CHAPTER 1

INTRODUCTION

1.1 GENERAL

Rapid advancement in the industrial sector has forced the industrialists and researchers to face severe challenges in improving both the quality and the quantity of the products of their interest. Researchers have been attempting various techniques such as surface coatings, metal matrix composites, etc., to improve the performance of the materials. Among the different methods, cryogenic treatment is one of the significant techniques. Cryogenic treatment is an ultra-low temperature process in which the constituents are exposed to cold treatment deep down to 87 K (−186°C). It is not a substitute for the conventional heat treatment process, but it is an addition to the traditional heat-treatment technique. Also, it is not a temporary process. It is a permanent one-time treatment. Cryogenic treatment will alter the entire portion of the materials [1-3].

Cryogenic treatment technique has been employed to a number of ferrous materials such as tool steels, valve steels, etc. It has been reported in many published literature that there has been a dramatic change in the mechanical and tribological properties due to cryogenic treatment. Tensile strength, hardness, wear resistance, dimensional stability and electrical conductivity are some of the properties which have been reported to be improved due to cryogenic treatment [4-10]. The mechanisms for the enhancement in various properties of different ferrous alloys due to cryogenic treatment are found to be the formation of carbide particles, grain refinement, conversion of retained austenite into martensite etc., [7, 9, 10] and it has been well-known that there is an enhancement in the properties of various metals and alloys due to cryogenic treatment. Next to ferrous materials research has been carried out on copper and its alloys. The thermal conductivity of copper has been predominantly focused, and it has been improved a lot.
### 1.1.1 History of Cryogenic Treatment

The word cryo means cold in Greek. The history of cryogenics dates back to the early periods of the 20th century. By the invention of liquefaction of gases, the cryogenics was possible. In the early 1930s, the tool makers in the UK and US were used to keep the tools in the cold environment during night time. They realised that the tools which were kept outside were possessing better properties. Later, in the 1950s, researchers and industrialists started to scrutinize the effect of lowering temperature on the properties of materials and began to realise the importance of reducing the temperature regarding improved tool life. In the 1970s R F Barron and others investigated the subzero temperature treatment process. They proved that with the improved treatment process the properties and life of the materials could be improved. Since the past three decades, researchers have been continuously working on various parameters of the cryogenic process on different materials and proved that it has a positive impact on the various properties. Also, they tried to explore the underlying mechanism behind the improvement. Much of the investigation on cryogenic treatment was carried out in the last three decades.

In the mid-20th century, the cryogenic treatment was carried out by immersing the part in the cryogenic fluid which is also known as cryo-quenching. Due to this, the parts develop micro-cracks on the surface. This behaviour is termed thermal shock. Hence, it is necessary to lower the temperature gradually. Due to the advancement in the technology the cryogenic treatment has been improved.

### 1.2 Cryogenic Treatment Process

The cryogenic treatment consists of three processes, namely the ramp-down process, soaking process, and ramp-up process. The usual cryogenic treatment cycle is given in Figure 1.1.
In cryogenic treatment cycle, the slow cooling of the specimen to the cryogenic temperature is called the ramp-down process or cool down the process. The ramp-down process should be carried out as gradually as possible. Because of the sudden exposure of the liquid nitrogen on the specimen will create thermal shocks. Due to the thermal shocks, the material will get microcracks which will deteriorate the properties of the materials. Once the ramp-down process is completed the materials will be held at the cryogenic temperature for a prolonged period. This process is called a soaking process. The soaking period should be sufficient enough to allow the materials to transform completely. The soaking period varies for different materials. For ferrous materials, the minimum soaking period should be 24 hours because the retained austenite has to completely transform into the martensite. Also, this transformation should take place in the entire region of the specimen. Hence significant time should be given for the transformation to get completed. For non-ferrous materials, the soaking period can be 8 hours [12].
The specimen has to be brought back to normal temperature after performing the soaking process. This process is called the ramp-up process. The ramp-up is usually performed by cutting off the nitrogen supply at the end of the soaking process and the specimen will reach the normal temperature naturally.

In view of the temperature, the cryogenic treatment can be sorted as follows:

1. Cold treatment or shallow cryogenic treatment (SCT)
2. Deep cryogenic treatment (DCT)

1.2.1 Shallow Cryogenic Treatment (SCT)

Heat treatment is a way of producing the desired properties by a controlled, intentional heating and cooling of metals and alloys. The purpose of heat treatment is to achieve the required properties by relieving the stress induced during various processes, to produce the desired microstructural changes in solid-state in order to obtain desired properties, to induce hardness etc., In ferrous metals and alloys, due to the presence of carbon, various heat treatments can be applied and the required properties can be achieved. Even though the heat treatment on ferrous metals and alloys produce significant effects, some amount of austenite will be retained in the materials, because the completion of phase transformation process from austenite to martensite takes place well below the room temperature. Since austenite is a soft phase, the retained austenite decreases the strength of the ferrous metals and alloys, hence it is prevalent to reduce the temperature of the materials below the room temperature to complete the martensitic transformation process. This can be achieved by reducing the materials to a very low temperature. Therefore, shallow cryogenic treatment can be applied to the materials. The shallow cryogenic treatment is a cold treating process in which materials are exposed to around 193 K (−80°C). Generally, shallow cryogenic treatment can be performed in three steps. Initially, the specimen temperature was lowered gradually from the room temperature to the cryogenic temperature. Then the sample is kept at that temperature for an extended period, finally, it is brought
back, to the room at a constant rate of warming. For most of the steels and alloys the martensitic transformation temperature finishes above 193 K (−80°C) therefore, due to shallow cryogenic treatment the retained austenite can be fully converted into the martensite. Formation of this martensite increases various mechanical properties such as strength, hardness, wear resistance, dimensional stability etc.

1.2.2 Deep Cryogenic Treatment (DCT)

In deep cryogenic treatment, the lowering of temperature has to be down well below shallow treatment temperature. The deep cryogenic treatment is performed by gradually cooling the materials from the ambient temperature to the cryogenic temperature. Slow cooling is a very essential part of the cryogenic treatment process because rapid cooling to cryogenic temperature can produce a thermal shock. Due to thermal shock, the microcracks can be developed in the materials which will eventually reduce the properties of the materials. Generally, less than 123K (−150°C) is termed as DCT or CT [13, 14] this can go up to liquid Helium temperature (20K) [15]. Since the boiling point of the liquid nitrogen is 77 K (−196 °C) which is below 123 K (−150 °C), besides, liquid nitrogen is very easily available and inert, it can be used as the cryogenic fluid. It was reported that thermal shock may occur at liquid nitrogen temperature. Therefore, the materials can be subjected to 87 K (−186°C), thereby, direct exposure of liquid nitrogen can be avoided. Then the materials can be held at that temperature for a sufficient time period. Since cryogenic treatment is a permanent, one-time process, which alters the whole material, sufficient time must be allowed. Finally, the materials are gradually brought back to the room temperature.

1.2.3 Significance of Cryogenic Treatment

The use of cryogenics and mechanical refrigeration varies from space to food processing which includes manufacturing sector, automotive, aerospace, etc., From the published literature it was evident that various mechanical and other properties have been improved due to cryogenic
treatment [11]. The improvement in these properties has been validated to be due to the changes in crystal and microstructural changes in various materials.

Mechanical properties which are said to be improved due to cryogenic treatment are:

- Tensile strength
- Yield strength
- Hardness
- Toughness
- Fatigue life
- Machining parameters such as tool wear, tool life during turning, milling, drilling etc.,
- Tribological properties which include wear resistance, etc.,
- Thermal properties, such as thermal conductivity, dimensional stability etc.,
- Electrical properties, such as electrical conductivity

Cryogenic machining has also been carried out for the past few years. In cryogenic cooling processes, cryogenic fluid during machining is used instead of coolant. The performance study of cryogenically treated materials was carried out by the researchers in the Electro-discharge machine, pin-on-disc tester, turning machines, drilling machine etc. In EDM machining the output responses considered are metal removal rate, TWR, electrode wear ratio and surface roughness. In pin-on-disc and ball-on-disc machines, wear resistance, wear rate, the COF etc., were considered for the performance study. In turning operation flank wear, the hardness of the sample, tool wear etc., are the important responses while conducting the performance study.
1.3 COPPER BERYLLIUM ALLOY

1.3.1 Introduction

Copper and its alloy have also been widely used by man for thousands of years now. People used to make different components by hammers. Pure copper was utilized for many centuries, later tin was added to pure copper to form Bronze and hence it was called Bronze Age. The Bronze Age lasted till 1200 BC. After the discovery of Iron, People started using Iron also. Till today copper is being extensively used because several unique properties of copper and its alloys make them peculiar [16].

1.3.2 Significance of copper and its alloys

Copper and its alloy are considered as one of the important materials in the industry due to some of their characteristics, such as,

- Extraordinary conductivity
- Non-corrosiveness
- Excellent ductility
- Good aesthetics

Pure copper is drawn as wire and used as cables, electrical contacts etc., Because of the high thermal conductivity they are most commonly used in heat exchangers like radiators, condensers, evaporators, also in piping and fittings. Copper alloy possesses excellent fatigue strength and cold working capacity. Hence they are used in springs, fasteners, electrical contacts and various other components. Non-corrosiveness is one of the important properties of copper. Therefore, they are used in certain corrosive environments. However, some alloys of copper are having hydrogen embrittlement issue under certain severe environment.

The addition of alloying element in copper makes it stronger and harder without much affecting the ductility. However, the electrical and thermal conductivity varies based on the alloying element and percentage of alloying elements. Usually, the strength of the copper alloys is increased by precipitation hardening because it has dual advantages of increased strength
in addition to comparable electrical and thermal conductivities [17]. The hardest of the copper alloy is copper-beryllium alloy. Copper-beryllium alloys can be precipitation-hardened, that increases its mechanical strength identical to that of the stainless steel.

1.3.3 Characteristics of copper-beryllium alloy

For some applications requiring a high-strength along with high thermal conductivity, copper-beryllium alloys are being used instead of steels. Particularly noteworthy is that the copper-beryllium alloy is non-magnetic, as distinguished from the ferrous materials. A typical example of the application of precipitation-hardened copper 2 wt. % beryllium alloy is in the preparation of diamond-anvil cells used in high-pressure experimentation. Aircraft landing gears, electrical contacts, etc.

Precipitation-hardening takes place in various alloys apart from the copper-beryllium alloy. This type of hardening attains in an alloy system when supersaturated solid-solution of two or more constituents are permitted to diffuse to form precipitates in the base matrix. With proper selection of heat-treating time and temperature, homogeneously dispersed secondary phase forms inside the solid-solution. These particles strengthen the alloy by appearing as a hindrance to displacement motion. In the Cu-Be alloy system, the alpha phase has the structure of copper, and the secondary phase consists of a Cu-Be intermetallic phase. In the alpha matrix, the Be is disorderly distributed, so this alloy cannot be said to be an intermetallic compound. When cobalt is added to the Cu-Be alloy, it forms as clusters of cobalt beryllide. The phase diagram copper-beryllium alloy is shown in Figure 1.2.
Figure 1.2 – Phase diagram of copper-beryllium alloy [18]

From Figure 1.2, it can be noticed that the copper-beryllium undergoes various transformation. Generally, in room temperature, the copper-beryllium alloy exists in the alpha copper matrix, which is a terminal solid solution of FCC crystal structure with a maximum solid solubility of 2.73% beryllium at 1039 K. The beta phase is stable above 893 K approximately. It is having a BCC crystal structure in a disordered solid solution state. The gamma phase is stable at room temperature. It has a simple cubic crystal structure of CsCl type. It is an orderly structured phase [19]. Generally, the gamma phase exists in grain boundaries [16].

1.3.4 Phase transformation in Cu-2 wt. % Be alloy

Copper-Beryllium alloy undergoes different changes in phase to attain the gamma phase from the alpha matrix phase as presented in the subsequent phase reaction [18, 20, 21].

$$\alpha_s \rightarrow \alpha + \text{GPZone} \rightarrow \alpha + \gamma' \rightarrow \alpha + \gamma' \rightarrow \alpha + \gamma$$ (1.1)
where,

\[ \alpha_s \] – Alpha solid solution of copper in FCC structure.

GP zone – Metastable multilayer coherent structure.

\[ \gamma'' \] – Metastable phase of Cu-Be alloy in the monoclinic structure.

\[ \gamma' \] – Metastable phase in BCC structure.

\[ \gamma \] – Equilibrium phase of Cu-2 wt. % Be alloy at room temperature.

From the published literature it can be inferred that the formation of GP zone and the precipitation of fine beryllide particles are the most influential parameters for the enhancement of the mechanical properties of Cu-2 wt. % Be alloy.

1.3.5 **Advantages of copper-beryllium alloy**

The advantages of copper Beryllium alloy over other copper alloys are:

- High strength
- Good electrical and heat conductivity
- Good fatigue resistant
- Low magnetic susceptibility
- High durability
- High resistance to galling
- Significant non-corrosiveness
- Excellent wear resistance

The mechanical properties of the Cu - 2 wt. % Be alloys are the best of all the copper and its alloys. These exceptional mechanical properties of Cu-2 wt. % Be alloy is achieved because of its excellent age-hardening characteristics even at low temperature [18, 20-23]. However, the increase in mechanical properties is accompanied by the reduction in its electrical and thermal conductivities. Even though the strength of Cu-2 wt. % Be alloy has improved to 1350 MPa, the electrical conductivity has drastically reduced to 20 % of IACS (International annealed copper standard). Exhaustive research
that has been conducted on the various properties and the mechanism for the property change of the copper-beryllium alloy showed that the increase in strength is due to the formation of GP (Guinier- Preston) Zone and the dispersion of fine beryllide particles [23].

1.3.6 Applications of copper-beryllium alloy

Cu-Be alloy possesses high strength along with high resistance to corrosion and, accordingly, it is utilised in diverse applications [16]. Such as,

- Electronic component connectors
- Bearings (aircraft landing gear and various aircraft components)
- Springs and diaphragms
- Dies
- Bushes
- Drill bits
- Fasteners
- Shafts
- Communication industries
- Aerospace industries
- Oil & Gas industries
- Electrodes in resistance welding systems.

1.4 NEED FOR THE PRESENT STUDY

From the above discussion, it is understood that cryogenic treatment is an extremely low-temperature, cold treatment process. It is not a substitute for the traditional heat treatment process, whereas it is an add-on process [13, 14]. Usually, this process is implemented after the completion of the usual heat treatment cycle.

It has been substantiated in the literature that cryogenic treatment is a very effective and efficient process to improve the mechanical and other properties of various materials especially ferrous metals and alloys. But its effect on non-ferrous materials especially Copper-Beryllium alloy has not yet been fully explored. Hence, in this study, an effort has been made to scrutinise
the impact of cryogenic treatment on microstructure, mechanical, electrical, tribological properties of Cu-2 wt. % Be alloy and also to evaluate the performance of cryogenically treated Cu-2 wt. % Be tool in EDM, and to identify the optimum EDM parameters to achieve multi-objective optimisation using Taguchi-Grey relational analysis.

1.5 OBJECTIVES

The present study focuses on the investigation of the properties of cryogenically treated copper 2 wt. % beryllium alloy and has the following objectives:

- To perform cryogenic treatment on the Cu 2wt. % Be alloy.
- To evaluate the microstructure of Cu 2wt. % Be alloy.
- To find the various phases present in the Cu 2wt. % Be alloy.
- To evaluate the mechanical and electrical properties, such as Tensile strength, Yield strength, Hardness and Electrical resistivity.
- To study the wear behaviour of the Cu 2wt. % Be alloy.
- To study the machining performance of cryogenically treated Cu 2wt. % Be tool using EDM.
- To find the optimum EDM parameters for achieving maximum metal removal rate (MRR) and minimum tool wear rate (TWR) & surface roughness using Taguchi-Grey relational analysis.

1.6 LAYOUT OF THE THESIS

The layout of the thesis in this study is as given below:

Chapter 1 presents a brief introduction and history about the cryogenic treatment, unique properties and applications of copper alloy especially Copper-Beryllium alloy, need for the present research and layout of the thesis.
Chapter 2 scrutinizes the available relevant literature which deals with the impact of cryogenic treatment on various properties, such as, tensile strength, hardness, dimensional stability, Tribological properties, of different substances and the influence of cryogenic treatment on machining parameters.

Chapter 3 illustrates the methodology followed and the standards maintained while conducting the experiments for finding the mechanical, electrical, wear and machining behaviours.

Chapter 4 deals with the detailed analysis of results obtained from the different experiments and establishes the relationship between microstructure obtained, the process followed and the property measured.

Chapter 5 describes the inferences drawn from the various experimental studies carried out in this study and offers suggestions for future work.

1.7 METHODOLOGY

Several processing techniques have been reported in the literature to enhance the properties of various metals and alloys. Among the different methods, cryogenic treatment is one where the materials are processing at ultra-low temperature. The main advantage of this process is that it is a permanent and one-time process. In this study, the microstructure of the Cu-Be2 alloy was evaluated using an optical microscope and a scanning electron microscope. Various phases were identified by X-ray diffractometer. The mechanical properties, such as tensile and yield strengths were evaluated using a computer-controlled Universal testing machine. The hardness of the alloy was measured in a Vickers hardness testing machine. The electrical resistivity was determined by standard two probe set-up, and the wear study was performed in a Pin-on-Disc Machine. The machining performance of cryogenically treated Cu-Be2 tool was studied on EDM. A combination of Taguchi approach and Grey-Relational-Analysis was implemented to optimize the process parameters of EDM to achieve maximum MRR and minimum TWR & surface roughness. Confirmation test was conducted to validate the test result. The layout of the methodology followed is presented below.
The Layout of the Methodology