



**EFFECT OF TITANIUM ADDITION ON THE
CORROSION BEHAVIOUR OF ALUMINUM
BRONZE CUAL10NI5FE4 FOR THE USAGE IN
INTERNAL COMBUSTION ENGINE**

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MASTER THESIS
MECHANICAL ENGINEERING**

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“I declare that all the information in this thesis has been obtained and presented in accordance with academic rules and ethical principles; I have also made all references not originating from this study as required by these rules and principles.”

Mukhtar Salem Ahmed ELKURTEHI

ABSTRACT

Master Thesis

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In this study, the effect of titanium addition on the corrosion behaviour of aluminum bronze CUAL10NI5FE4 for the usage in internal combustion engine is studied. The samples were produced at the Sağlam Metal Industry and Trade Research and Development Center. The melting process was executed using a 10-kilogram, 5M medium frequency induction furnace. Two experiments were performed: one without titanium and another with a titanium concentration of 0.2%. The castings were positioned at a temperature of 1230 degrees Celsius. The casting process utilized a permanent mold. For the immersion corrosion test, each sample's surface area was estimated separately. Immersion corrosion persisted for 12 to 72 hours in a 3.5% NaCl solution. Every hour, ethanol and chromatic acid (180 g/L) were used to remove any remaining corrosion residue from the sample surface. After being allowed to dry, the

corrosion samples were individually weighed using calibrated scales, and then they were exposed to immersion corrosion once more.

The incorporation of Titanium did not produce a discernible alteration in the β phase of the microstructures; instead, regional shrinkage in the soft α phase and an augmentation in the κ phase ratio were observed. The hardness data indicate that the addition of Titanium elevated the hardness from 226.17 HB (without titanium) to 237.80 HB (with 0.2% titanium). Corrosion testing indicated that the absence of titanium alloy resulted in adverse corrosion performance. After 72 hours, the minimum weight loss recorded in the CuAl10Ni5Fe4-0.2%Ti alloy was 0.009305 mg/dm². The greatest weight reduction was seen in the absence of titanium alloy, measuring 0.010015 mg/dm².

Keywords: CuAl10Ni5Fe4, titanium, corrosion, hardness, microstructure.

Science Code : 91518

ÖZET

Yüksek Lisans Tezi

İÇTEN YANMALI MOTORLARDA KULLANIM İÇİN ALÜMİNYUM BRONZ CUAL10NI5FE4'ÜN KOROZYON DAVRANIŞI ÜZERİNE TİTANYUM EKLENTİSİNİN ETKİSİ

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Bu çalışmada, içten yanmalı motorlarda kullanım için alüminyum bronz CUAL10NI5FE4'ün korozyon davranışı üzerine titanyum ilavesinin etkisi incelenmiştir. Numuneler Sağlam Metal Sanayi ve Ticaret Araştırma ve Geliştirme Merkezi'nde üretildi. Eritme işlemi 10 kilogramlık 5M orta frekanslı indüksiyon ocağı kullanılarak gerçekleştirildi. İki yükleme gerçekleştirildi: biri titanyum olmadan, diğeri ise %0,2 titanyum içeriğiyle. Dökümler 1230 santigrat derece sıcaklıkta yerleştirildi. Döküm kalıcı kalıp kullanılarak yapıldı. Daldırma korozyon testinde her numunenin yüzey alanı hesabı tek tek hesaplandı. Daldırma korozyonu %3,5 NaCl'de 12-72 saat sürdü. Numune yüzeyini korozyon kalıntılarından temizlemek için her saat başı kromik asit (180 g/L) ve etanol kullanıldı. Kurutma işleminin ardından korozyon numunelerinin tek tek ağırlık ölçümleri hassas terazilerle yapılarak tekrar daldırma korozyonuna bırakıldı.

Titanyum ilavesi mikroyapıların β fazında gözle görülür bir değişikliğe neden olmasa da yumuşak α fazında lokalize büzülme ve κ faz oranında ise artış olduğu belirlendi. Sertlik sonuçlarına göre Titanyumun eklenmesi sertliğin 226,17 HB'den (titanyumsuz) 237,80 HB'ye (%0,2 titanyumlu) yükselmesine neden oldu. Korozyon testlerinde titanyum içermeyen alaşım korozyona karşı olumsuz davranış göstermiştir. 72 saat sonra en az ağırlık kaybı CuAl10Ni5Fe4-0,2%Ti alaşımında gözlemlendi ve bu değer 0,009305mg/dm² oldu. En yüksek ağırlık kaybı 0,010015 mg/dm² değeriyle titanyumsuz alaşımında gözlemlendi.

Anahtar Sözcükler : CuAl10Ni5Fe4, titanyum, korozyon, sertlik, mikroyapı.

Bilim Kodu : 91518

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SYMBOLS AND ABBREVIATIONS INDEX

SYMBOLS

Cu : Copper

Fe : Iron

Ni : Nickel

Al : Aluminum

Ar : Argon

Ti : Titanium

Li : Lithium

H₂ : Hydrogen

ρ : Unit mass

σ : Normal Stress

ABBREVIATIONS

ASTM : American Society for Testing and Materials

DIN : Deutch Industrie Normen

EN : European Norm

TS : Turkish Standard



PART 1

INTRODUCTION

Pure copper was first used by humans approximately 10,000 years ago. Enhanced electrical and thermal conductivity and corrosion resistance are among its well-established qualities. Nonetheless, the insufficient strength of copper has constrained its use. The Bronze Age started around 5,000 years ago with the alloying of copper and tin to enhance its strength. Currently, various copper alloys constitute one of the most extensively utilized material categories in engineering applications due to their diverse qualities. Copper alloys can be categorized into high-strength copper alloys, copper alloys with notable tribological properties, corrosion-resistant copper alloys, and high-conductivity copper alloys based on their intended function and requisite properties for specific applications [1]. High-strength copper alloys are utilized in applications necessitating elevated mechanical strength, including deep drawing, spinning, gears, and copper beryllium and copper aluminum alloys with high aluminum content are included in this category. Corrosion-resistant copper alloys, particularly copper-nickel alloys and nickel-aluminum bronzes, are utilized mostly in the maritime industry. High conductivity copper alloys, particularly copper chromium and copper beryllium alloys, are utilized primarily in resistance welding applications within the electrical and electronics industry. Copper alloys exhibiting significant tribological qualities are utilized in machine components subjected to friction and wear, including bearings and wear plates; aluminum and some bronzes belong to this category.

Nickel aluminum bronzes comprise copper, aluminum, nickel, and iron. They are among the alloys that are extensively favored in engineering applications because to their superior wear resistance, high strength, and corrosion resistant qualities. Numerous research in the literature have employed various approaches to enhance the mechanical characteristics and wear resistance of nickel aluminum bronzes.

In contrast to methods like excessive plastic deformation or further heat treatments, the incorporation of alloying elements is a more economical and pragmatic strategy, since it does not extend the manufacturing timeline. Studies reported in the literature suggest that adding different alloying elements improves strength and resistance to wear. Titanium is an element utilized in copper alloys for this reason. The wear resistance of nickel aluminum bronzes is enhanced by incorporating titanium into the alloy surface through various surface treatments [2,3]. The incorporation of titanium at a constant rate, alongside B and Pb, enhanced wear resistance and strength [4].

The purpose of this work is to evaluate the effects of 0.2% titanium incorporation on the CuAl10Ni5Fe4 alloy's microstructure and corrosion resistance. To this end, titanium-free CuAl10Ni5Fe4 with 0.2% titanium content was manufactured; variations in corrosion resistance were examined using corrosion testing, and alterations in microstructure were analyzed using an optical microscope.

PART 2

COPPER ALLOYS

2.1. GENERAL COPPER ALLOY PROPERTIES

Copper usage dates back 10,000 years. Copper items initially appeared in the Middle East around 8700 BC. Early molten metal art was constructed from copper [5]. Its corrosion resistance and electrical and thermal conductivity make copper famous. However, it is non-magnetic, recyclable, easy to alloy, and robust [6]. Copper alloys developed in Mesopotamia approximately 3500 BC, and copper-tin initiated the Bronze Age. Bronze and brass were popular before iron was discovered. After electricity was discovered in the 19th century, copper alloys became popular [7]. Copper alloys are a popular industrial metal group. Copper alloys are easy to machine, have good electrical and thermal conductivity, corrosion resistance, strength, and fatigue resistance. Some copper alloys can be welded using gas metal arc and resistance welding [5–7].

2.2. COPPER ALLOY GROUPS

Casting and wrought copper alloys are categorized by application. Based on solidification range, cast copper alloys are categorized into three classes. Group 1 alloys include manganese, aluminum, and copper chromium alloys having a limited solidification range. Group 2 alloys have a modest solidification range, with a 50–110 °C liquidus–solidus difference. Group 2 alloys include beryllium coppers, silicon bronzes, and copper nickel. Group 3 alloys solidify around 110–170 °C. This category includes tin and lead bronzes [8]. The alloying components of copper alloys split them into 9 categories. Pure coppers, high conductivity copper alloys, copper-zinc, copper-tin, aluminum, silicon, nickel, zinc nickel, copper, and specific alloys.

Commercially named alloys are patented in addition to these criteria. Commercial alloys like Muntz Metal and Moldmax are best known.

2.2.1. Pure Coppers

Pure copper metals contain 99.3% copper [5]. In EN (European standards) standards, Cu-ETP electrolytic solid copper, Cu-OF oxygen-free copper, and Cu-OFE oxygen-free electronic grade copper are included.

2.2.2. High Conductivity Coppers

High conductivity coppers have 94% copper and little other alloying elements. Strength and thermal stability are the major goals of alloying. This includes beryllium coppers and copper chromium alloys [5].

2.2.3. Copper Zinc Alloys

Copper-zinc alloys are referred to as brasses. These are alloys including up to 40% zinc by mass [5]. Their internal structure and mechanical qualities fluctuate based on the zinc concentration. They are categorized into two classes based on its copper content: alpha brasses, which contain above 61% copper, and alpha+beta brasses, which contain between 54% and 61% copper [9].

2.2.4. Copper Tin Alloys

It is a category of alloys referred to as phosphor bronze or tin bronze. They comprise up to 10% tin and 0.2% phosphorus. Cast iron comprises 1.25% to 10% tin [5].

2.2.5. Copper Aluminum Alloys

These are alloys of aluminum and other alloying elements in concentrations of 3% to 15% [5]. They may be categorized into two groups based on their chemical compositions: alpha simple aluminum alloys, which include just copper and aluminum

as alloying elements, and complex aluminum alloys, which include additional alloying elements such as iron, nickel, and magnesium alongside aluminum. Iron is a commonly utilized alloying ingredient in aluminum bronzes. They dissolve up to 2% in the alpha phase. Iron constitutes the FeAl₃ intermetallic phase that reduces the thickness of the structure with aluminum. Manganese is used into complicated alloys for its deoxidizing properties. It solubilizes up to 12% in the alpha phase and exhibits effects analogous to iron. Nickel is the predominant alloying ingredient in aluminum bronzes. Nickel may dissolve up to 5% in the alpha phase and produces the Ni₃Al phase, which exhibits a precipitation action with aluminum [8].

2.2.6. Copper Silicon Alloys

Copper-silicon alloys are copper alloys that include a maximum of 3% silicon, sometimes referred to as silicon bronzes. They may comprise zinc, manganese, aluminum, or iron. The predominant silicon bronzes are high-alloy silicon bronzes with 3% silicon and low-alloy silicon bronzes with 1.5% silicon [5].

2.2.7. Copper Nickel Alloys

Copper alloys with a nickel content of up to 30% are referred to as copper-nickel alloys. These alloys, referred to as nickel bronzes, are categorized into four classes based on their nickel concentration. These consist of alloys with less than 5% nickel, alloys with 5%-10% nickel, alloys with 10%-20% nickel, and specialized alloys where nickel is the predominant ingredient [9]. The use of Cu-Ni binary alloys with a nickel content of up to 10% is significantly restricted. Alloys comprising 15%-30% nickel are predominantly favored for their cold formability and superior corrosion resistance. The most prevalent alloys including several alloying components are Cu-Ni-Fe-Mn alloys. Additions of iron and manganese in these alloys enhance corrosion resistance [8].

2.2.8. Copper Nickel Zinc Alloys

Copper alloys that include nickel and zinc, commonly referred to as German silver. An established example is the copper alloy including 12% nickel and 23% zinc, designated as C75700 in ASTM standards. It is utilized in deep-drawing components and contact springs.

2.2.9. Special Alloys

They are alloys that incorporate components designed to impart a certain characteristic primarily for application.



PART 3

BRONZES

3.1. ALUMINUM BRONZES

Copper alloys known as aluminium bronzes have aluminium as the main alloying element. They are recognized for their superior amalgamation of mechanical attributes and corrosion resistance [10]. Aluminum bronzes are extensively utilized in diverse applications such as maritime propellers, shipbuilding, hydroelectric power generation, and industrial gear [11,12].

A key benefit of aluminum bronzes is their resistance to corrosion. They have significant corrosion resistance in many conditions, such as saltwater, river water, and alkaline solutions [13,14]. The corrosion resistance of aluminum bronzes is due to a protective oxide coating on the surface that serves as a barrier against corrosive substances [15]. The use of aluminum as an alloying ingredient markedly improves the corrosion resistance of the alloy [14].

Aluminum bronzes exhibit not just corrosion resistance but also superior mechanical qualities. They possess elevated strength, commendable ductility, and significant wear resistance [16]. These characteristics render aluminum bronzes appropriate for applications necessitating both strength and corrosion resistance, particularly in maritime conditions [17]. Aluminum bronzes are often utilized in the production of propellers, bearings, valves, and pumps [10,12].

The microstructure of aluminum bronzes plays a crucial role in determining their properties. Heat treatment and alloy composition can influence the microstructure and, consequently, the mechanical and corrosion properties of aluminum bronzes [18]. For example, the addition of nickel and iron to aluminum bronzes can improve their

strength and hardness [19]. The presence of intermetallic phases, such as α and γ phases, also contributes to the mechanical properties of aluminum bronzes [20].

Erosion and erosion-corrosion resistance are important considerations for materials used in applications exposed to abrasive and corrosive environments. Studies have investigated the erosion and erosion-corrosion performance of aluminum bronzes, both in cast and thermally sprayed forms [21]. The results showed that thermally sprayed nickel-aluminum bronze exhibited better erosion and erosion-corrosion resistance compared to cast nickel-aluminum bronze. The microstructure and coating characteristics were found to influence the erosion and erosion-corrosion behavior of aluminum bronzes [21].

Surface modification techniques have also been explored to enhance the properties of aluminum bronzes. For example, selective surface diffusion processes have been used to modify the surface of aluminum bronzes using waste materials, resulting in cost-effective and environmentally friendly surface modifications [22]. In an effort to enhance the tribological properties of the alloys, more research has looked into the creation of secondary structures on the friction surface of aluminium alloys for monometallic journal bearings [23].

To sum up, copper alloys known as aluminium bronzes combine exceptional mechanical qualities with resistance to corrosion. They are extensively utilised in many different industries, including as industrial machinery, maritime, and power generating. Although the existence of a protective oxide covering is responsible for aluminium bronzes' resistance to corrosion, other parameters including alloy composition and microstructure affect their mechanical qualities. In order to improve the qualities of aluminium bronzes, more study has concentrated on modifying their surface and investigating erosion-corrosion resistance strategies.

3.2. ALUMINUM BRONZE CUAL10NI5FE4

CuAl10Ni5Fe4, or aluminium bronze, is an alloy based on copper that is alloyed with iron, nickel, and aluminium. It is renowned for having superior tribological qualities,

resistance to corrosion, and mechanical qualities [10,24–27]. Numerous industries, including aerospace, automotive, marine, and manufacturing, employ aluminium bronze extensively [23,24,28].

One of the key advantages of aluminum bronze is its high strength and hardness, which make it suitable for applications that require good load-bearing capacity and wear resistance [24–27]. It has been used as a tool material for deep drawing of high alloy steel due to its excellent friction properties and high load capacity [26,29]. In dissimilar metal connections, aluminium bronze has also been utilised as a surface layer to provide resistance against impact attacks and cavitation erosion [30].

In terms of tribological properties, aluminum bronze exhibits good friction and wear characteristics. It has been studied as a bearing material and has shown favorable performance in terms of wear resistance and low friction coefficient [23,31–34]. The self-lubricating ability of aluminum bronze allows it to absorb impact forces and accommodate small hard particles, reducing the risk of surface scratches [35]. Additionally, aluminum bronze has been used in the manufacturing of self-lubricating bearing materials [33].

Corrosion resistance is another important characteristic of aluminum bronze. It has been found to have better corrosion resistance compared to other copper alloys, especially at high temperatures [27]. Aluminum bronze is commonly used in applications where resistance to corrosion is crucial, such as valves, fittings, pump castings, and heat exchanger water boxes [10]. It has also been studied as a potential replacement for monometallic bronze journal bearings, offering improved tribological properties [23].

The microstructural evolution of aluminum bronze has been investigated in various studies. Nickel aluminium bronze has been created via wire-arc additive manufacturing (WAAM), and the mechanical and microstructural qualities of the finished product have been examined [24,25]. Directional solidification has been employed to investigate the effects of thermal variables on the microstructure, hardness, and microhardness of aluminum bronze alloys [36]. It has also been

investigated how production processes affect the mechanical characteristics and microstructures of aluminium bronze [37].

To sum up, aluminium bronze, or CuAl10Ni5Fe4, is an alloy based on copper that has superior tribological qualities, corrosion resistance, and mechanical qualities. It is frequently utilised for applications requiring high strength, wear resistance, and corrosion resistance in a variety of industries. A lot of research has been done on the microstructural evolution of aluminium bronze, and several production techniques have been investigated to maximise its characteristics. All things considered, aluminium bronze is a flexible material with a number of advantageous qualities for a variety of engineering uses.

3.3. FABRICATION OF ALUMINUM BRONZE CUAL10NI5FE4

CuAl10Ni5Fe4, an alloy based on copper, is commonly utilised in numerous applications because of its superior mechanical and tribological characteristics [38]. The fabrication of this alloy involves several processes and techniques to achieve the desired properties. One approach to fabricating aluminum bronze CuAl10Ni5Fe4 is through the use of powder metallurgy. The addition of mechanically alloyed copper-based granules to powder bronze containing 5 weight percent tin was studied by Smirnov & Shalunov [38]. By adding these granules, antifriction composite materials were produced that were better than conventional antifriction tin and aluminium bronzes in terms of mechanical and tribotechnical qualities. This suggests that the addition of mechanically alloyed copper-based granules can enhance the properties of aluminum bronze CuAl10Ni5Fe4. Another method of fabricating aluminum bronze CuAl10Ni5Fe4 is through accumulative roll bonding (ARB) process. Alizadeh & Dashtestaninejad [39] studied the fabrication of manganese-aluminum bronze as a shape memory alloy using the ARB process. However, the specific fabrication of aluminum bronze CuAl10Ni5Fe4 using the ARB process was not reported in this reference.

The fabrication of aluminum-bronze coatings can also be achieved through thermal spraying processes. Morales et al. [40] investigated the corrosion resistance of

aluminum-bronze coatings as a function of gas pressure used in the thermal spraying process. Although this reference does not directly discuss the fabrication of CuAl10Ni5Fe4, it provides insights into the fabrication of aluminum-bronze coatings, which can be relevant to the fabrication of CuAl10Ni5Fe4 coatings. In terms of tribological characteristics, Tan et al. [31] studied the tribological characteristics of nickel-aluminum bronze CuAl10Ni5Fe4 against 30CrMnSiA steel after prior corrosion treatment. The study focused on the tribological behavior of the alloy and its performance against steel. This information can be useful in understanding the tribological properties of CuAl10Ni5Fe4 and its suitability for specific applications. Furthermore, the fabrication of aluminum bronze coatings using high-velocity oxy-fuel (HVOF) was investigated by [28]. The study demonstrated that the aluminum bronze coating fabricated via HVOF exhibited excellent resistance performance, even at high frequencies. This suggests that the fabrication process can significantly influence the tribological properties of aluminum bronze CuAl10Ni5Fe4. Micro casting is another technique that can be used for the fabrication of aluminum bronze CuAl10Ni5Fe4. Rögner et al. [41] studied the microstructure and mechanical properties of micro tensile specimens made of CuAl10Ni5Fe4 produced by micro casting. The study highlighted the influence of process parameters on the microstructure of the alloy, indicating that the fabrication process can affect the material's properties.

In the field of tribology, Çakir & Tunay [42] investigated the tribological properties of journal bearings used in tamping units of railway tamping machines. The study compared the performance of CuSn14 tin bronze with CuAl10Fe5Ni5 aluminum bronze. The use of aluminum bronze as a replacement for tin bronze suggests that aluminum bronze CuAl10Ni5Fe4 may exhibit favorable tribological properties. Corrosion and wear resistance are important considerations for aluminum bronzes. The impact of cobalt and titanium additions on the corrosion and wear resistance of aluminum bronzes containing nickel was examined by Kulakli et al. [27]. In comparison to other copper alloys, the study indicated that CuAl10Ni5Fe4 aluminum bronzes showed superior wear resistance and corrosion resistance at high temperatures. This shows that aluminum bronze CuAl10Ni5Fe4 can be made more resistant to corrosion and wear by adding cobalt and titanium. The effect of heat

treatment on the tribological characteristics of CuAl10Ni5Fe4 nickel aluminum bronze was investigated by [43]. The study examined the influence of different heat treatment processes on the tribological characteristics of the alloy. This information can be valuable in understanding the effect of heat treatment on the properties of CuAl10Ni5Fe4 and optimizing the fabrication process. In summary, the fabrication of aluminum bronze CuAl10Ni5Fe4 involves various processes and techniques such as powder metallurgy, accumulative roll bonding, thermal spraying, micro casting, and heat treatment. These processes can significantly influence the mechanical, tribological, and corrosion properties of the alloy.

The addition of mechanically alloyed copper-based granules, the use of thermal spraying processes, and the optimization of heat treatment can enhance the properties of CuAl10Ni5Fe4. Further research is needed to explore the specific fabrication methods and parameters for achieving the desired properties of CuAl10Ni5Fe4.

3.4. MECHANICAL PROPERTIES OF ALUMINUM BRONZE CUAL10NI5FE4

Aluminum bronze CuAl10Ni5Fe4 is a copper alloy that is widely used due to its superior mechanical properties. It possesses high strength, oxidation and corrosion resistance in marine environments, as well as excellent wear, cavitation, and impact resistance [44]. The addition of niobium carbide to aluminum bronze alloy through high-energy milling has been shown to improve its properties, making it a promising material for various applications [44]. In addition, compared to other copper alloys, aluminium bronze CuAl10Ni5Fe4 offers higher wear resistance and superior corrosion resistance at high temperatures [27].

The microstructural transformations and mechanical properties of cast NiAl bronze, which is similar to aluminum bronze CuAl10Ni5Fe4, have been studied. It was found that fusion welding and friction stir processing can significantly affect the microstructure and mechanical properties of the alloy [45]. Investigations have also been conducted into the effects of various production techniques on the mechanical characteristics and microstructures of aluminium bronze. The investigation

demonstrated that the alloy's microstructure and mechanical characteristics can be significantly influenced by the production process [37].

Tribological properties, such as friction and wear, are important considerations for materials used in journal bearings. CuAl10Fe5Ni5 aluminum bronze has been studied as an alternative to tin bronze for journal bearings in railway tamping machines. The experiments conducted showed promising results in terms of tribological properties [42]. Similarly, tribological characterization of Al-bronzes used as mold materials has been investigated. The study found that CuAl10Ni5Fe4 alloy has lower coefficient of friction compared to CuAl14Fe4Mn2Co alloy, but it suffers from wear under dry sliding conditions [32].

Numerous research have examined the microstructure and mechanical characteristics of aluminium bronze CuAl10Ni5Fe4. Research has been done on the effects of annealing, quenching, and ageing on the alloy's microstructure and mechanical characteristics [46]. The effects of dopant and heat treatment on the microstructure and mechanical properties of nickel-aluminum bronze have also been studied [47]. Additionally, the estimation of microstructure and corrosion properties of peened nickel aluminum bronze has been analyzed [48]. These studies highlight the importance of heat treatment and microstructure in determining the mechanical properties of aluminum bronze CuAl10Ni5Fe4.

Analysis of the densification of aluminium bronze powders with various carbides demonstrates that aluminium bronze alloy is used in settings that call for good mechanical resistance and wear resistance [49]. The synthesis and characterization of nanocrystalline Al-Cu powders produced by mechanical alloying have also been investigated, demonstrating the potential of mechanical alloying in producing aluminum bronze alloys [50].

In summary, aluminum bronze CuAl10Ni5Fe4 is a copper alloy with superior mechanical properties, including high strength, corrosion resistance, and wear resistance. The addition of niobium carbide and the use of different production methods can further enhance its properties. Heat treatment, microstructure, and dopant

elements also play a significant role in determining the mechanical properties of the alloy. Tribological properties, such as friction and wear, are important considerations for applications such as journal bearings. Overall, aluminum bronze CuAl10Ni5Fe4 is a promising material for various engineering applications.

3.5. CORROSION PROPERTIES OF ALUMINUM BRONZE CUAL10NI5FE4

Aluminum bronze CuAl10Ni5Fe4 is a copper-based alloy that contains up to 10% aluminum, 5% nickel, and 4% iron [36]. This alloy is widely used in various applications due to its superior properties, including high strength, corrosion resistance, and wear resistance [44].

The corrosion resistance of aluminum bronze CuAl10Ni5Fe4 is attributed to the formation of a passive film on the surface, which reduces the corrosion rate by inhibiting the transport of corrosive ions [14]. This passive film is composed of protective layers such as Al₂O₃ and Cu₂O [14]. The corrosion resistance of aluminum bronze can be further enhanced by heat treatment, which affects the microstructure and erosion-corrosion behavior of the alloy [18].

Studies have shown that aluminum bronze CuAl10Ni5Fe4 exhibits excellent corrosion resistance in various environments, including alkaline solutions [14], chloride solutions [18], and marine environments [44]. The alloy has been found to have higher corrosion resistance compared to other commercially available nickel-aluminum-bronze alloys [19]. It also shows good resistance to cavitation corrosion [51].

In addition to corrosion resistance, aluminum bronze CuAl10Ni5Fe4 also possesses high wear resistance, making it suitable for applications where tribological properties are important [31]. The alloy has been used as a mold material and in drawing dies due to its excellent mechanical and tribological properties [32,51]. It has also been used in ship propellers, where it exhibits superior corrosion-erosion resistance [12].

Various factors can influence the corrosion properties of aluminum bronze CuAl10Ni5Fe4. For example, the addition of cobalt and titanium has been found to

improve the corrosion and wear resistance of nickel-containing aluminum bronzes [27]. The particle size of Al₂O₃ in a high-aluminum bronze coating can also affect its corrosion resistance [52]. Surface treatments such as shot peening have been shown to enhance the cavitation resistance of nickel aluminum bronze alloys [53].

In conclusion, aluminum bronze CuAl10Ni5Fe4 is a copper-based alloy with excellent corrosion resistance, wear resistance, and mechanical properties. Its corrosion resistance is attributed to the formation of a passive film on the surface, which inhibits the transport of corrosive ions. The alloy has been used in various applications, including marine environments, mold materials, and ship propellers. Factors such as heat treatment, alloy composition, and surface treatments can influence its corrosion properties. Further research is needed to explore the specific corrosion properties of aluminum bronze CuAl10Ni5Fe4 in different environments and under different conditions.

3.6. USAGE FIELDS OF ALUMINUM BRONZE CUAL10NI5FE4

Aluminum bronze CuAl10Ni5Fe4 is a copper alloy that is widely used in various fields due to its superior properties. It possesses high strength, oxidation and corrosion resistance in marine environments, as well as wear, cavitation, and impact resistance [44]. These properties make it suitable for applications such as marine propellers, shipbuilding, aircraft industry, oil and gas industry, valves, fittings, pump castings, pump shafts, valve stems, heat exchanger water boxes, and anti-wear coatings [10,17,44,54].

In terms of tribological behavior, aluminum bronze CuAl10Ni5Fe4 exhibits high hardness, low friction coefficient, and excellent wear resistance, making it suitable for industrial applications as an anti-wear coating [55]. It also has high load capacity and excellent friction properties, making it advantageous for forming tools, particularly in the cold forming of high alloy austenitic steel [26]. Furthermore, compared to other copper alloys, aluminium bronze CuAl10Ni5Fe4 has been discovered to have superior wear resistance and better corrosion resistance at high temperatures [27].

The microstructure of aluminum bronze CuAl10Ni5Fe4 plays a significant role in its mechanical properties. Research has shown that the microstructure of aluminum bronze CuAl10Fe5Ni5 (BA1055) castings used for marine propellers affects their mechanical properties [56,57]. The addition of nickel to aluminum bronze alloys has also been found to influence their structure and mechanical properties [57].

Aluminium bronze CuAl10Ni5Fe4 has a good mix of strength, toughness, and corrosion resistance, which makes it a popular choice for marine applications [17]. It has been found to exhibit excellent resistance to corrosion fatigue and compares favorably with stainless steels [58]. However, it is important to note that the corrosion resistance of aluminum bronze can be influenced by factors such as weld and surface defects [10].

Overall, aluminum bronze CuAl10Ni5Fe4 is a versatile copper alloy that finds applications in various fields due to its superior properties. Its high strength, corrosion resistance, wear resistance, and low friction coefficient make it suitable for marine applications, shipbuilding, aircraft industry, oil and gas industry, and as an anti-wear coating. Its microstructure and the addition of certain elements can influence its mechanical properties, and it exhibits good resistance to corrosion fatigue. However, its corrosion resistance can be affected by factors such as weld and surface defects.

3.7. TITANIUM ADDITION TO ALUMINUM BRONZE CUAL10NI5FE4

Titanium addition to aluminum bronze CuAl10Ni5Fe4 is a topic of interest in the field of materials science and metallurgy. The addition of titanium to aluminum bronze alloys can have various effects on the microstructure, mechanical properties, corrosion resistance, and wear resistance of the alloy.

Several studies have investigated the impact of titanium addition on aluminum bronze alloys, considering different processing methods and alloy compositions. The effects of cobalt and titanium additions on the characteristics of nickel-containing aluminium bronze (CuAl10Ni5Fe4 alloy) under cast and forged conditions were examined in one study by Kulakli et al. [27]. The study found that the addition of titanium as a grain

refiner improved the properties of the alloy, including corrosion and wear resistance. Another study by Ma et al. [59] focused on the microstructure and mechanical properties of Al/Ti/Al laminated composites prepared by roll bonding. The study highlighted the economic attractiveness of the Ti/Al system compared to monolithic titanium, due to the joining of relatively inexpensive aluminum. This suggests that the addition of titanium to aluminum bronze could provide cost benefits.

The use of titanium alloys as a replacement for aluminum in certain applications has also been explored. The possibility of titanium alloy 6Al-4V as an aluminium substitute was examined by Sanders & Edwards [60] because of its favourable coefficient of thermal expansion, light weight, good corrosion resistance, compatibility with composite materials, and capacity to tolerate higher temperatures. This suggests that the addition of titanium to aluminum bronze could enhance its high-temperature performance and corrosion resistance. Regarding manufacturing techniques, Lee & Chung [61] investigated the self-propagating high-temperature synthesis process in the titanium, carbon, and aluminium system, as well as its ignition phenomena and reaction mechanisms. The study investigated the effect of aluminum addition on the ignition and reaction mechanisms. This suggests that the addition of aluminum, along with titanium, could influence the ignition and reaction behavior of the alloy.

Furthermore, the addition of other elements to aluminum bronze alloys, such as boron carbide particles, has been investigated. The friction behaviour of aluminium bronze enhanced with boron carbide particles was studied by Smolin et al. [62]. The study prepared powder mixtures with different boron carbide/aluminum bronze weight ratios and deposited them on a Cu-7.5 wt%Al alloy. This suggests that the addition of titanium, along with boron carbide particles, could potentially enhance the mechanical properties and wear resistance of aluminum bronze.

To summarise, the incorporation of titanium into aluminium bronze CuAl10Ni5Fe4 can result in diverse outcomes for the alloy's microstructure, mechanical characteristics, resistance to corrosion, and endurance against wear. The precise effects rely on variables like the composition of the alloy, the production technique, and the

existence of additional components. Properties including cost-effectiveness, wear resistance, corrosion resistance, and high-temperature performance can all be enhanced by the addition of titanium. To completely comprehend the impact of titanium addition on aluminium bronze alloys and to optimise the alloy composition for particular applications, more research is necessary.



PART 4

EXPERIMENTAL STUDIES

4.1. PRODUCTION OF ALLOYS

This study investigated the impact of titanium incorporation on the microstructure, hardness, and wear resistance of nickel aluminium bronze. A CuAl10Ni5Fe4 alloy with 0.2% titanium was fabricated using the gravity mold casting technique. The characterisation of the alloy, including metallographic procedures, microstructural analysis, chemical analysis, hardness testing, and corrosion characteristics of the generated materials, was conducted.

In order to create the samples, the casting process was executed at the Sağlam Metal Industry and Trade R&D Center. Casting processes required pre-prepared nickel-aluminum bronze ingot, which was made under production circumstances. Materials for tests were created in a controlled laboratory environment, whereas ingots were made under production settings to serve as raw materials.

4.1.1. Production of Raw Materials to be Used in Casting Works

Ingot, utilized as a raw material in casting processes, is manufactured using the gravity mold casting method employing pure copper scrap, pure aluminum, iron, and nickel. The melting procedure was conducted in a 300 kg capacity induction furnace. Figure 4.1 illustrates the melting processes.



Figure 4. 1. Melting process of ingots to be used in casting works.

4.1.2. Casting Work

Samples included in experimental research were cast under laboratory circumstances and in ambient atmospheric conditions. The research was conducted at the casting laboratory of the Sağlam Metal R&D center. A 5M brand medium-frequency induction furnace with a 10 kilogram capacity was utilized for melting. The melting procedure utilized previously manufactured nickel aluminum bronze ingot, which was chopped for this purpose. CuLi pre-alloy was employed for deoxygenation in the liquid metal, whereas a 30% copper titanium pre-alloy was utilized for titanium supplementation. Following the melting of nickel aluminum bronze, copper lithium pre-alloy was employed for degassing. Three distinct charges were formulated: one without titanium, one with 0.20% titanium, and one with 0.90% titanium. In the last step of melting, 30% copper titanium pre-alloy was incorporated into the liquid metal, and casting commenced. Castings were conducted at 1230°C. The samples generated by the permanent mold casting technique were prepared for testing sample sizes and utilized in the research.

4.2. CHEMICAL ANALYSIS

The chemical composition of the ingot, manufactured under industrial circumstances for casting processes, was analyzed using an Oxford optical emission spectrometer at

the casting facility. The chemical analyses of the materials generated in the casting tests conducted under laboratory settings and utilized in the experiments were ascertained by the age analysis method. Samples were extracted from various sections of the cast ingots, and chips were collected for the wet analytical procedure.

4.3. METALLOGRAPHIC PROCESSES AND MICROSTRUCTURAL CHARACTERIZATION

Surface pictures of the synthesized CuAl10Ni5Fe4 and CuAl10Ni5Fe4-0.2% Ti alloys were captured using a Nikon inverted metallurgical optical microscope at the MARGEM-Metallography Laboratory of Karabük University Iron and Steel Institute. Samples measuring 10 mm in thickness were sectioned for microstructure surface imaging. The cut samples were positioned in epoxy molds and their surfaces were polished with sandpapers ranging from 320 to 2500 grit. The sanded surfaces were subsequently polished using a polishing felt utilizing a 3 µm pure aqueous alumina solution. The etching method utilized a picral etchant composed of 5 g FeCl₃, 50 ml HCl, and 100 ml distilled water.

4.4. HARDNESS TEST

Hardness measurements of the synthesized CuAl10Ni5Fe4 and CuAl10Ni5Fe4-0.2% Ti alloys. The hardness of the samples was assessed using an 187.5 N load and a 2.5 mm diameter ball in a Brinell hardness tester. Samples with a thickness of 10 mm were produced for measurement. Hardness tests were conducted on each prepared sample five times, and the average Brinell hardness values were determined by measuring the diameters of the indentations. Figure 4.2 presents an example picture from the hardness measurements conducted using the Brinell hardness apparatus.



Figure 4. 2. Brinell hardness testing procedure.

4.5. CORROSION TEST

Using a Precisa scale with a 0.1 mg accuracy, the surface area and weight of each sample were separately calculated for the immersion corrosion test. In a 3.5% NaCl solution, immersion corrosion lasted for 12 to 72 hours. Every hour, ethanol and chromatic acid (180 g/L) were used to remove any remaining corrosion residue from the sample surface. Hourly intervals of 180 g of CrO₃ and 1 L of distilled water were used to prepare ethanol and chromatic acid, which were used to remove corrosion residues from the sample surface. To get rid of the chromic acid, the corrosion samples were first submerged in it for around three minutes. Then, they were rinsed with pure water. After being cleaned with distilled water, corrosion samples were soaked in ethanol for about two minutes before being dried. After being allowed to dry, the corrosion samples were individually weighed using precision scales, and then they were exposed to immersion corrosion once more.

The average weight losses in grammes as a result of the immersion corrosion process were converted to milligrammes at each hourly interval. The corrosion sample's surface area, measured in mm³, was translated to dm². The average weight loss (mg) was divided by the surface area (dm²) to determine the milligramme loss per square decimetre per hour. Using these measurements, weight losses were calculated by deducting the pre-corrosion value from the post-corrosion value. By deducting the pre-corrosion weight and surface area value from the post-corrosion weight and surface

area value, the weight loss after 24 hours was calculated. Milligrammes per square decimetre per day, or mdd, was used to calculate the corrosion rate. We calculated the corrosion rates per day by dividing weight losses by the total number of days. For example, since 72 hours is equivalent to three days, the weight loss after 72 hours was divided by three to get the rate of corrosion over three days. The Karabük University Iron and Steel Institute's MARGEM-Metallography Laboratory used a Carl Zeiss Ultra Plus Gemini Fesem SEM for microsurface scanning electron microscopy (SEM) research. CuAl10Ni5Fe4 and CuAl10Ni5Fe4-0.2% Ti alloys were subjected to SEM studies in order to better investigate the post-corrosion oxide layers. The setup of the scanning electron microscope used for SEM research is shown in Figure 4.3.

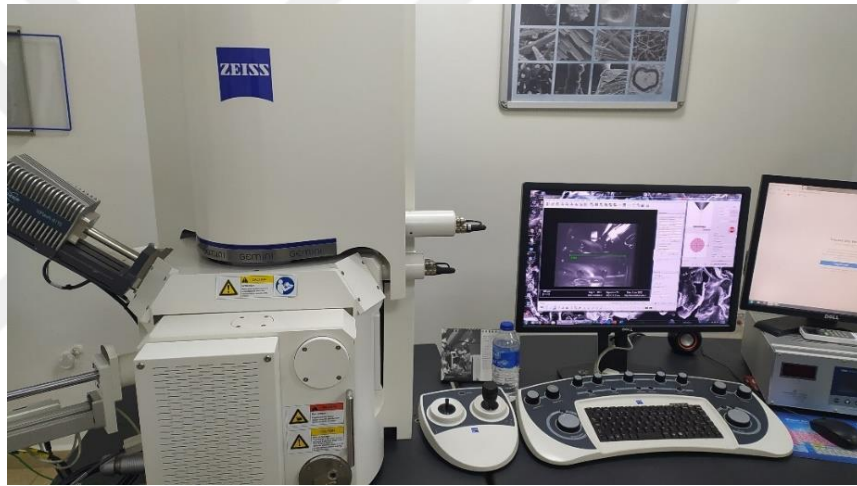


Figure 4. 3. Configuration of the scanning electron microscope (SEM).

PART 5

RESULTS AND DISCUSSION

5.1. RESULTS OF CHEMICAL ANALYSIS

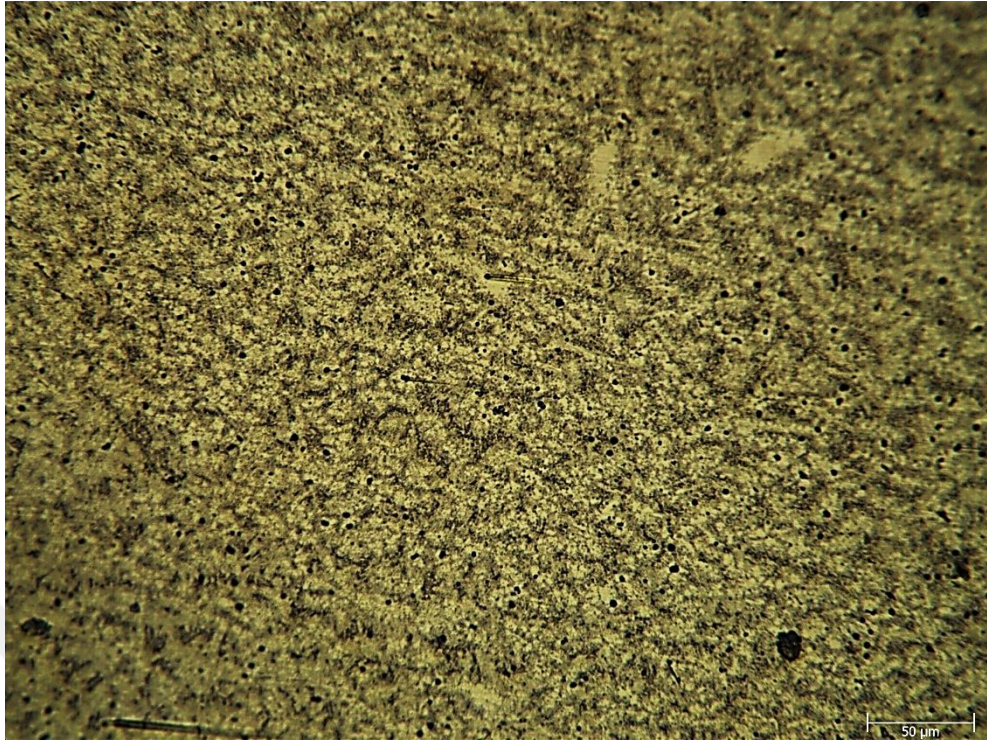
This study presents the chemical analysis of the ingot utilized as raw material and the resultant alloys. The chemical composition of the ingot, ascertained prior to the casting procedures using optical emission spectrometry, is presented in Table 5.1.

Table 5. 1. Chemical compositions of the alloys used in the studies.

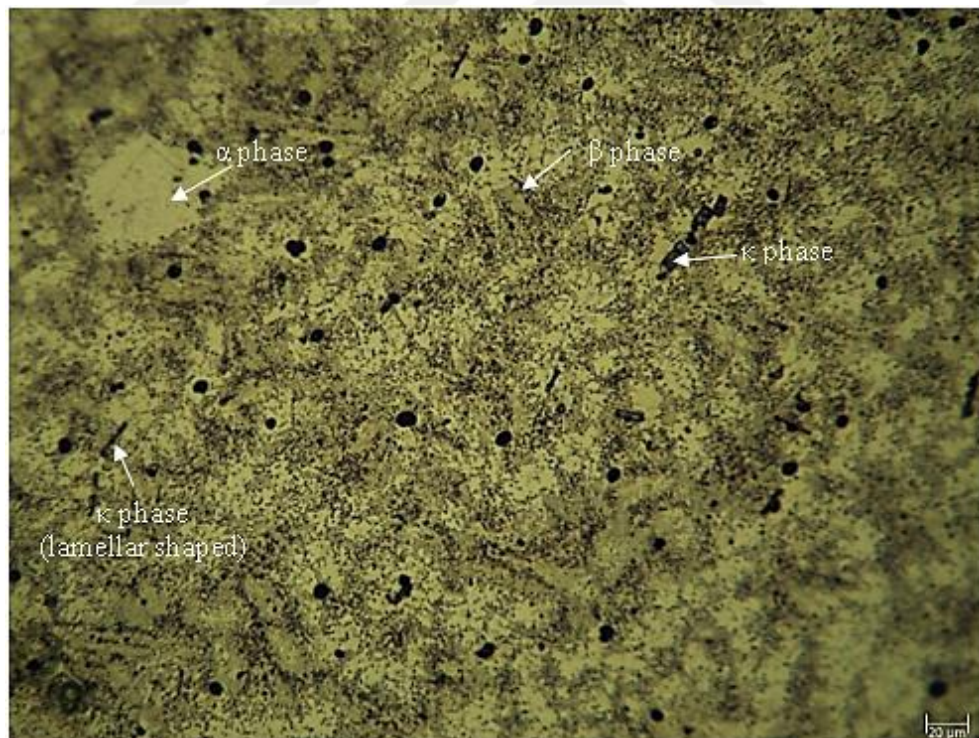
Alloy	Chemical Composition (wt.%)				
	Al	Fe	Ni	Ti	Cu
CuAl10Ni5Fe4	10.19	3.01	4.41	-	Bal.
CuAl10Ni5Fe4-%0.2 Ti	9.99	3	4.3	0.2	Bal.

5.2. RESULTS OF MICROSTRUCTURAL CHARACTERIZATION

Figures 5.1 and 5.2 illustrate the alterations in phase morphologies of the CuAl10Ni5Fe4 alloy, both in the absence of titanium and with the incorporation of 0.2% Ti. The alloy's microstructure typically comprises the α phase, a copper-rich solid solution, various intermetallics known as the κ phase, and the dark intergranular areas identified as the remaining β phase [63]. The white regions observed in the microstructures are referred to as the copper-rich α phase, whilst the dark intergranular portions are designated as the residual β phase. The κ phase was identified as diminutive solutions and lamellar structures. κ intermetallics were detected within the α grains. No additional alterations were seen in the β phase with the incorporation of titanium; nevertheless, a localized shrinkage was noticed in the soft α phase, accompanied by an increase in the ratio of the κ phase.

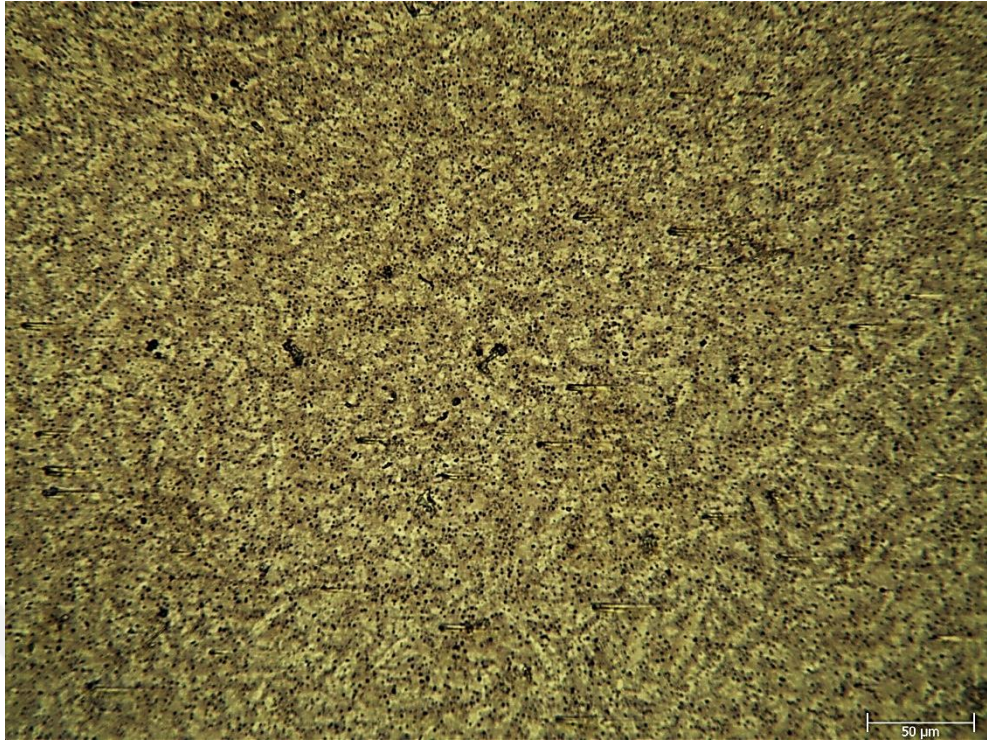


(a)

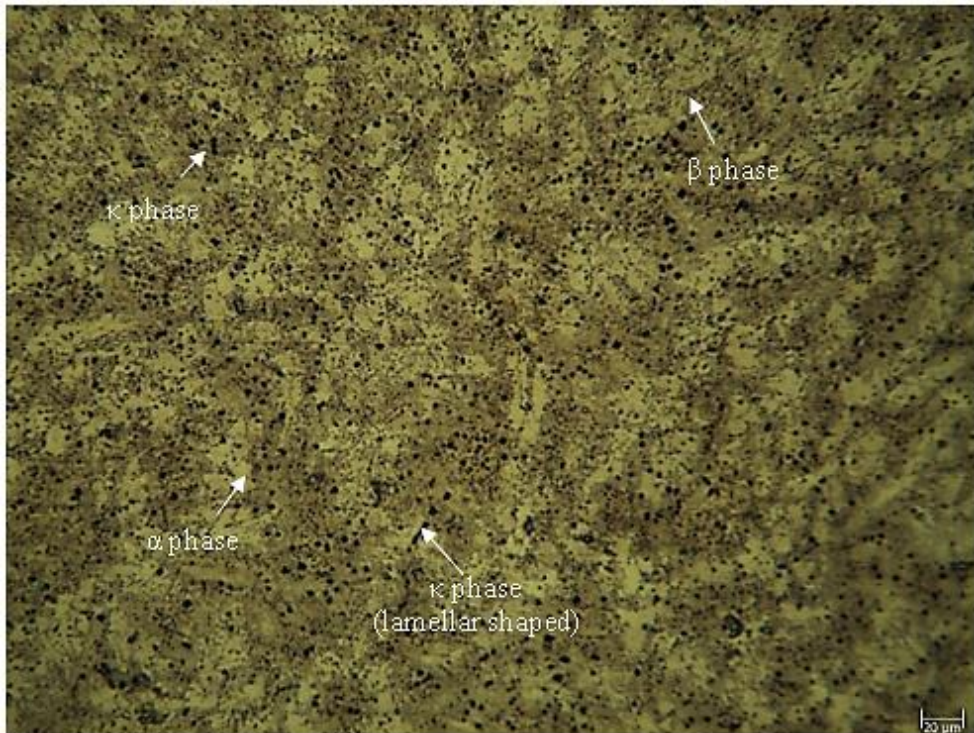


(b)

Figure 5. 1. (a) 20X and (b) 50X microstructure images of wrought CuAl10Ni5Fe4 sample.



(a)



(b)

Figure 5. 2. (a) 20X and (b) 50X microstructure images of wrought CuAl10Ni5Fe4-0.20 Ti sample.

5.3. RESULTS OF HARDNESS TEST

Figure 5.3 illustrates the hardness comparison between CuAl10Ni5Fe4 and CuAl10Ni5Fe4-0.2%Ti alloys. Typically, hardness values augment with the incorporation of titanium. Figure 3.3 indicates that the most rigid alloy is CuAl10Ni5Fe4-0.2%Ti, exhibiting a hardness of 237.80 HB, whilst the least rigid is CuAl10Ni5Fe4, with a hardness of 226.17 HB.

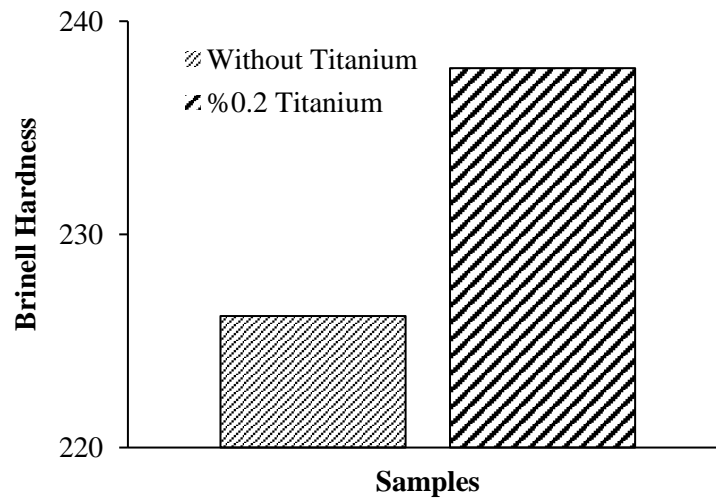


Figure 5. 3. Hardness values of the investigated alloys.

5.4. RESULTS OF CORROSION TEST

Figure 5.4 illustrates the weight loss graph attributable to corrosion after 72 hours for CuAl10Ni5Fe4 alloys, both in the absence of titanium and with a 0.2% titanium addition. The CuAl10Ni5Fe4 demonstrated enhanced corrosion resistance with the use of titanium. The absence of titanium alloy shown detrimental effects on corrosion resistance. After 72 hours, the minimal weight loss recorded in the CuAl10Ni5Fe4-0.2%Ti alloy was 0.009305 mg/dm². The greatest weight reduction was seen in the absence of titanium alloy, measuring 0.010015 mg/dm². Titanium, employed as a grain refiner, influences the microstructure of CuAl10Ni5Fe4, hence influencing its corrosion resistance[64]. The microstructure design to improve the corrosion and cavitation resistance of CuAl10Ni5Fe4 frequently incorporates titanium [65].

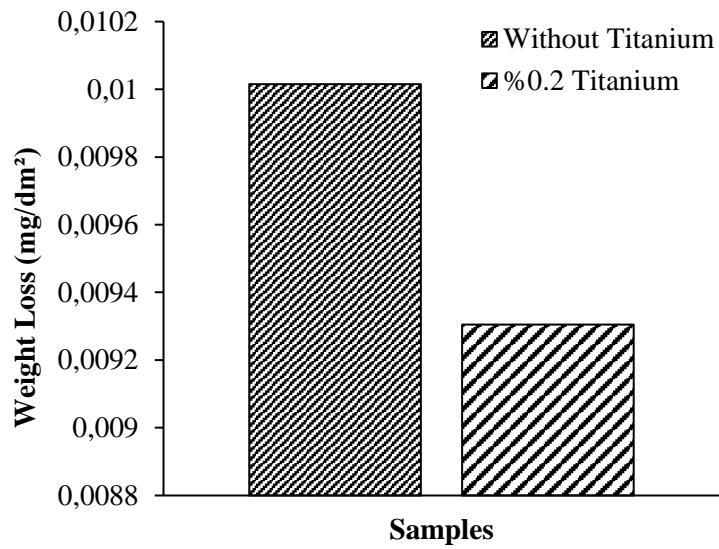
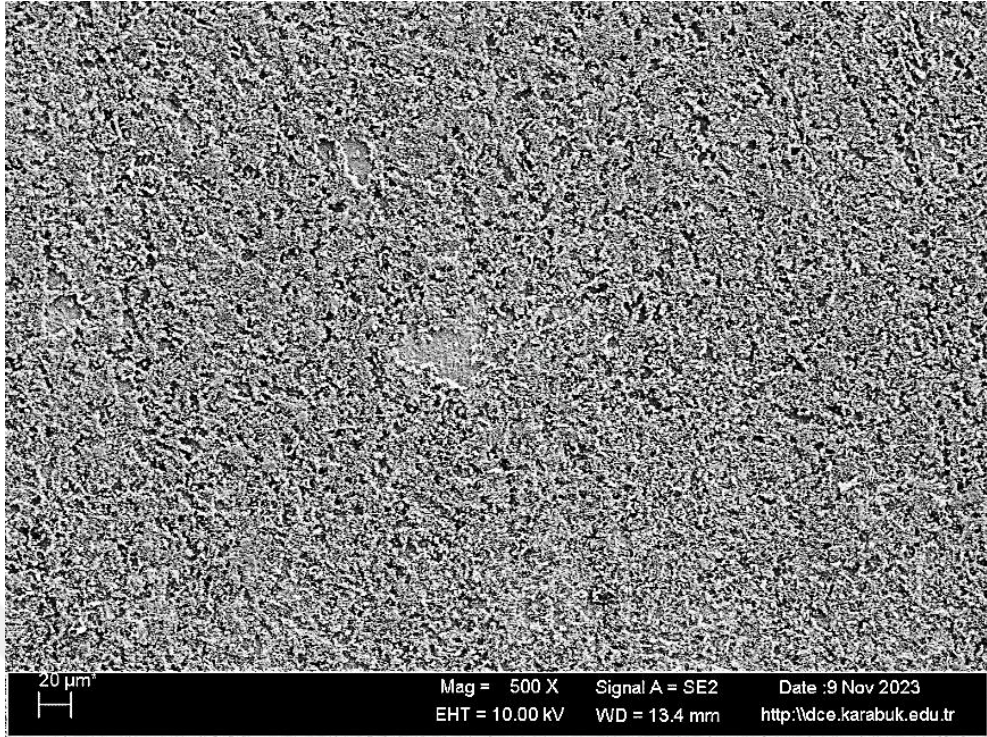
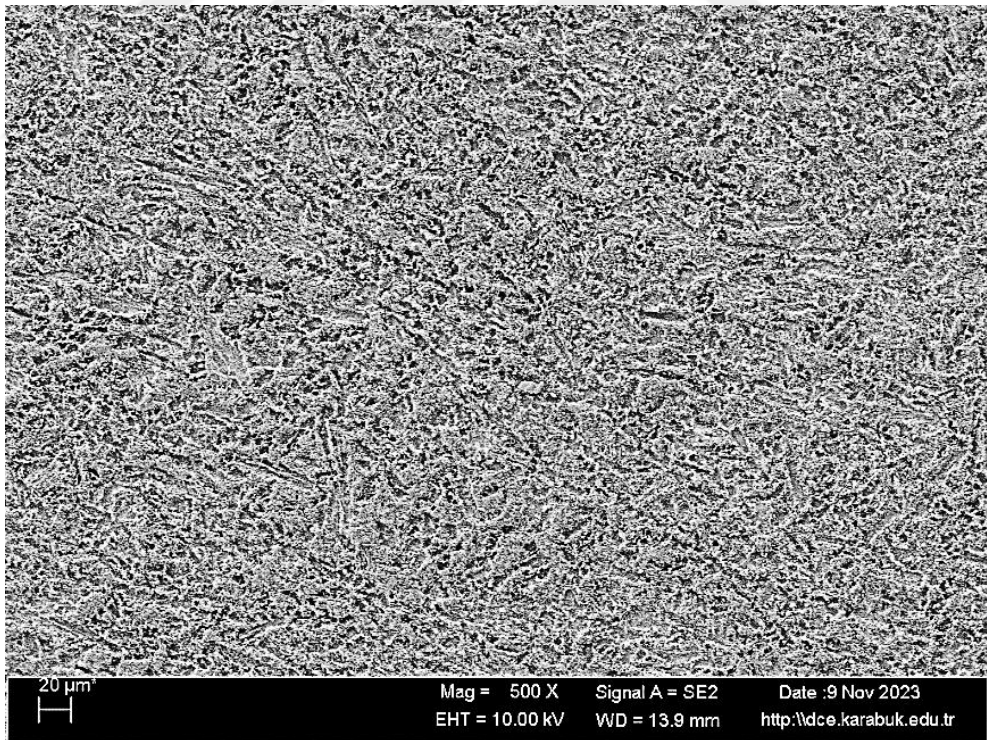


Figure 5. 4. Post-corrosion weight loss graph of without titanium and 0.2% titanium of CuAl10Ni5Fe4 alloys.

Figure 5.5 displays the SEM images of alloys without titanium and CuAl10Ni5Fe4-0.2%Ti following immersion corrosion. SEM pictures of corrosion post-casting reveal a greater prevalence of pit-shaped corrosion surfaces and porous structures in the absence of titanium alloy compared to CuAl10Ni5Fe4-0.2%Ti. The structure without titanium alloy has a heavily indented configuration, whereas the CuAl10Ni5Fe4-0.2%Ti alloy features tiny pits amid the porous surfaces.



(a)



(b)

Figure 5. 5. (a) without titanium (500X) and (b) 0.2% titanium (500X) corrosion mechanism images of CuAl10Ni5Fe4 alloys.

PART 6

CONCLUSION

In this study, phase morphologies, hardness tests and corrosion properties of CuAl10Ni5Fe4 (Nickel Aluminum Bronze) alloys without titanium addition and with 0.2% Ti addition were examined. The results of the examinations are summarized below:

- The incorporation of titanium did not produce any discernible alterations in the β phase of the microstructures; instead, regional shrinkage was seen in the soft α phase, accompanied by an increase in the ratio of the κ phase.
- The incorporation of titanium led to a hardness enhancement from 226.17 HB (without titanium) to 237.80 HB (with 0.2% titanium).
- Corrosion testing indicated that the absence of titanium alloy resulted in adverse corrosion performance. After 72 hours, the minimal weight loss was recorded in the CuAl10Ni5Fe4-0.2%Ti alloy, amounting to 0.009305 mg/dm². The greatest weight reduction was seen in the absence of titanium alloy, measuring 0.010015 mg/dm².

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RESUME

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