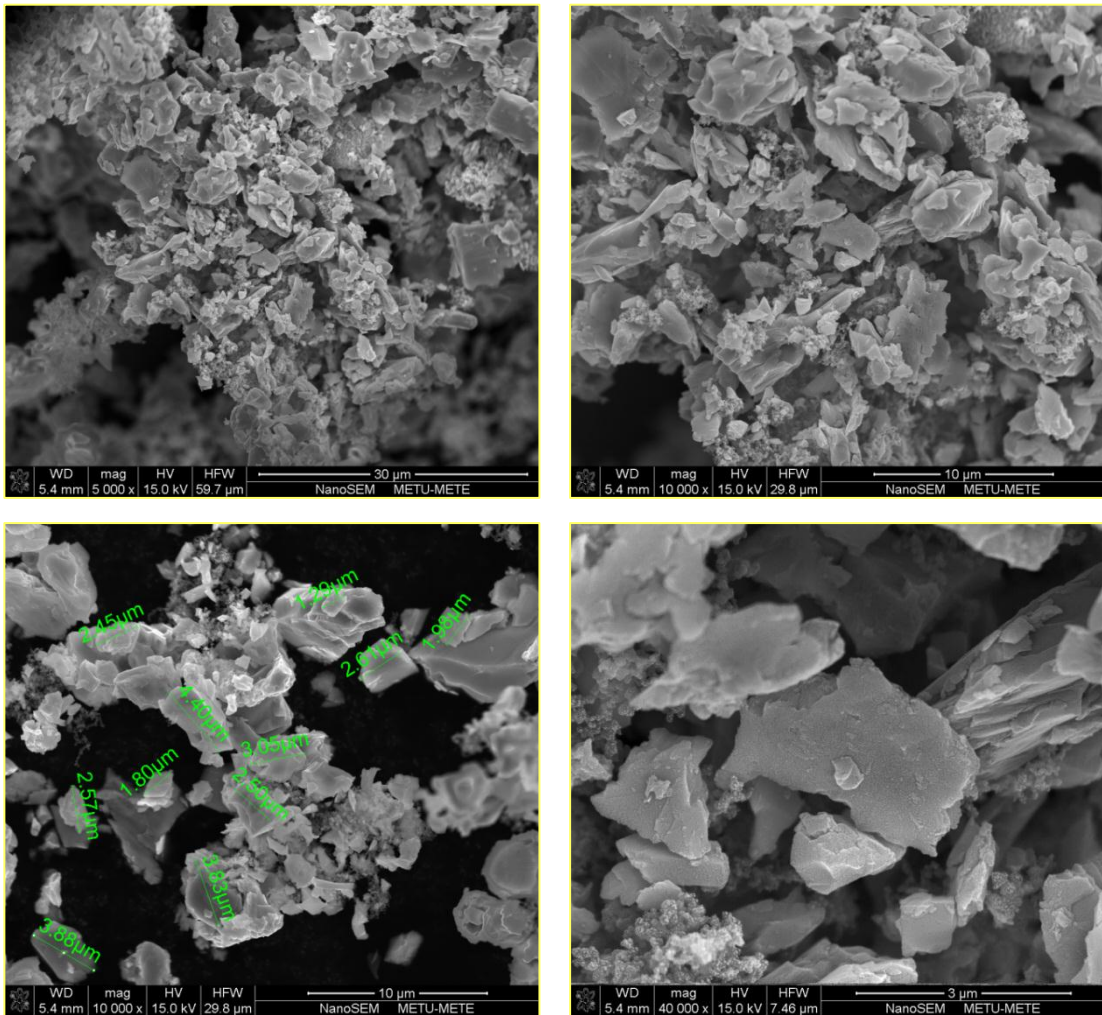


Figure 5.19 Microstructure of Cr - alloyed compound at 5000x, 10000x and 40000x.

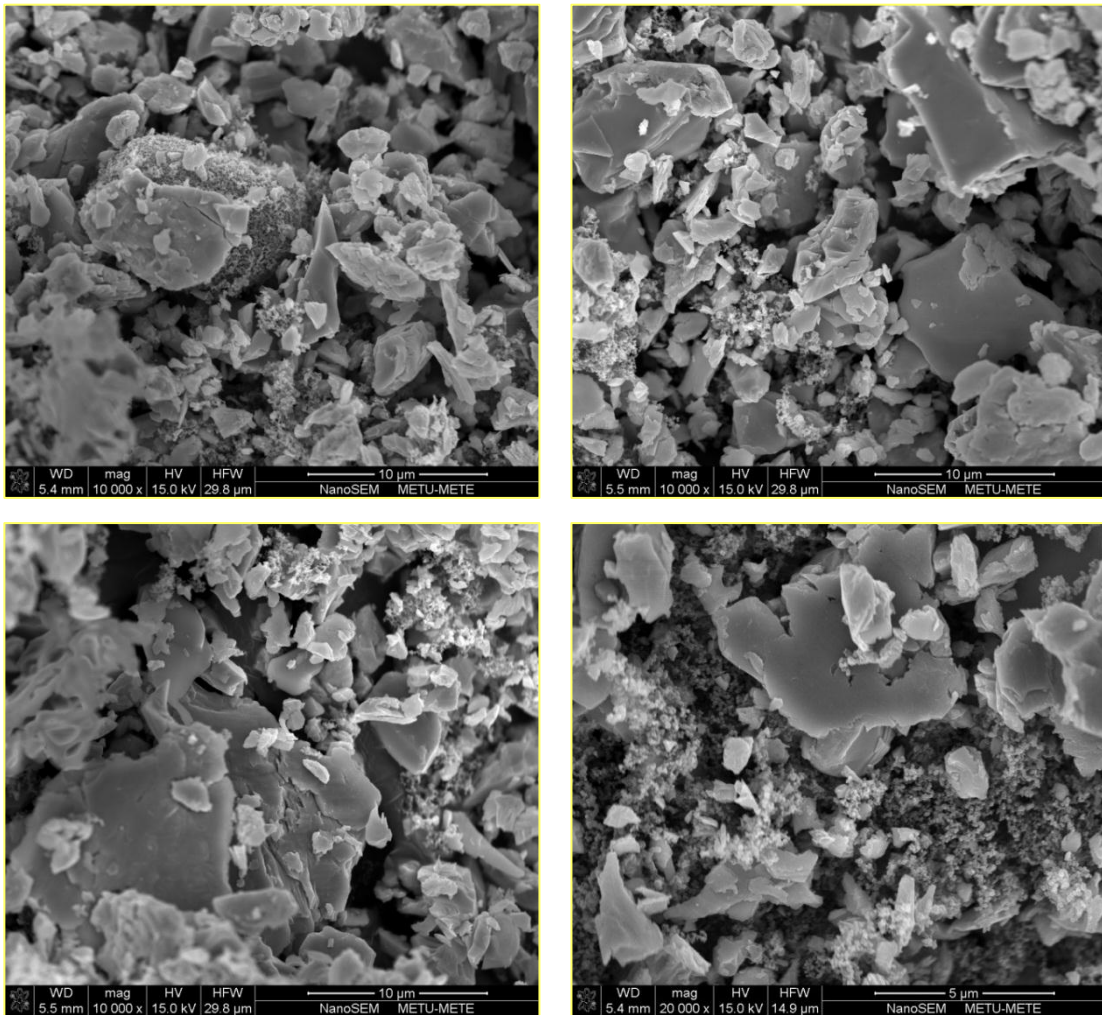


Figure 5.20 Microstructure of Mg - alloyed compound at 10000x and 20000x.

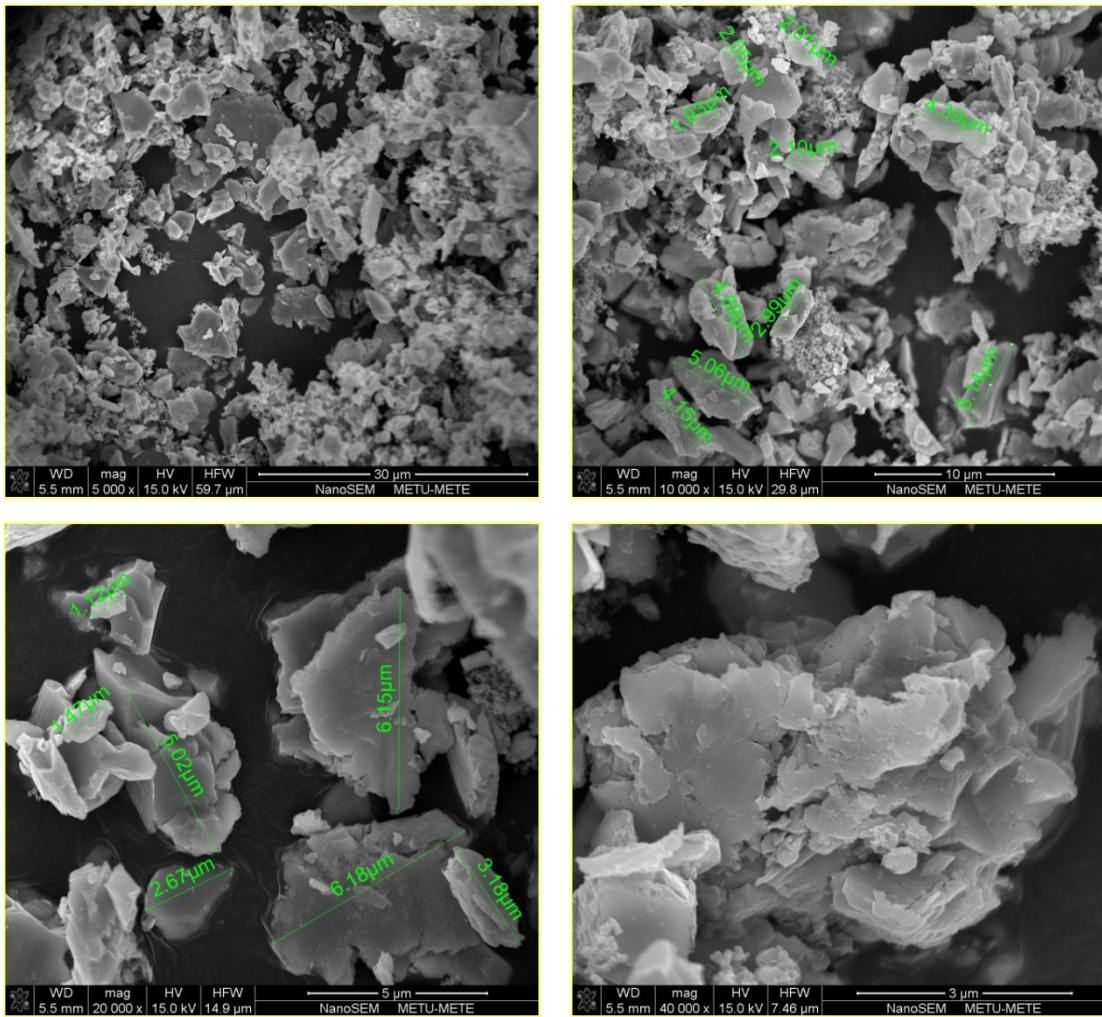


Figure 5.21 Microstructure of Fe - alloyed compound at 5000x, 10000x, 20000x and 40000x.

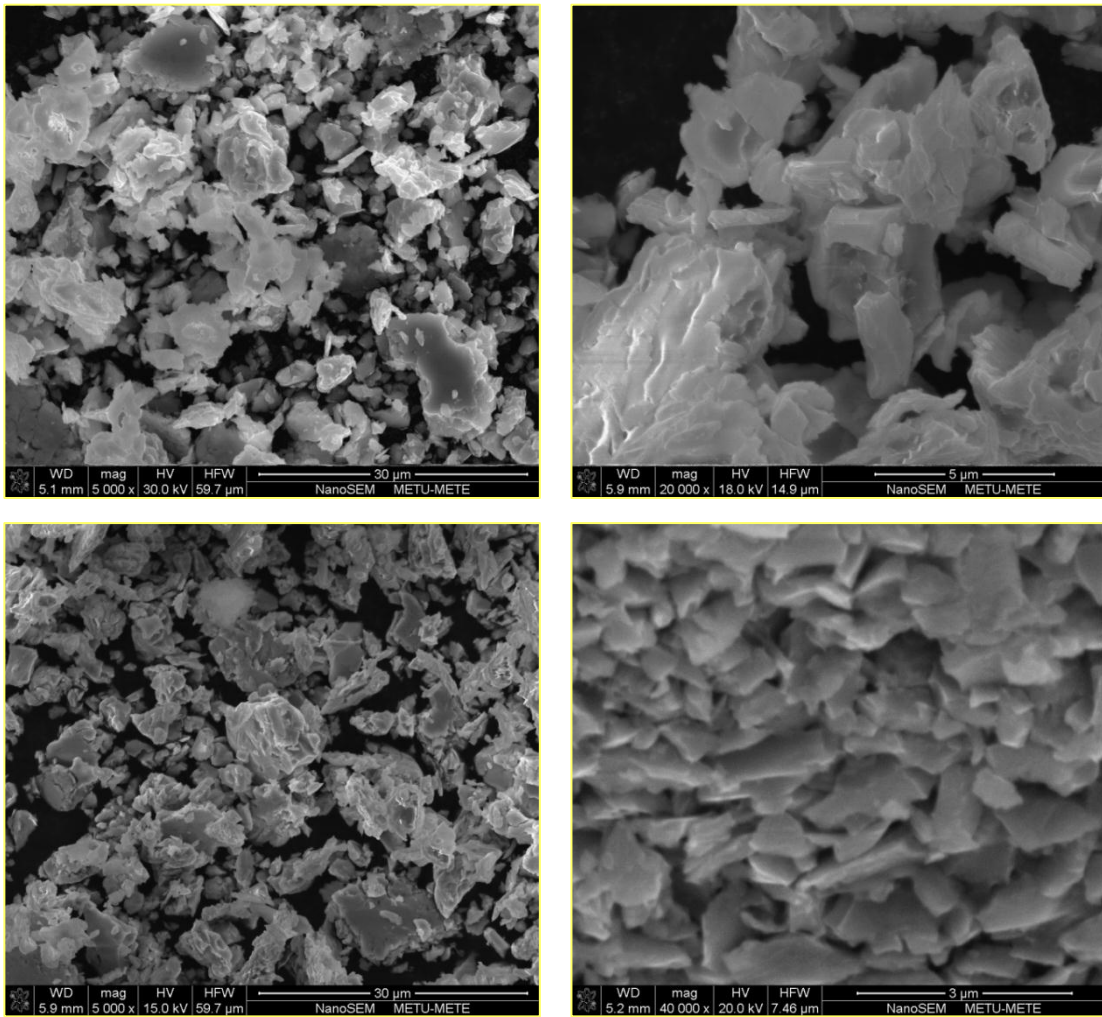


Figure 5.22 Microstructure of Dy - alloyed compound at 5000x, 20000x and 40000x.

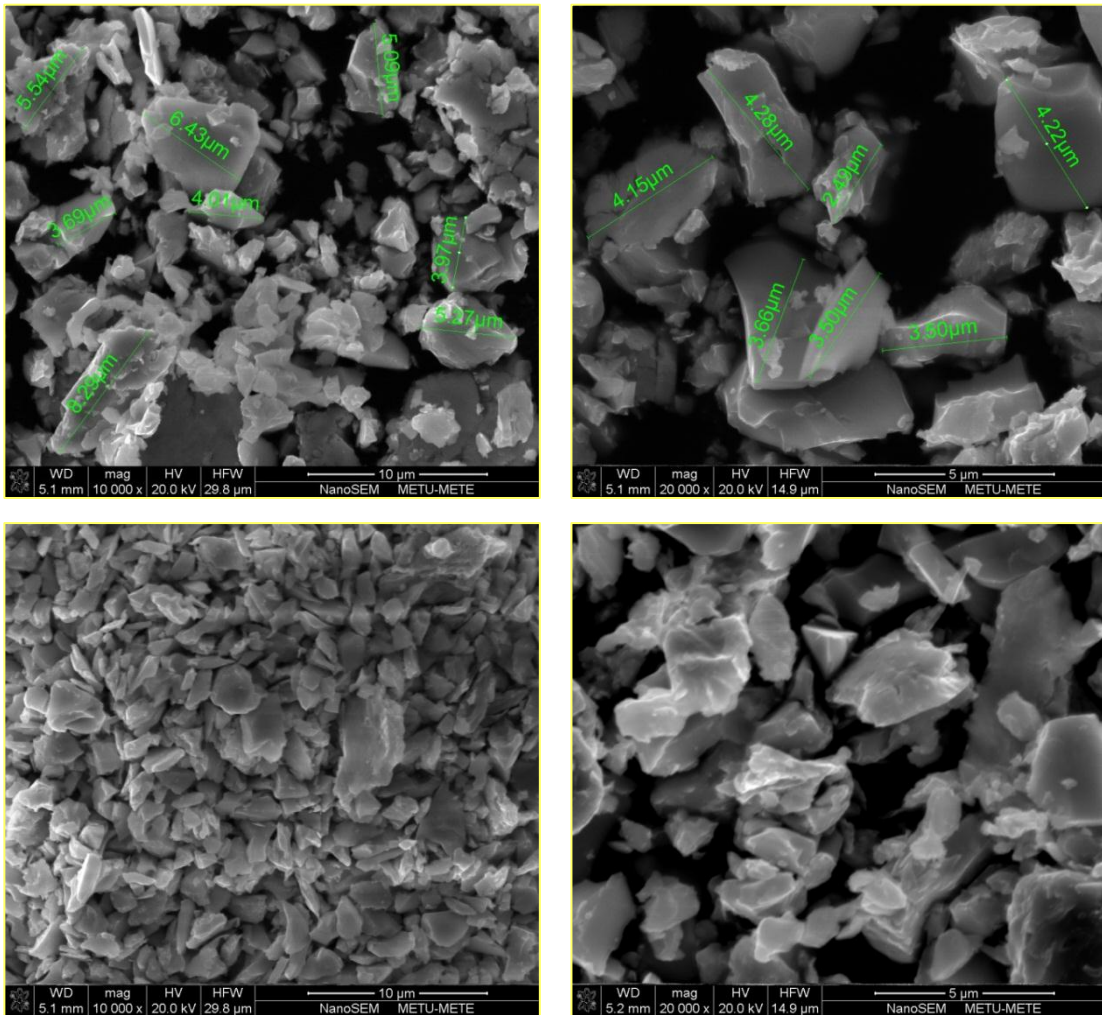


Figure 5.23 Microstructure of V - alloyed compound at 10000x and 20000x.

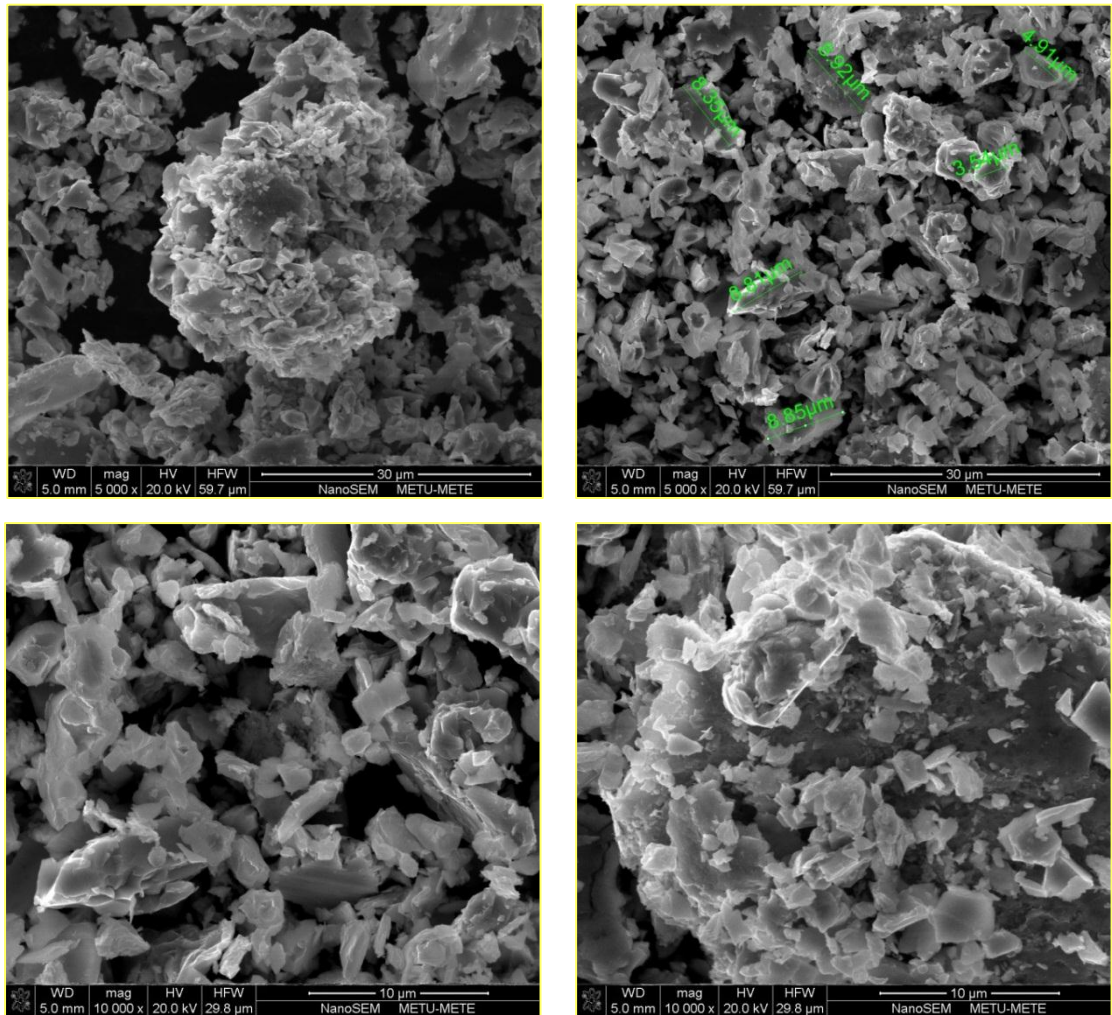


Figure 5.24 Microstructure of Ti - alloyed compound at 500x, 5000x and 10000x.

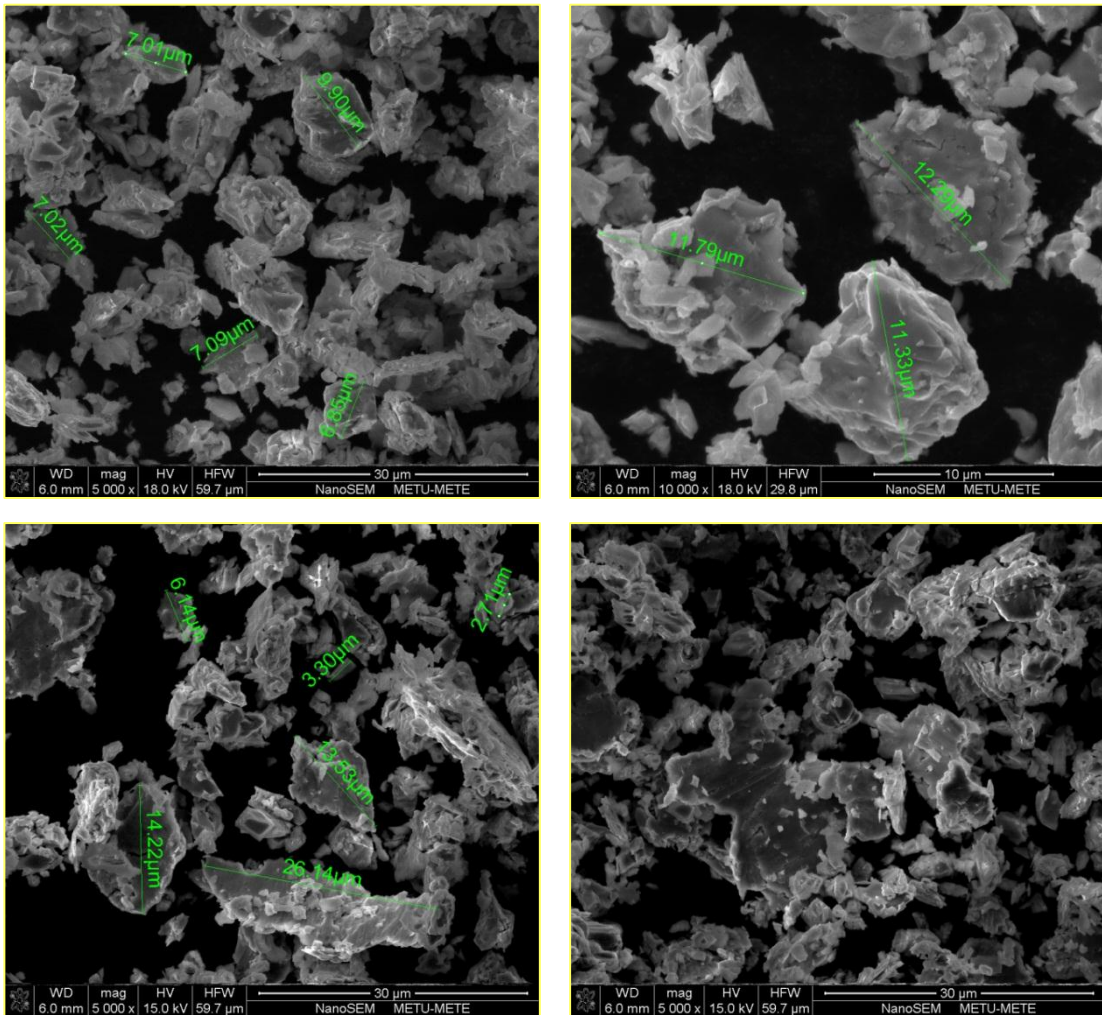


Figure 5.25 Microstructure of Hf - alloyed compound at 5000x and 10000x.

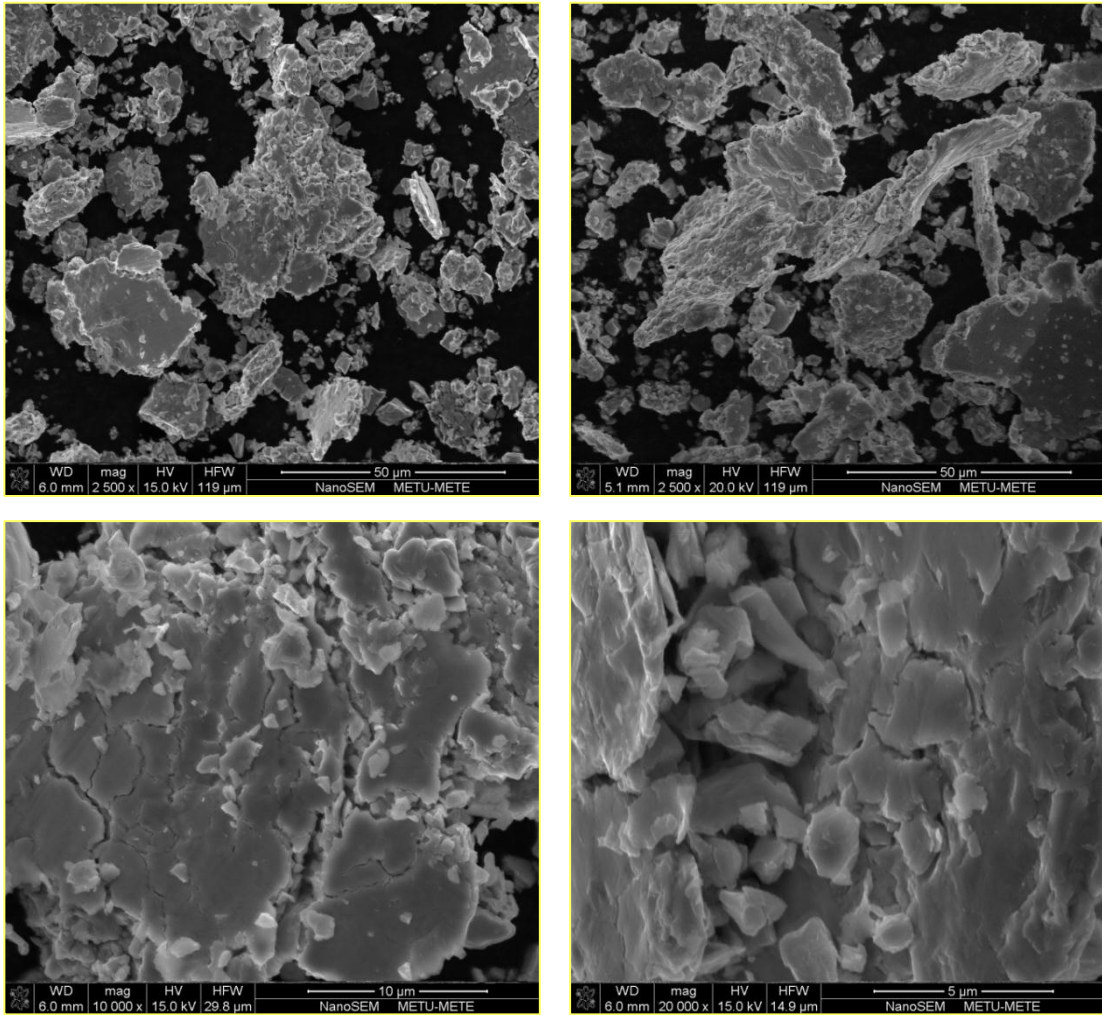


Figure 5.26 Microstructure of Er - alloyed compound at 2500x, 10000x and 20000x.

5.6 Electrochemical Characterization

Produced active material was used to form cell and potentiostat was used to carry out galvanostatic charge and discharge cycles. Characteristics of Ni – MH batteries is activation of anode materials storing hydrogen. Thus, it was expected increasing capacity in first charge – discharge cycles. The electrodes were cycled by charging at 20 mA / g for 8 h and discharging 2 mA / g for 8 h down to 1 V.

Typical charge – discharge profile is shown for few cases in Figure 5.27. Capacity versus cycle life graphs of batteries are shown in Figure 5.28, 5.29 and 5.30. Discharge capacities of the alloy were determined by time integration at the current profile.

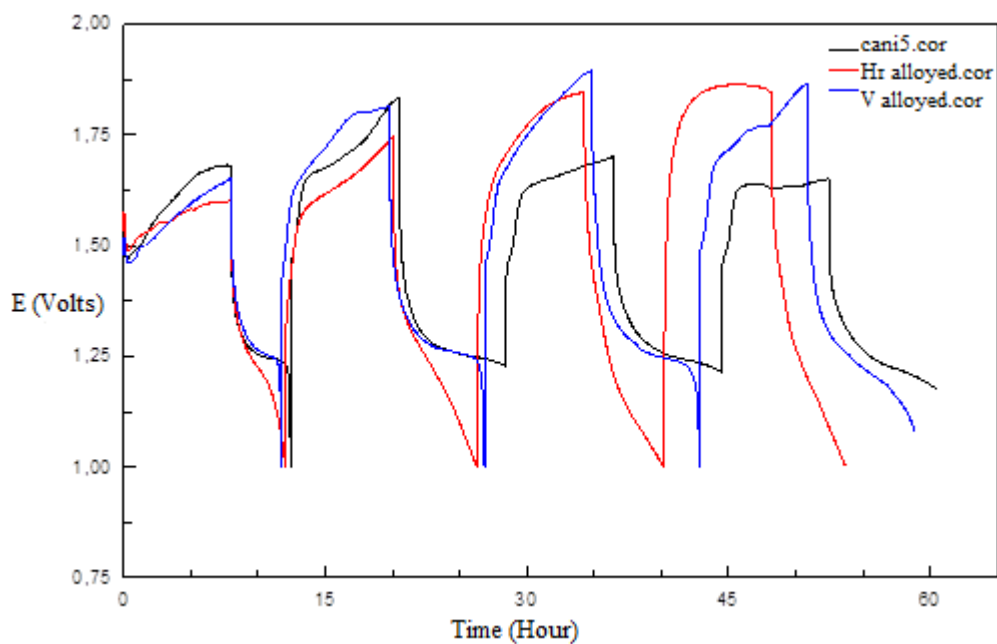


Figure 5.27 V – t graph for the selected compounds (Unalloyed, V and Hf – alloyed).

When discharging capacities of alloy compounds are considered, there are three different aspects. In the first aspect, there can be no change in capacity of compound, so it can be commented as active material stored and released the same amount of hydrogen. This aspect is not observed in our results.

There can be second possibility which is the degradation of active material. In this situation, capacity of compound decreases slightly because of reactions that occur during charging – discharging. After each reaction, amount of active material reduced, therefore less amount of hydrogen released for the followed reactions. Sm, Sn, Al, Y and Cu show that kind of discharging profile in our experiments. In the existence of the hydride phase of active material, slightly decreasing in capacity can be also shown. Thus, released hydrogen amount will be less and capacity will be less, too. However, in parallel with theoretical studies, formation of stable hydride phase was not observed [38].

There is another possibility that active material is needed to be activated. This activation profile is generally observed in Ni – MH batteries. In this profile, capacity has significant increase for few cycles to be activated than is stable for cycles and starts to decrease. This profile is almost observed in our most of selected elements. Cu, Si, Zn, Cr, Mg, Fe, Dy, V, Ti, Hf and Er were needed to be activated. In discharging capacities profile, important aspects are; time that holds the capacity stable, capacity that has higher values and need of activation.

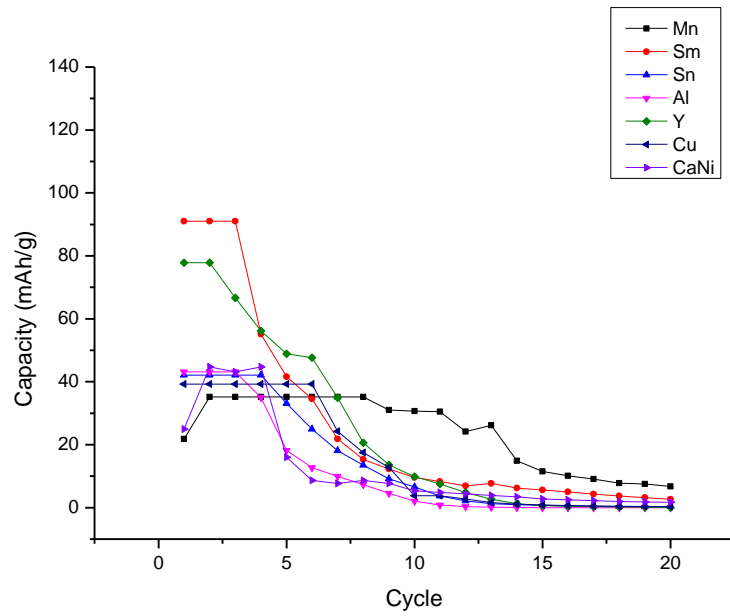


Figure 5.28 Discharging capacities of Mn, Sm, Sn, Al, Y and Cu – alloyed compounds.

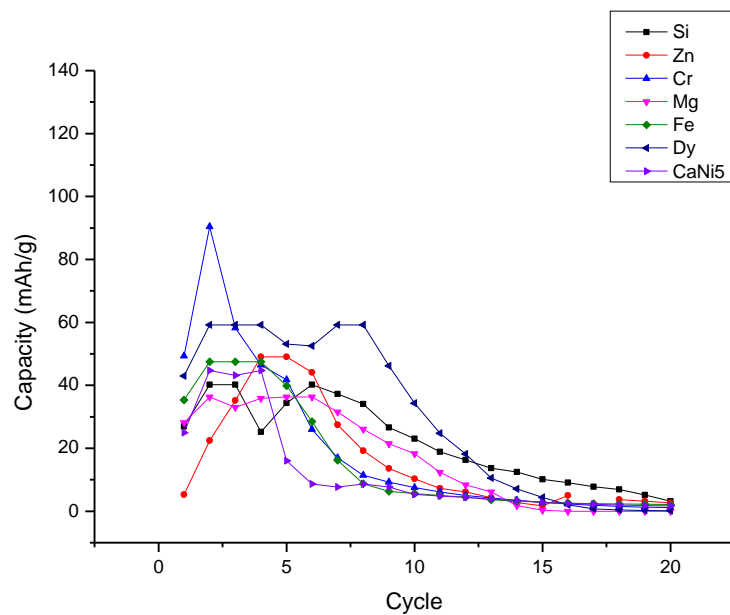


Figure 5.29 Discharging capacities of Si, Zn, Cr, Mg, Fe and Dy - alloyed compounds.

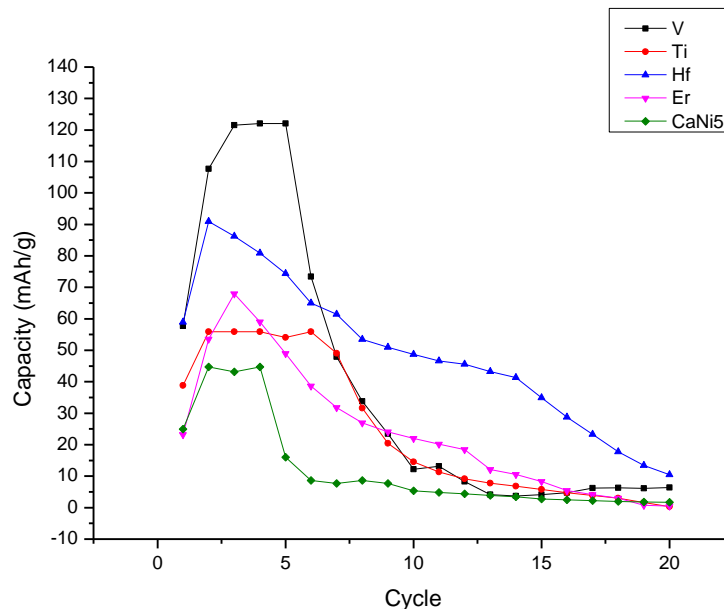


Figure 5.30 Discharging capacities of V, Ti, Hf and Er - alloyed compounds.

When the results are considered, maximum discharging capacities are lower than expected. For instance, theoretical capacity of CaNi_5 compound is 482 mA /g whereas experimental value is of 122 mA / g. This can be because of two different mechanisms which are insufficient activation of batteries and/or degradation of active material during activation. The latter seems more possible. During preparation of cell, active material is in contact with electrolyte. Thus, self-discharge of the battery and losing of active material may start even before it is activated. This situation was also faced in the commercial applications of LaNi_5 [42]. In this situation, surface modification that protects the alloy from corrosion could be a solution. Active material has covered with a protective film to prevent corrosion of the particles before integration of active material in the battery and completing of electrochemical activation.

After the consideration of results, there are two different discharging profiles in our selected elements and activation is needed almost for all alloying elements. In this

manner, there is some point which is standing out when the subject is effects of alloying elements on activation profile. Capacity of unalloyed compound is not sufficient, although it has stable discharging profile. This may be the result of the degradation of the active materials. Same problems are observed in the alloyed compounds with Mn, Cu, Al, Sn, Si, Zn and Fe. Even so, Sm, Y, Cr, Dy, V, Ti, Hf and Er – alloyed compounds preserve the capacity of batteries and specially, alloying elements, V, Hf and Cr has significant effect on the capacity and cycle durability.

Discharging profile of CaNi_5 is not related with only degradation of compound but also stability of hydride phase that occurs during charging. During discharging, compound cannot be able to restore hydrogen. In this situation, it is normal obtaining lower capacity than expected. Mn, Y, Cu, Si Mg, Dy, Ti, Hf and Er are effective elements on durability of discharging profile. If we also considered first higher capacities of the compounds, Y and Hf have better results. All these results show that unalloyed compound has problems about durability of discharging profile and capacity.

According to our studies, alloyed compound have better cycle life and durability as expected. However, the compounds do not exhibit their potential electrochemical properties, cycle life and durability. There is an explanation of the reason of low capacity in the literature with LaNi_5 alloys that belong the same crystal structure with CaNi_5 alloys [43]. This study is about phase structure and electrochemical characteristics of LaNi_5 and La_2Ni_7 . There is a formation of La_2Ni_7 during the production of LaNi_5 as CaNi_5 production in this study. Moreover, it is stated that electrochemical tests show that the maximum discharge capacity and high rate discharge ability can be improved by adjusting the stoichiometric ratio. By the formation of other phase, Ca_2Ni_7 , stoichiometric ratio is not achievable. Thus, this can result with decreasing in capacity and discharge ability.

There are some effective elements when the results are compared with unalloyed compound. These effective alloying elements are; Y, Dy, Ti, Hf and Er (instead of Ca). There is not much effect of Sm on the activation of battery compared to other alloying elements. In the decreasing of the cycle life, there are different mechanism which can be dominant are durability of compounds or diffusion mechanism of Ca element in the structure. All elements which are mentioned above makes the durability of compounds higher whereas this effect is less for Hf element. However, experimental results showed that Hf has much more effect when it is compared with theoretical results. Therefore, it can be explained that diffusion mechanism of Ca is much more effective for cycle life of the battery.

Al, Sn and Zn have no effect on the cycle life of the battery where they affect the durability of compound in the alloying by replacing Ni atom. All information which was gathered from theoretical studies are also investigated by the experimental studies. All selected elements were used for substitution of the system and and tested for measurement of capacity and cycle life. Effects of alloying elements on formation and activation energy are shown in Table 5.4. In this table, diffusion activation energy of Ca atom is given for alloying of Ni atom which is most constant. (Ni – 2 position is found as most constant). Correspondingly, results of experimental studies on effects of alloying elements on maximum capacity of the compounds and cycle life are shown in Table 5.5.

Table 5.4 Effects of alloying elements on formation and diffusion activation energy of Ca atom [38].

Alloying element	Stability of alloyed compound (%)		Diffusion activation of Ca atom (%)		Stability of alloyed hydride compound(%)	
	Replacement of		Replacement of		Replacement of	
	Ca	Ni	Ca	Ni	Ca	Ni
CaNi₅	0	0	0	0	0	0
Mn	27.82	1.42	-	-	10.02	-0.98
Sm	-19.42	12.76	0.8	-	2.51	-15.74
Sn	15.04	-10.76	-	-16.10	8.73	-7.73
Al	10.54	-22.35	-	-15.51	10.94	4.72
Y	-21.71	8.56	2.65	-	4.57	-16.03
Cu	42.33	-1.42	-	-	5.49	-0.37
Si	26.60	-30.24	-	-8.75	9.10	9.02
Zn	26.09	-10.24	-	-10.57	5.40	3.67
Cr	55.50	12.21	-	-	-1.99	-4.24
Mg	10.44	-0.68	-	-	5.21	-5.40
Fe	38.44	3.25	-	-8.67	13.86	1.38
Dy	-22.80	5.85	3.77	-	5.00	-14.35
V	27.41	0.73	-	-20.42	10.74	-4.03
Ti	1.09	-10.51	22.41	-	13.61	-4.82
Hf	-17.54	-8.11	15.71	-	16.85	-7.78
Er	-23.38	3.07	4.52	-	6.18	-13.85

Table 5.5 Effects of alloying elements on maximum capacity of the compounds and cycle life.

Alloying elements	Max.capacity (mAh/g)	Cycle life at half of its capacity
CaNi₅	44	5
Mn	35	14
Sm	91	5
Sn	42	7
Al	43	5
Y	77	8
Cu	39	8
Si	40	10
Zn	49	7
Cr	90	5
Mg	36	10
Fe	47	6
Dy	59	10
V	122	7
Ti	56	8
Hf	91	14
Er	67	7

CHAPTER 6

CONCLUSION

As a conclusion of all studies, it is understood that CaNi_5 has not sufficient properties to use in Ni – MH batteries instead of LaNi_5 . Two main problems are; compound does not have resistance to degradation and cycle - capacity durability is lower of the compound.

Capacity loss is an outstanding problem which is caused by activation and self – discharge. In experimental studies, there is not found effective elements on this subject. Hf and Y alloying elements can be noticed as improving cycle life of the battery. Also, Sm has effects on the capacity. V and Cr alloying elements have significant effect; therefore it is thought that they form a protective layer around the powder particles.

All these experimental studies were carried out with theoretical studies to understand the mechanism of degradation of Ca element in the crystal structure [38]. There are two main profiles on discharging capacity profile of the alloyed compounds. There are some alloyed compounds that lose their capacities due to the degradation of active material. Therefore, there was not enough active material for storing hydrogen. In the second and most common observation is that almost all alloying elements were needed to be activated. However, after activation capacities of compounds would not be stable for more cycles. The reason of this situation is insufficient activation and degradation of active material.

Two main problems researched which is degradation of the compound and lower cycle durability. Formation energy of the compounds was calculated and elements that are improved cycle durability were established. Also, elements that made diffusion difficult were established by calculating of diffusion activation energy of Ca atom in the structure. Formation energy of hydride phases were also calculated in the case of durability of the hydrides of alloying elements.

Hydride phase of the structure provides resistance from corrosion and this gives the durability of cycles of discharging. During discharging, stored hydrogen cannot be released, therefore it is expected to obtain less capacity rather than expected. These results were also studied by experimental and discharging capacities were calculated of produced alloyed compounds.

Effective elements are Mn, Y, Cu, Si, Mg, Dy, Ti, Hf and Er for the durability of discharging capacities. If it is evaluated with the first maximum capacities Y and Hf elements have better results. It is obviously showed that unalloyed compound has problematic during discharging and cycle durability.

As a conclusion, alloying of CaNi_5 compound by Hf, Ti, Y, Dy and Er by replacing Ca element and Si and Mn by replacing Ni element can be resulted with an improvement in the cycle life of the batteries. Moreover, V and Cr alloying elements can be used to prevent self – discharge of the batteries.

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