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A structural and mechanical study of the maintenance of archaeological Al-brass alloy by simulation method

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The purpose of this research is to investigate the casting process of producing Al-brass alloy (76% Cu, 22% Zn, 2 % Al) and destroying it chemically in accordance with the methods used in simulating damaged archaeological samples; this was achieved by immersing the alloy in a dilute solution of sulfuric acid (H_2SO_4) with a concentration of 8% molar for 24 hours. This was followed by treatment with a 300 mJ, Nd: YAG laser for 10 seconds at 100 cm, leading to the four stages of the alloy. The damaged alloy had the lowest levels of structural properties with a low hardness value, as opposed to the laser-treated alloy, which had the best structural properties. The results of X-ray diffraction and microscopic imaging by an atomic force microscope and hardness values show that this method is the best way to maintenance.

Keywords: Mechanical properties, archaeological Al-brass alloy, simulation method.

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Introduction

Minerals are essential to human life; they resulted in a qualitative advancement when humans obtained them through mining to produce their tools rather than relying solely on wood, bone and stones. Because of the significance of this discovery, that era was dubbed the Stone-Metal Age [1]. Copper ores were at the forefront of the newly discovered minerals, with their beautiful, bright colours that attracted the ancient explorers as they extracted minerals from their ores at the extraction sites. The ores' contents dissolve when heated to a specific temperature [2]. Thus, melting and casting metals paved the way for the development of mining technologies, as well as the growing significance of copper and its alloys in the lives of ancient societies [3]. Soon, copper and its alloy, brass, were used in various ancient industries, such as jewellery, utensils, death masks and many others. Later, they were used to produce numismatic coins, mainly because gold and silver coins were limited to the wealthy and influential people, and copper coins were prevalent among the common people and the poor [4,5]. When miners discovered that copper could be melted in coal furnaces, they began to exploit copper-rich ores in large quantities; the practice became popular across Europe and portions of Asia throughout the second millennium BC [6].

Much research has been conducted on the treatment and maintenance of ancient metal components. Mereu et al. [7] conducted a structural and microscopic study of copper alloys dating back to the end of the eighth century BC. They discovered study models for X-ray diffraction and the study of the elements and phases in each model in the area (Casale del Fosso). In addition, a researcher [8] conducted maintenance on an alloy (Cu-Sn-P) utilising a simulation technique, both mechanically and in conjunction with a laser. The second approach was deemed the best for maintenance after an X-ray diffraction inspection and hardness evaluation of the samples. In a case study involving silver-plated copper alloy coins, Giraud et al. [9] used gels for archaeological metal cleaning. Physical peelable gels produced the best post-treatment results regarding efficiency and the overall aesthetics of the object.

I. Theoretical Framework

1.1. The ancient alloy-making techniques

Brass is a metal alloy of copper, zinc and some other elements. It has improved physical and chemical properties such as strength, hardness and corrosion resistance, and it is a colour similar to the yellow lustre of the noble element gold. The alloy was produced mainly from the smelting of copper ores (malachite and azurite), with deposits of other mineral elements such as (zinc, tin, nickel, aluminium and iron). The percentage of zinc ranged from about 40% to 50%, as in pieces discovered by Nael Hanoun in the 1977 excavations at Tell Al-Sibu in the Hamrin Basin, 2 km west of the Diyala River [10]. This suggests that the first usage of a primitive form of brass alloys dates from the first millennium to the second century BC. Laboratory examinations of the Al-Seeb hill piece revealed variable mineral compositions (copper, zinc, tungsten, thorium, sodium, silicon and antimony). Moulds made of wax were among the most prominent techniques of forming and plumbing in the past; this approach is characterised by manufacturing a wax template for all the inscriptions to be exhibited and then coating the mould with a layer of sand. The mould has holes at the bottom and top; it is vigorously heated after drying to melt the wax and let it flow from the lower hole. Some frills are included to draw attention to the inscriptions [11].

Gigantic sculpture pieces were manufactured in a mould, then assembled and connected with a type of nail. They were employed to manufacture parts of sharp tools like knives, spears and bayonets, as well as parts of pots such as handles made of wood and ivory [12].

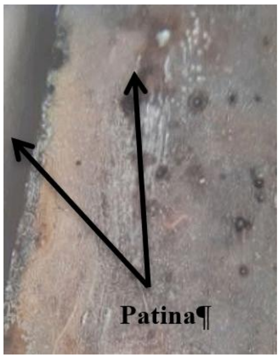
1.2. Causes and ways of archaeological alloy destruction

Metals are regarded as one of the most challenging archaeological materials to engage with, whether at the excavation site or in museum storage; it is because they interact with the surrounding weather and environmental factors, forming corrosion products and layers that can destroy either the whole or part of the metal structure. Although copper has qualities similar to noble elements, it is susceptible to substantial harm, even if the processes causing the damage are gradual. Whether it is a single metal or its alloys, rust and corrosion are caused by the presence of a large number of impurities, primarily due to the manufacturers' lack of understanding of the conventional production procedure, as well as the simplicity of manufacturing methods at the time [13]. The patina layer on the surface of copper alloys is just one example of gradual corrosion in the presence of moisture; it is particularly sticky to the surface and has various hues: green, dark green, blue, brownish-red and black. Depending on the oxidation state of the layer, impacts of Turkish media (terrestrial, near rivers and locations with air pollution), natural activities from streams and tectonic activities have a significant role in weakening the metal structure; biological activity and air activities impact the artefacts if they are on display and there is water or water vapour in the atmosphere. The existence of porosity in the alloy during production aids in forming a layer of salts located in the centre of the alloy surface to generate electrical cells that corrode and penetrate the depth of the metal [14].

II. Experimental Methods

2.1. Destruction of the alloy

The most relevant scientific approaches were applied in the chemical treatment of archaeological objects. For 24 hours, the alloy was immersed in a dilute solution of sulfuric acid (H_2SO_4) at a concentration of 8% molar (PH≈0.2), in room temperature [7]. After removing the sample from the solution, rinsing it with distilled water and drying it, a green (patina) rust layer (copper sulphate) formed on its surface, imparting a vivid red colour. Figure (2) presents a picture of the brass alloy before and after immersion.



(a)


(b)

Fig. 1. Images of the alloy (a) Before immersion (b) After immersion.

2.2. Mechanical grinding

Because the samples are intact with no loss of any part, they required manual mechanical cleaning operations for protective maintenance. Because the rust layers were not very thick (the material being a copper alloy), the sanding method [12] was adopted, using smoothing paper with values of 1000 and 800 microns, respectively. Subsequently, the samples were washed with distilled water and alcohol and dried using a particular cling film. Following that, the samples were polished using a special polishing cloth and diamond paste in three stages (3/4, 1/2 and 1/4 micron), washed with distilled water, then alcohol, and lastly, dried with a special towel.

After the smoothing and polishing processes, we conducted the etching with a suitable reagent. We placed a quantity of the show solution for copper and its alloys ($FeCl_3$ 5 mg, Alcohol 95 ml, HCl 2 ml) in an hour bottle and submerged the sample for 8 to 10 minutes. Then, the sample was washed with distilled water, then alcohol, and dried with fabric [15].

2.3. Laser surface treatment

The laser surface treatment was performed using a pulse ND: YAG laser at 300 mJ energy with a 1064 nm wavelength and 10 sec pulse time at a distance of 100 cm with frequency 2.82×10^{14} Hz and spot diameter 1 mm by energy per unit area (5-20) J/cm^2 to observe the improvement in the structural properties of the alloy on which the destruction process was conducted; this provided us with four samples of brass alloy, as shown in

Table (1) below.

Table 1.
The samples of alloys used in the research

Alloy Symbols	Sample Status
A	Base
B	Chemically destroyed
C	Mechanically restored
D	Laser treated

2.4. Structural properties

2.4.1. X-ray diffraction examination

The crystal structure of the alloys was investigated using the XRD-6000 diffract meter and angle 2θ =30°–70°. According to Bragg's law [13]:

$$2d\sin\theta = n\lambda \quad (1)$$

Where d refers to the distance between two parallel levels, θ represents the diffraction angle and λ is the x-ray wavelength.

The full width at half maximum (FWHM) was used to compute grain size for all peaks using the Debye-Scherrer equation [13]:

$$V = \frac{K_{sch}\,\lambda}{\beta\cos\theta} \quad (2)$$

Where V denotes grain size, β the FWHM and θ_B the Bragg diffraction angle.

The crystal lattice constant, a was obtained using the below equation [13]:

$$a = \sqrt{d^2.(h^2+k^2+l^2)} \quad (3)$$

Where d denotes the distance between parallel levels and h, k and l, the Miller coefficients.

The theoretical density value of any sample was computed using the following formula [14]:

$$\rho = \frac{ZM}{V_{cell}N_A} \quad (4)$$

Where Z is the atomic number according to the crystal structure, M is the atomic mass and V_{cell} and N_A are constants.

The International Centre for Diffraction (ICDD) also calibrated and confirmed that all phases and Miller indices appeared at diffraction angles according to the American Standard for Testing Materials (ASTM).

2.4.2. Atomic force microscope examination

The four samples' surface properties, roughness and thickness were determined using an atomic force microscope (AFM) type (AA 3000 SPM User's Manual).

2.5. Hardness testing

The hardness of the manufactured samples was measured using the Rockwell Hardness scale (HRC) through the Sinowon device. Five microscopic hardness tests were conducted for each sample. The arithmetic average of its hardness value was in units g/mm^2.

III. Results and Discussion

Figures (2–5) exhibit X-ray diffraction data for the alloy models in various stages: healthy, before destruction, damaged, mechanically treated and laser-processed. The four figures show that the alloys are polycrystalline with an Face Centre Cubic (FCC) structure. Miller's coefficients (h, k and l) are $h^2 + k^2 + l^2 = 35, 3, 11, 8, 24...$, as seen from the diffraction peaks. This means that the following values will be within the crystalline structure (FCC): 531, 111, 113, 220, 422, ... This is consistent with the findings of the research [6]. Figure (4) highlights the high oxidation of both copper and tin elements, as shown by the phases (CuO and ZnO_2), with a notable drop in the strength of the diffraction peaks. The intensity of the peaks begins with a slight increase and elimination of oxidation based on Figure (4), indicating the heterogeneity of the crystal structure because of treating the alloy with dilute sulfuric acid for 24 hours. When we performed the laser surface treatment, we noticed a clear improvement in the intensity of the diffraction peaks, as shown in Figure (5); this indicates crystal growth and homogeneity of the crystal structure, showing the strong cohesion of the alloy crystalline and its appearance as a single piece. Table (2) displays the X-ray diffraction analytical findings for all models [15].

Figure (6) shows three-dimensional AFM pictures of the produced samples. It can be observed that the improvement began with sample B, followed by sample C, with the best results by sample D, the laser-treated

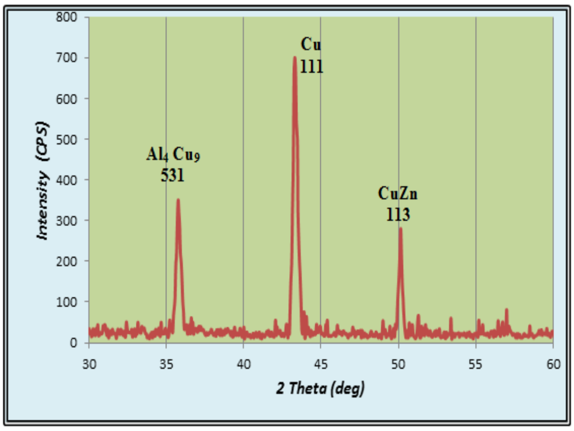


Fig. 2. X-ray diffraction for sample (A).

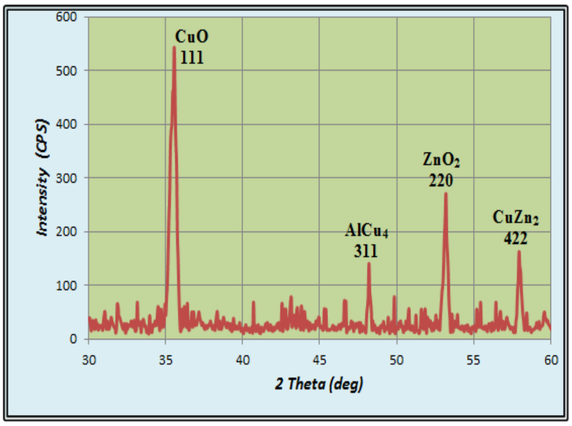


Fig. 3. X-ray diffraction for sample (B).

alloy. Atomic microwave morphology (AFM) results for the four samples (A–D) show clear and distinct changes in surface structure and an increase in surface nano-protrusions, demonstrating the influence of the alloy's state on its surface structural properties. Sample (A) exhibits moderate roughness and nano-protrusions of approximately 4.9 nm [16]. Sample (B), which was chemically damaged, is significantly rougher and has a much higher surface protrusion, reaching 30.16 nm. This indicates severe corrosion and a lack of surface homogeneity. Sample (C), which underwent mechanical rehabilitation, shows a marked change in surface regularity and improvement, with the roughness decreasing to approximately 11.38 nm due to the removal of damaged layers and resurfacing [17,18]. Finally, the laser-treated sample (D) exhibits the most uniformity and a reduction in nano-protrusions to 3.72 nm. This demonstrates the effectiveness of laser treatment in reorganizing and fusing surface layers and reducing external defects, thus achieving optimal results. On surfaces with granular regularity, this method can also be effective in surface treatments of turbine blades, oil pipes, etc [19].

Table (3) indicates that surface roughness values were reduced, indicating improvement. The table indicates that the laser-treated sample D has the best surface smoothness and the most homogenous structure.

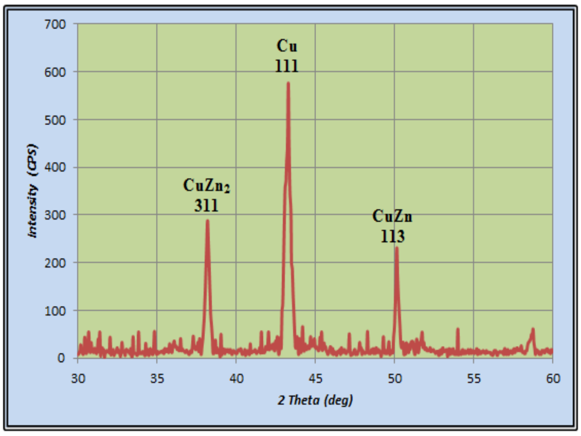


Fig. 4. X-ray diffraction for sample (C).

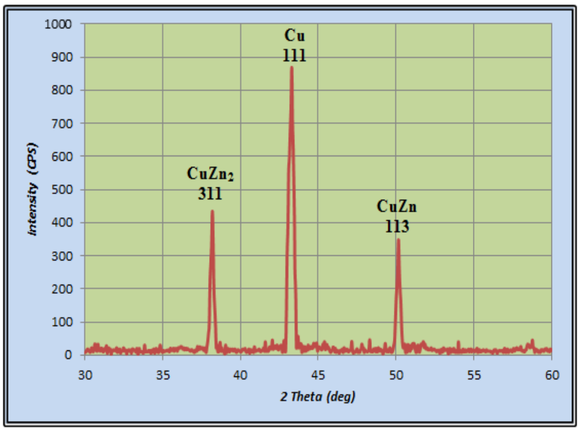


Fig. 5. X-ray diffraction for sample (D).

Table 2.

Analytical results of X-ray diffraction for samples

	Alloy A	Alloy B	Alloy C	Alloy D
Lattice Constant (Å)	3.16	4.373	3.16	3.16
Grain size (Debye-Scherrer) (μm)	18.32	26.88	22.81	15.75
Phases	Cu (2θ=43.3)	CuO (2θ=35.553)	Cu (2θ=43.3)	Cu (2θ=43.3)
Theoretical Density (g/cm^3)	8.9	2.508	8.91	8.91
Atomic Radius (Å)	1.27	1.89	1.27	1.27

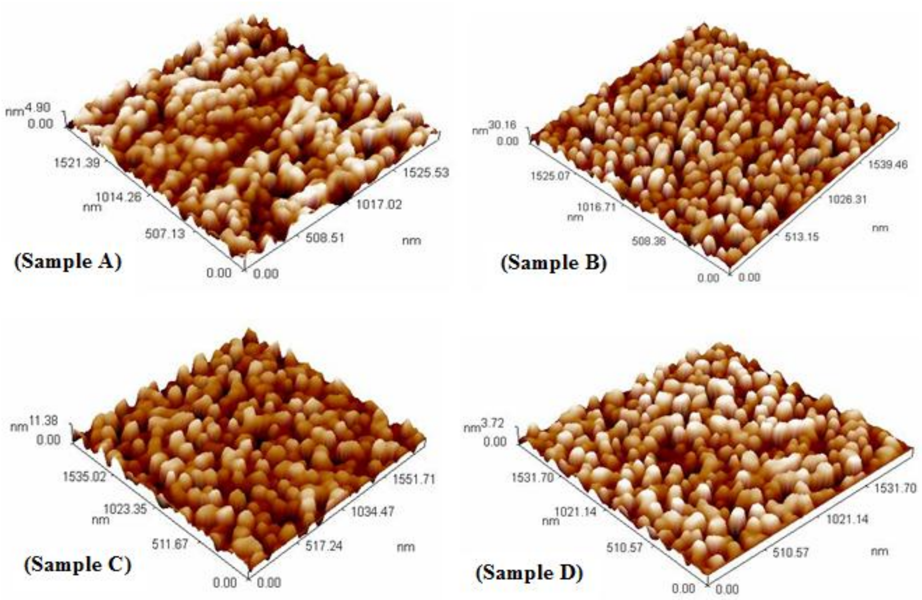


Fig. 6. Atomic force microscope images of the four samples in three dimensions.

Table 3.
Analytical results of atomic force microscope images

Sample	Surface thickness (nm)
A	4.9
B	30.16
C	11.38
D	3.72

Mechanical treatment raised hardness values. However, laser surface treatment produced a larger and better increase, as indicated by the hardness values. This shows the uniform and homogenous distribution of crystallinity following laser treatment because of the melting of the surface molecules, which improved the alloy's composition, as shown in Figure (7) [20].

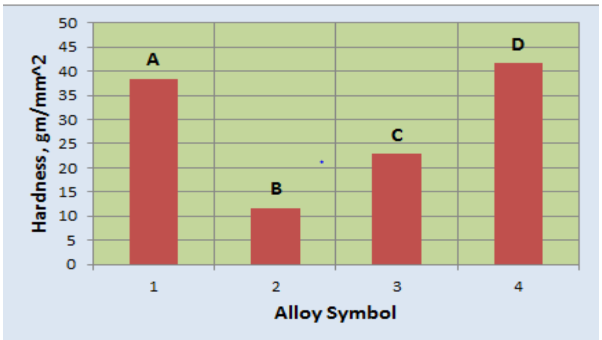


Fig. 7. Hardness values for alloy symbol.

Conclusion

According to the XRD results, all generated samples had a polycrystalline structure with differences in peak intensity, width half maximum and diffraction angle location. The chemical damage caused significant oxidation of both copper and zinc components, as well as a reduction in the strength of the diffraction peaks. When laser therapy is employed, the strength of the diffraction peaks and the uniformity of the crystal structure appear to improve. The hardness values rose following mechanical treatment, but they were higher after surface laser treatment, as was the uniform and homogenous distribution of the crystalline as confirmed by the AFM examination; the best surface smoothness was for the laser-treated sample.

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Структурно-механічне дослідження збереження археологічного алюмінієвого латунного сплаву методом моделювання

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Метою даного дослідження є вивчення процесу лиття алюмінієвого латунного сплаву (76 % Cu, 22 % Zn, 2 % Al) та його хімічного руйнування відповідно до методик, що застосовуються при моделюванні пошкоджених археологічних зразків. Це здійснювалося шляхом занурення сплаву в розбавлений розчин сірчаної кислоти (H_2SO_4) з концентрацією 8 % (мол.) протягом 24 годин. Після цього проводили обробку лазером Nd:YAG з енергією імпульсу 300 мДж протягом 10 с на відстані 100 см, що призводило до формування чотирьох стадій стану сплаву. Пошкоджений сплав характеризувався найнижчими значеннями структурних властивостей із малою твердістю, на відміну від зразків, оброблених лазером, які продемонстрували найкращі структурні характеристики. Результати рентгеноструктурного аналізу, мікроскопічних досліджень за допомогою атомно-силового мікроскопа та вимірювання твердості свідчать, що запропонований метод є найбільш ефективним для консервації (збереження) таких сплавів.

Ключові слова: механічні властивості, археологічний алюмінієвий латунний сплав, метод моделювання.