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RISK FACTORS OF TRIBOLOGICAL PROCESSES AND THEIR ENVIRONMENTAL IMPACT

Disertation thesis

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Declaration

I hereby declare I have written this doctoral thesis independently and quoted all the sources of information used in accordance with methodological instructions on ethical principles for writing an academic thesis. Moreover, I state that this thesis has neither been submitted nor accepted for any other degree.

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Abstract

Tribology deals with the interaction of surfaces during relative motion, depending on their design, friction, wear and lubrication. However, tremendous development has been done for tribology in manufacturing, in the past 100 years, to transform this phenomenon to a known and avoidable nuisance from a sophisticated discipline, there is still many new challenges coming up due to upcoming scientific achievements.

One of these challenges is estimating risk behind material's wear and friction existing by tribology. Therefore a clear need came up to scientific committees in order to approach new studies and ideas, How to minimize and limit this risk either by improving material resistance or having new lubrication fluid formulas.

According to various experiences and areas of application, tribological coatings play a key role in the performance of mechanical components and products by reducing wear and friction, increasing the life of the working material and reducing energy dissipation as heat, thus increasing the efficiency of the moving.

This research will take proper use of PTA coatings as case study, which can significantly reduce friction and wear, leading to reduced energy consumption and extended service life. Studied material will be cermets based on B_4C particles in Ni-based matrix. A tribology analyze for wear, abrasion, resistance of plasma deposited cermets, will be concluded with target to show impact of these phenomenon on industrial tribology and related processes on the environment.

Goal of this case study, is collecting discharged particles from tribology tests and prepare a risk Assessment. The estimation of risk factor for plasma-welded material on tribologically treated surfaces will be shown by possible impurities generated during this process on the environment and possible proof improvement for wear resistance.

Risk assessment will be prepared based on Agency of European Union regulations and standards, by showing hazard classifications and labelling for produced particles after tests running and notifying for after treatment necessity, which would be considered as future work.

Keywords: Tribology, Risk Assessment, Environmental Risks, Cobalt, Nickle alloys, Friction, wear, Powder Plasma Transferred ARC Welding, Surface Coating, Electro-microscope.

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usa, usa
eu, eu
ussr, ussr

Chapter 1

Introduction

As our modern industry undergoes a push towards optimization and increased efficiency, a necessary growing becomes more desirable feature within the industry to follow up market needs.

To guide these improvements and being sure that it will fulfill standards and regulations, there will be important factors need to be controlled, and one of these factors is tribology and its side effects.

However, many advanced methods have been proposed in the field of tribology, concentrating on two main factor: friction and wear resistance. Modern technologies can be in some cases quite over-engineered or too complex especially when scientific committee proposing new methods, such as lubricating oil new composites or surface treatment by using new materials.

Over the last few decades there has been considerable activity in the field of risk assessment. This has mainly taken place in international organizations such as European Chemicals agency.

A high motivation has been noticed here and will be considered in this dissertation, by presenting and concentrating on new invented materials, which can be used in tribological applications as robust future material in industrial usage, and showing clearly advantages and disadvantages of this usage.

As this dissertation is focused on cermets as promising material to be used in tribological applications, the aim is to summarize and estimate risk factors, produced by combining Nickel alloys 625 and Boron Carbide particles in plasma powder transferred arc welding (PPTAW).

Till today's date, Cermets, including Ni625 and B_4C, are nowadays reaching a great level of development, to prove its optimal properties, Boron Carbides (B_4C) ceramic, as high temperature resistance and hardness material and Inconel® metal, as corrosion resistant material, high yield and tensile, high temperature strength, excellent weld ability and creep strength.

Each of the various tribological processes, by which material can be lost from a surface in service, leaves its fingerprint both in the topography of the worn surface and in the size, shape and number of the particles, which make up the wear debris. The size of material removal from work piece surface as well as the rate of material removal are the prime dependent outcome parameters, which depend on the wear-mechanism taking place during tribological operation.

Cermets optimal properties bring improvement to tribological properties, wear resistance and friction, as advantage. Nevertheless, from other hand, general overview for disadvantages, which could be brought by this usage, need to be considered here by risk assessment preparation according to European Chemical Agency standards and classifications.

The necessity to study this risk came from lack of knowledge and experience with this new combination of cermets (Ni625 and B_4C), that is why collecting particles, produced by tribology test, for confocal microscope analyses, is necessary for this research, to distinguish micro/ nano particles existence. Electro-microscope analyze was performed to confirm cobalt/ Nickel particles existence in free micro/ nano particles, which is considered as hazard, allergic particles for human being and prohibited material to be found in micro/ nano size particles. [1]. According to European chemical agency Nickel can be announced clearly as dangerous material. [1], [2].

Cobalt substance is registered under the REACH Regulation and is manufactured in and / or imported to the European Economic Area, at 10 000 tonnes per annum.

This substance is used by consumers, in articles, by professional workers (widespread uses), in formulation or re-packing, at industrial sites and in manufacturing.

Talking about Cobalt and it's existence in industry, this substance is used in the following products: metals and metal surface treatment products. Other release to the environment of this substance is likely to occur from: indoor use and outdoor use resulting in inclusion into or onto a materials (e.g. binding agent in paints and coatings or adhesives).

[3]

According to European chemical agency, Cobalt considered as Dangerous material. "According to the harmonised classification and labelling (ATP14) approved by the European Union, this substance may cause cancer, may damage fertility, is suspected of causing genetic defects, may cause long lasting harmful effects to aquatic life, may cause an allergic skin reaction and may cause allergy or asthma symptoms or breathing diffi-

[1]https://echa.europa.eu/substance-information/-/substanceinfo/100.028.283
[2]https://echa.europa.eu/substance-information/-/substanceinfo/100.028.325
[3]https://echa.europa.eu/substance-information/-/substanceinfo/100.028.325

culties if inhaled."

Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance is fatal if inhaled, is very toxic to aquatic life with long lasting effects, may damage fertility or the unborn child, is very toxic to aquatic life, is harmful if swallowed, causes serious eye irritation, may cause damage to organs through prolonged or repeated exposure and is suspected of damaging fertility or the unborn child.

Therefore, risk assessment and diagnostic aid in assessing the health of operating plant, which may contain many tribological contacts, requires not only appreciation of the mechanisms, by which wear occurs, but also careful and standardized procedures for debris extraction and observation either by solving these particles in liquids or using cleaning oils to prevent having hazard materials in free movement atmosphere.

The remainder of this thesis is organized as follows: Section 2 reviews the necessary background for this work. Section 3 presents the existing works. In section 4, present and discuss the practical experiments and results. section 5 discuss results and finally, section 6 concludes what has been done in this work and what are further next steps.

Chapter 2

Theoretical Background

Nowadays, manufacturing technologies are being highly developed to gain most efficient and highest quality of production processes. As a part of this development, a need to invent new materials combinations raised up with high demand to show impact of these materials in industrial field. One of these combinations is having Cobalt and Nickel particles in on composite called cermets in tribological behaviour, which will be the main case of study in this thesis.

According to previous studies it is clearly known that Cobalt compounds (metal, salts, hard metals, oxides, and alloys) are used widely in various industrial, medical and military applications.[2] Cobalt compounds listed in many health agencies as probable or possible human harmfully, and to use this material it is needed to have risk assessment.

Nickel is ubiquitous in the industrial work field even though it causes serious eye irritation, causes skin irritation and may cause respiratory irritation according to previous studies.[3]

Nickel hydroxide is on the hazardous substance list because it is regulated by many health, industrial and chemical societies. Nickel Hydroxide can affect human when breathed in. Therefore it should be handled as a carcinogen-with extreme caution. ON other hand any contact with Nickel hydroxide can irritate and burn skin and eyes. Breathing Nickel Hydroxide can irritate the nose, throat and lungs causing cough, phlegm and shortness of breath.[4]

Depending on mentioned information and facts and due to lack of previous data and researches, the necessity to define risk of cobalt Nickel cermets usage is so high, in order to avoid it's negative impact in industry specially when it will be used in tribological applications.

2.1 Tribology principles and risks

Tribology is the science and technology consists of surfaces interacting in relative motion and with associated matters (as friction, wear, lubrication, surface treatment). The term Tribology was introduced and defined for the first time in 1966 by Prof. H. Peter Jost[5]. It was reported that huge sums of money have been spent around the world owing to the consequences of friction, wear and corrosion.

Many typical previous tribological studies concentrating on friction, wear, lubrication and adhesion have been done involving also efforts of mechanical engineers, material scientists, chemists and physicists to have an interface of various scientific disciplines, and various aspects (nanotribology, biotribology, the tribology of magnetic storage devices and micro electromechanical systems(MEMS)/nano electromechanical systems and adhesive contact) of interacting surfaces in relative motion.

New concept of 'green tribology' has been defined recently as 'the science and technology of the tribological aspects of ecological balance and of environmental and biological impacts'. elaborated on the need for risk assessment for tribology and has mentioned that 'the influence of economic, market and financial triumphalisms have retarded tribology and could retard "green tribology" from being accepted as a not-unimportant factor in its field. Therefore, by highlighting the economic benefits of tribology, tribology societies, groups and committees are likely to have a far greater impact on the makers of policies and the providers of funding than by only preaching the scientific logic. Tribology societies should highlight to the utmost the economic advantage of tribology. It is the language financial oriented policy makers and markets, as well as governments, understand'.The specific field of green or environment-friendly tribology emphasizes the aspects of interacting surfaces in relative motion, which are of importance for energy or environmental sustainability or which have impact upon today's environment. This includes tribological technology that mimics living nature(bio mimetic surfaces) and thus is expected to be environment friendly, the control of friction and wear, which is of importance for energy conservation and conversion, environmental aspects of lubrication and surface-modification techniques and tribological aspects of green applications, such as wind-power turbines, tidal turbines or solar panels. It is clear that a number of tribological problems could be put under the umbrella of green tribology and are of mutual benefit to one another. Green tribology can be viewed in the broader context of two other 'green'areas: green engineering and green chemistry. The US Environmental Protection Agency defines green engineering as 'the design, commercialization and use of processes and products that are technically and economically feasible while minimizing

1- generation of pollution at the source and

2- risk to human health and the environment' (US Environmental Protection Agency2010).

The three tiers of green engineering assessment in design involve [6]:

(i) process research and development,

(ii) conceptual/preliminary design

(iii) detailed design pollution prevention

The paradigm of green tribology:

(a) Renewable energy (represented by a wind turbine),

(b) Bio mimetic surfaces (represented by a gecko foot)

(c) biodegradable lubrication (represented by natural vegetable oil).

Another related area is green chemistry, also known as sustainable chemistry,which is defined as the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances (US Environmental Protection Agency 2010). Green chemistry technologies provide a number of benefits, including reduced waste, eliminating costly end-of-the-pipe treatments,safer products, reduced use of energy and resources and improved competitiveness of chemical manufacturers and their customers. Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components and improved efficiency.

The 12 principles of green chemistry that provided a road map for chemists to implement green chemistry are:[6]

1) Prevention of waste is better than cleaning up.

2) Maximum incorporation into the final product of all materials used in the process.

3) Chemical synthesis should incorporate less hazardous or toxic materials, when possible.

4) Chemical products should be designed to reduce toxicity.

5) Auxiliary substances, such as solvents, should be safe whenever used.

6) Energy efficiency requirements should be recognized. Synthetic methods should be conducted at ambient temperature and pressure, whenever possible.

7) A raw material or feed stock should be renewable, whenever possible.

8) Reduce unnecessary derivatives.

9) Catalytic reagents are superior to stoichiometric reagents.

10) Chemical products should be degradable at the end of their function.

11) Real-time analysis, monitoring and control should be implemented to prevent the formation of hazardous substances.

12) Substances and their use in the chemical process should be chosen to minimize the risk of accidents and prevent fires, explosions, spills, etc.

A number of green chemistry metrics have been suggested to quantify the environmental efficiency of a chemical process. These metrics include the environmental factor

('E-factor').

Since tribology is an interdisciplinary area that involves, among other fields,chemical engineering and materials science, the principles of green chemistry are applicable to green tribology as well. However, since tribology involves, besides the chemistry of surfaces, other aspects related to the mechanics and physics of surfaces, there is a need to modify these principles. The principles of green tribology will be formulated in the following section.

Even though the name tribology implies inter facial sliding, the discipline considers static contact as well. Lubrication to reduce friction and wear has been intimately involved with the empirical development of machinery through the ages. Tribology, therefore, has been basically a "catch-up" science; trying to explain physical phenomena which were known phenomenogically for decades. The pervasive concept in all tribology is the elastoplastic interaction at the microscopic irregularities on engineering surfaces. Some of the major advances in tribology in the past ten years have been the definition of engineering surfaces on this microscopic scale and the analysis of the thermo-mechanical situation, which develops when such surfaces are slid against each other under load.

The phenomena at the surfaces in contact include the transfer of energy as the result of the actions of normal and shearing forces and temperature differences. The nature of the phenomena depends on the thermal, geometrical, mechanical, chemical and physical attributes of the surfaces and those of the bulk materials.

It is appropriate to discuss the nature of surfaces first as this governs subsequent events. This will be followed by a description of wear, its importance and its mechanisms. The fundamental ideas governing friction and heat transfer, causing wear, will follow [7].

2.1.1 Friction and Wear Resistance Resulted During Tribology

Although the subject of tribology is wider than friction study, friction does play a key role in the performance of many mechanical systems. Work done in overcoming friction in bearing and gears in machines is dissipated as heat and by reducing friction, we can achieve and increase in overall efficiency. Whenever surfaces move over each other, wear will occur: damage to one or both surfaces, generally involving progressive loss of material. Sometimes the wear is imperceptibly slight, bit it can be also extremely rapid. In most cases, wear is detrimental, perhaps causing increased clearance between the moving components, unwanted freedom of movement and loss of precision. It often leads to vibration, to increased mechanical loading and yet more rapid wear, and sometimes to fatigue failure. The small amount of lost material by wear can be enough to cause complete failure for large and complex machines, and there are unfortunately cases where the root causes of major engineering disasters can be traced back to wear [8]. Result from this wear and friction can be observed as particles growing between these two moving metals. These particles can have disadvantages on production processes and environment [9].

Nowadays there are many methods to reduce friction and often wear, to lubricate the system in some way, and the study of lubrication is very closely related to that of friction and wear.

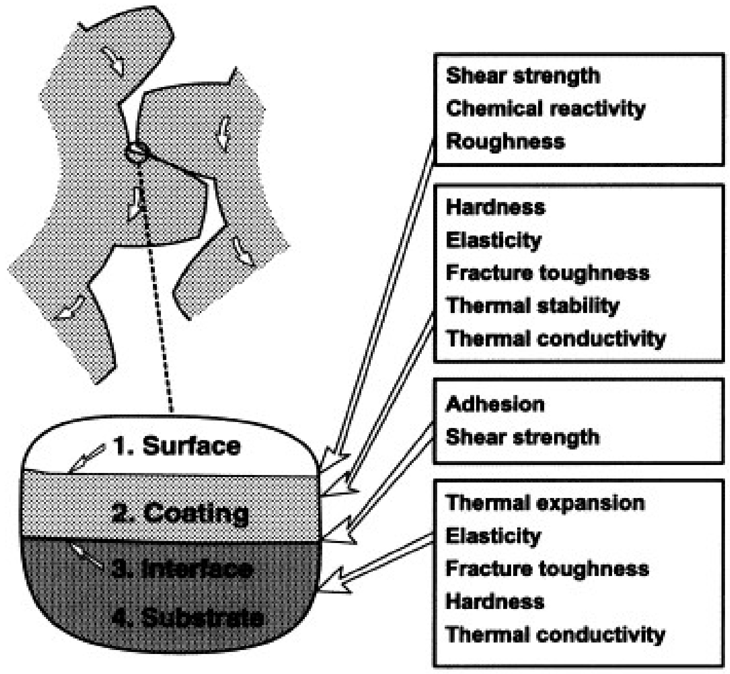

Figure 2.1: Tribologically important properties in different zones of the coated surface

According to previous studies, financial savings can be made through improved trbilogical practice by system lubrication [7]. Where, Savings in maintenance and replacement costs 45 %. Savings in losses resulting from breakdowns 22%. Savings in investment through increased of of plants 20%. Reduction in Energy consumption through lower friction 5%. Savings in investment through greater.

On other hand, surface treatment brings different method to reduce friction and wear, by applying multilayer and multi-component coatings. In recent years, the use of multilayers has often been cited as the way forward to improve the mechanical, tribological and chemical properties of coatings. See figure 2.1 [10].

2.2 Materials – Ni Alloy Type 625, Boron Carbide, Cermets, Ni Based Cermets with B4C

Ni-based super alloy type Inconel® is a solid-solution derived from refractory elements including niobium and molybdenum, in a nickel-chromium matrix. Alloy of the type 625 alloy has good corrosion resistance, good combination of yield, tensile, high temperature strength, excellent weld ability and creep strength that led to its application in different areas such as aeronautics, aerospace, marine, nuclear, chemical and petrochemical industries [11]–[13].

Chemical Properties Of Inconel 625 Bar in Figure 2.2

Nickel	Chromium	Molybdenum	Iron	Niobium and Tantalum	Cobalt	Manganese	Silicon
58%	20%-23%	8%-10%	5%	3.15%-4.15%	1%	0.5%	0.5%

Figure 2.2: Chemical Properties Of Inconel 625 Bar

Inconel® usage and applications in manufacturing technologies is remarkably difficult and expensive, due to fact that it has low wear resistance characteristics [12].

The frictional wear between the moving parts have to be considered. Subsequently, on one hand, deformation of the sealing surface geometry during operation because of high load and impact forces is unavoidable but needs to be limited. On the other hand, the wear resistance of moving parts has to be improved to reduce deterioration and extend service life. Therefore, continuous improvement in the performance in terms of shape stability, impact resistance and wear resistance of valve components is required [14], [15], [16]. Figure 2.3

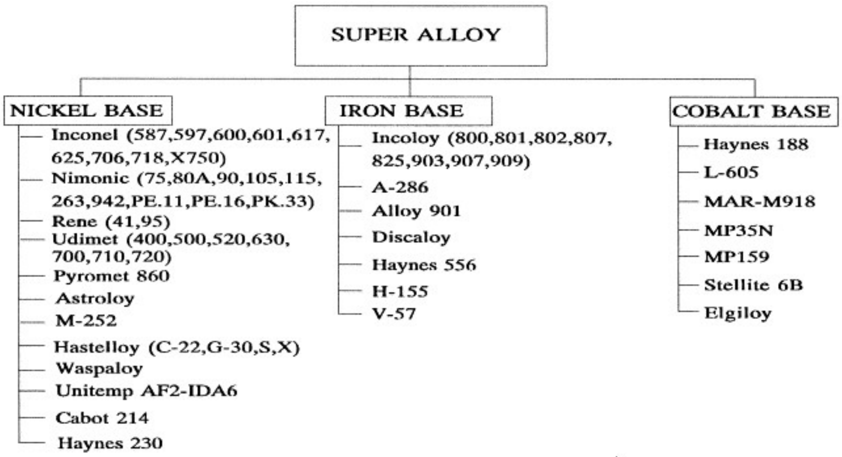

Figure 2.3: Alloy Variants and Types

Inconel-625 is a solid solution-strengthened alloy used for long-duration applications at high temperatures and moderate stresses. Different heat treatment cycles have been studied to obtain optimum mechanical properties suitable for a specific application. It has been observed that room temperature strength and, hardness decreased and ductility increased with increase in heat treatment temperature [17].

2.3 Boron Carbide

Boron carbide is characterized by a unique combination of properties that make it a material of choice for a wide range of engineering applications. Boron carbide is used in refractory applications due to its high melting point and thermal stability; it is used as abrasive powders and coatings due to its extreme abrasion resistance; it excels in ballistic performance due to its high hardness and low density; and it is commonly used in nuclear applications as neutron radiation absorbent. In addition, boron carbide is a high temperature semiconductor that can potentially be used for novel electronic applications. This paper provides a comprehensive review of the recent advances in understanding of structural and chemical variations in boron carbide and their influence on electronic, optical, vibrational, mechanical, and ballistic properties. Structural instability of boron carbide under high stresses associated with external loading and the nature of the resulting disordered phase are also discussed [12], [18], [19].

2.4 Plasma Powder Transferred Arc Welding (PPTAW)

PPTAW is one of the techniques used in modification and regeneration of the surfaces of machine components. By correctly adjusting the arc power, this method allows control of the substrate penetration depth with high accuracy, achieving less than 5% base metal content in the surfacing weld. Thus, in order to obtain a coating with specific operating characteristics, it is sufficient to create a surface weld of small thickness, which has a measurable economic effect. In addition, selecting appropriate plasma welding parameters allows surface layers obtain with thicknesses from 0.25 to 5– 7 mm and a high level of metallurgical purity [1]. Plasma plum/ jet is heating both parent and filler material Fig.02 Uniform power distribution of the plasma arc spot on surface of welded object and the use of swinging movement of the plasma torch ensures obtaining surface of uniform thickness across the width of the layer and with a smooth face, often without the need for machining. Precise control of linear welding energy during the welding process allows to adjust the width and structural changes in the heat affected zone of the surface weld, without excessive grain growth and underbid cracking. The efficiency of the plasma welding process is high and, depending on the design of the burner, can reach up to 22 kg of melted powder per hour [4]. The surfacing process can be applied to flat and rotational objects made of carbon steel, alloy steel and corrosion resistant steel, as well as cast steel and some grades of cast iron. Surfacing is used for example for camshafts, valves and valve seats of internal combustion engines, bolts and bearing pins, homogenizer plungers, molds for precision forming of glassware, turbine vanes, cutting tools, cutting edges of earthmoving tools, extruder screws, components of hydraulic fittings and equipment for oil extraction installations [6]. Due to the cost of equipment for plasma welding and additional welding materials (powders), this method is mainly used for applying layers with special properties, i.e. high hardness and wear resistance. [4] A cermet is a composite material composed of ceramic (cer) and metal (met) materials. A cermet is ideally designed to have the optimal properties of both a Boron Carbides (B4C) ceramic, such as high temperature resistance and hardness, and those of a Inconel® metal, such as the ability to undergo plastic deformation [16], [20]. The effect of an individual welding parameter on the PTA welding method has to be known for optimizing welding parameters and to learn interactions between different welding parameters. In the mass production to obtain equal quality onto the deposited components, the surfacing process has to be consistent enough. The main advantages of the PTA welding method are heat input and cooling rate, which are in the range suitable for depositing a component with a broad range of alloys as well as for surface alloying or surface hardening. Usually brittleness, cracking, and gas porosity can be avoided [12].

The most important factors are:

1. Plasma arc current
2. current upslope
3. plasma gas flow rate
4. composition of plasma, carrier, and shielding gas
5. powder consumable feed rate
6. moisture content of powder and gas pipes
7. chemical composition of powder consumable
8. overlapping
9. preheating temperature
10. interpass temperature
11. working distance
12. arc voltage

13. arc polarity
14. electrode diameter
15. electrode type
16. electrode setback
17. substrate shape and size.

2.5 Tribology And Its Impact On The Environment

The specific field of green or environment-friendly tribology emphasizes the aspects of interacting surfaces in relative motion, which are of importance for energy or environmental sustainability or which have impact upon today's environment. This includes tribological technology that mimics living nature (biomimetic surfaces) and thus is expected to be environment friendly, the control of friction and wear, which is of importance for energy conservation and conversion, environmental aspects of lubrication and surface-modification techniques and tribological aspects of green applications, such as wind-power turbines, tidal turbines or solar panels. It is clear that a number of tribological problems could be put under the umbrella of green tribology and are of mutual benefit to one another. Previous studies selected a single tribo-pair, and just paid close attention to the tribo-chemical reactions of B_4C, but lost sight of having cermet's based on B_4C particles in Ni-based matrix [18], [21]. And hence, it is necessary to further investigate the effect of the mating material on the tribological performances of the cermet's based on B_4C particles in Ni-based matrix with various normal loads and sliding frequencies. Target is to estimate risk of damaged and occurred wear to Cermet (B_4C Ceramics with Inc.625, applied by plasma welding on surfaces), by tribological in-vitro test.

2.6 Risk In General

Nano/ Micro particles are the materials with at least two dimensions between 1 - 100 nm for nanoparticles and 1 – 1000 µm for micro particles, mostly these particles are natural products but their tremendous commercial use has boosted the artificial synthesis of these particles (engineered particles). Accelerated production and use of these engineered particles may cause their release in the environment and facilitate the frequent interactions with biotic components of the ecosystems. Despite remarkable commercial benefits, their presence in the nature may cause hazardous biological effects. Therefore, detail understanding of their sources, release interaction with environment, and possible risk assessment would provide a basis for safer use of engineered nano/ micro particles with minimal or no hazardous impact on environment. Keeping all these points in mind the present review provides updated information on various aspects, e.g. sources, different types, synthesis, interaction with environment, possible strategies for risk management of engineered particles [22], [23].

2.7 Study objective

Nowadays, the environment pollution produced by metal traces is a highly concerned issue. One of the important causes of trace metal pollution is particles discharging out of industrial processes which normally exist in micro/ nano size particles. These metal traces pose life-threatening effects on human kind health and safety. The aim of this dissertation is to determine cobalt (Co) and Nickel (Ni) existence which are produced from cermets, consist of boron carbide and Ni 625 alloys, used in tribology applications to evaluate Co and Ni toxicities in these samples.

According to previous studies and occupational exposure to cobalt mostly occurs via inhalation as part of the refining, alloy production and hard metal industries, but dermal exposure is also possible. It is known that different forms of cobalt can have different toxicological effects.[24]

Cobalt is a technically important metal, used mainly as a binder in hard-metal industry and as a constituent of many alloys. Boron Carbide and Nickel alloys compounds are used as case study in this dissertation. Implantation and preparation of cobalt alloys has been prepared by plasma powder transferred arc welding, and cobalt compounds induced local and sometimes metastasizing sarcomas in life being. An indication of possible harmful effects of cobalt alloys or compounds in human populations has arisen from medical use, in hard-metal industries, and at cobalt production. Unfortunately, having boron carbide and nickel alloys has a major problem, and the size of most of the investigated populations has been rather small, so none of the investigations alone gives sufficient evidence of a carcinogenic effect in humans, but taken together there is an indication of a potential risk that should be explored further.[25]

Nickel is one of the most common allergens causing allergic contact dermatitis worldwide. The aim of the study is to evaluate the contributing factors to nickel contact allergy (NiCA) and it's great negative impact on working atmosphere in tribological areas.

Main target out of this dissertation is to proof possible risk of using these cermets in tribological applications by finding, during tribological experiments, that cobalt and Nickel particles produced and this can be dangerous for health of people working in this field.

Secondary objective is to further investigate the tribological behaviour of cermets B_4C/ Ni alloys 625, as a promising composite to reduce friction, material loss and increase wear resistance.

Expected findings from this study:

1. Existence of cobalt and Nickel micro & nano particles resulted from tribology.

2. Heat treatment effect on cermets physical characteristics and how it will change tribology efficiency.

3. Micro & nano sized cobalt and Nickel particles existence in free movement.

4. Conclude the effectiveness of the approach as a means of showing risk of this material usage and possible impurities during manufacturing processes.

The remainder of this thesis is organized as follows: Section 2 reviews the necessary background for this work. Section 3 presents the existing works. In section 4, present and discuss the practical experiments and results. section 5 discuss results and finally, section 6 concludes what has been done in this work and what are further next steps.

Chapter 3

State Of The Art

This chapter presents the related works and running endotoxin test to estimate risk Of using nanomaterials in tribological process which is our previous work that have done as a study w.r.t this thesis.

3.1 Related Work

Growing attention has been given to the risk factors in tribological process. Thus, there are many previous works discussing its methods. In [11], the authors investigate the influences of interpass cooling strategy (ICS) and continuous deposition strategy (CDS) on microstructure and mechanical properties of the PPAD Inconel 625 non-ferrous alloy. The as-deposited samples in the two conditions were subjected to the post heat treatment: 980 C solution treatment plus direct aging (STA). The microstructures and mechanical properties of the samples were characterized by means of scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS), transmission electron microscopy (TEM), micro-hardness and tensile testers. It was found that the as-deposited microstructure exhibited homogenous cellular dendrite structure, which grew epitaxially along the deposition direction. The as-deposited microstructure of ICS sample revealed smaller dendrite arm spacing, less niobium segregation and discontinuous finer Laves phase in the inter dendrite regions compared to the case of continuous deposition strategy (CDS). The ICS sample exhibited better mechanical properties than CDS sample. After STA heat treatment, a large amount of Laves particles in the inter dendrite regions were dissolved, resulting in the reduction of Nb segregation and the precipitation of needle-like δ(Ni3Nb) . The tensile and yield strength of the as-deposited samples were improved, while the elongation slightly decreased.

Ni-based super alloy Inconel 625 components fabricated by using Pulsed plasma arc deposition (PPAD) which combines pulsed plasma cladding with rapid prototyping. [15].

Microstructures and mechanical properties of deposits were investigated by scanning electron microscopy (SEM), optical microscopy (OM), transmission electron microscopy (TEM) with energy dispersive spectrometer (EDS), micro hardness and tensile testers. It was found that the as-deposited structure exhibited homogenous columnar dendrite structure, which grew epitaxially along the deposition direction. Moreover, some inter metallic phases such as Laves phase, minor MC (NbC,TiC) carbides and needle-like δ-Ni_3Nb were observed in γ-Ni matrix. The study analyzed the precipitation mechanism and distribution characteristics of these inter metallic phases in the as-deposited 625 alloy sample. In order to evaluate the mechanical properties of the deposits, micro hardness was measured at various location(including transverse plane and longitudinal plane). The results revealed hardness was in the range of 260-285 $HV_0 \cdot _2$. As a result, micro hardness at the interface region between two adjacent deposited layers was slightly higher than that at other regions due to highly refined structure and the disperse distribution of Laves particles.

According to previous researches [20] the current state of research about composite coatings created by means of the plasma transfer method. Regarding their research were discussed and compared. The increasing industrial use of composite layers on the surface of components is due to their excellent properties, including tribological characteristics, but also their favourable design parameter, which is their high strength to weight ratio.

Also, composite surface welds obtained by means of the PPTAW technique have high quality, and their properties such as hardness and abrasive wear resistance are superior to the substrate material, which usually consists of iron alloys as well as nickel and cobalt, aluminium and titanium. These are generally coatings reinforced with carbides of transition metal or borides. The high properties of these coatings are due to the presence of hard phase particles in the metallic matrix.

Results indicate that laser cladded Inconel 625 coating has finer microstructure, alleviated segregation of Mo and Nb and lower dilution of iron compared with arc welded one as revealed by XRD, SEM and EDS results. The hardness profile at room temperature can be divided into four regions, namely coating zone, iron dilution zone, heat affected zone and substrate. Laser cladded Inconel 625 coating has slightly higher hardness in coating zone, whereas much higher hardness in iron dilution zone, indicating that iron distribution plays important role in the hardness. At elevated temperatures, the hardness of laser cladded Inconel 625 coating is higher due to finer microstructure and alleviated segregation. The wear test results show that abrasive wear is apparent at room temperature, whereas adhesive wear is dominant at elevated temperature. In comparison, laser cladded coating has lower wear rate because of lower dilution of iron and higher hardness. Therefore, laser cladded Inconel 625 coating is preferred due to its better mechanical performance at both room and elevated temperature.

Pulsed plasma arc deposition (PPAD) was successfully used to fabricate the Ni-based super alloy Inconel 625 samples [17].

The effects of three heat treatment technologies on microstructure and mechanical properties of the as-deposited material were investigated. The study found that the as-deposited structure exhibited homogenous cellular dendrite structure, which grew epitaxially along the deposition direction. Moreover, some intermetallic phases including Laves phase and MC carbides were precipitated in the region as a result of Nb segregation. Compared with the as-deposited microstructure, the direct aged (DA) microstructure changed little except the precipitation of hardening phases γ' and γ'' (Ni_3Nb), which enhanced the hardness and tensile strength. But the plastic property was inferior due to the existence of brittle Laves phase. After solution and aging heat treatment (STA), a large amount of Laves particles in the interdendritic regions were dissolved, resulting in the reduction of Nb segregation and the precipitation of needle-like δ (Ni_3Nb) in the interdendritic regions and grain boundaries. The hardness and tensile strength were improved without sacrificing the ductility. By homogenization and STA heat treatment (HSTA), Laves particles were dissolved into the matrix completely and resulted in recrystallized large grains with bands of annealing twins. The primary MC particles and remaining phase still appeared in the matrix and grain boundaries. Compared with the as-deposited sample, the mechanical properties decreased severely as a result of the grain growth coarsening. The failure modes of all the tensile specimens were analyzed with fractography. The authors in [23] studied recent developments in nanotechnology including current manufacturing techniques, uses of nanoscale particles, and implications for particle toxicity and human exposure pathways. They reviewed the current risk assessment methods in the context of nanoparticle exposure routes and regulation for human and environmental health protection. According to their study from a risk assessment respects, environmental and human health issues need to be determined and relevant test procedures developed to address these concerns. Also, in the absence of quantitative data in these areas, a qualitative framework for risk assessment is required. [26] provides a comprehensive study of the mechanisms of wear and friction that can be achieved by careful analyses of wear products. Electron microscopy and associated spectroscopic analyses provide a powerful tool in the comprehensive characterization of wear products. Scanning electron microscopy (SEM), especially the high-resolution SEM equipped with field emission gun (FEG), can greatly increase the spatial resolution in microscopic observations as compared to Optical microscopy (OM) which is often employed to observe the wear phenomena of microstructure at micrometre scale. The study defends that, scanning electron microscope (SEM) based imaging and spectroscopic analyses are straight forward in assessing worn surfaces and wear debris, where FEG-SEM is capable of observing wear induced features in up to nano-scale, and the Back-scattered electron (BSE) imaging and energy dispersive X-ray spectroscopy (EDX) spectroscopy are applied to deal with tribo-chemical wear. transmission electron microscope (TEM) based wear mechanism study has been attributed to the successful preparation of cross-sectional worn surface samples using the ion beam milling techniques. On the prepared cross-sectional samples, TEM provides sufficiently high spatial resolution in observing wear induced microstructure changes in certain depths of the worn surface layer, including tribofilms and other types of worn surface attachments.

Relation to our work:

3.2 Running Endotoxin Test To Estimate Risk Of Using Micro/ Nano materials In Tribological Process

To improve the oil-lubricity using micro/ nano particles, a new technology was used to prepare a kind of lubricant containing titanium dioxide (TiO_2) and other micro/ nano particles. Tribological properties of this micro/ nano particles are used as an additive in base oil. Other technologies also concentrate on the possibility of adding micro/ nano particles and use it in the surface painting. The main aim of this paper lies in estimating the toxicity effect of using micro/ nano particles after solving and how to prevent the side effects of using materials in micro/ nano particles shape. By this paper we will be able to understand the theory of micro/ nano materials as a first step and after that explain the theory of tribology including wear that occurs to metal during work. As a last part will be estimation of the risk factor for utilization micro/ nano material in tribological processes by running endotoxin tests [27], [28].

3.2.1 Theory of Micro/ Nano materials

Micro particles are the particles with size ranging from 1 to 1000 micro meter and made up of either natural or synthetic polymers. Nano particles have one dimension that measures 100 nanometers or less. The properties of many conventional materials change when formed from micro/ nano particles. This is typically because these particles have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules. Micro/ Nano particles are used, or being evaluated for use, in many fields. We can mention and introduce several of the uses under development like: Applications in Medicine, applications in Energy and Electronics, applications in

Manufacturing and Materials and their effect on the environment. Classification of micro & nano particles: Micro & Nano particles can be broadly grouped into two: namely organic and inorganic micro/ nano particles. Organic particles may include carbon Micro & Nano particles (fullerenes) while some of the inorganic Micro & Nano particles may include magnetic Micro & Nano particles, noble metal Micro & Nano particles (like gold and silver) and semiconductor nanoparticles (like titanium dioxide and zinc oxide).

3.2.2 Theory Tribology And Wear Or Endurance

The proper use of process fluids or lubricants can bring a significant reduction in friction and the amount of wear, thereby leading to a reduction in power consumption and better performance from tribology perspective. During different technological operations contamination of used process fluids or lubricants occurs. Such contamination leads not only to a reduction of the lifetime of the lubricants but it can also change the functional properties and increase the health risks for operators. The quality of the process fluid is among other things influenced by bacterial attacks. The use of Micro/ Nano additives is one method for inhibiting the bacteria and improving the bio availability and stability of the technological fluids. micro Nano lubricant is a new system composed of micro/ nano metre-sized particles dispersed in a base lubricant. The doping of lubricants with micro/ nano particles is one of the ways to solve problems with the removal of bacteria, whereby improving the biological, chemical and technological stability of process fluids. As an example we could monitor the effects of doping process fluids with micro/ nano particles of silica (SiO_2), titanium dioxide (TiO_2), silver nitrate ($AgNO_3$) and ascorbic acid ($C_6H_8O_6$) on the friction coefficient and on the wear of friction pairs of Si3N4 balls against steel 16MnCr5. Experimental results with micro/ nano particles used as additives in oil lubricants show that they deposit on the friction surfaces and improve the tribological properties of the base oil, displaying good friction and wear reduction features, even at low concentrations. Inter alia, titanium dioxide (TiO_2) micro/ nano particles as lubricant additive were studied with much more attention, because of their good performance on anti-oxidant features, relatively low toxicity, pleasant odor, and non-volatility. We would like to understand more clearly how the TiO_2 nanomaterial will react after adding it to lubricating oil. Titanium (Ti) atoms of TiO_2 coordinate with either two or three oxygen atoms (O) to form TiO_2 or Ti_2O_3 groups, so they are hybridized to a planar or three dimensional structure. Such structure units can comprise several different typical groups through various combinations, which lead to a structure more complex and cause the difficulty of surface modification of TiO_2. However, the transfer and adhesion of the micro/ nano particles accelerates surface modification, self-reduction, and the formation of a fine TiO_2 tribofilm that reduced the coefficient friction, pressure, and temperature in contact area and hence wear. Thus, it can be concluded that both methods (listed above) are classical and have their own defects (the addition of dispersant or usage of surfactant into base oil) for solving the oil solubility of TiO_2 micro/ nano particles.

According to many researches which approve that the nano material TiO_2 is a suitable material for reducing tribological disadvantages, we will concentrate on the side effect of using this material and its risk factors utilization of micro/ nano material TiO_2 in tribological Processes.

3.2.3 Harmlessness Tests (Health Safety) Utilization Of Micro/ Nano materials

The safety of micro/ nano materials has become a crucial question in the last few years, particularly as the number of consumer products containing them has been rising every year. The fact that micro/ nano materials, by definition, are materials that have a size comparable to biomolecules (e.g. proteins, DNA) raises the question of their safety. Could nanomaterials interact with biomolecules in an adverse manner, triggering a toxic effect? Could nanomaterials pass protection barriers in cells? What happens when materials containing micro/ nano particles reach landfills and degrade? Will micro/ nano materials be dispersed in the environment? In what dose? Could this cause harm to ecosystems?

It would be incorrect to say that we know nothing about the toxicological properties of micro/ nano materials. In the last years, a wealth of information has been collected and reported by authoritative research groups. What it is not clear is how relevant these results are for humans, since not all tests according to standards have been conducted in vitro for all used micro & nano particles. Researches so far has mainly focused on two groups of materials: carbon-based micro/ nano materials (carbon nanotubes and fullerenes) and metal or metal-oxide nanoparticles (e.g. ultrafine titanium dioxide, TiO_2). Several studies seem to indicate that some forms of carbon nanotubes show pulmonary toxicity and that this depends on the production method and the length and surface properties of the carbon tubes. Similarly, TiO_2 has been reported to cause inflammation in the lungs when inhaled in high doses. These results guide us to one fact that whole nano technology society should cooperate together to fulfill all requirements and to estimate the risk factor for micro & nano particles usage. To go more deeply in this issue, first we should recognize that before a full assessment of nanomaterial toxicity can proceed, some fundamental issues need to be resolved.

1. The need for a definition of micro/ nano material is crucial. It is not just a matter of nomenclature; it is, more importantly, a matter of defining what 'cut size' should be considered in Nano-toxicology. It is a common belief among toxicologists that the

conventional scale 1–100 nm now used to define a nanomaterial in Nano-toxicology is not exhaustive, as nanomaterials often aggregate or agglomerate in larger particles with dimensions ranging from hundreds of nanometers to microns.

2. The reference materials must be defined and fully characterized, which means deciding what standard measuring methods to use (or, possibly, developing new ones, if the existing ones prove inadequate).

3. It is important to test materials pure and free from contamination.

4. The medium used to disperse the micro/ nano material during the toxicological testing is crucial. For example fullerenes are best dispersed in calf serum, whereas they cannot be dispersed at all in water. Lack of dispersion can lead to false results or confused toxicological results: therefore, it is essential that dispersion media are defined for each micro/ nano material to be tested.

Based on these facts and in parallel with following standards (for example: ČSN EN ISO 29701)[1]. We would like to introduce a way for testing toxicity of using micro & nano particles.

Standard LAL test according to ČSN EN ISO 29701: Endotoxins (lipopolysaccharides LPS) are part of the outer membrane of the cell wall of Gram-negative bacteria such as E. coli, Salmonella, Shigella, Pseudomonas, Neisseria, Haemophilus. Endotoxins can cause a variety of systemic reactions in mammals, including humans, such as fever, disseminated intravascular coagulation, hypotension, shock and death: the responses are mediated by production of various kinds of cytokines, activation of the complement cascade, activation of the coagulation cascade, etc.

Endotoxins are present in the ordinary environment. Since most test samples of nanomaterials intended for in vitro and in vivo test systems require various preparation procedures, endotoxins might contaminate the test nanomaterials if the samples are prepared without special care. For the purpose of toxicity screening or biocompatibility testing of nanomaterials, or mechanism studies on the possible toxicity induced by nanomaterials, various cell-based in vitro test systems and in vivo animal models are being developed and employed.

In in vitro test systems, macrophages and other relevant mammalian cells are frequently used as the test cells especially for nanomaterials because they are primarily the responsible surveillance cells in the body. However, these cells are highly reactive to endotoxins; therefore it is difficult to distinguish the response to endotoxins from that to nanomaterials. Consequently, contamination by endotoxins would confound the result of

[1] https://www.unmz.cz/

tests in vitro. Contamination by endotoxins of test samples may be reduced if appropriate precautions are followed in preparation of the test sample. Therefore the preliminary detection of endotoxins is required to minimize the contamination by endotoxins or confirm the insignificant levels of endotoxins in the test sample. It is also important to quantify endotoxin levels for the adequate interpretation of data obtained by in vitro biological test systems.

Since endotoxins may contaminate medical devices and medicines for parenteral use, quantitative and semi-quantitative assay methods to test for endotoxins both in vivo and in vitro have been developed and used for regulatory purposes as well as laboratory standard operational procedures for nanomaterials.

The bacterial endotoxin test using Limulus amebocyte lysate (LAL) reagent has been developed as an in vitro assay method to test for the presence of endotoxin contamination as an alternative to the pyrogenicity test using rabbits, and methods are described in the pharmacopoeia of many countries.This International Standard provides considerations for the application of the LAL test to nanomaterial samples intended for in vitro biological tests. To have a clear idea about what is LAL test main idea, Endotoxins activate a factor in the LAL and trigger a proteolytic cascade.

The clotting enzyme, which is released from the proclotting enzyme by one of the activated factors, catalyses a proteolysis of coagulogen in the LAL and the resulting fragments, coagulins, spontaneously bind to each other through disulfide linkage to develop the turbidity of the LAL and finally form a gel-clot. The gel-clot formation is principally determined by visual inspection after inverting test tubes. This method requires no optical reader and the procedures are easy to perform. The most sensitive gel-clot method using commercially available reagents measures 0,015 EU/mL.

3.2.4 Endpoint Photometric Method

The optical density (OD) of the reaction mixture is measured after a certain period of reaction time. With regard to endpoint photometric methods, there are two techniques; the turbidimetric technique measuring the turbidity of the reaction mixture and the chromogenic technique measuring p-nitroaniline (p-NA) liberated from a synthetic substrate, such as Boc-Leu-Gly-Arg-p-NA or Boc-ThrGly-Arg-p-NA for the clotting enzyme. There are at least two procedures for measuring p-NA in the reaction mixture:

- one measures the OD of p-NA directly at a wavelength of 405 nm, and
- the other measures the diazotized magenta derivative of p-NA photometrically at a wavelength of between 540 nm and 550 nm.

The sensitivity of endpoint photometric method using commercially available reagents by measuring the OD at a wavelength of 405 nm is 0,01 EU/mL while that of the diazo-coupling method is 0,001 EU/mL.

3.2.5 Kinetic Methods

The time required to reach the predetermined OD of the reaction mixture or the rate of colour or turbidity development is determined by an optical reader. With regard to kinetic procedures, the OD of p-NA liberated from the synthetic peptide stated above or turbidity of the reaction mixture is read at multiple time points as the reaction proceeds, and thus several types of automated instruments have been developed. To detect endotoxins more precisely and accurately with kinetic methods, sophisticated automated instruments are necessary. The best sensitivity of the kinetic method using a commercially available automated instrument is 0,001 EU/mL.

3.2.6 Summary

After presenting all of these facts we can say that we live in a world where ‘saving energy’ and ‘cost cut down’ are two important notions. The tribological issue involves both, i.e., friction = energy loss and wear = increase in maintenance costs. Both friction and wear can only be mitigated, never eliminated.

Nanostructured coatings serve as good alternatives to the conventional materials thanks to their superior mechanical and tribological properties. Industrial data on the performance of nanostrucutured coatings in the field are still scarce. More tribological data illustrating their superior reliability compared to current industrial benchmarks are needed to establish confidence in the technology among end users. The search for optimum materials with multifunctional properties will continue. Features such as selfhealing, smart coatings capable of adjustment based on tribological needs, and compatible surfaces with an affinity towards lubricant additives are some promising research avenues.

From other hand we have to concentrate more often on risk factor before, during and after utilization of nanomaterials for raising the efficiency of tribological phenomenon. LAL test results indicate that nanoparticles (TiO_2, Ag, CaCO3, SiO2) can interfere with certain endotoxin detection methods (gel clot LAL assay, endotoxin extraction protocol), while other assays (chromogenic-based LAL assay, TLR4 reporter cells) are not hampered. Dependent on the particle and its concentration used, a convenient endotoxin detection test method must be chosen [27].

3.3 Risk factors for B4C composite utilization in tribological processes

Tremendous development has been done for tribology in manufacturing, in the past 100 years, to transform this phenomenon from a known and unavoidable nuisance to a sophisticated discipline, there is still many new challenges coming up due to upcoming scientific achievements. One of these challenges is materials' wear resistance increasement and higher friction avoidance. Therefore new studies and ideas have been done with approach to either improve material resistance or having new lubrication fluid formulas.According to various experiences and areas of application, tribological coatings play a key role in the performance of mechanical components and products by reducing wear and friction, increasing the life of the working material and reducing energy dissipation as heat, thus increasing the efficiency of the moving.This research will take proper use of PTA coatings as case study, which can significantly reduce friction and wear, leading to reduced energy consumption and extended service life. [29]

Studied material will be cermets based on B4C particles in Ni-based matrix. A tribology analyze for wear, abrasion, resistance of plasma deposited cermets, will be concluded with target to show impact of these phenomenon on industrial tribology and related processes on the environment.

Goal of this case study, is collecting discharged particles from tribology tests and prepare a risk Assessment. The estimation of risk factor for plasma-welded material on tribologically treated surfaces will be shown by possible impurities generated during this process on the environment and possible proof improvement for wear resistance.

Based on Agency of European Union regulations and standards, hazard classifications and labelling for produced particles needs to be shown and necessary treatment after tests running will be required also to be considered as research future work.

Cermets, as promising material to be used in tribological applications, has been studied and analyzed with target to show, summarize and estimate risk factors, produced by combining Nickel alloys 625 and Boron Carbide particles in plasma powder transferred arc welding (PPTAW).

Till date, Cermets, including Ni 625 and B4C, are nowadays reaching a great level of development, to prove its optimal properties, Boron Carbides (B4C) ceramic, as high temperature resistance and hardness material and Inconel® metal, as corrosion resistant material, high yield and tensile, high temperature strength, excellent weld ability and creep strength.

These optimal properties bring improvement to tribological properties, wear resistance and friction factor, as advantage. Nevertheless, from other hand, general overview for disadvantages, which could be brought by this usage, need to be considered here by risk assessment.

3.3.1 2.1 Inconel 625 samples preparation

Samples were deposited by a manually controlled procedure, with a commercially available plasma hard facing automate PPC 250 R6 according to to fixed parameters (Peak current 100 [A], Pulse frequency 28.7 [Hz], Welding speed 0.4 [m.min^{-1}], Powder filler material 1.5 [g.min^{-1}], Oscillation 28 [mm] by 28 [mm.s^{-1}]). One layer coating (Ni 625 70

3.3.2 Samples heat treatment before tribology test

Heat Treatment is necessary for the precipitation of strengthening phases and improvement of the mechanical properties. Therefore a detailed conditions of applied heat treatment method is:

Step 01 aging: Heat to 720^{o}C during 180 [min], hold for 8 [h], furnace cool to 620 ^{o}C, hold for 8 [h], air cool.

Step 02 solution:Heat to 980^{o}C during 180 [min], hold for 1[h], air cool.

Due to fact that samples surface is rough and would make a high deformation during tribology test. Grinding for samples' surface was done to make surface suitable for testing applications.

3.3.3 Surface roughness / Friction coefficient

Two roughness parameters namely average roughness [Ra] and mean peak to valley height [Rz], which are used to determine quantities surface characteristics of the panels, were measured. Showing three measuring points on the same horizontal line. Each one of these measuring points has 1 [cm] length.

Result of surface roughness of the parts before and after heat treatment are the same. No remarkable differences according to figure 3.1

Table 2 – Surface roughness values

Measuring Point			1		2		3	
Axis	Surface Polishing	HT	Ra [µm]	Rz [µm]	Ra [µm]	Rz [µm]	Ra [µm]	Rz [µm]
X	Yes	Yes	1.4275	11.78	1.595	13.06	1.8575	14.76
Y	Yes	Yes	2.025	14.6575	2.2325	14.2	2.415	15.9675
X	Yes	No	1.0475	10.6775	1.05	9.65	1.745	15.1825
Y	Yes	No	1.9525	14.385	2.17	17.8575	2.32	16.3675

Figure 3.1: Inconel 625 Samples prepared by PTA

3.3.4 Ball on flat disk Tribology Test

Measured distance 30 [mm], Velocity: 1 [mm/s], Acceleration: 0.1 [s], Duration: 30 [min], Force 10 [N]. By running this test. The friction coefficient, of Inconel with B4C composite welded by PTA deposits without heat treatment, was (0.166) lower than heat-treated samples (0.30675).

3.3.5 Tribometer dry test

Tribometer or Tribotester is a generic name for a device, which is used to simulate friction and wear at the interface between surfaces in a relative motion under controlled conditions.

Tablet on Plate (Disk) Linear Reciprocating For this test, it is needed to have Disk and Tablet. Tablet will be fixed with applied load on it, while disk connected to motor to give the Linear Reciprocating movement.

One Disk was cut by using cutting machine square shape 1 [cm2].Cutting disk with cutting machine square shape 1 [cm2] Tribometer test performed into these parameters:

1. Applied load on disk: 3 [Kg] 2. Speed: Stroke (Step): 2*35 [mm]

Main target of this test is to measure tablet weight during test running to recognize how much material we lose and how big is wear rate for this material.

First study case, heat-treated tablet vs heat-treated disk. Test lasted for 1335min and during this time, 15 measurements were conducted for tablet's weight.

Second study case, non-heat treated tablet vs heat-treated disk. Test lasted for 1620min and during this time 13 measurements were conducted for tablet's weight,

Figure 2 shows heat treated tablet vs Heat treated disk: discharged material as average 0.00036 [gram] / 120 [min]

Figure 3 shows Non Heat treated tablet vs heat treated disk: discharged material as average 0.00026 [gram] / 120 [min]

3.3.6 Confocal Microscopy Particles Analyze After Test

This thesis demonstrates the potential of confocal laser scanning microscopy (CLSM) as a characterization tool for different types of micro and nano particles. Micro/ Nano particles were prepared by collecting particles produced from Tribometer testing equipment. This technique can be used to determine the shape and outer structure of the micro/ nano particles;

Nevertheless, it has certain limitations when used for this analysis of the particles' internal structure. Observed photos and analyze from this technique will give remarkable traces for micro nano sized particles existence. Observed projection views produced from a series of optical sections pro-vides gave important information about a three-dimensional specimen than a multi-dimensional view, including mapping and distance for dimensional points.

As result of confocal microscope analyze and measuring size of existing particles, comparing to measurement scale. An existence of micro nano particles (1 to 100 nanometers) is clearly noticeable by this analysis.

As conclusion an investigation to the tribological behavior of cermets B4C/ Ni alloys 625, as a promising composite to reduce friction, material loss and increase wear resistance. Study was fulfilled under special conditions of heat treatment and different methods of tribology testing methods were done. Further investigation behind the advantages and disadvantages of these materials on industrial tribology and related processes on the environment. Particles analyze was done by different methods, starting with Confocal microscope as first step and electro-microscope as second step. Findings from this study:

1- Existence of micro nano particles was noticed clearly by confocal.

2- Samples with heat treatment has higher average material loss during tribology test.

3- Micro Nano sized Cobalt particles were noticed in particles produced by tribology test (variant heat-treated disk vs heat-treated tablet) more than variant (heat-treated disk vs non heat-treated tablet).

4- Micro Nano sized Nickel particles were noticed in particles produced by tribology test.

Chapter 4

Experiments And Results

Following the theoretical background of tribology, cermets and risk assessment, in this section a practical view into samples preparation, running required tests, observing results and analysing these results will discussed clearly.

Depending on fact that tribology, nowadays, plays a key role in manufacturing technologies, by showing and improving production efficiency and performance.

On other hand it is can not be avoided or hidden the negative impact which we would have here as humankind from these processes, in a form of discharged materials produced by tribological phenomenon.

Therefore a high concentration is required here to show what impact does it have and such concentration will be formalized as risk assessment. This risk assessment will be main part of this thesis by showing a clear study case which was not studied before in scientific committees and was not clearly estimated for these cermets in tribological fields.

Several practical applications are implemented on real-time engineering processes in the proceeding chapter, to justify its use for real industrial applications. In addition a top punch technologies have been used here in this thesis to analyse particles after testing including Confocal/ Electro microscope to demonstrates the effectiveness of having cermets (Ni625 and B_4C) in tribological applications.

4.1 Inconel 625 Samples Preparation

Samples were deposited by plasma transferred arc (PTA) using the Nickel-based super alloy Inconel 625, manually controlled procedure, with a commercially available plasma hard-facing automate PPC 250 R6 (KSK, s.r.o., Czech Republic) in a tight chamber. Used machine is designated for glass industry applications, mainly for hard-facing of glass mold edges. The hard-facing automate can work with plasma current pulses up to 200 Hz between 50 and 250A with 30 percent B_4C and 70 percent Ni625 alloys. [16] [30]. See figure 4.1

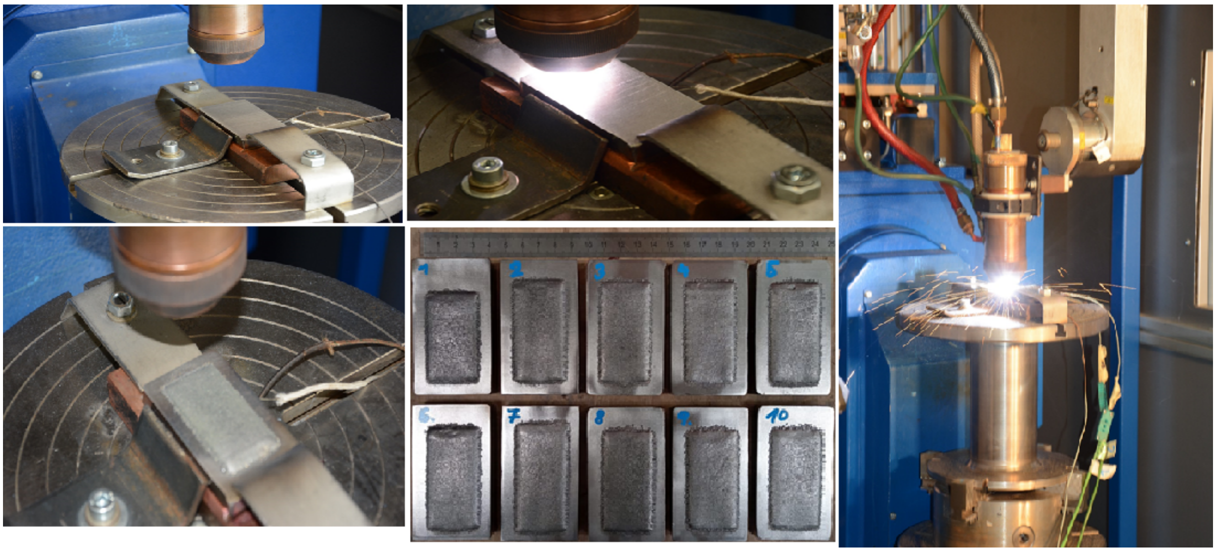

Figure 4.1: Inconel 625 Samples prepared by PTA

Chosen parameters for study experiment in figure 4.2 :

Parameters	**Peak current I_P (A)**	**Background current I_b (A)**	**Pulse frequency f (Hz)**	**Duty cycle (%)**	**Welding speed (m/min)**	**Powder Filler material (g/min)**	**Oscillation**
Value	100	45	28.7	-	0.4	1.5	28mm by 28 mm/s

Figure 4.2: Processing parameters of pulsed plasma arc deposition

4.2 Temperature Measurement During Samples Preparation

Manufacturing of 3D-parts by plasma transferred arc (PTA) powder deposition process involves repeated heating and cooling processes at the same location causing thermal distortion and residual stresses in the substrate and deposited material.

Samples' temperature were tracked during this preparation, so that a clear understanding clarified by temperature diagram, showing which tempo-behaviour can be shown here in a diagram and how it will affect samples quality.

Therefore, pre-heating was used to the working piece and measured by Tempo measuring points T1, T2, and T3. These measuring points where attached to samples according to figure 4.3.

Welding procedure took from 2 to 6 min. During this waiting time the temperature of the work piece increased rapidly to reach maximum limit approx. 900oC on T1 point [15].

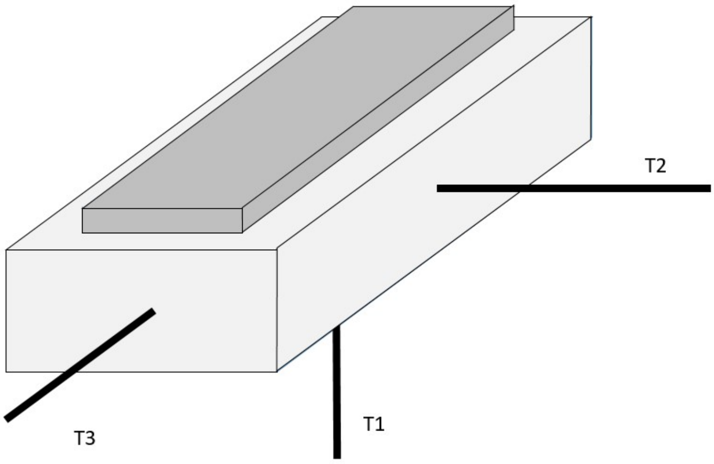

Figure 4.3: Attached Temperature Measuring Points on testing samples

Welding process was continuous and no fast decreasing temperature of the work piece was obtained. temperature change was the biggest for the deposits welded with welding parameters T1, because of high heating temperature, up to 900 °C.

Figures 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 4.10, 4.11, 4.12 and 4.13 show the Temperature Diagram during PTA application on Cermets on ten samples.

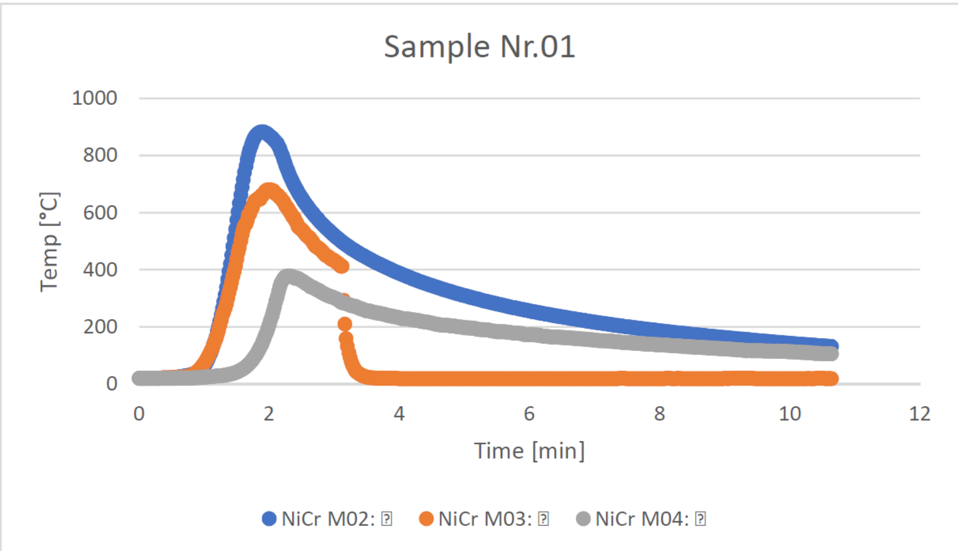

Figure 4.4: Temperature Diagram during PTA application on Cermets

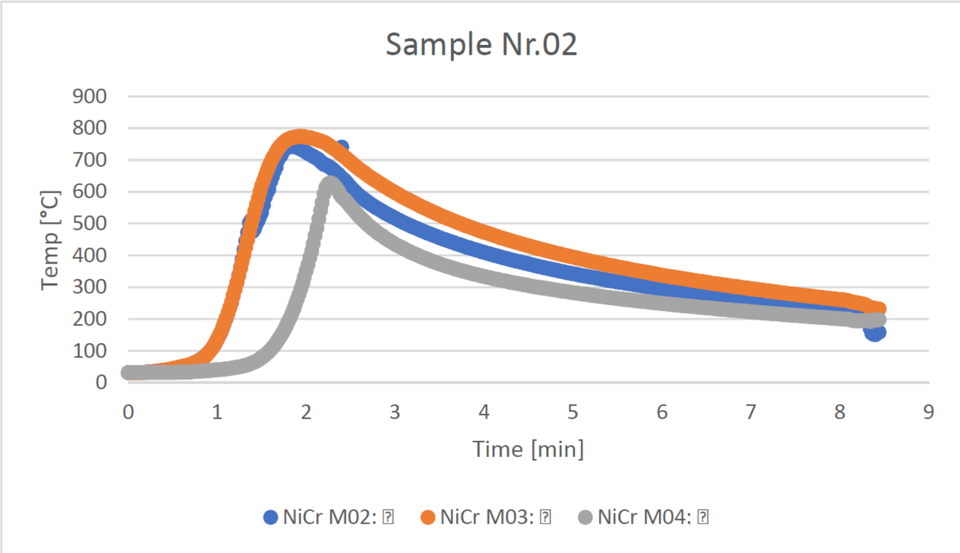

Figure 4.5: Temperature Diagram during PTA application on Cermets

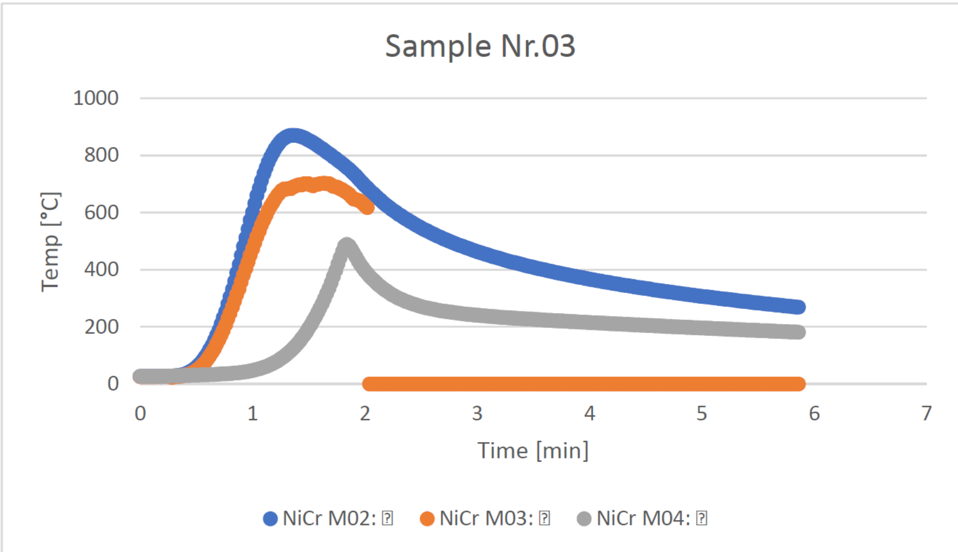

Figure 4.6: Temperature Diagram during PTA application on Cermets

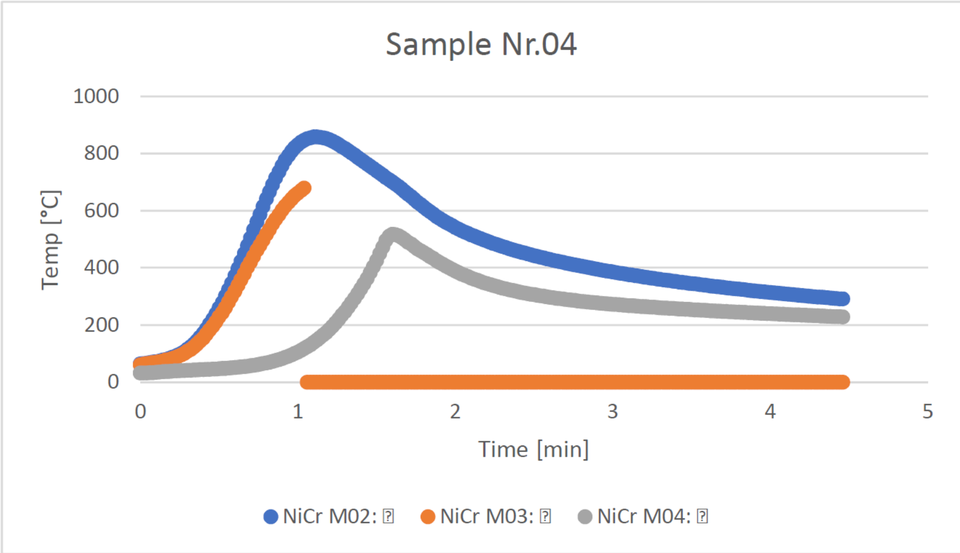

Figure 4.7: Temperature Diagram during PTA application on Cermets

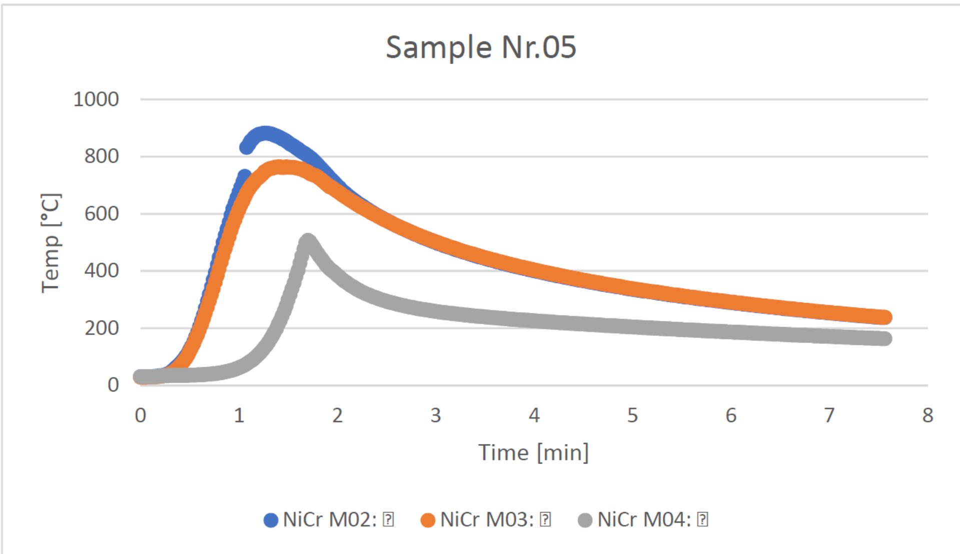

Figure 4.8: Temperature Diagram during PTA application on Cermets

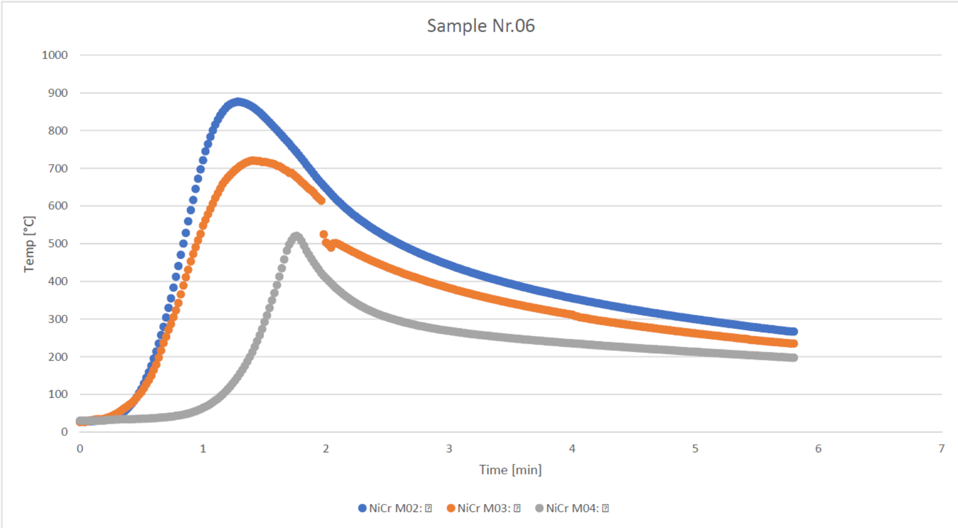

Figure 4.9: Temperature Diagram during PTA application on Cermets

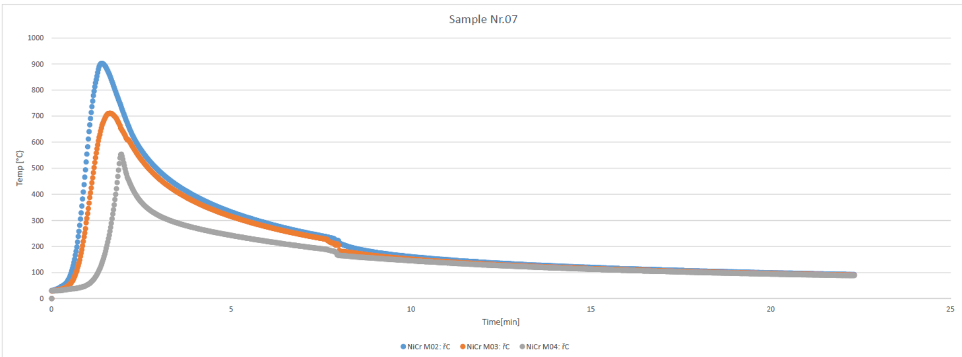

Figure 4.10: Temperature Diagram during PTA application on Cermets

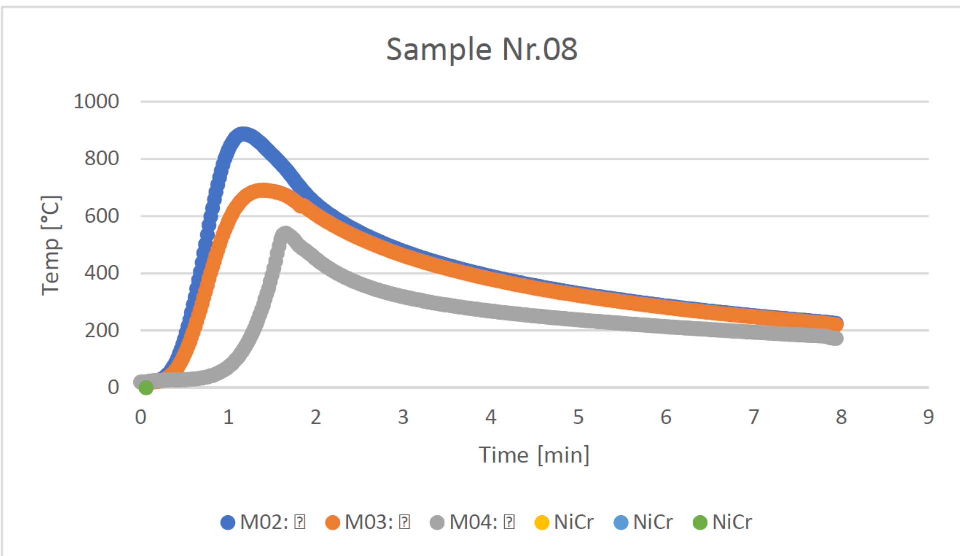

Figure 4.11: Temperature Diagram during PTA application on Cermets

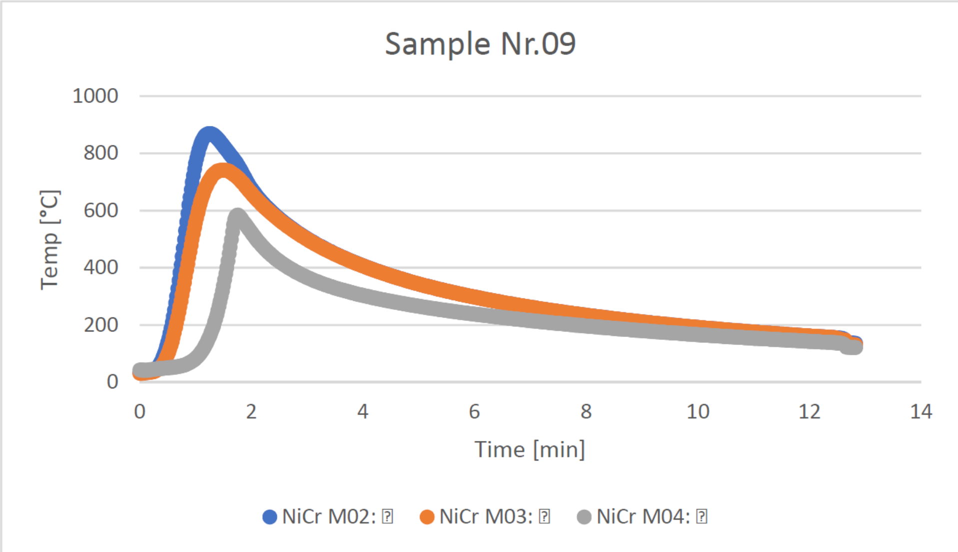

Figure 4.12: Temperature Diagram during PTA application on Cermets

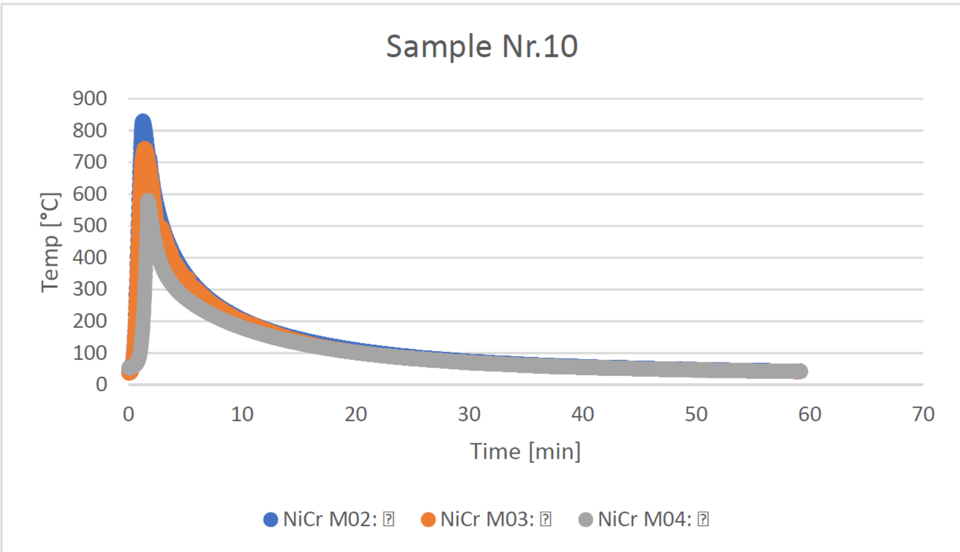

Figure 4.13: Temperature Diagram during PTA application on Cermets

By analyzing temperature diagram for T1 measuring point, see figure 4.14. Duration of time between preheating up to 300oC and getting back to same temperature after passing arc weld on sample, takes between 3.6-5.36 min depending on processing parameters.

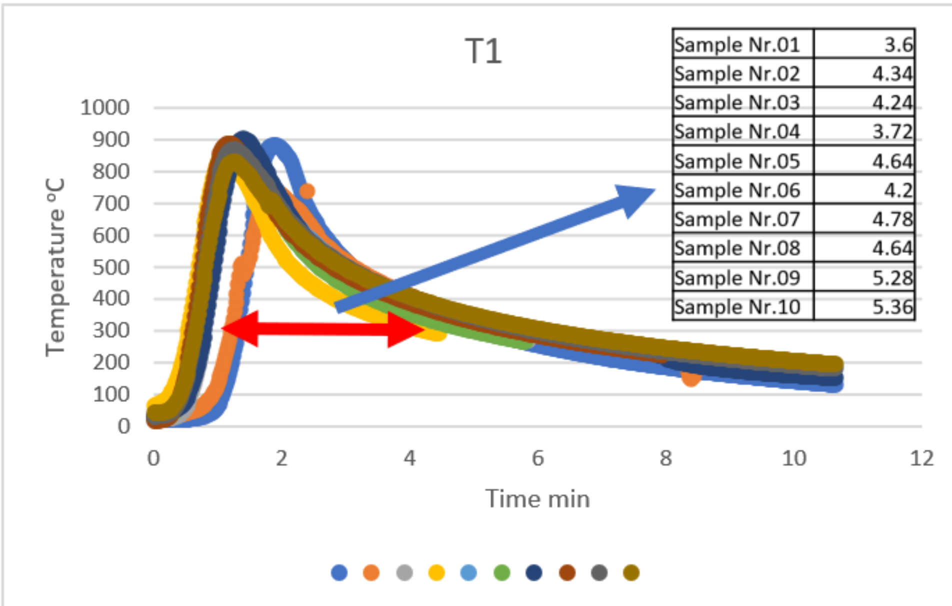

Figure 4.14: Time difference on 300oC for all Samples

4.3 Testing Samples Heat Treatment Before Tribology Test

According to previous studies, heat Treatment is necessary for the precipitation of strengthening phases and improvement of the mechanical properties. therefore a detailed conditions of applied heat treatment method is listed in Figures 4.15 and 4.16 [11], [12], [15].

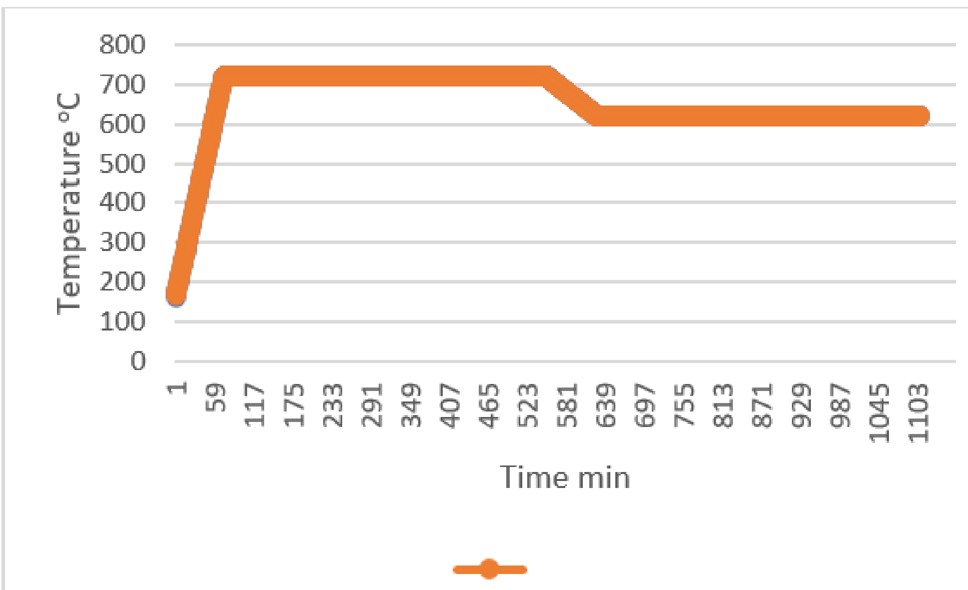

Figure 4.15: Heat Treatment Plan

Step 1 aging	Heat to 720°C during 180 min, hold for 8h, furnace cool to 620 °C, hold for 8h, air cool
Step 2 solution	Heat to 980°C during 180 min, hold for 1h, air cool

Figure 4.16: Heat Treatment Plan Steps

4.4 Polishing and Samples Preparation For Tribology Test

Due to fact that samples surface is rough and would make a high deformation during tribology test. Polishing/grinding for samples' surface was done to make surface more smooth and suitable for testing applications, figure 4.17, 4.18.

Figure 4.17: Parts polished and prepared for tribology test

Sample	Axis	Grinding	HT
1	X	No	Yes
	Y	No	Yes
2	X	Yes	Yes
	Y	Yes	Yes
3	X	Yes	Yes
	Y	Yes	Yes
4	X	Yes	Yes
	Y	Yes	Yes
5	X	Yes	Yes
	Y	Yes	Yes
6	X	Yes	No
	Y	Yes	No
7	X	Yes	No
	Y	Yes	No
8	X	No	No
	Y	No	No
9	X	Yes	No
	Y	Yes	No
10	X	Yes	No
	Y	Yes	No

Figure 4.18: Samples for tribology test

4.5 Tribology Test

4.5.1 Roughness Measurement

To predict the two roughness parameters namely average roughness (Ra) and mean peak to valley height (Rz) which are used to determine quantities surface characteristics of the panels, we measure these two parameters according to 4.19. Showing three measuring points on the same horizontal line. Each one of these measuring points has 1cm length.

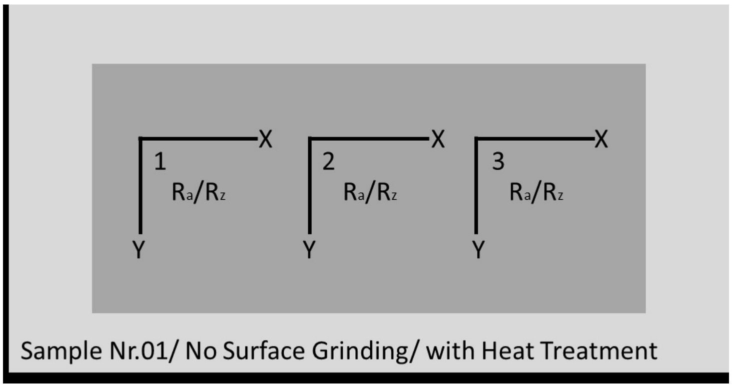

Figure 4.19: Surface roughness measuring points

According to figures 4.20 and 4.21, Ra, Rz values have similar average values.

			Measuring Point	1		2		3	
Sample	Axis	Surface Polishing	HT	Ra µm	Rz µm	Ra µm	Rz µm	Ra µm	Rz µm
1	X	No	Yes	8.72	46.61	10.87	65.66	9.77	46.24
	Y	No	Yes	11.4	62.2	8.28	45.12	8.99	54.3
2	X	Yes	Yes	0.73	6.65	1.39	11.95	0.91	7.22
	Y	Yes	Yes	1.46	10.74	1.89	13.3	1.5	11.11
3	X	Yes	Yes	1.34	10.12	1.72	12.34	2.82	20.51
	Y	Yes	Yes	2.21	18.14	3.04	18.35	2.49	17.53
4	X	Yes	Yes	2.22	14.54	1.87	14.02	1.19	9.35
	Y	Yes	Yes	2.49	14.9	1.81	11.11	2.79	17.04
5	X	Yes	Yes	1.42	15.81	1.4	13.93	2.51	21.96
	Y	Yes	Yes	1.94	14.85	2.19	14.04	2.88	18.19
6	X	Yes	No	1.4	13.35	1.75	16.23	1.39	11.9
	Y	Yes	No	1.76	14.65	1.93	14.86	2.48	18.63
7	X	Yes	No	0.71	8.92	0.87	7.5	2.54	19.48
	Y	Yes	No	1.82	14.26	1.77	15.92	2.69	17.96
8	X	No	No	12.45	65.22	9.65	47.53	9.23	52.37
	Y	No	No	9.92	52.36	14.17	69.08	9.81	55.45
9	X	Yes	No	1.25	8.6	0.55	5.43	1.5	15.73
	Y	Yes	No	2.61	16.5	2.55	23.02	1.4	11.34
10	X	Yes	No	0.83	11.84	1.03	9.44	1.55	13.62
	Y	Yes	No	1.62	12.13	2.43	17.63	2.71	17.54

Figure 4.20: measuring points on Testing samples

Measuring Point			1		2		3	
Axis	Surface Polishing	HT	Ra µm	Rz µm	Ra µm	Rz µm	Ra µm	Rz µm
X	Yes	Yes	1.4275	11.78	1.595	13.06	1.8575	14.76
Y	Yes	Yes	2.025	14.6575	2.2325	14.2	2.415	15.9675
X	Yes	No	1.0475	10.6775	1.05	9.65	1.745	15.1825
Y	Yes	No	1.9525	14.385	2.17	17.8575	2.32	16.3675

Figure 4.21: Testing samples roughness values

4.5.2 Tablets Preparation For Tribometer Tribology Test

Part of tribometer test is having tablets with diameter 1*1 [cm]. This has been done by cutting one disk into these tablets, by using cutting Metallographic abrasive cutting machine, which is provided by Manufacturing Technologies department, Czech Technical University in Prague. Figure 4.23 shows prepared tribometer tablets for test.

4.5.3 Tribometer Tribology Test:

Tribometer or Tribotester is a generic name for a device which is used to simulate friction and wear at the interface between surfaces in a relative motion under controlled conditions. In this testing phase it will be needed to have tablet on plate (Disk) Linear Reciprocating. For this test we need to have Disk and Tablet. Tablet will be fixed with applied load on it, while disk connected to motor to give the Linear Reciprocating movement. See Fig.4.22. One Disk was cut by using cutting machine square shape 1 [cm^2]. See figures 4.23, 4.24, 4.25, 4.26, 4.27, 4.28

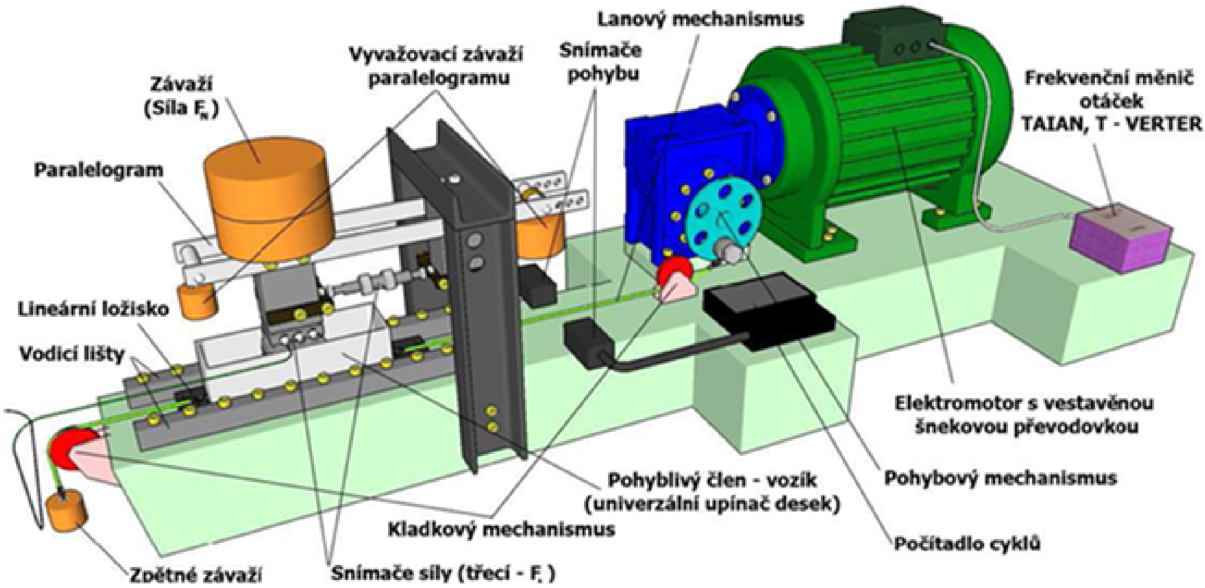

Figure 4.22: Tribometer tribology machine

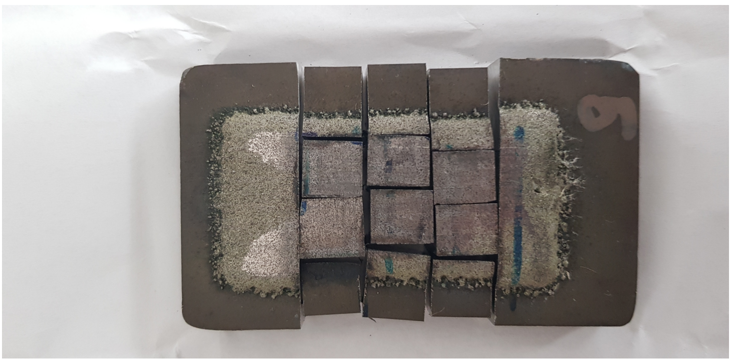

Figure 4.23: Cutting disk with cutting machine square shape (1 cm2)

Figure 4.24: Cutting disk with cutting machine square shape (1 cm2)

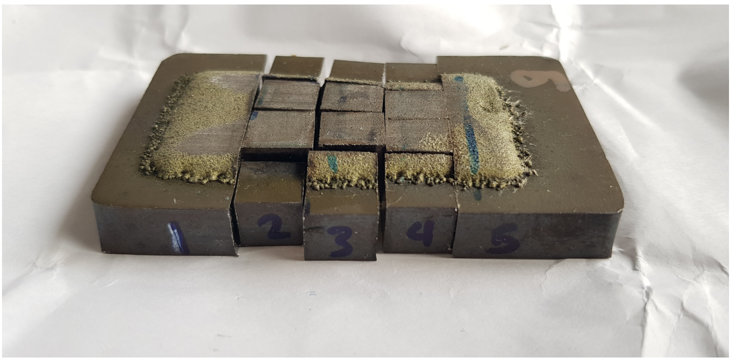

Figure 4.25: Cutting disk with cutting machine square shape (1 cm2)

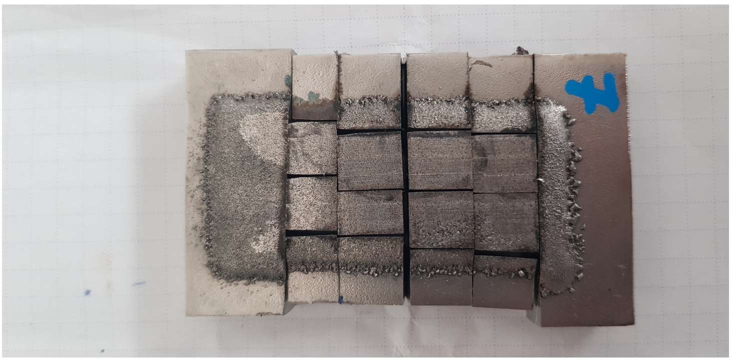

Figure 4.26: Cutting disk with cutting machine square shape (1 cm2)

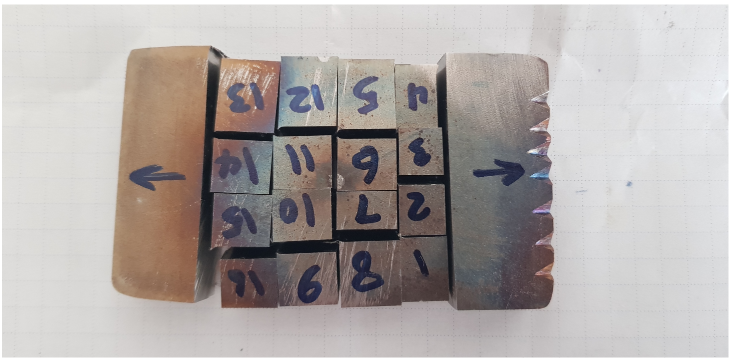

Figure 4.27: Cutting disk with cutting machine square shape (1 cm2)

Figure 4.28: Cutting disk with cutting machine square shape (1 cm2)

Tribometer test performed into these parameters:

1. Applied load on disk: 3 [Kg].
2. Speed: Stroke (Step): 2*35 [mm]

Main target of this test is to measure tablet weight during test running to recognize how much material we lose and how big is wear rate for this material. First study case, heat treated tablet vs heat treated disk. Test lasted for 1335 [min] and during this time 15 measurements were conducted for tablet's weight. Second study case, non heat treated tablet vs heat treated disk. Test lasted for 1620[min] and during this time 13 measurements were conducted for tablet's weight, figures 4.29,4.30

Tablet	Disk	Applied Force	Tablet weight before test/ Gram	Tablet weight after test Gram	Lost Martial	elapsed time
5,2,2	4	3 Kg	10.0096	10.0087	0.0009	30
5,2,2	4	3 Kg	10.0087	10.008	0.0007	60
5,2,2	4	3 Kg	10.008	10.0077	#VALUE!	105
5,2,2	4	3 Kg	10.0077	10.0074	0.0003	165
5,2,2	4	3 Kg	10.0074	10.0069	0.0005	225
5,2,2	4	3 Kg	10.0069	10.0062	0.0007	315
5,2,2	4	3 Kg	10.0062	10.0059	0.0003	405
5,2,2	4	3 Kg	10.0059	10.0056	0.0003	495
5,2,2	4	3 Kg	10.0056	10.0053	0.0003	615
5,2,2	4	3 Kg	10.0053	10.0049	0.0004	735
5,2,2	4	3 Kg	10.0049	10.0045	0.0004	825
5,2,2	4	3 Kg	10.0045	10.0042	0.0003	945
5,2,2	4	3 Kg	10.0042	10.0039	0.0003	1155
5,2,2	4	3 Kg	10.0039	10.0034	0.0005	1335

Figure 4.29: measuring heat treated tablet weight

Tablet	Disk	Applied Force	Tablet weight before test Gram	Tablet weight after test Gram	Lost Material	Elapsed Time
7,5,14	4	3 Kg	9,1214	9,1209	0,0005	90
7,5,14	4	3 Kg	9,1209	9,1204	0,0005	225
7,5,14	4	3 Kg	9,1204	9,1202	0,0002	285
7,5,14	4	3 Kg	9,1202	9,1198	0,0004	405
7,5,14	4	3 Kg	9,1198	9,1195	0,0003	585
7,5,14	4	3 Kg	9,1195	9,1191	0,0004	765
7,5,14	4	3 Kg	9,1191	9,1181	0,001	945
7,5,14	4	3 Kg	9,1181	9,1177	0,0004	1065
7,5,14	4	3 Kg	9,1177	9,1175	0,0002	1185
7,5,14	4	3 Kg	9,1175	9,1171	0,0004	1365
7,5,14	4	3 Kg	9,1171	9,117	0,0001	1485
7,5,14	4	3 Kg	9,117	9,1167	0,0003	1665
7,5,14	4	3 Kg	9,1167	9,1165	0,0002	1785

Figure 4.30: measuring non heat treated tablet weight

Heat treated tablet vs Heat treated disk: discharged material as average 0.00036/ 120 [min].

Non Heat treated tablet vs Heat treated disk: discharged material as average 0.00026/ 120 [min], [30], figure 4.31.

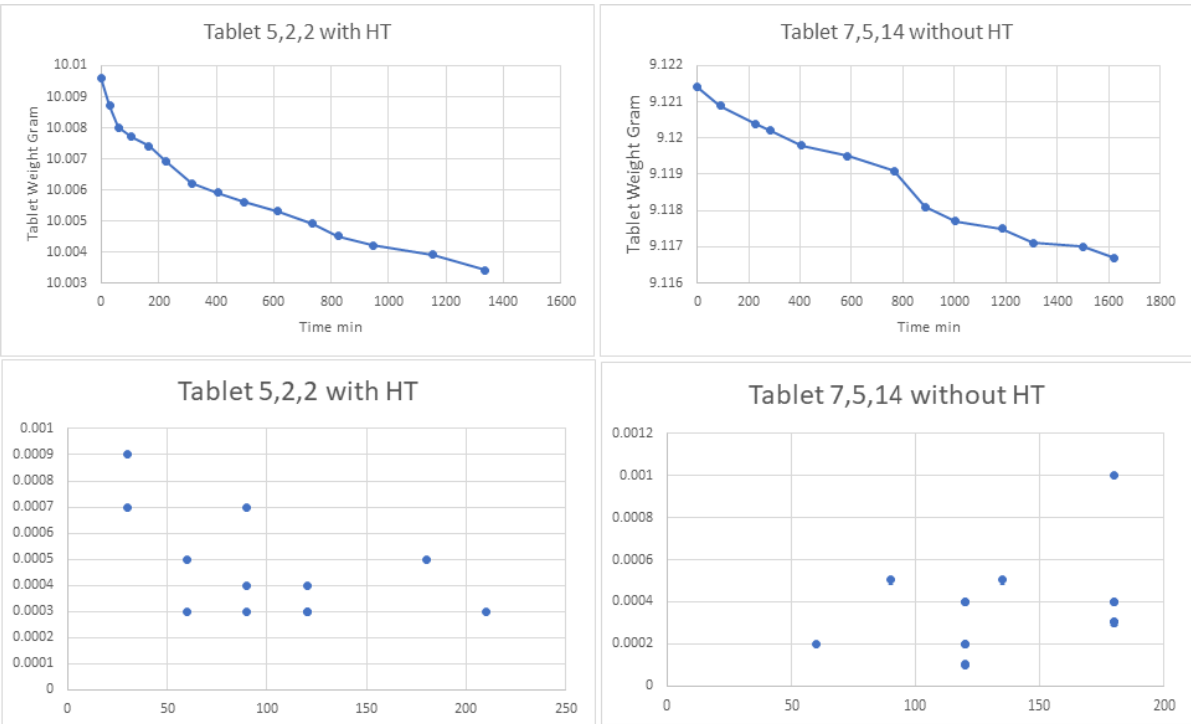

Figure 4.31: measuring tablet weight tests results

4.6 Confocal Microscope

Confocal microscopy[1] is a technique in optical imaging that uses point illumination via a spatial pinhole to eliminate out of-focus signals. The excitation light in confocal microscopy is usually provided by a laser to generate high intensities of fluorescence or reflectance from the focal spot. Fluorescence confocal microscopy is the most used in dermatology to analyze ex vivo and in-vitro samples. Reflectance confocal microscopy can be used for real-time microscopy and uses melanin as a natural contrast agent. Confocal microscopy has many advantages, including increasing the optical resolution and contrast of an image of a specimen; facilitating reconstruction of 3-D images; enabling collection of serial optical sections from thick specimens; and enabling in vivo imaging without the artifact induced by tissue processing (Pawley, 2006). In addition to LSCM, 3-D images of nonliving samples can also be acquired by SCEM, where an electron beam is used for illumination, resulting in higher resolution compared with confocal microscopy. Limitations of confocal microscopy include the depth of imaging within thick samples and cost compared with conventional microscopes. The problems of fluorescent probe photobleaching and phototoxicity inherent in conventional fluorescence microscopy are also present with confocal microscopy [31].

There has been a tremendous explosion in the popularity of confocal microscopy in recent years, due in part to the relative ease with which extremely high-quality images can be obtained from specimens prepared for conventional fluorescence microscopy, and the growing number of applications in cell biology that rely on imaging both fixed and living cells and tissues. In fact, confocal technology is proving to be one of the most important advances ever achieved in optical microscopy.

4.7 Confocal Microscopy Particles Analyze After Test

This study demonstrates the potential of confocal laser scanning microscopy (CLSM) as a characterization tool for different types of micro-particles.Micro-particles were prepared by collecting particles produced from tribometer testing equipment.

This technique can be used to determine the shape and outer structure of the micro-particles; nevertheless, It has certain limitations when used for the analysis of the internal structure of such particles [32].

Observed photos and analyze from this technique will give remarkable traces for micro & nano sized particles existence.

The following figures 4.32, 4.33, 4.34, 4.35, 4.36, 4.37, 4.38, 4.39, 4.40, 4.41, 4.42

[1]https://www.olympus-lifescience.com/en/microscope-resource/primer/techniques/confocal/confocalintro/

and 4.43 projection view produced from a series of optical sections provides important information about a three-dimensional specimen than a multi-dimensional view, including mapping and distance for dimensional points.

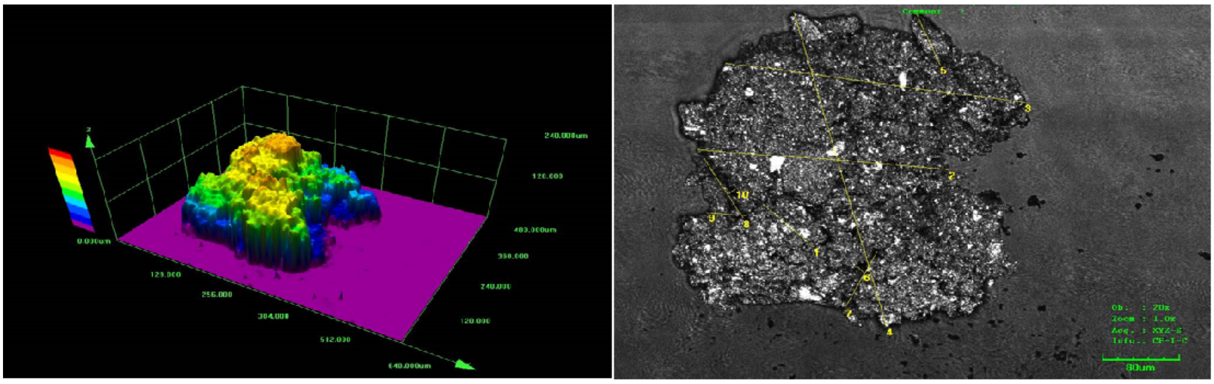

Figure 4.32: Confocal analyze for particle1

Dimension point	Judge	Length[um]	dZ[um]
1		75.6801	4.336
2		272.7893	-26.032
3		326.21	-68.088
4		399.6017	94.836
5		68.6843	41.58
6		10.6213	-46.676
7		77.4198	-117.988
8		84.823	49.74
9		40.3877	-12.572
10		9.3942	46.012

Figure 4.33: Confocal analyze for particle1 measurements

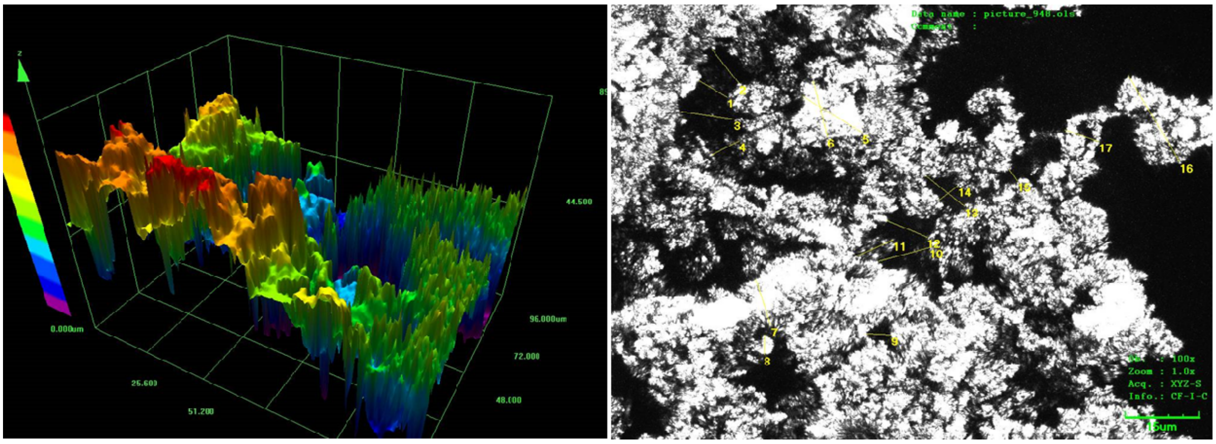

Figure 4.34: Confocal analyze for particle2

Figure 4.35: Confocal analyze for particle2 measurements

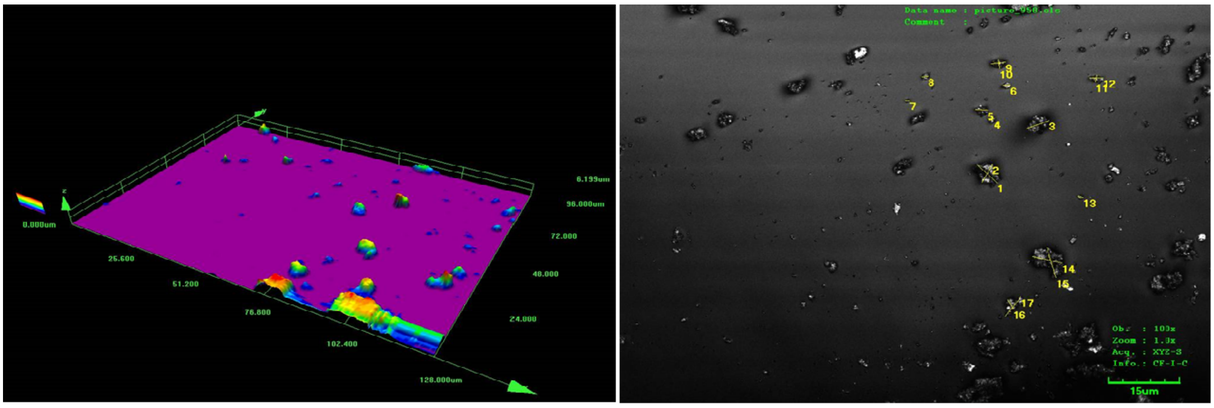

Figure 4.36: Confocal analyze for particle3

Dimension point	Length[um]	dZ[um]
1	6.2025	-0.831
2	4.9449	0.533
3	5.4845	0.328
4	1.2738	-0.096
5	2.678	-0.065
6	1.5286	0.016
7	0.8917	0.04
8	1.4069	0.198
9	3.0808	0.343
10	2.297	0.005
11	1.6683	0.216
12	2.9298	-0.208
13	1.2988	-0.005
14	6.6724	-0.119
15	7.5109	-1.224
16	2.5546	0.271
17	5.8942	0.192

Figure 4.37: Confocal analyze for particle3 measurements

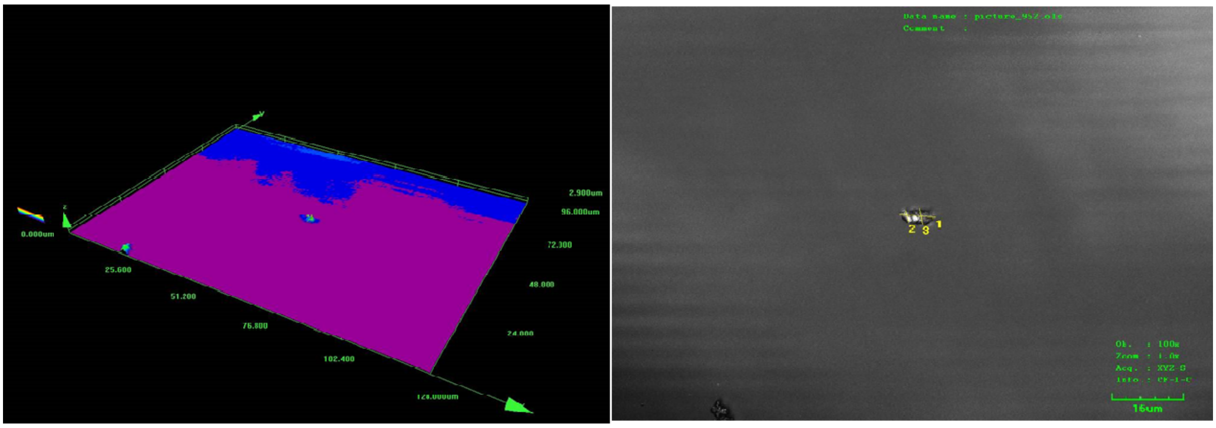

Figure 4.38: Confocal analyze for particle4

Dimension point	Length[um]	dZ[um]
1	7.8075	0.368
2	2.8619	-0.067
3	3.6078	0.042

Figure 4.39: Confocal analyze for particle4 measurements

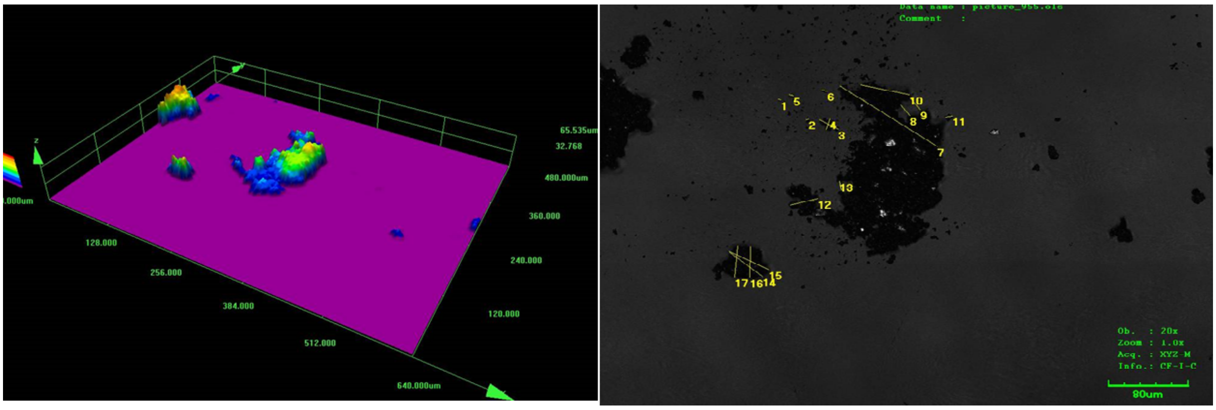

Figure 4.40: Confocal analyze for particle5

Dimension point	Length[um]	dZ[um]
1	2.5859	0.475
2	2.5859	0.4
3	22.4618	1.271
4	12.446	0.025
5	4.5656	1.566
6	5.6806	0.305
7	122.6921	14.232
8	15.1422	-3.189
9	15.6362	-0.497
10	51.4312	-0.248
11	7.013	0.17
12	29.2082	1.192
13	10.1657	0.648
14	44.0124	0.594
15	45.9728	1.686
16	36.2192	0.562
17	36.3494	0.052

Figure 4.41: Confocal analyze for particle5 measurements

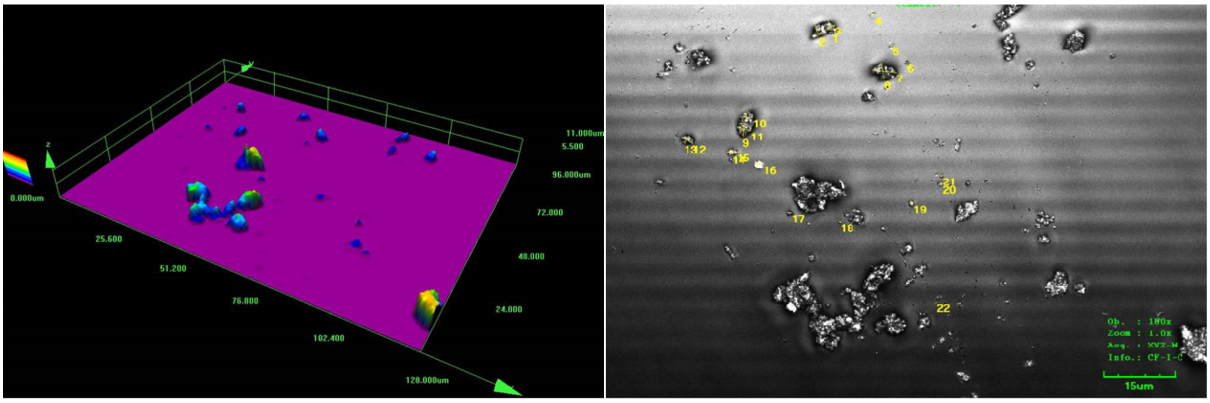

Figure 4.42: Confocal analyze for particle6

Dimension point	Length[um]	dZ[um]
1	3.0165	0.155
2	2.6887	1.673
3	5.8092	-0.146
4	1.0191	-0.112
5	0.7747	0.08
6	0.6369	0.017
7	5.1346	-0.556
8	3.8577	1.373
9	6.1724	0.021
10	2.9407	1.732
11	3.1222	1.885
12	3.2514	0.167
13	2.101	-0.092
14	1.0842	0.172
15	2.1692	0.003
16	1.7833	-0.122
17	1.1534	0.129
18	0.5095	0.066
19	0.7747	0.087
20	0.8053	-0.089
21	0.6494	0.038
22	0.6359	0

Figure 4.43: Confocal analyze for particle6 measurements

As result of confocal microscope analyze and measuring size of existing particles, comparing to measurement scale. An existence of micro & nano particles (1 to 100 nanometer) is clearly noticeable by this analysis.

Particles dimension 0.6 - 300 micrometer size were detected and existence of micro & nano particles clearly can be seen up to 10 nano particles per 15 micrometer.[30]

4.8 Electron Microscope

An electron microscope[2] is a microscope that uses a beam of accelerated electrons as a source of illumination, figure 4.44. Electron microscopes are used to investigate the ultra-structure of a wide range of biological and inorganic specimens including microorganisms, cells, large molecules, biopsy samples, metals, and crystals.

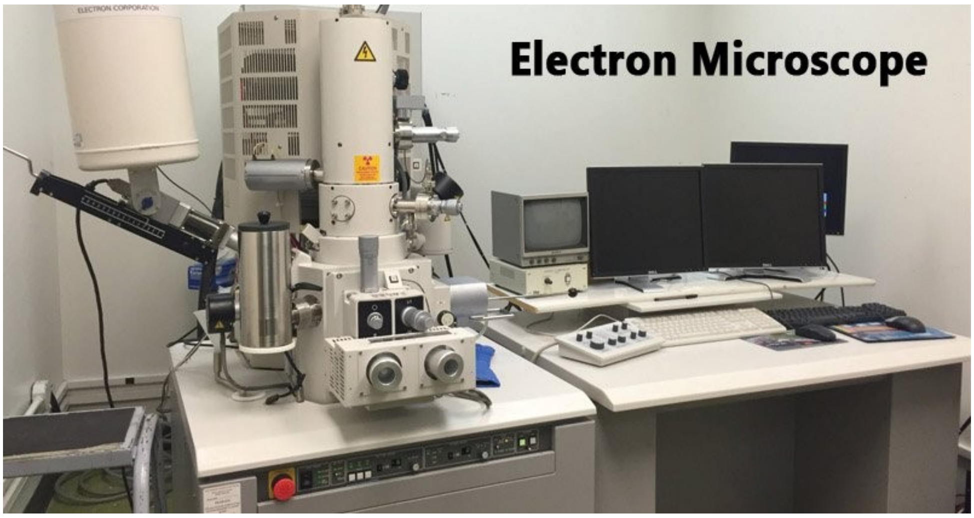

Figure 4.44: Electron Microscope

Electron microscope Definition:

- An electron microscope is a microscope that uses a beam of accelerated electrons as a source of illumination.
- It is a special type of microscope having a high resolution of images, able to magnify objects in nanometres, which are formed by controlled use of electrons in vacuum captured on a phosphorescent screen.
- Ernst Ruska (1906-1988), a German engineer and academic professor, built the first Electron Microscope in 1931, and the same principles behind his prototype still govern modern EMs.

[2]https://microbenotes.com/electron-microscope-principle-types-components-applications-advantages-limitations/

Working principle of electron microscope:

- An electron microscope is a microscope that uses a beam of accelerated electrons as a source of illumination.
- It is a special type of microscope having a high resolution of images, able to magnify objects in nanometres, which are formed by controlled use of electrons in vacuum captured on a phosphorescent screen.

Sample Electron interactions: The scanning electron microscope (SEM) produces images by scanning the sample with a high-energy beam of electrons. As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by one or more detectors to form images which are then displayed on the computer screen. When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Many signals, like secondary electrons and X-rays, are produced as a result of this interaction inside the sample, figure 4.45 .

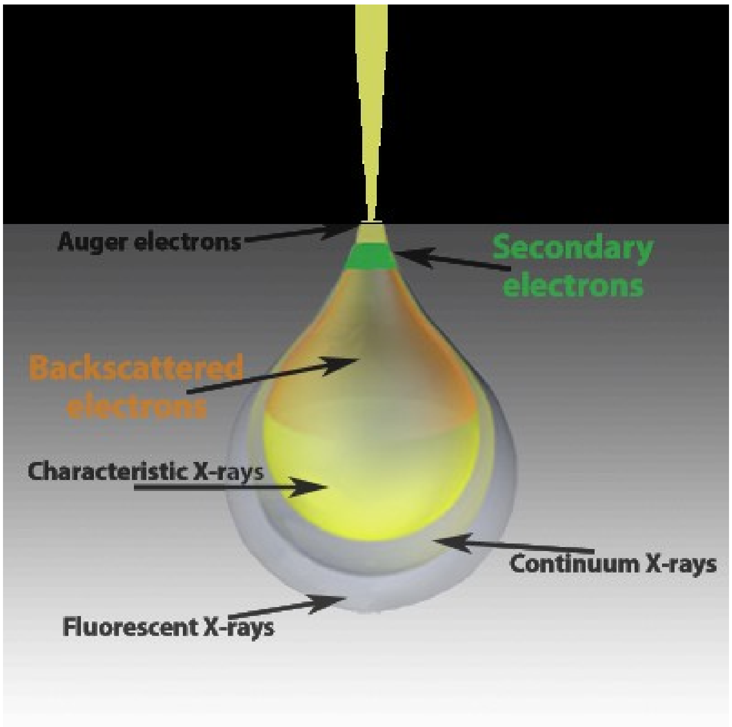

Figure 4.45: Electron Microscope Beam

Parts of Electron Microscope:

EM is in the form of a tall vacuum column which is vertically mounted. It has the following components:

- Electron gun: The electron gun is a heated tungsten filament, which generates electrons.
- Electromagnetic lenses:
  - Condenser lens focuses the electron beam on the specimen. A second condenser lens forms the electrons into a thin tight beam.
  - The electron beam coming out of the specimen passes down the second of magnetic coils called the objective lens, which has high power and forms the intermediate magnified image.
  - The third set of magnetic lenses called projector (ocular) lenses produce the final further magnified image.
  - Each of these lenses acts as an image magnifier all the while maintaining an incredible level of detail and resolution.
- Specimen Holder: is an extremely thin film of carbon or collodion held by a metal grid.
- Image viewing and Recording System.
  - The final image is projected on a fluorescent screen.
  - Below the fluorescent screen is a camera for recording the image.

Electron Microscope Applications:

- Electron microscopes are used to investigate the ultrastructure of a wide range of biological and inorganic specimens including microorganisms, cells, large molecules, biopsy samples, metals, and crystals.
- Industrially, electron microscopes are often used for quality control and failure analysis.
- Modern electron microscopes produce electron micrographs using specialized digital cameras and frame grabbers to capture the images.
- Science of microbiology owes its development to the electron microscope. Study of microorganisms like bacteria, virus and other pathogens have made the treatment of diseases very effective.

4.9 Analytical Scanning Electron Microscopy

Human beings have been subjected continually to naturally occurring, as well as anthropogenic, nanoparticles produced from mechanical and manufacturing processes. The persistent growth in the engineering of nanomaterials has immensely led to a polluted environment triggered by lack of safety monitoring and lack of available risk assessments, starting from nanomaterial production process to the disposal causing various health concerns.

There are several researches proving that pollution caused by nanomaterials have effects on the respiratory and cardiovascular systems thereby causing higher death rate.

Due to this, relevant studies have been carried out to understand toxic affect of nano particles existence and epidemiology affect on human beings. Norms and standards show clearly risk of nanoparticles mainly by harming and penetrating human kind skin and can travel quickly to any organ through blood circulation. In this study, we explore pioneering ways of using transmission electron microscopy in diagnostic pathology to determine potential risks of nanomaterials to human health.[33]

4.9.1 Scanning Electron Microscopy

SEM is the most widely used instrument in routine materials characterization for its advantages of flexibility in sample preparation, easy data interpretation, and multiple functions of imaging, chemical analysing, and the recently developed electron back scattered diffraction (EBSD). For dozens of years, SEM has been one of the essential tools in failure investigation, including comprehensive analyses of wear debris, worn samples, and subsurface micro-structure.

In SEM, an electron beam that is generated in the filament, which can be tungsten, LaB6 ceramic, or a field emission gun, is focused to an extremely small size to scan over a defined area of a sample surface. During the scanning, several signals are emitted as a result of the physical interactions between the electron beam and the sample volume in the small volume beneath the beam-focused area. These signals are simultaneously collected by various detectors either to form images or to perform spectroscopic analyse [34].

4.9.2 Secondary Electron (SE)

Secondary electron (SE) imaging is the most straightforward analysis of surface morphology. Because of the very low energy, secondary electrons that are generated in the interaction volume are mostly absorbed by the sample matrix, except those emitting from the extreme surface. Therefore, the spatial resolution of SE imaging is the best in all of the SEM image modes. Also, for this reason, the SE intensity depends strongly on the geometric orientation of the electron beam scanned surface, which makes it sensitive to the variation of surface morphology. Consequently, SEM images in SE mode provide a tool to observe the three-dimensional morphology of rough surfaces, such as worn surfaces, fractures, and chemically etched metallographic surfaces. SE imaging is the mostly used technique to observe wear products, including worn surfaces and wear debris [35]–[37].

4.9.3 Back-scattered electron (BSE)

Back-scattered electron (BSE) imaging provides a tool to characterize the variation of chemical compositions in a sample. Because the energy of electrons back scattered from nuclei strongly depend on the mass density of the nuclei, the BSE intensity varies with the local chemical compositions. In other words, the contrast of a BSE image is generated from the difference in chemical compositions in the two-dimensional scanning area. In this mode, an area that is rich in light elements, such as oxides, carbides, or nitrides, exhibits dark contrast, while another area containing heavy elements exhibits bright contrast, see figure 4.46. Therefore, SEM images in BSE mode provide a convenient tool to characterize the distribution of secondary phases, the presence of oxides, or other compounds [37], [38]

In addition, BSE imaging can also be employed to detect cracks and metallurgical defects, such as porosity and non-metallic inclusions [39].

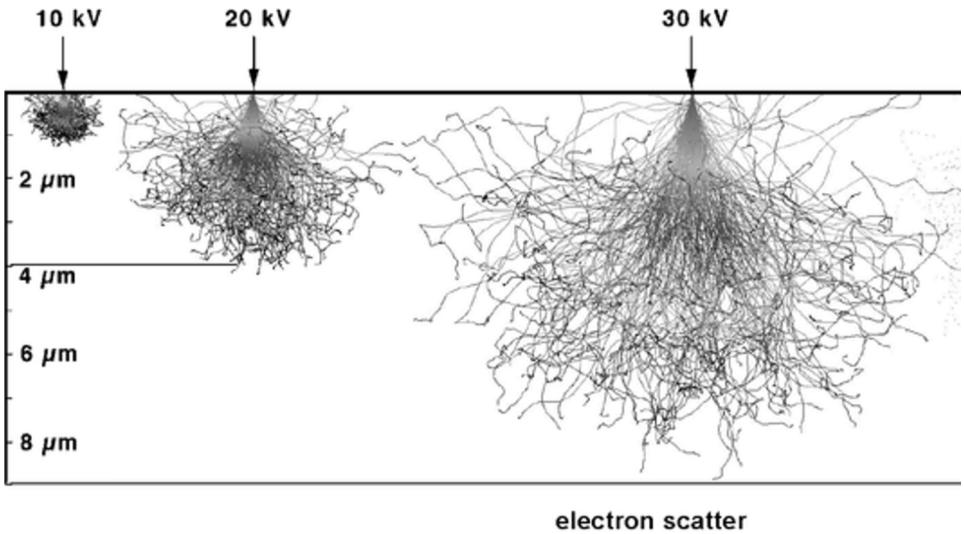

Figure 4.46: Simulation showing the scattering behaviour of electrons within the spciment

4.9.4 Energy Dispersive X-ray (EDX)

Energy dispersive X-ray (EDX) spectroscopic analyses have become an essential attachment of most SEM instruments, which allow simultaneous chemical analysis during SE or

BSE observation. Especially, recently developed software packages have enabled several modes of SEM-EDX analyses. When the incident electron beam is fixed at a point or is defined to scan within a special area or line, a spectrum can be obtained, from which the chemical compositions of the electron-hit point or area can be determined either qualitatively or quantitatively. Using the SEM-EDX spectroscopic analysis, it is convenient to analyse the overall chemical composition of a sample or the chemical compositions of various areas [39].

SEM-EDX analyses provide reasonable accuracy to the analyses of heavy elements, e.g., most metals in the periodic table. However, its accuracy is greatly restricted in the analysis of light elements, i.e., from boron to oxygen in the periodic table. The characteristic X-rays of these light elements have very low energies, which makes them mostly absorbed by the sample matrix, except the X-rays emitting from the outmost surface. Consequently, the integrated intensities of these X-rays are much lower than the characteristic X-rays of heavier elements, because the latter emit both from the outmost surface and from certain depth (up to several micrometres). Although SEM-EDX is less sensitive in analysing light elements, nevertheless, it provides the feasibility to detect dissimilar matters, such as tribo-oxidation films or particles, as compared to the bulk worn surface. Another limitation of SEM-EDX is the scattering data in analysing carbon, which arises from the unavoidable presence of carbon contamination of samples.

4.9.5 Interactions of Electrons with Specimens

When electrons enter the specimen, the electrons are scattered within the specimen and gradually lose their energy, then they are absorbed in the specimen. This behaviour is shown in Fig.4.46. The scattering range of the electron energy, the atomic number of the elements making up the specimen and the density of the constituent atoms. As the energy is higher, the scattering range is larger, the scattering range is smaller [3].

Electro-microscope measurement steps involves accelerating voltage 15KV, which is considered as the effective voltage in this case study, surpassed by a charged particle along a defined straight line. Two types of photos have been taken by electro-microscope.

4.9.6 Influence of Accelerating Voltage

When the accelerating voltage is changed, the penetration depth of the incident electrons changes. As the accelerating voltage is higher, the penetration depth is larger. If the accelerating voltage is increased, information from the inside of the specimen gives rise to the background, degrading the contrast on the specimen surface.

[3] https://www.jeol.co.jp/en/applications/pdf/sm/sem$_a$$toz_a$$ll.pdf$

Two types of electron images will be presented here in this dissertation:

- LEI is detector for secondary electrons/ Illumination effect of Secondary Electron Detector.
- COMPO - Back-scattered electrons/ Illumination effect of back-scattered electron detector.

4.9.7 X-ray Mapping Particles

Non heat treated tablet vs heat treated disk (7,5,14 tablet vs 4 disk)

Electron 3D Model

X-ray mapping is used to obtain the distributions of specific elements. In this analysis, the electron probe is scanned over a specific area and characteristics X-ray with specific energies are acquired.

From figures 4.47, 4.48, 4.49, 4.50, 4.51, 4.54, 4.54, 4.54, 4.55 bellow, show X-ray mapping for particles from tribometer test under electron microscope. Particles are from tribometer test combination non-heat treated tablet vs heat treated disk.

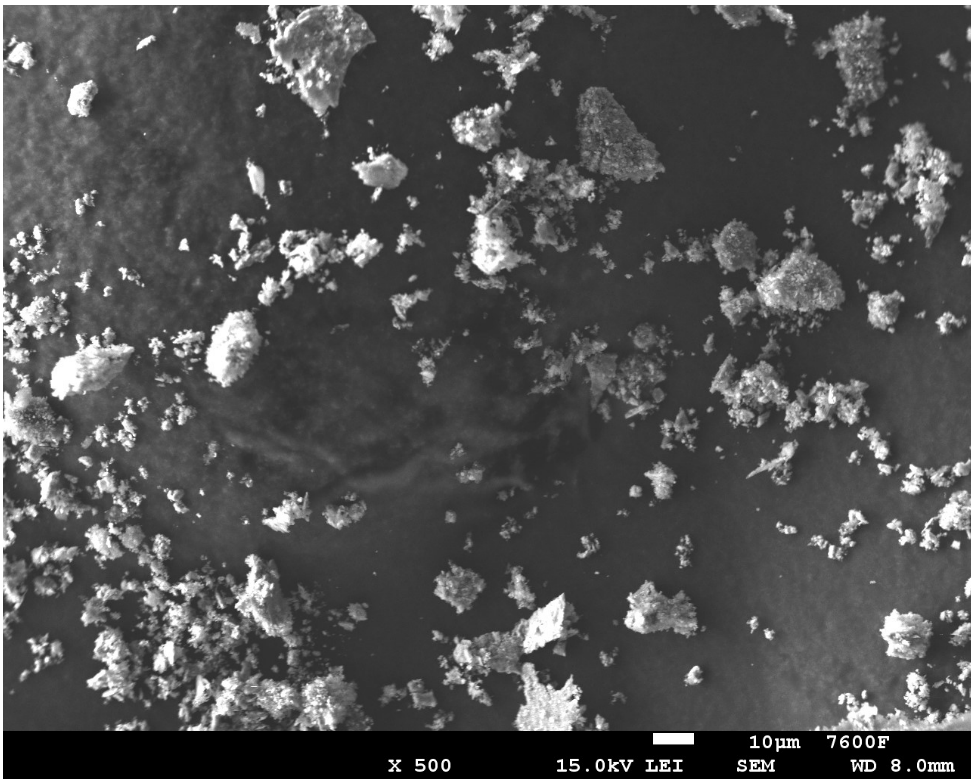

Figure 4.47: LEI 10µm scale, non-heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM SE imaging mode showing nano sized particles

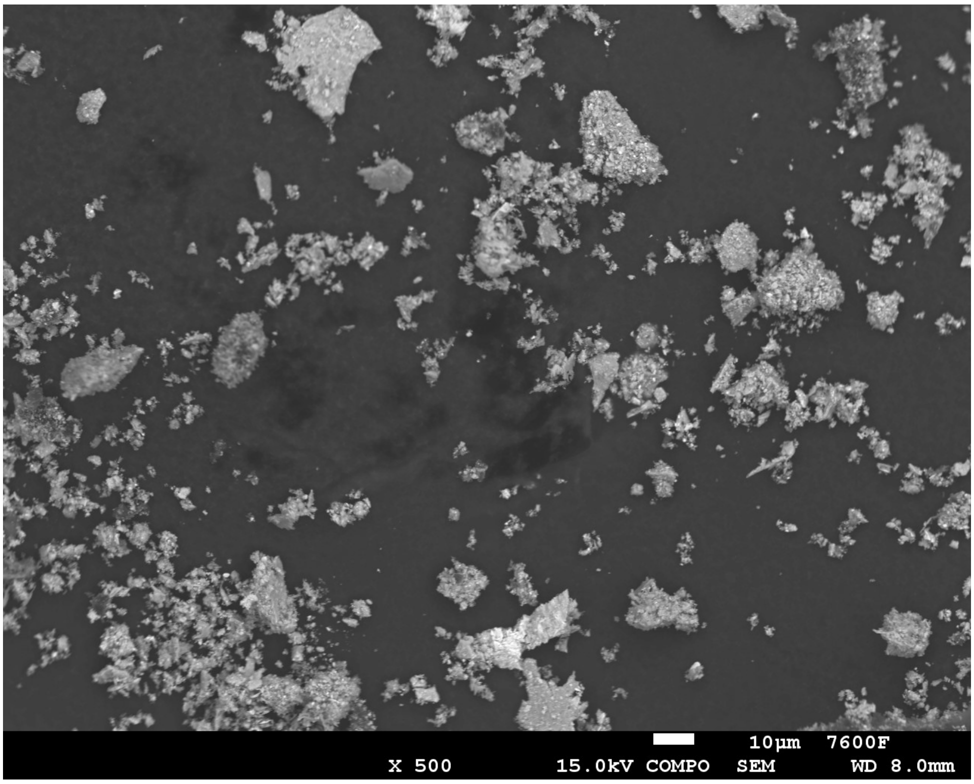

Figure 4.48: COMPO 10µm scale non-heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM back-scattered electron (BSE) imaging mode showing nano sized particles existence

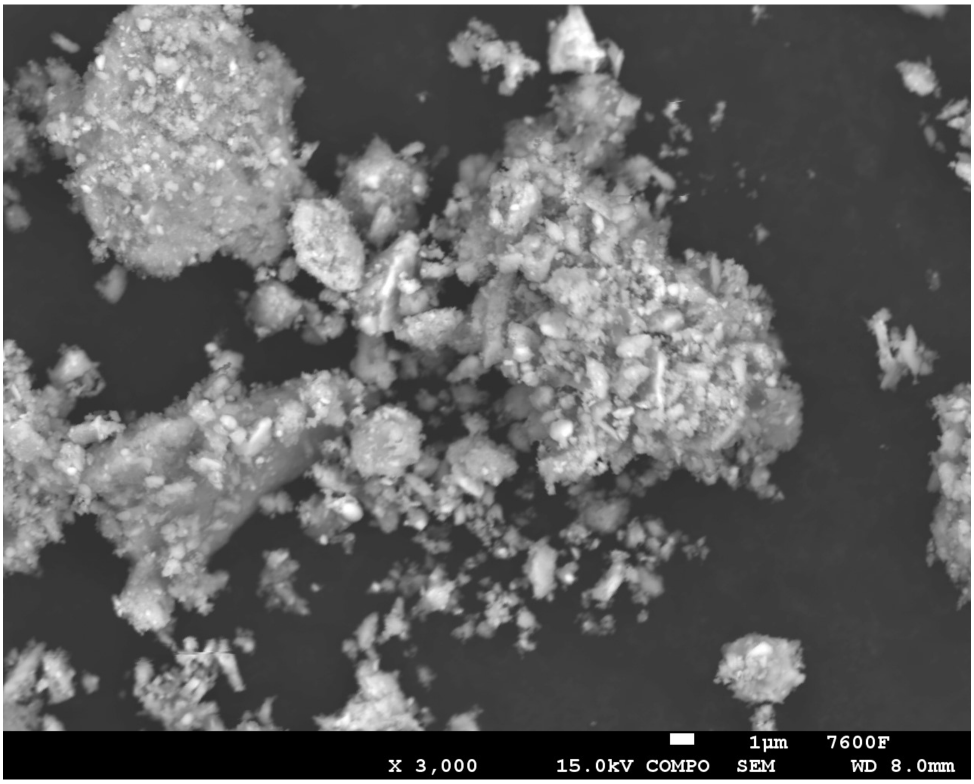

Figure 4.49: COMPO 1µm scale, non-heat treated tablet vs heat treated disk showing nano sized particles existence

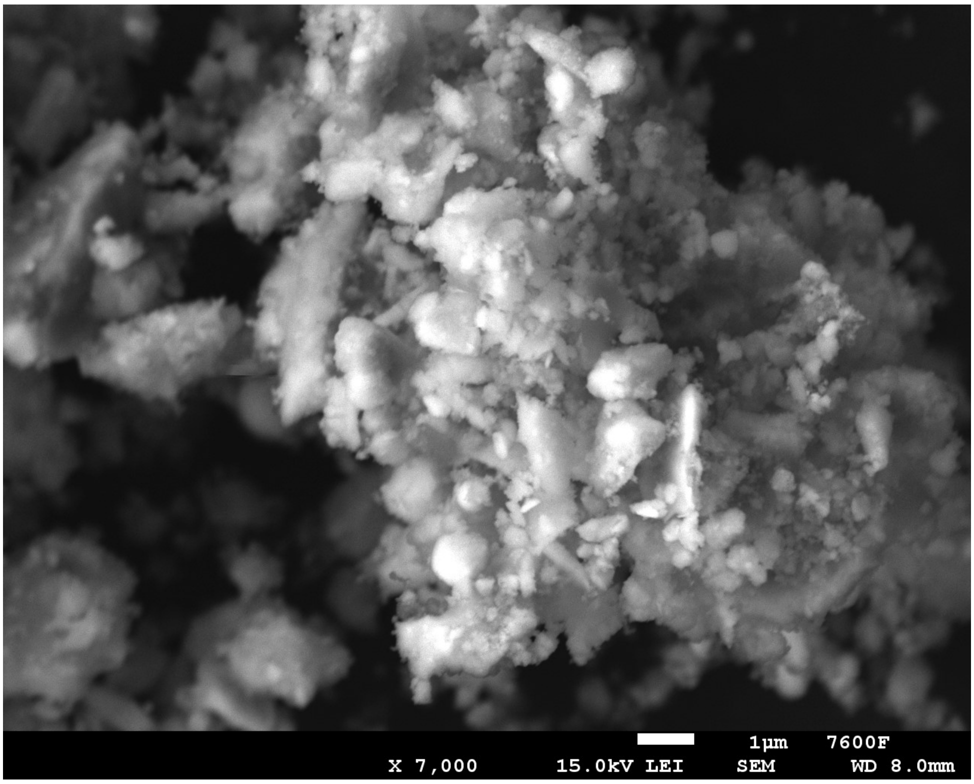

Figure 4.50: LEI 1µm scale, non-heat treated tablet vs heat treated disk showing nano sized particles existence

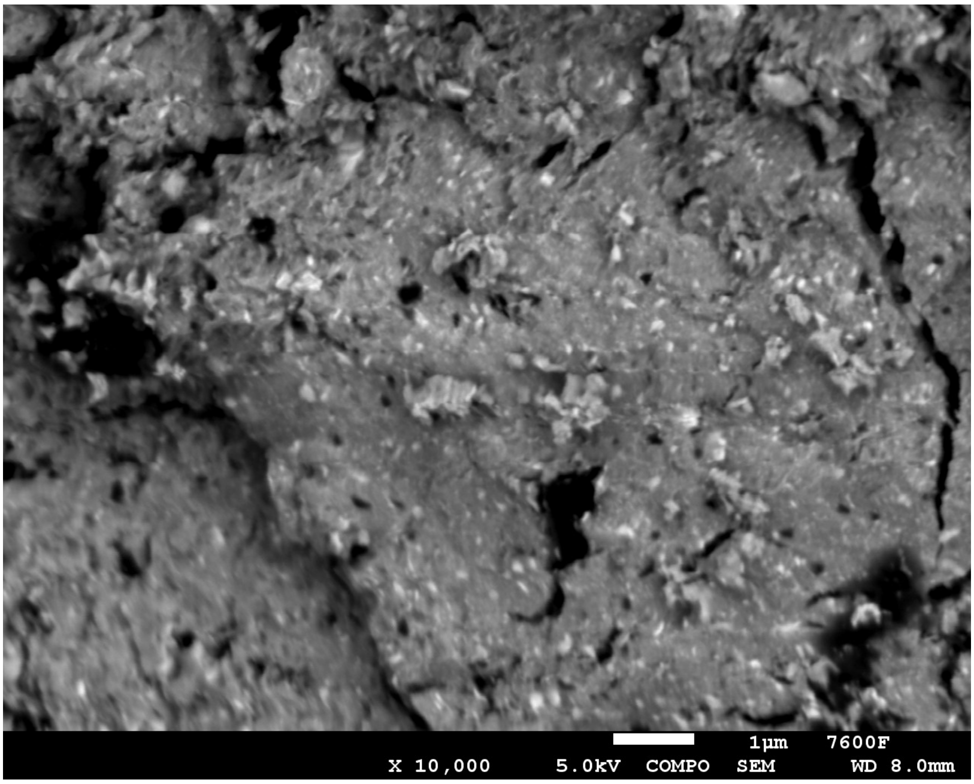

Figure 4.51: COMPO 1µm scale, non-heat treated tablet vs heat treated disk showing nano particles existence

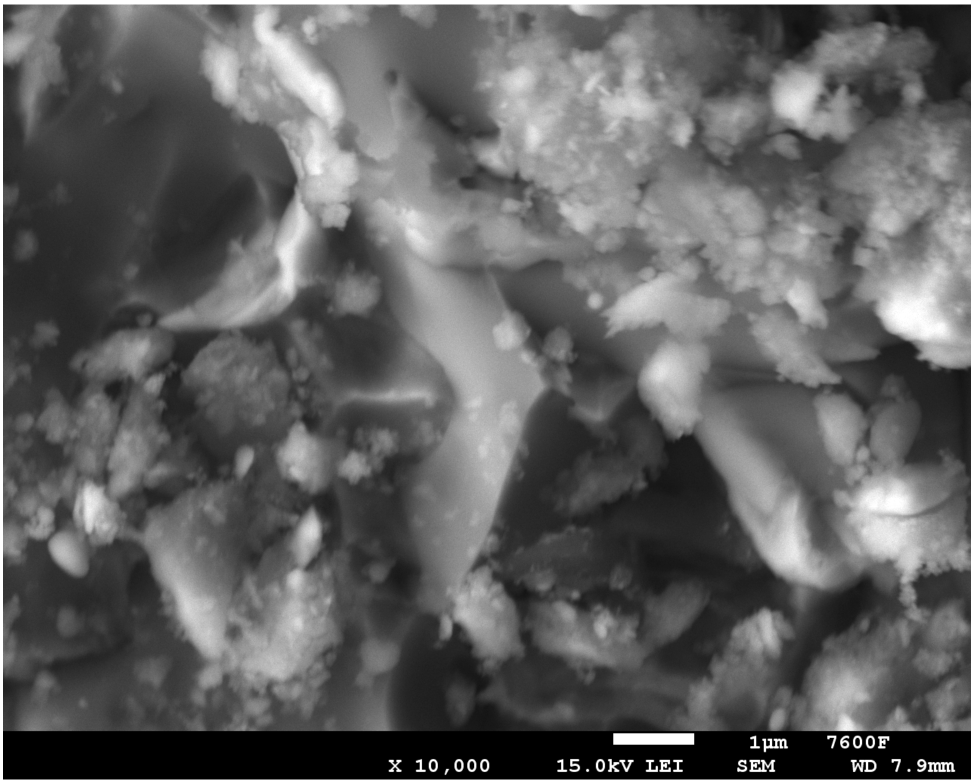

Figure 4.52: LEI 1µm scale, non-heat treated tablet vs heat treated disk showing nano particles existence

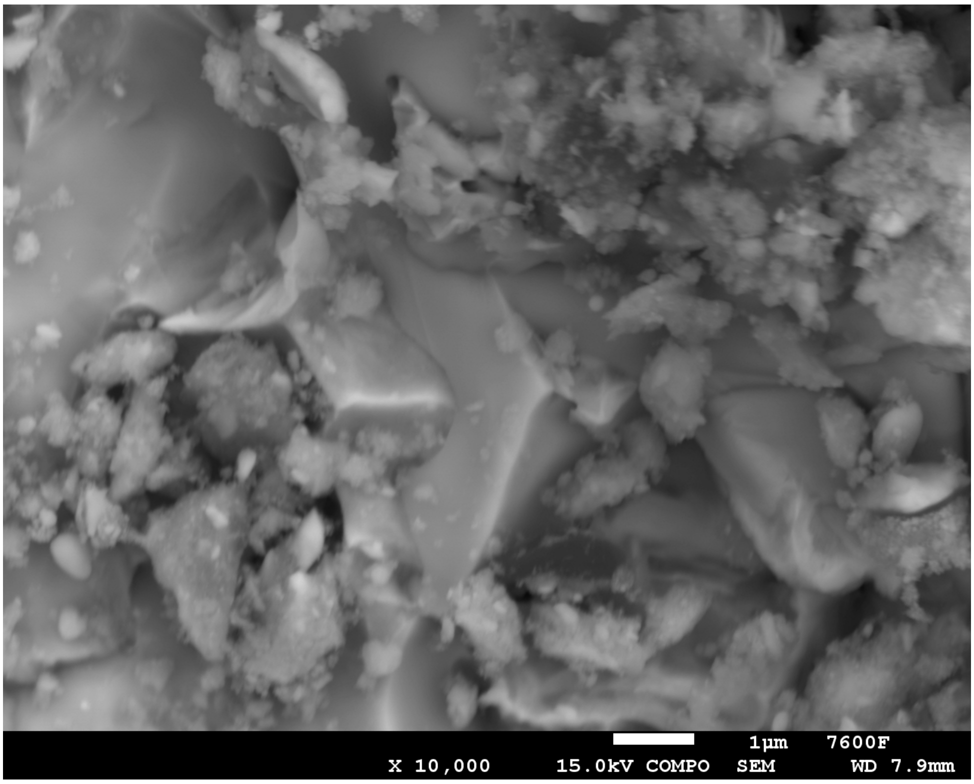

Figure 4.53: COMPO 1µm scale, non-heat treated tablet vs heat treated disk showing nano particles existence

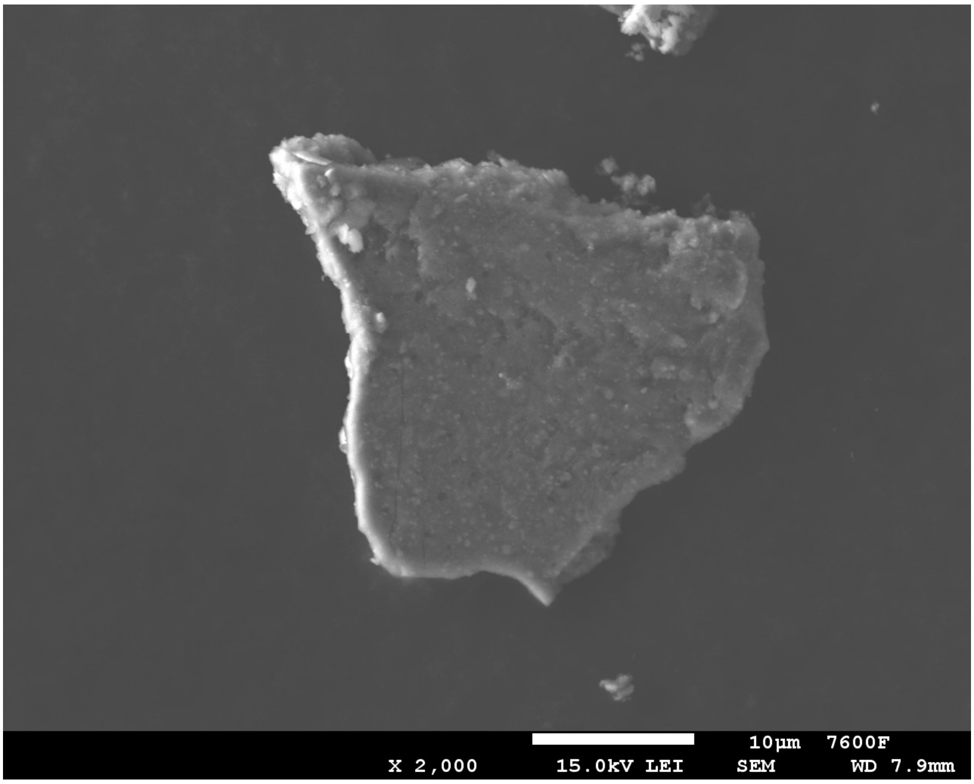

Figure 4.54: LEI 10µm scale, non-heat treated tablet vs heat treated disk showing nano particles existence

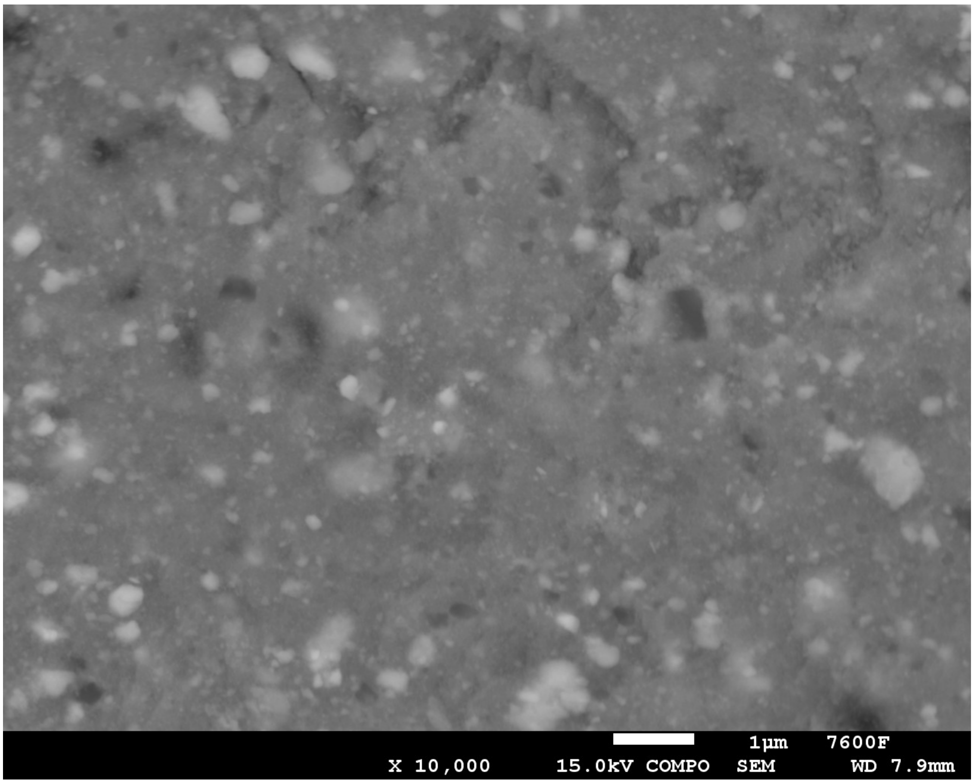

Figure 4.55: COMPO 1µm scale, non-heat treated tablet vs heat treated disk showing nano particles existence

Chemical Mapping by backscattered electrons:

Backscattered electrons are those scattered backwards and emitted out of the specimen. When the incident electrons are scattered in the specimen. They are sometimes called reflected electrons. Since backscattered electrons possess higher energy than secondary electrons, information from a relatively deep region is contained in the backscattered electrons. The backscattered electrons are sensitive to the composition of the specimen. The atomic number of the constituent atoms in the specimen is larger, the backscattered electrons yield is larger. That is, an area that consists of a heavy atom appears bright in the backscattered electron image. Thus, this image is suitable for observing a compositional difference.

In this dissertation experimental the scanning was done by electron microscope equipped with EDS (Energy dispersive X-ray spectroscopy), detector Oxford X-Max $50mm^2$ for chemical analysis (element mapping)[4].

If the specimen surface has irregularity, the intensity of backscattered electrons becomes higher in the direction of specular reflection. The feature can be used to observe the topography of the surface.

Therefore, chemical analyze by using electron beam will show chemical map for ma-

[4]https://nano.oxinst.com/products/ultim-max

terials existence in particles shape, which can move freely in testing atmosphere and surroundings.

Figures 4.56, 4.58, 4.59 , 4.60, 4.61, 4.62, 4.63, 4.64 show visible particles by Electroscope are the following: Chromium , Nickel, Iron, Molybdenum, Cobalt, Copper, Zink, Silica, Boron, Carbon, and Oxygen.[30]

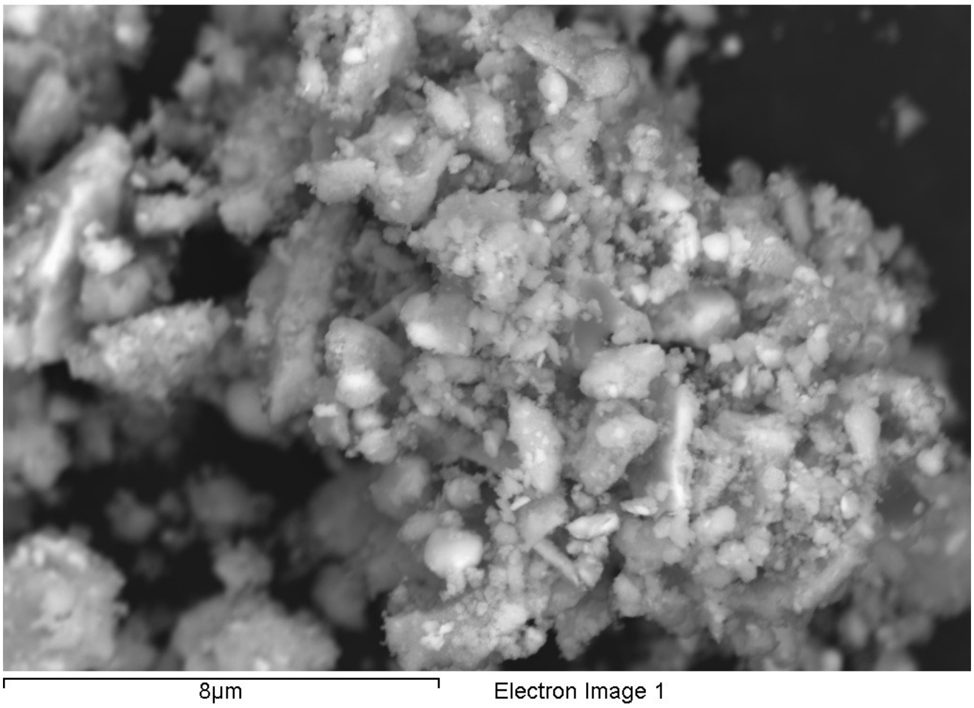

Figure 4.56: COMPO 1 non-heat treated tablet vs heat treat: provides the application of SEM SE imaging. The imaging mode has very powerful spatial resolution in resolving nano-scale features, owing to the field emission gun and the SE imaging mode

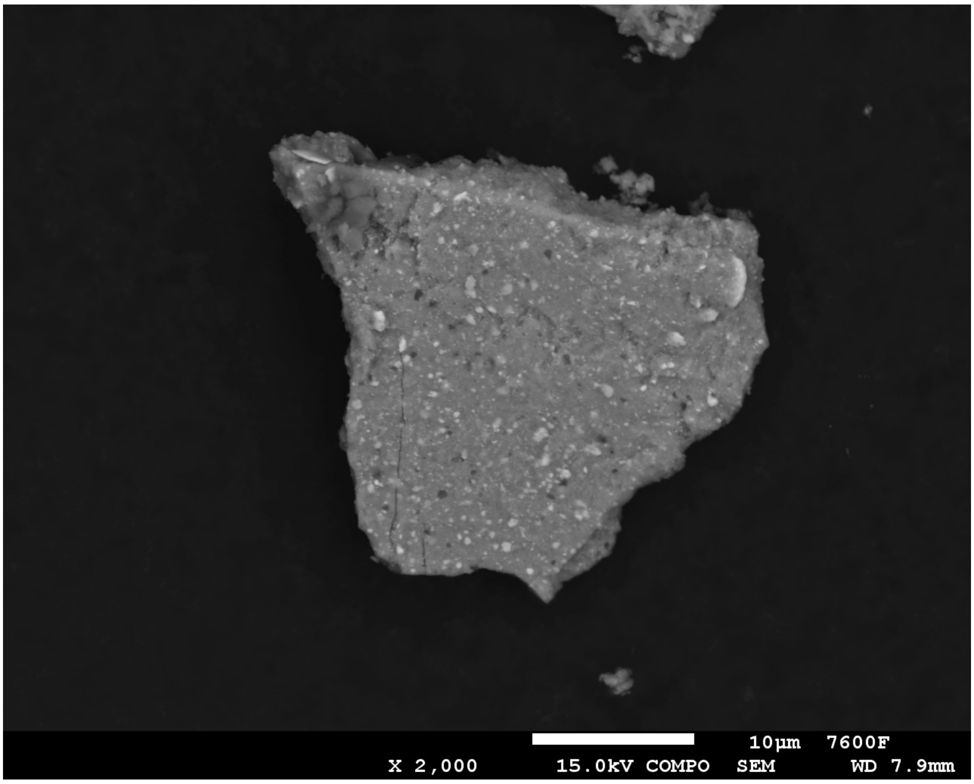

Figure 4.57: COMPO 10µm non-heat treated tablet vs heat treated disk

Figure 4.58: Chemical and elemental mapping by Electro microscope showing Cr, Ni, Mo existence

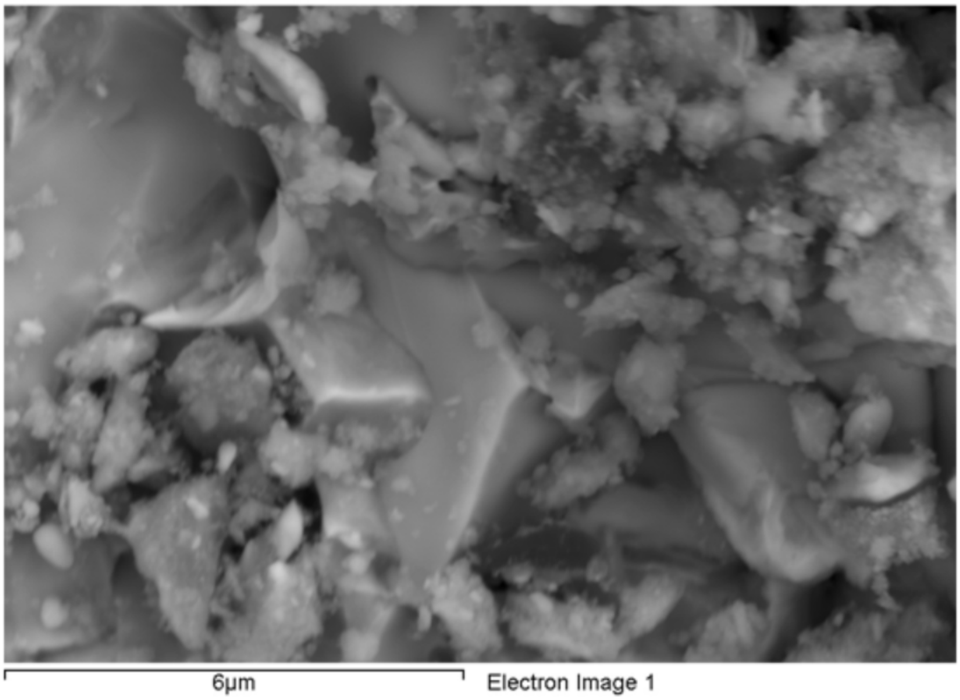

Figure 4.59: Visible particles by Electroscope

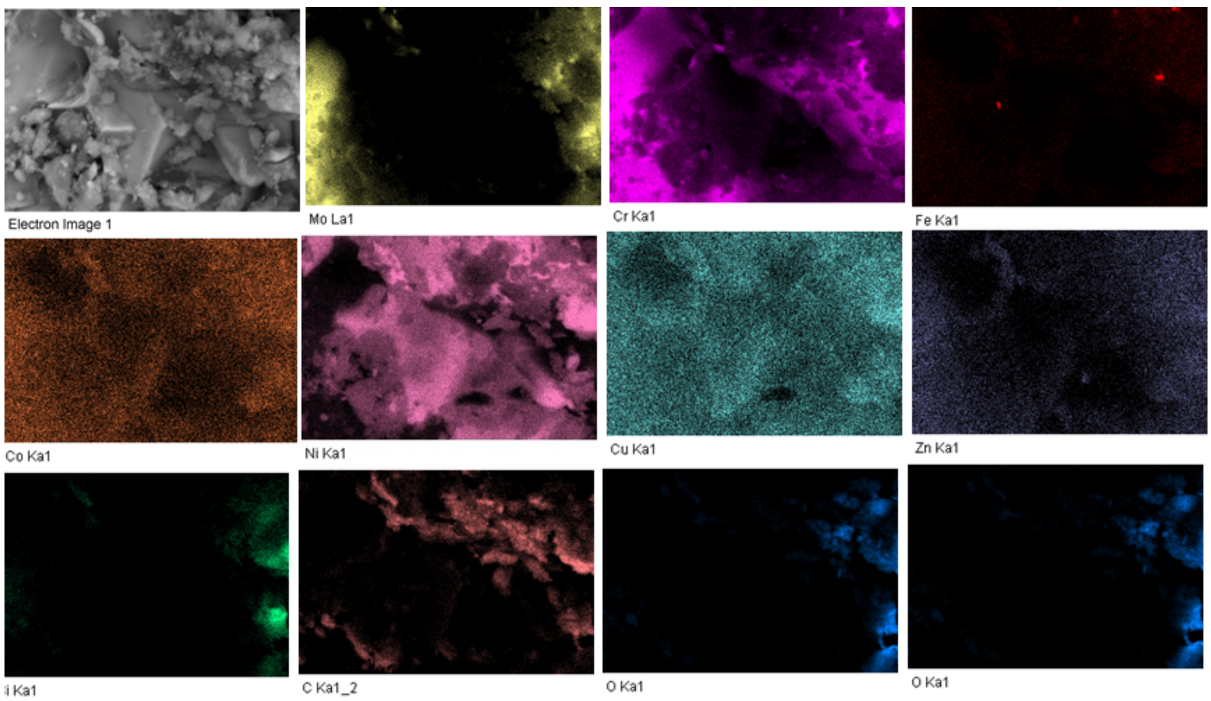

Figure 4.60: Cr, Fe, Mo, I, C Visible particles by Electroscope

Spectrum	In stats.	B	C	O	Si	Cr	Fe	Co	Ni	Cu	Zn	Mo	Total
Sum Spectrum	Yes	22.50	12.81	2.13	0.10	17.73	0.46	0.02	40.74	0.18	0.10	3.23	100.00
Spectrum 2	Yes	19.30	8.11	0.56		10.54	0.43		60.45	0.25	0.12	0.24	100.00
Spectrum 3	Yes	21.34	10.04	0.81	0.03	6.74	0.29		60.15	0.19	0.09	0.31	100.00
Spectrum 4	Yes	16.97	9.32	4.44	0.32	12.40	0.42		52.67		0.26	3.18	100.00
Spectrum 5	Yes	17.93	8.15	0.98	0.14	12.53	0.51		58.50	0.21	0.12	0.93	100.00
Spectrum 6	Yes	28.60	23.78	3.08	0.08	15.15	0.37	0.05	24.41	0.17	0.07	4.24	100.00
Spectrum 7	Yes	11.16	6.22	0.58	0.03	53.50	0.28		18.02	0.30	0.11	9.79	100.00
Max.		28.60	23.78	4.44	0.32	53.50	0.51	0.05	60.45	0.30	0.26	9.79	
Min.		11.16	6.22	0.56	0.03	6.74	0.28	0.02	18.02	0.17	0.07	0.24	

Figure 4.61: Processing option : All elements analysed (Normalised) all results in weight%

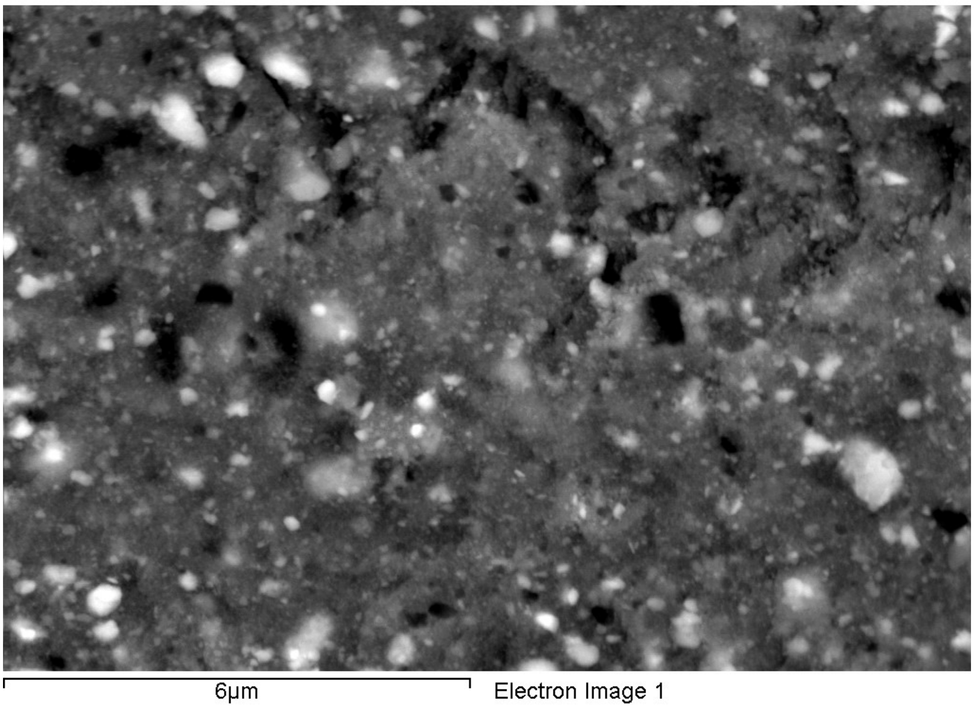

Figure 4.62: Electron Image

Incident electron beam is fixed at defined points to scan within a special area or line, a spectrum can be obtained, from which the chemical compositions of the electron-hit point or area can be determined either qualitatively or quantitatively. Figure 4.63 shows spectrum material analyse for specified points.

Figures 4.58, 4.60 show the comparative SEM-EDX analysis of the two regions.

The only difference between the two regions is in the low-energy period of the spectra, i.e., the presence of light elements Ni, B, Mo, Cr, Fe.

So, profiles of the light element spectra are highlighted to show more details in better energy resolution.

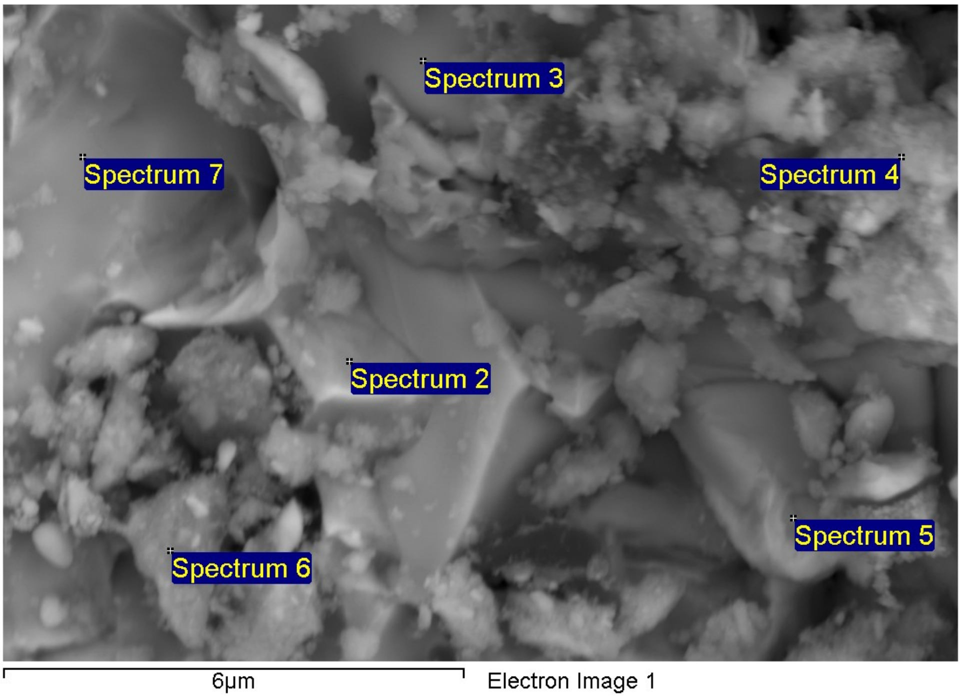

Figure 4.63: Spectrum Material analyse

In figure 4.61 demonstrates the application of Scanning Electron Microscopy Backscattered Electron and Secondary Electron imaging modes and Energy Dispersive X-ray analysis in the characterization of tribology produced particles. The images were taken on specified spectrum areas on surface of a particles generated after tribology cycles of unlubricated non heat treated tablet sliding against a heat treated disk.

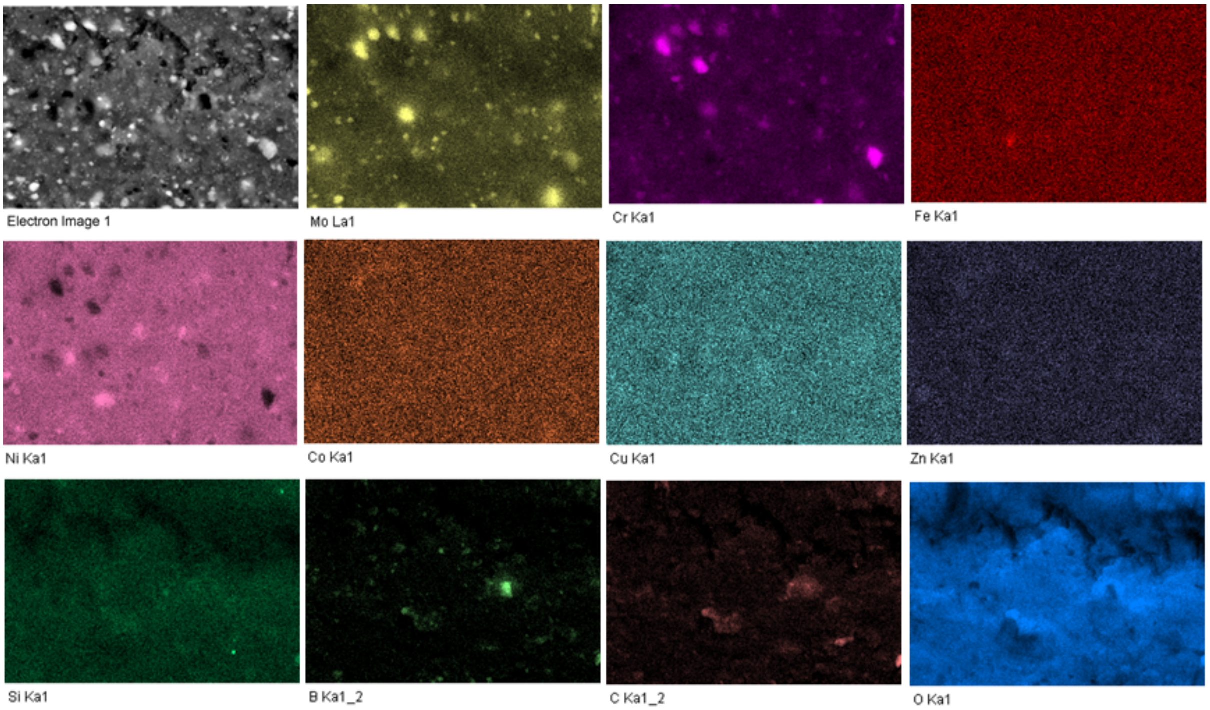

Figure 4.64: Electron Image showing Mo, Cr, Fe, Ni, B, Si, C existence

Heat Treated Tablet vs Heat Treated Disk (5,2,2 Tablet vs 4 Disk)

Electron 3D Model:

X-ray mapping is used to obtain the distributions of specific elements. In this analysis, the electron probe is scanned over a specific area and characteristics X-ray with specific energies are acquired.

From figures 4.65, 4.66, 4.67, 4.68, 4.69, bellow, show X-ray mapping for particles from tribometer test under electron microscope. Particles are from tribometer test combination heat treated tablet vs heat treated disk.

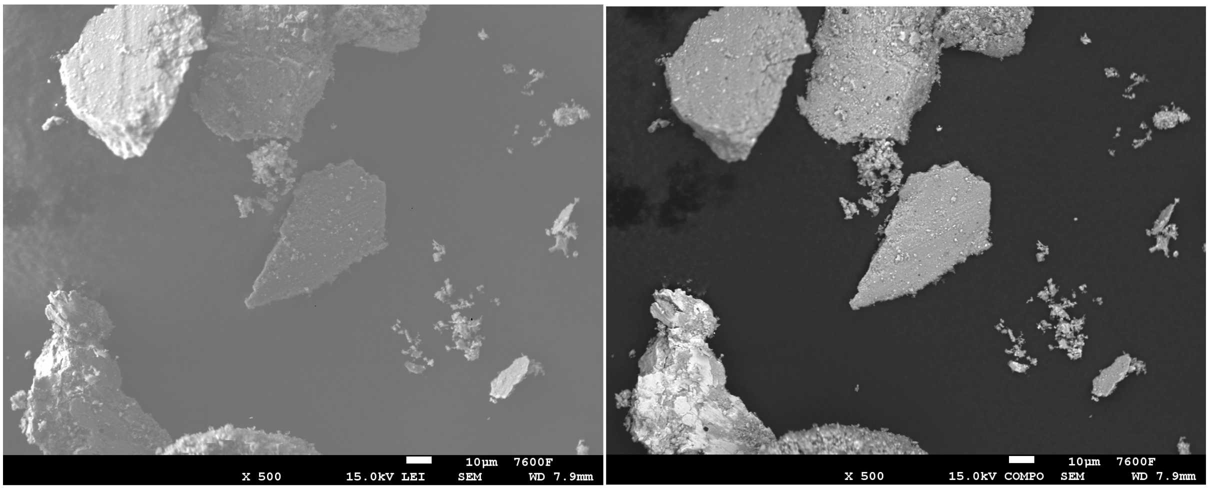

Figure 4.65: LEI/ COMPO 10µm heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM SE imaging mode

Figures 4.66, 4.67

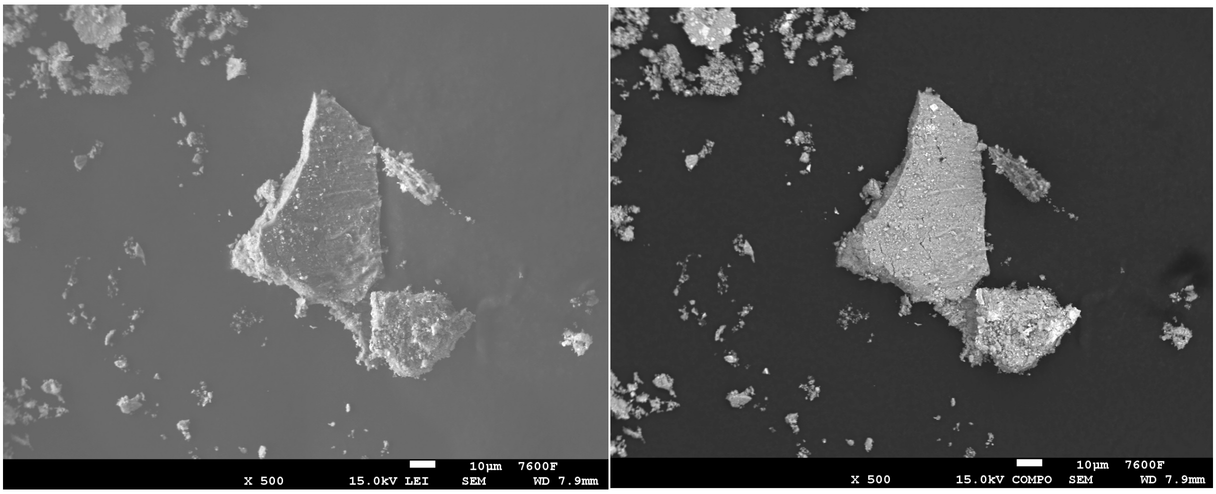

Figure 4.66: LEI/ COMPO 10µm heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM SE imaging mode

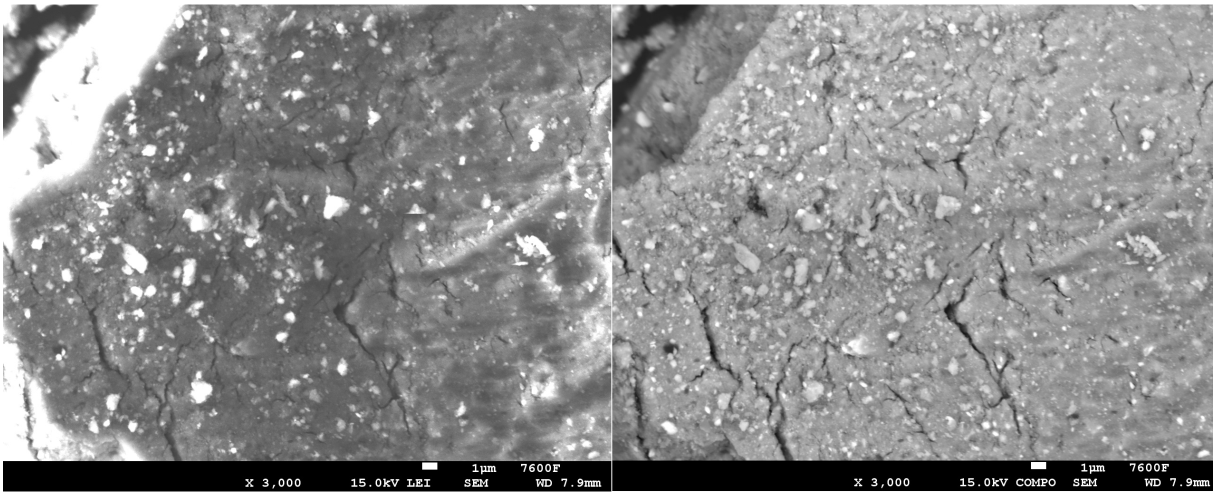

Figure 4.67: LEI/ COMPO 10µm heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM SE imaging mode

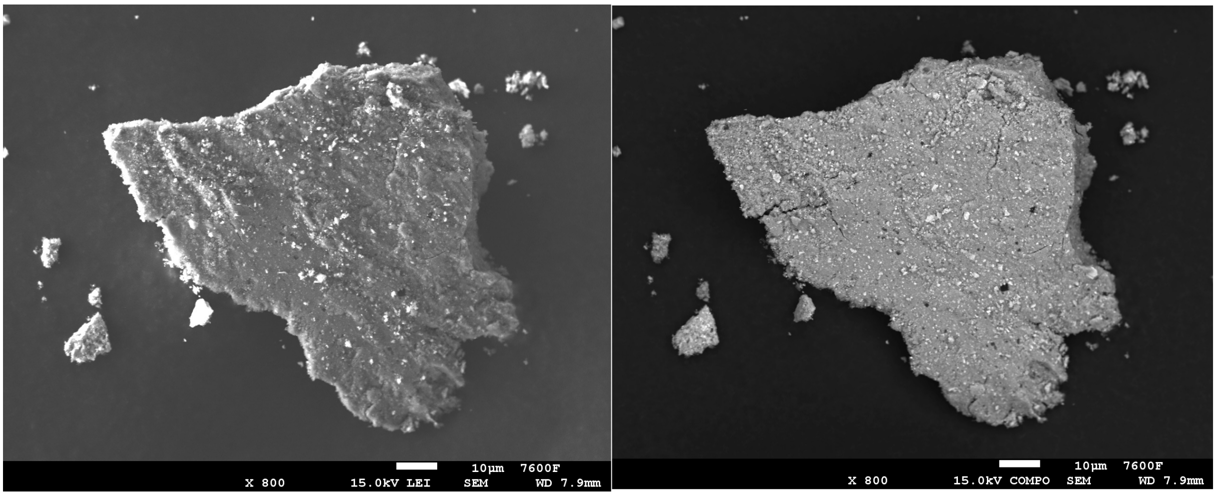

Figure 4.68: LEI/ COMPO 10µm heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM SE imaging mode

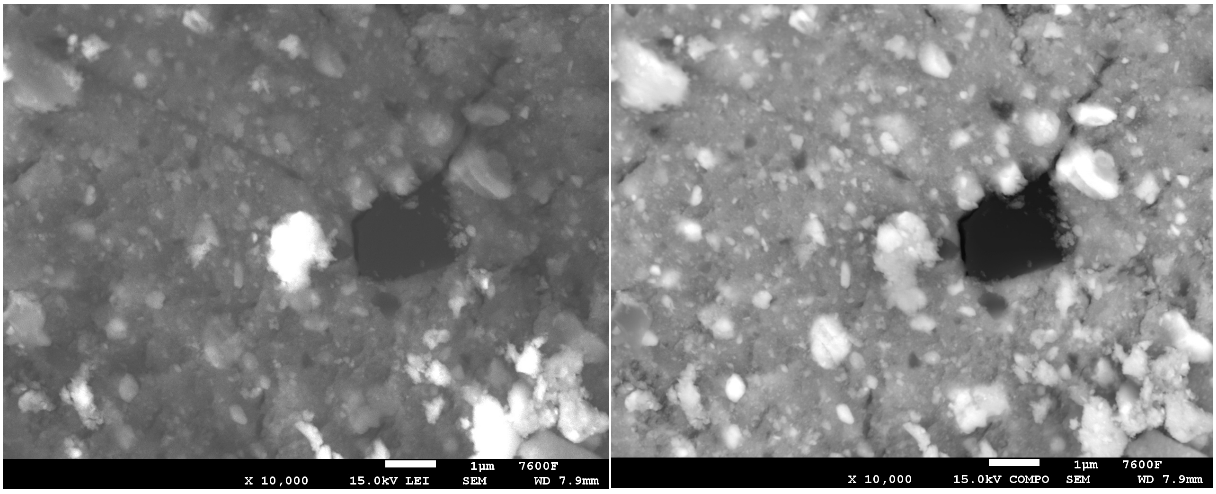

Figure 4.69: LEI/ COMPO 10µm heat treated tablet vs heat treated disk; Analysis of particles by means of three SEM modes, the SEM SE imaging mode

Chemical Mapping by backscattered electrons:

Backscattered electrons are those scattered backwards and emitted out of the specimen. When the incident electrons are scattered in the specimen. They are sometimes called reflected electrons. Since backscattered electrons possess higher energy than secondary electrons, information from a relatively deep region is contained in the backscattered electrons. The backscattered electrons are sensitive to the composition of the specimen. The atomic number of the constituent atoms in the specimen is larger, the backscattered electrons yield is larger. That is, an area that consists of a heavy atom appears bright in the backscattered electron image. Thus, this image is suitable for observing a compositional difference.

In this dissertation experimental the scanning was done by electron microscope equipped with EDS (Energy dispersive X-ray spectroscopy), detector Oxford X-Max $50mm^2$ for chemical analysis (element mapping)

If the specimen surface has irregularity, the intensity of backscattered electrons becomes higher in the direction of specular reflection. The feature can be used to observe the topography of the surface.

Therefore, chemical analyze by using electron beam will show chemical map for materials existence in particles shape, which can move freely in testing atmosphere and surroundings.

Figures 4.70, 4.71, 4.72 , 4.73 show visible particles by Electroscope are the following: Chromium , Nickel, Iron, Molybdenum, Cobalt, Copper, Zink, Silica, Boron, Carbon, and Oxygen.

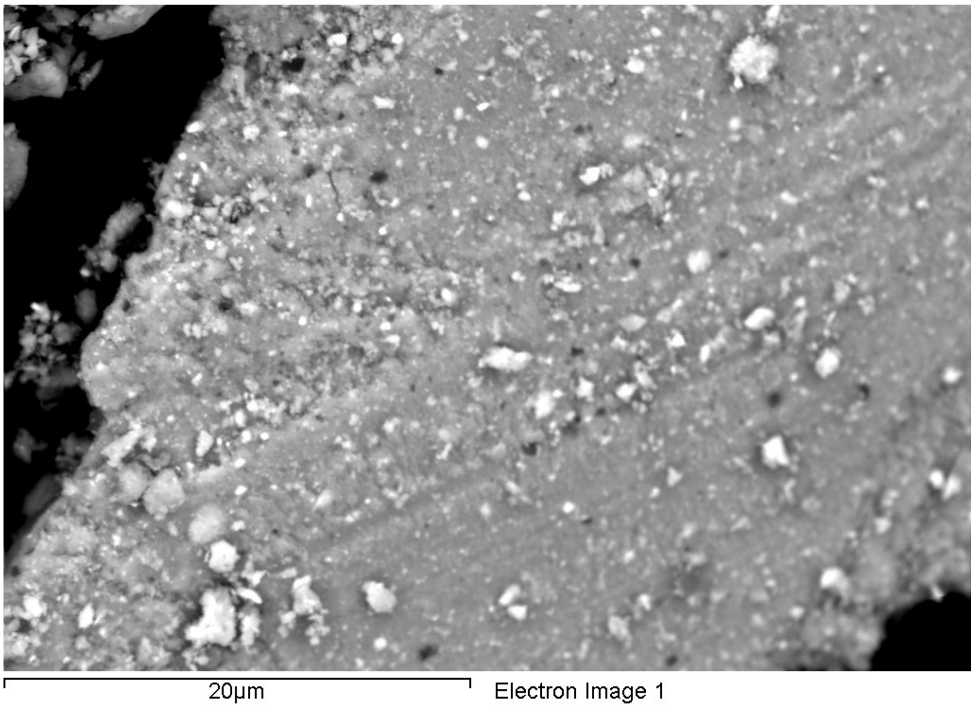

Figure 4.70: Heat treated tablet vs Heat treat disk with scale diameter 20m, Micro & Nano sized particles are visible

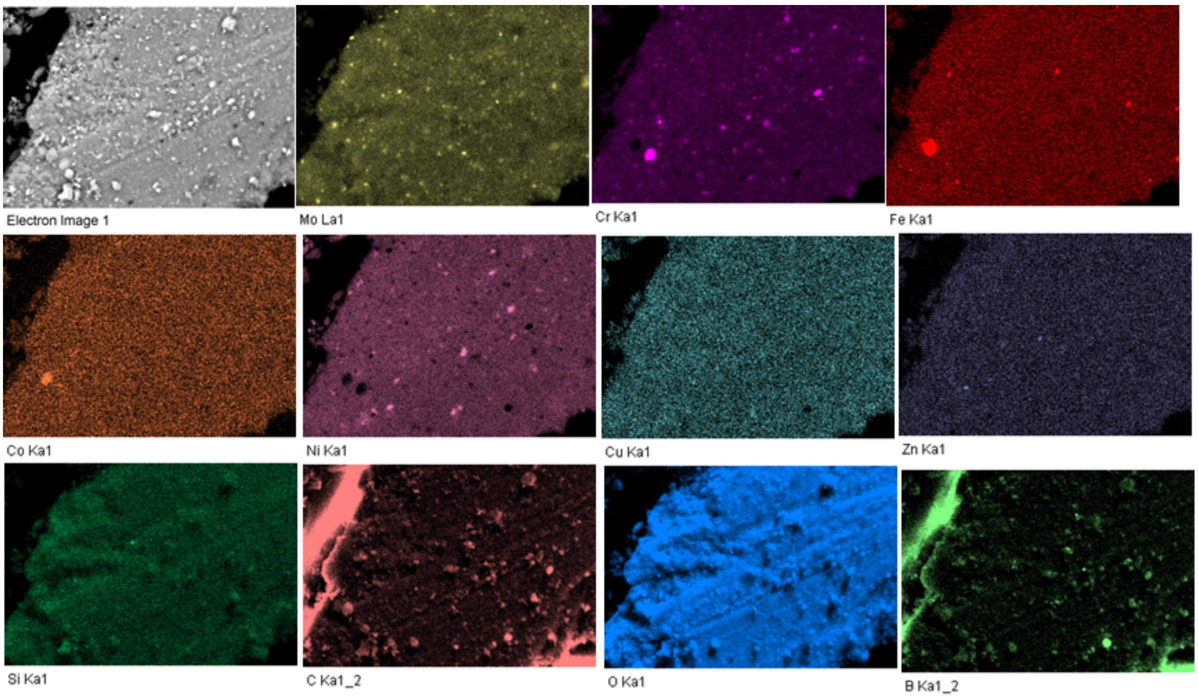

Figure 4.71: Heat treated tablet vs Heat treat disk, Chemical mapping showing MO, Cr, Fe, Co, Ni, Cu, Zn, Si, C, O, B

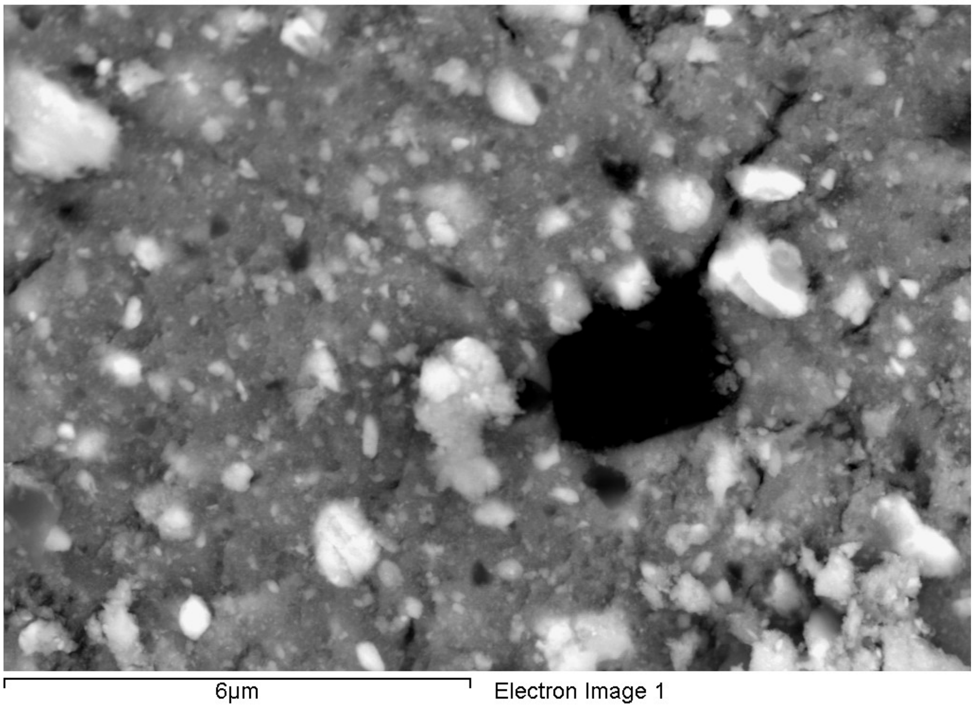

Figure 4.72: Heat treated tablet vs Heat treat disk with scale diameter 20m, Micro & Nano sized particles are visible

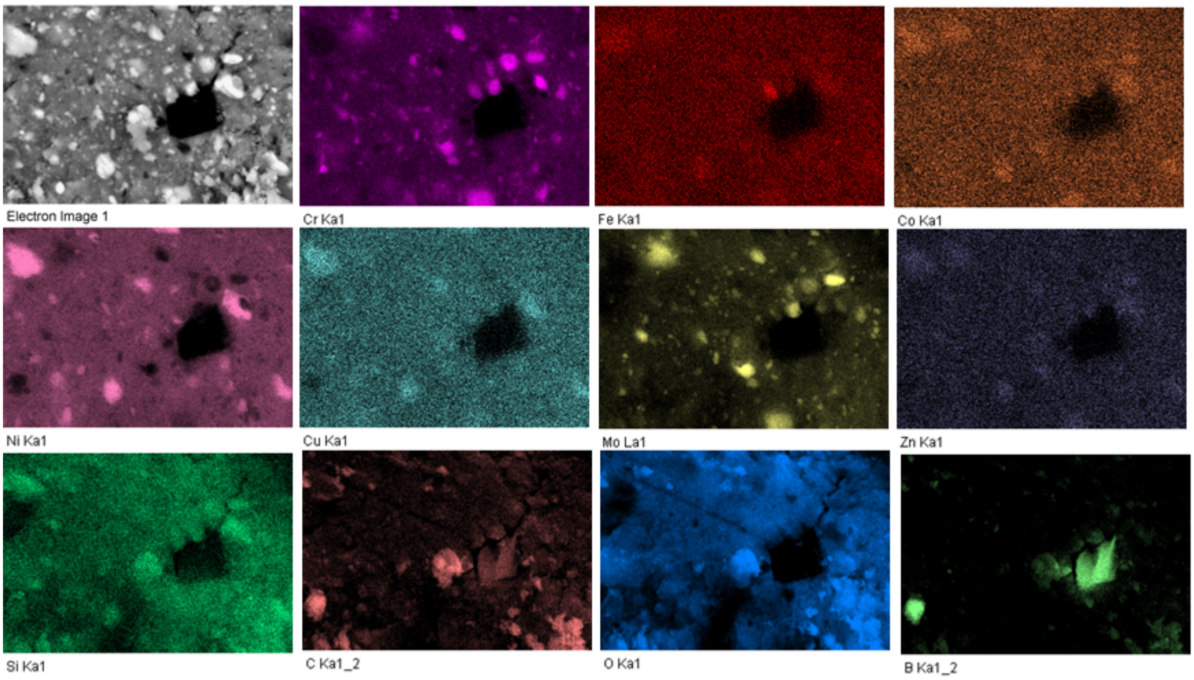

Figure 4.73: Heat treated tablet vs Heat treat disk, Chemical mapping showing MO, Cr, Fe, Co, Ni, Cu, Zn, Si, C, O, B

4.10 X-ray Mapping Tablet

Scanning Electron Microscope was used in tribology test tablet materials characterization. It is one of the essential tools in failure investigation, including comprehensive analyses of wear debris, worn samples, and subsurface micro-structure. Therefore SEM will bring an analyze for tablet surface, showing size of particles located on it surface, and chemical analyze, to show which particles are visible and could increase risk of this application.

4.10.1 Heat Treated Tablet

Energy dispersive X-ray (EDX) spectroscopic analyses is an essential attachment of SEM instruments, which allow simultaneous chemical analysis during SE or BSE observation.

In this thesis we have software packages, which enable several modes of SEM-EDX analyses.

When the incident electron beam is fixed at a point or is defined to scan within a special area or line, a spectrum can be obtained, from which the chemical compositions of the electron-hit point or area can be determined either qualitatively or quantitatively.

Using the electron microscope equipped with EDS (Energy dispersive spectroscopy) detector Oxford X-Max $50mm^2$ spectroscopic analysis, it is convenient to analyse the overall chemical composition of a sample.

Electron 3D Model

X-ray element mapping analyze is used to obtain the distributions of specific elements. In this analysis,the electron probe is scanned over a specific area and characteristics X-ray with specificenergies are acquired.From figures 4.74, 4.75 bellow, show X-ray mappingfor particles from tribometer test under electron microscope. Particles are from tribometertest combination non-heat treated tablet vs heat treated disk.

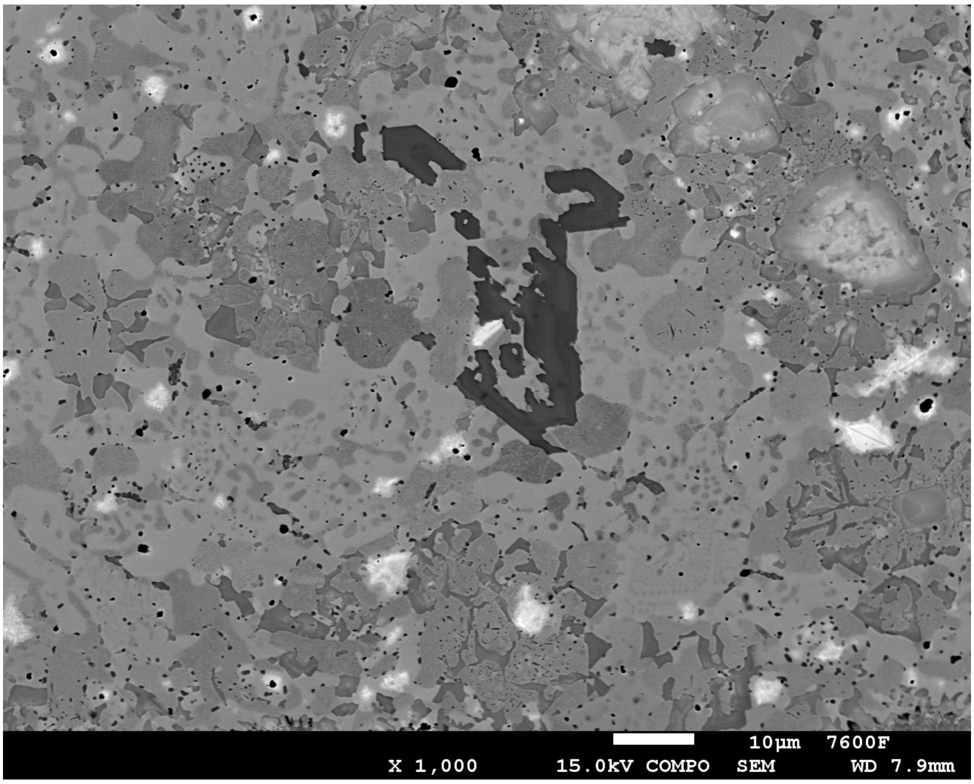

Figure 4.74: Heat treated tablet 5:2:2 surface, diameter 10m. Particles with micro & nano particles in size 1 to 100 nanometers

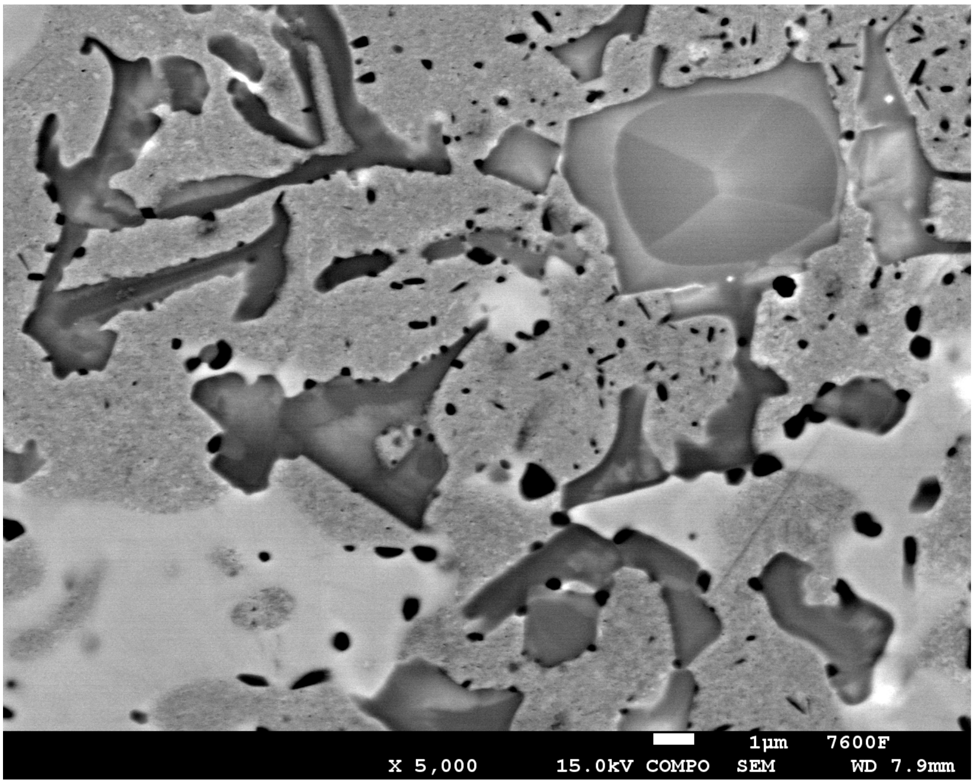

Figure 4.75: Heat treated tablet 5:2:2 surface, diameter 10m. Particles with micro & nano particles in size 1 to 100 nanometers

Chemical Mapping by Backscattered Electrons

Figures 4.76, 4.77, 4.78 and 4.79 showing the reaction of backscattered electrons which going backwards and emitted out of the specimen.

They are sometimes called reflected electrons. Since backscattered electrons possess higher energy than secondary electrons, information from a relatively deep region is contained in the backscattered electrons. The backscattered electrons are sensitive to the composition of the specimen. The atomic number of the constituent atoms in the specimen is larger, the backscattered electrons yield is larger. That is, an area that consists of a heavy atom appears bright in the backscattered electron image. Thus, this image is suitable for observing a material compositions.

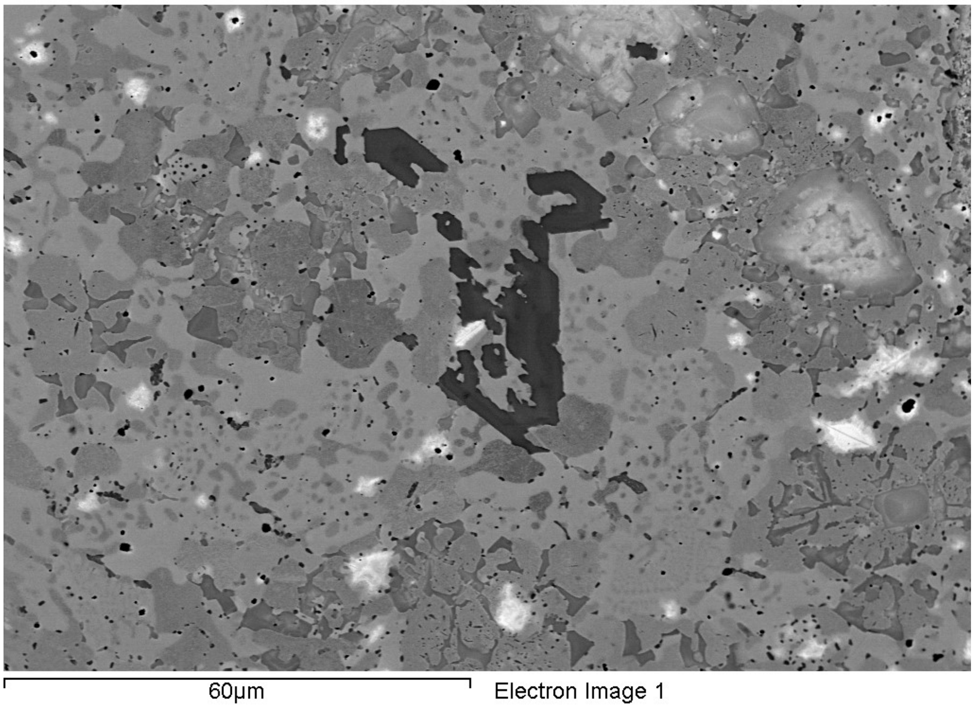

Figure 4.76: Heat treated tablet 5:2:2 surface, Chemical mapping showing Mo, Cr, B, C, O, Si

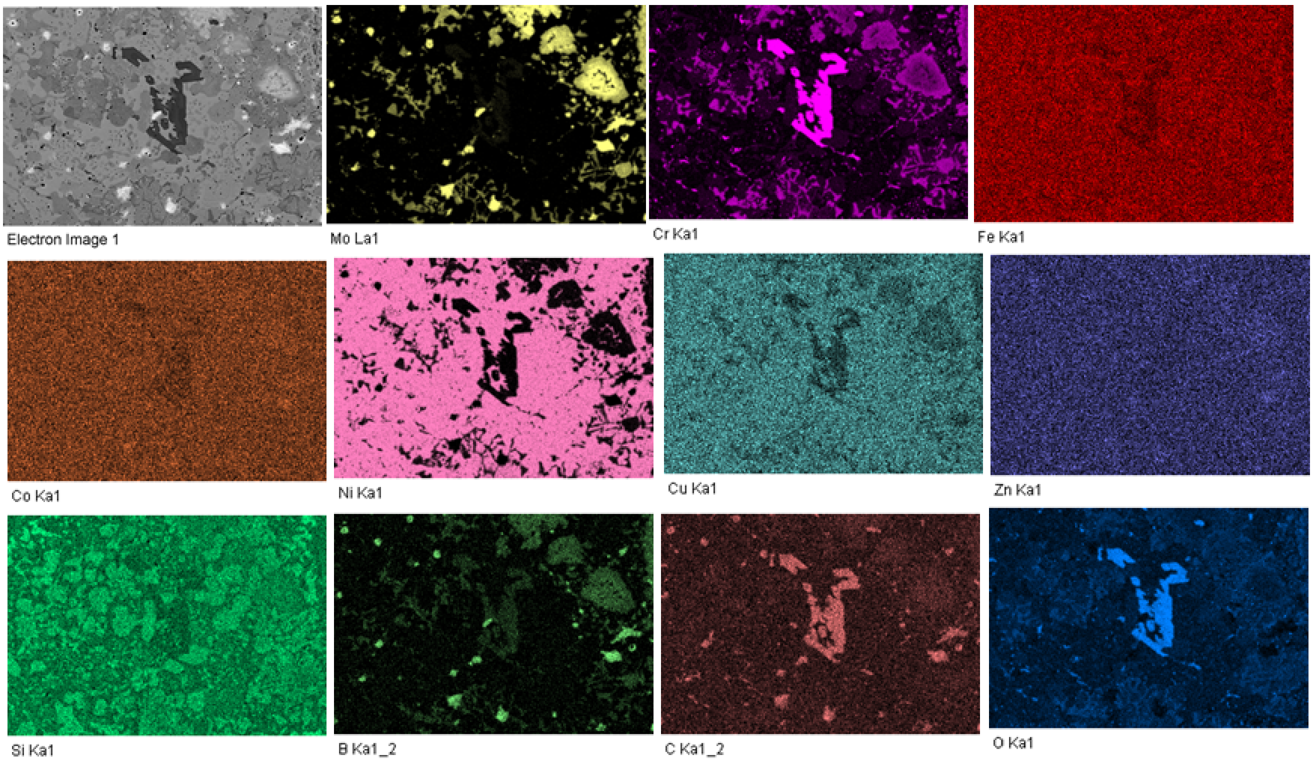

Figure 4.77: Heat treated tablet 5:2:2 surface, Chemical mapping showing Mo, Cr, B, C, O, Si

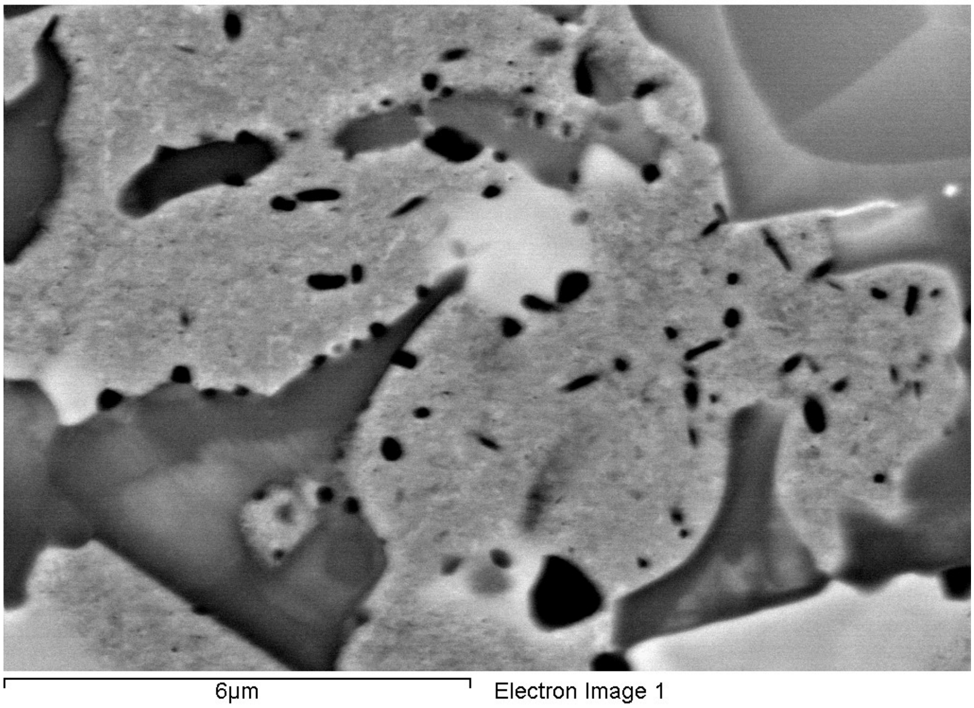

Figure 4.78: Heat treated tablet 5:2:2 surface, Chemical mapping showing Cr, B, C, O, Cu, MO

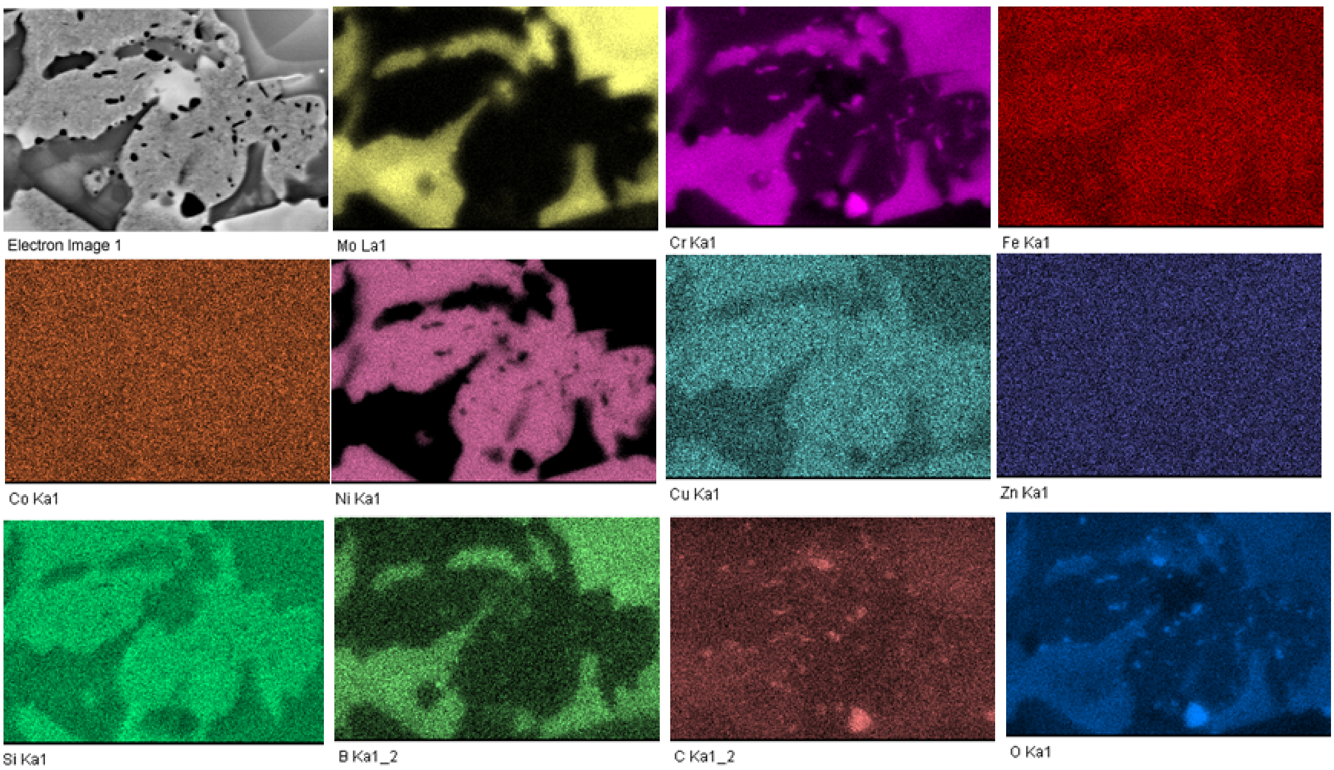

Figure 4.79: Heat treated tablet 5:2:2 surface, Chemical mapping showing Cr, B, C, O, Cu, MO

4.10.2 Non Heat Treated Tablet

Same study has been repeated here for non heat treated tablet.

Electron 3D Model

According to figure 4.80, It is noticeable to see particles in nano size.

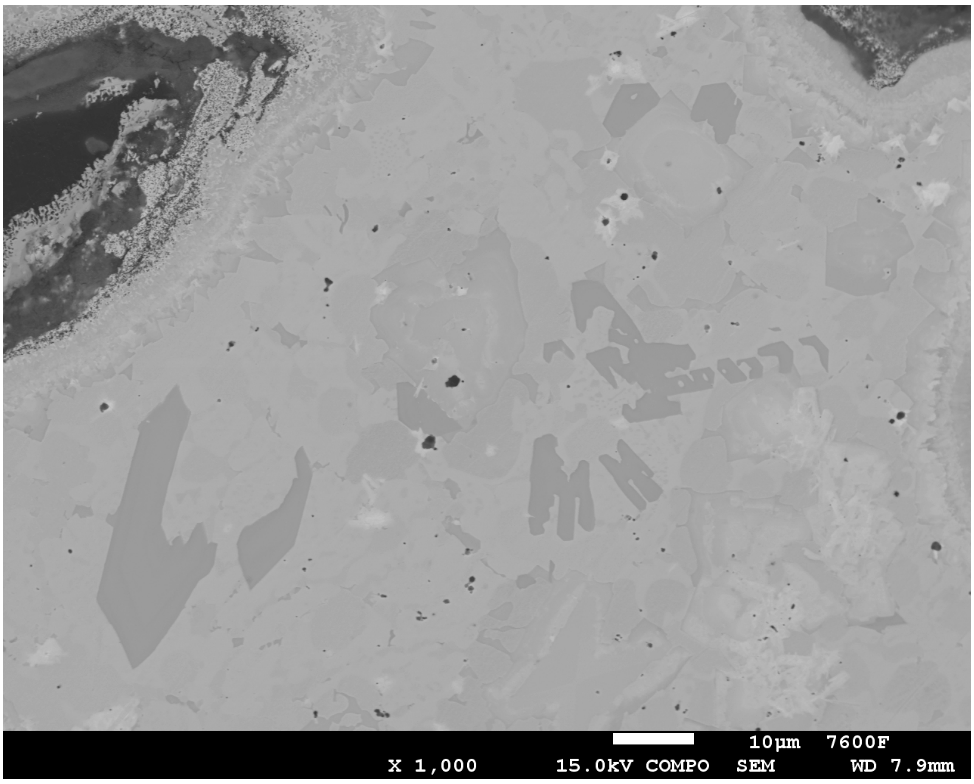

Figure 4.80: Non Heat treated tablet 7:5:14 surface, diameter 10m. Particles with micro & nano particles in size 1 to 100 nanometers

Chemical Mapping by Backscattered Electrons

Chemical Mapping is prepared with purpose to proof type of existed material on tablet surface. These particles could be a risk of releasing these particles.

Figures 4.81, 4.82, 4.83,4.84 show type of material.

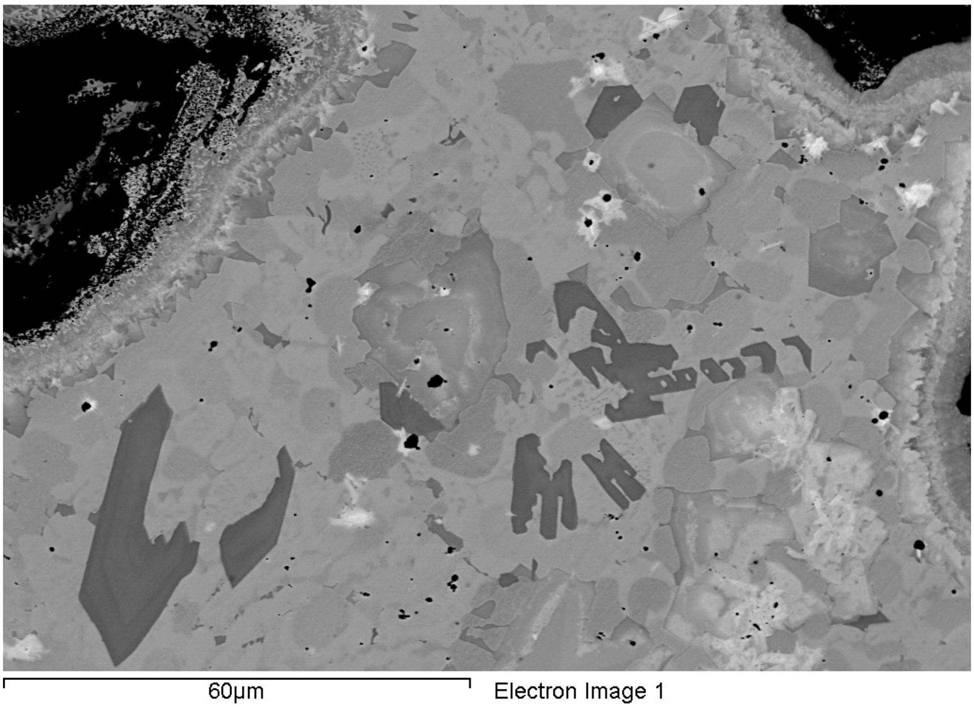

Figure 4.81: Non Heat treated tablet 5:2:2 surface, Chemical mapping showing Cr, C, O, B, Si, Mo

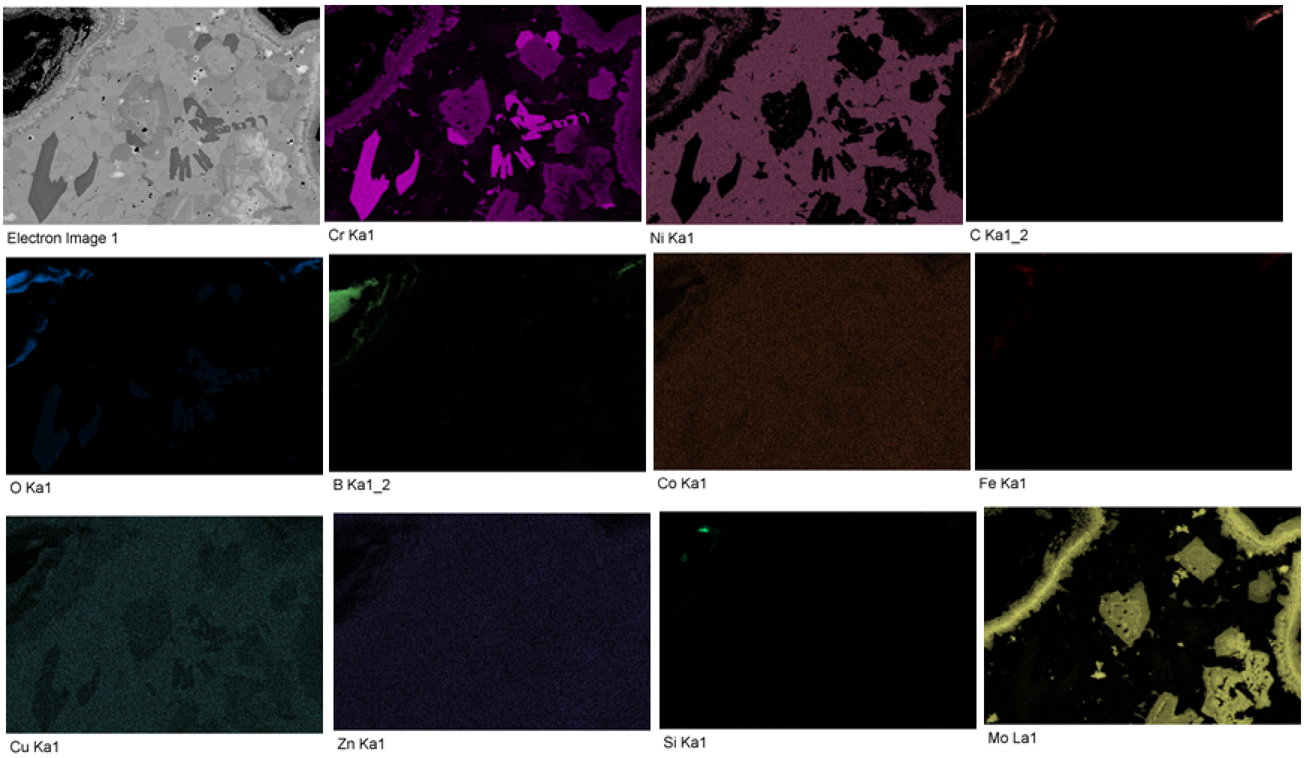

Figure 4.82: Non Heat treated tablet 5:2:2 surface, Chemical mapping showing Cr, C, O, B, Si, Mo

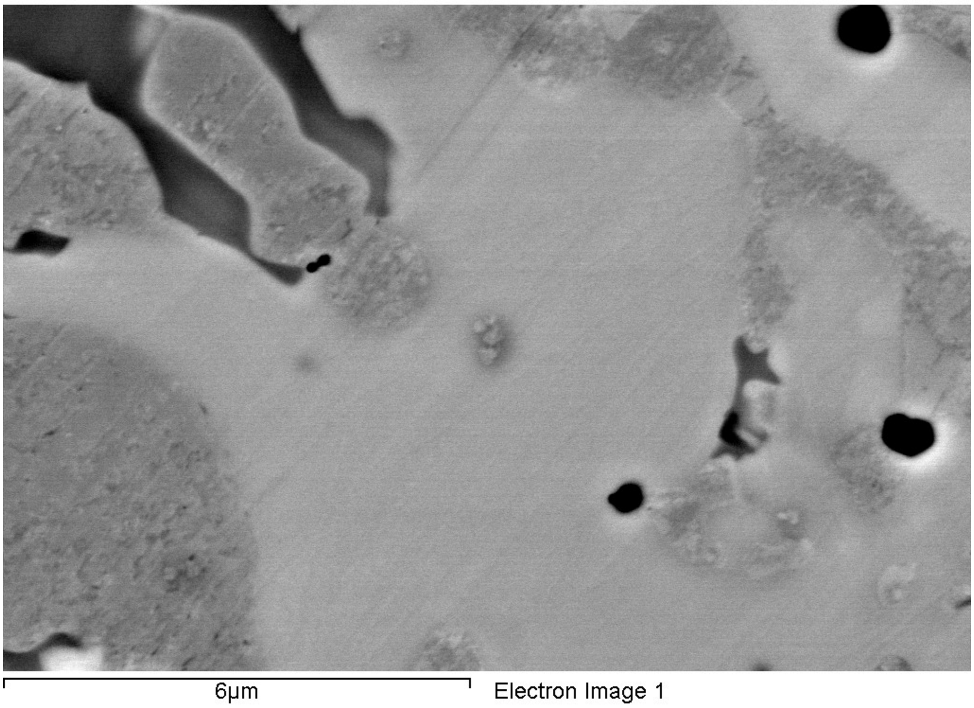

Figure 4.83: Non Heat treated tablet 5:2:2 surface, Chemical mapping showing Cr, Mo, Si, C, O, B

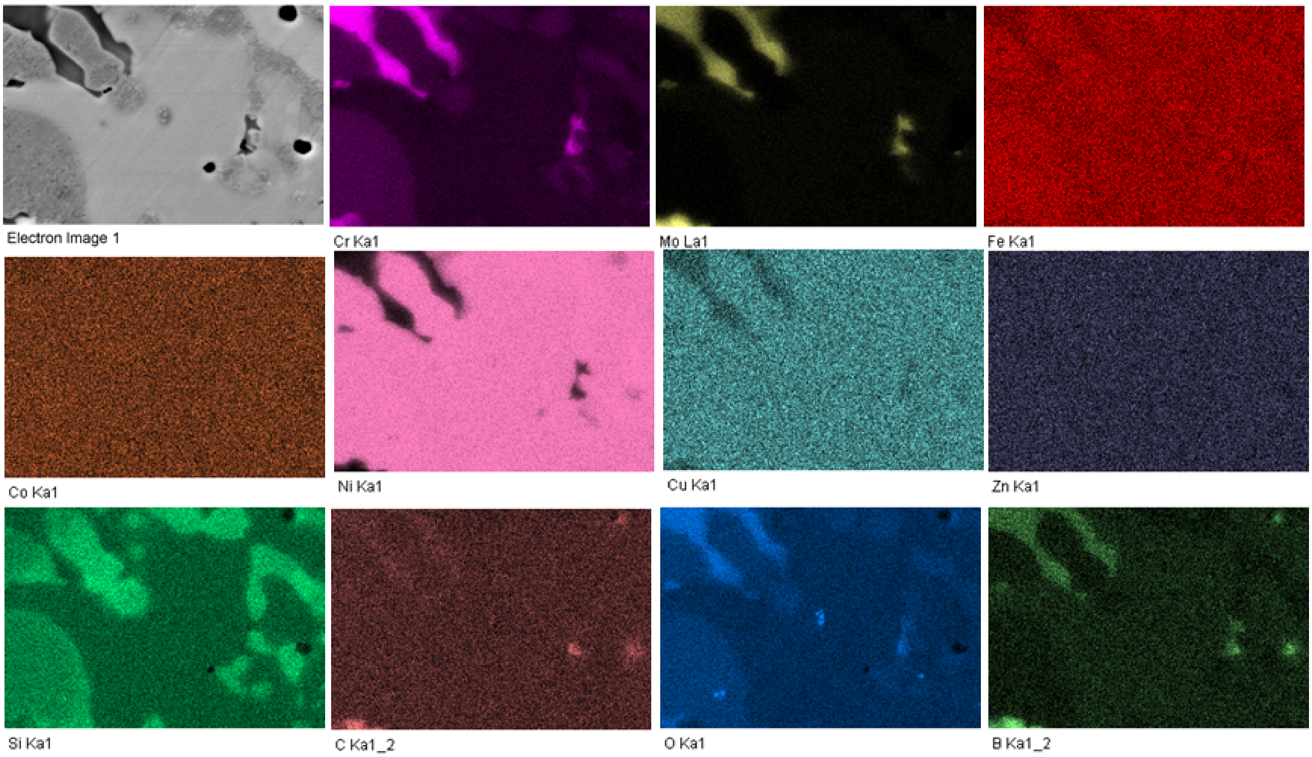

Figure 4.84: Non Heat treated tablet 5:2:2 surface, Chemical mapping showing Cr, Mo, Si, C, O, B

Chapter 5

Discussion

According to previous discussion and explanation, the necessity to estimate risk resulted from previous studies concluded that Cobalt (Co) can be found in rocks, soil, water, plants, and animals, including people. It can harm human kind by different ways. The way how it will harm is mentioned here: eyes, skin, heart, and lungs. Exposure to cobalt may cause cancer, therefore workers may be harmed from exposure to cobalt and cobalt-containing products. The level of harm depends upon the dose, duration, and work being done.[40]

Some examples of workers at risk of being exposed to cobalt include the following:

1. Workers who work in industries processing cobalt-alloys.
2. Miners who work in the metal mining industries.
3. Workers involved in the production or use of cutting or grinding tools
4. Employees who work at nuclear or irradiation facilities

According to European chemical agency and the classification provided by companies to ECHA in REACH registrations identifies, Cobalt considered as Dangerous material and can cause serious danger on human being.

In addition to cobalt, this thesis concentrating on nickel particles existence due to face that it is part of cermets composites study case.

People are exposed to nickel and nickel compounds in many common workplaces, such as mining, welding, casting, and grinding. Occupational exposure to nickel occurs mainly through inhalation of dust particles and fumes or through skin contact, which can increase risks of lung cancer and nasal cancer.

The necessity to study this risk came from lack of knowledge and experience with this new combination of cermets (Ni625 and B_4C), that is why collecting particles, produced by tribology test, for confocal microscope analyses, is necessary for this research, to distinguish micro/ nano particles existence. Electro-microscope analyze was performed to confirm cobalt/ Nickel particles existence in free micro/ nano particles, which is considered as hazard, allergic particles for human being and prohibited material to be found in micro/ nano size particles. [1].

Clear intersect between authors from the same field opinion and this doctoral thesis to show necessity of having risk assessment for any cobalt/ nickel usage as a risk material for any industrial usage. This idea was also supported by thesis author's published article on Metal 2021 conference.[30]

in this thesis cermets containing B_4C and Ni625 alloys as promising composite for better industrial efficiency. Target here is to show that usage of these cermets will emit particles which contain cobalt and nickle particles in nano/ micro size.

- The first main objective of this dissertation was to extend on the till now developed approaches of tribological coating and it's risk of usage in manufacturing applications.

- The risk assessment prepared by this work includes practical analysis of Inconel cermets applications in tribological testing areas.

- Further, as was seen in Section 4.2 Temperature Measurement during samples Preparation. Welding process was continuous and no fast decreasing temperature of the work piece was obtained. Highest temperature obtained from Thermocouple point T1 and it did not increased over 900°C. Duration of time between preheating up to 300^oC and getting back to same temperature after passing arc weld on sample, takes between 3.6-5.36 [min] depending on processing parameters, which is matching with researchers: Fujia Xu, Yaohui Lv, Yuxin Liu, Fengyuan Shu, Peng He, Binshi Xu, who have published the same conclusion in there article "Microstructural Evolution and Mechanical Properties of Inconel 625 Alloy during Pulsed Plasma Arc Deposition Process" [15]

- Depending on fact that studied cermets material in this thesis is quite new and promising, a comparison for samples characteristics before and after heat treatment was able to be done. Such analyse can bring more value for this thesis by giving result was not considered in previous studies. Measurement of surface roughness was executed in section 4.5.1, figure 4.21 shows that roughness Measurement Ra, Rz values have similar average values between heat treated and non heat treated samples.

- By this section 4.5.3 Tribometer Tribology Test, a result was introduced clarifying that, combination of heat treated tablet vs heat treated disk has higher average discharged material comparing to Non Heat treated tablet vs Heat treated disk. This result was published by thesis author in conference Metal 2021 under title "Risk factors for B_4C composite utilization in tribological processes".[30] This result differ from what previous researches done on the same field of study.[11], [12], [15] These previous studies proved that heat treatment can bring better wear resistance to material during tribology while this thesis's result showing opposite results. This deviation can be promising for further studies and analyses.

In fact having these particles, caused by material wear, and lack of knowledge with cermets consists of (Ni625 and B_4C), will motivate to have risk assessment for this special material to proof cobalt/ nickel particles existence in free movement after testing.

Nickel considered as hazard, allergic particles for human being and prohibited material to be found in micro/ nano size particles. [1]. According to many chemical agencies, Cobalt compounds listed in many health agencies as probable or possible human harmfully, and to use this material it is needed to have risk assessment.[2]

This info used as base point for showing this risk by distinguishing micro/ nano particles existence. Electro-microscope analyze was performed to confirm cobalt/ Nickel particles existence in free micro/ nano particles,

- By these sections 4.7 Confocal Microscopy Particles Analyze After Test and 4.9 Microscopic analyze was derived and developed as key contribution of this dissertation work for evaluating the micro & nano particles visibility.

Particles with size up to 0,1-1,0 [µm] were visible clearly by using confocal microscope and nano particles with size 1,0 - 100 [nm] were traced by using electro microscope.

- Referring to section4.10, running an X-ray chemical mapping, Cobalt and Nickel particles were observed and as already mentioned in European standards [EC / List no.: 231-158-0], [CAS no.: 7440-48-4], that Nickel and cobalt considered as high risk materials [EC / List no.: 231-111-4], [CAS no.: 7440-02-0]. Nickel micro & nano particles as allergic particles. Cobalt particles as prohibited material in EU.

- Impact of possible impurities generated by Cobalt and Nickel existence during this process on the occupational and environmental health was analyzed by Electro microscope by finding Nickel and Cobalt particles.

Exposure to cobalt can lead to adverse health effects related to various organs or tissues. Cobalt can harm human organs such as respiratory organs, the skin, the hematopoietic tissues, the myocardium, the thyroid gland, as well as teratogenic and carcinogenic effects.[41], [42], [43]

Based on previous studies which give an overview on the analysis of inorganic nickel species and their toxic effects, occupationally exposed people have a higher risk of respiratory tract cancer due to inhalation of nickel at their workplace in the nickel-producing or using industries. In contrast, within the general population the most harmful health effect related to nickel exposure is allergic contact dermatitis. [44], [45], [46]

This dissertation is considered as a risk assessment for the industrial fabrication and application of these cermets. The production processes for these materials were selected for this analysis, based on their current or near-term potential for large-scale production and commercialization.[30]

Chapter 6

Conclusion

In this chapter, we summarize what we have done in this work and what are the further steps for future work.

6.1 Summary of thesis

In this dissertation work, a preliminary objective was to further investigate the tribological behaviour of cermets B_4C/ Ni alloys 625, as a promising composite to reduce friction, material loss and increase wear resistance. Study was fulfilled under special conditions of heat treatment and different methods of tribology testing methods were done. Further investigation behind the advantages and disadvantages of these materials on industrial tribology and related processes on the environment. Particles analyze was done by different methods, starting with Confocal microscope as first step and electro microscope as second step. Findings from this study:

1. Confocal microscope and electro microscope were used to identify and recognize size of produced particles. Nano sized particles and micro sized particles have been observed clearly.

2. Samples with heat treatment has higher average material loss during tribology test.

3. Micro & Nano sized Cobalt particles were noticed in particles produced by tribology test (variant heat treated disk vs heat treated tablet) more than variant (heat treated disk vs non heat treated tablet).

4. Micro & Nano sized Nickel particles were noticed in particles produced by tribology test (variant heat treated disk vs heat treated tablet) more than variant (heat treated disk vs non heat treated tablet).

5. Higher care is needed here for handling discharged particles from this studied material.

6. It is important to destroy these harmful particles as preventive action by solving it into liquid or by another possible after treatment methods (Burning, Liquidation, Chemical reaction, ...), which could be part of case study future work.

6.2 Fulfillment of targets

Cobalt is a technically important metal, used mainly as a binder in hard-metal industry and as a constituent of many alloys. Boron Carbide and Nickel alloys compounds are used as case study in this dissertation. Implantation and preparation of cobalt alloys has been prepared by plasma powder transferred arc welding, and cobalt compounds induced local and sometimes metastasizing sarcomas in life being. An indication of possible harmful effects of cobalt alloys or compounds in human populations has arisen from medical use, in hard-metal industries, and at cobalt production. Unfortunately, having boron carbide and nickel alloys has a major problem, and the size of most of the investigated populations has been rather small, so none of the investigations alone gives sufficient evidence of a carcinogenic effect in humans, but taken together there is an indication of a potential risk that should be explored further.[25]

From these respective results, this work may conclude the effectiveness of the approach as a means of showing risk of this material usage and possible impurities during manufacturing processes. In addition, a major component of this dissertation work was to provide mechanical properties during all tests running to highlight possible mechanical advantages by using this material in tribological applications.

6.3 Further extensibility and recommendations

From this dissertation, two novel tribological methodologies were derived and tested, namely the ball on surface test and linear tablet on disk. Both tests brought mechanical properties, basic substances for microscopic/ chemical analyse. Nevertheless, for future work further methods of analyze are recommended here: 1- High temperature tribometer. 2- Dry sand/ rubber wheel abrasion test. 3- Wet sand/ rubber wheel abrasion test 4- Pin abrasion test.

As a further means of validation, to check and confirm existence of high risk particles. Use of transmission EM (TEM) and the scanning EM (SEM) electron microscope is highly recommended for more tribology cases to show and confirm best way to achieve safe application of this material.

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