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THE EFFECT OF HEAT TREATMENT ON THE STRUCTURE AND HARDNESS OF CuAl10Ni5Fe4 NICKEL ALUMINIUM BRONZE

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The paper concerns the influence of heat treatment (annealing, quenching and aging) on the microstructure and hardness of flat bars samples from the CuAl10Ni5Fe4 alloy. The microstructures were observed in light and scanning electron microscopes. The appearance and area fractions of the martensite beta phase and their influence on the mechanical properties were examined. The annealing study at a temperature of 950 °C for 1 hour, followed by rapid quenching in water and subsequent tempering at a temperature of 350-500 °C for 15-120 minutes, demonstrated the potential for a significant increase in the hardness of aluminum bronze from approximately 200 HV3 up to 600 HV3. This suggests new possibilities for the material's applications.

Keywords: nickel aluminium bronze, heat treatment, microstructure, beta phase, hardness

INTRODUCTION

Aluminum bronzes constitute copper-based alloys with approximately 6 % to 12 % aluminum and varying proportions of iron, nickel, manganese, and/or silicon as alloying elements, providing a diverse range of mechanical properties [1]. These properties span from high ductility, as seen in tin-bronze, to the elevated strength levels found in high-tensile manganese bronze. Since small changes in chemical composition can result in significantly different properties, it is crucial to recognize that maintaining the consistency and reliability of aluminum bronze products necessitates close control of both chemical composition and manufacturing methods [2-4].

Aluminum bronzes are extensively applied in situations demanding superior strength, hardness, ductility, and corrosion resistance. Their bearing and wear-resistant qualities, when appropriately lubricated, prove valuable in various applications, including gears, slides, gibs, cams, bushings, bearings, molds, and dies [5]. Nickel-aluminum bronzes see wide usage in environments involving saltwater or oxidizing media. Maritime propellers are crafted using nickel-aluminum bronze alloys conforming to go

US government specification MIL-B-21230A. Manganese-nickel-aluminum bronze was initially designed for marine propellers. The favorable casting characteristics, coupled with high strength and ductility, along with effective resistance to cavitation erosion, make these alloys suitable for turbine castings, impellers, and hydrofoil components. Additional applications for aluminum bronze alloys encompass components for combustion engines, steam and chemical apparatus requiring service at elevated temperatures ranging from 316 to 399 °C, valve components, spark-resistant tools, forming dies, rolls, and shoes used in metal shaping [6].

The copper-aluminum equilibrium diagram shown in Figure 1a signifies that alloys containing up to approximately 9,4 % aluminum should exhibit a single-phase alpha (α) structure at room temperature. Nevertheless, at higher temperatures, alloys containing more than 8 % aluminum invariably solidify as a two-phase material consisting of alpha + beta (α + β). The equilibrium diagram reveals that the high-temperature β phase will transform into α, but the transformation rate is so gradual that alloys containing more than 8 % aluminum eventually end up as two-phase materials. In alloys containing more than 9,4 % Al, the β phase undergoes a eutectoid transformation, if slowly cooled in the region of 900 °C to 565 °C, forming a mixture of alpha + gamma2 ($\alpha + \gamma_2$).

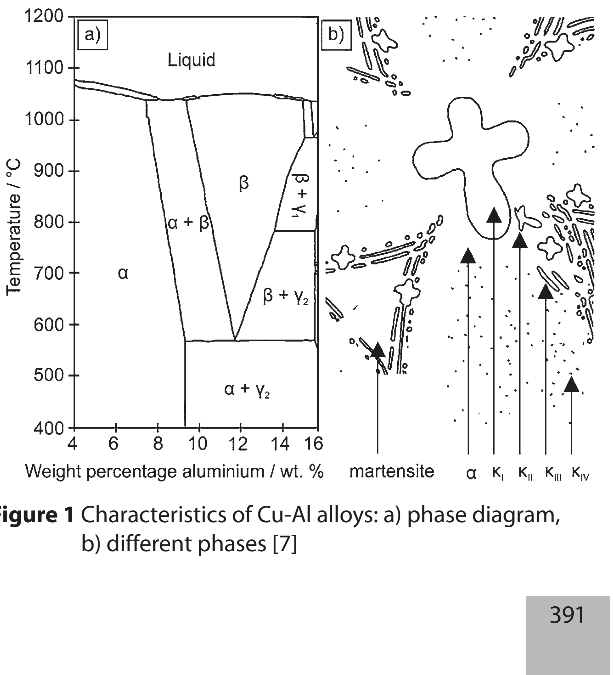

Figure 1 Characteristics of Cu-Al alloys: a) phase diagram, b) different phases [7]

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For nickel-aluminum bronzes, which include nickel, iron, and manganese as alloying elements, the microstructure consistently comprises different kappa (κ) phases rich in nickel or iron within an alpha matrix. Depending on their morphology and compositions, these κ phases are categorized as κ_I, κ_{II}, κ_{III}, and κ_{IV} [7-9]. Figure 1b illustrates a schematic diagram highlighting these diverse phases in nickel-aluminum bronzes.

EXPERIMENTAL PROCEDURE

In the current experiment square-shaped samples with a side length of 30 mm were used. These samples were cut from an extruded flat bar with an alloying elements content of 10 % Al, 5 % Ni and 4 % Fe, in accordance with the EN 12163 standard. The chemical composition of the alloy is presented in Table 1.

Samples were subjected to heat treatment at temperature 950 °C for 1 hour using a muffle heat treatment furnace. Subsequently, one sample was slowly air-cooled, another sample was quenched in oil, and the remaining 16 samples were rapidly quenched in water. Then, the 16 samples subjected to the water quenching process were annealed at a temperature of 350 – 500 °C for 15 – 180 minutes.

The microstructures were observed on conventional metallographic sections in light and scanning electron microscopes (SE detector, magnification: x 150 – x 4000). The evolution of the structure were monitored using an optical microscope Epityp-2 (Carl Zeiss, Germany) and SEM (FEI Inspect S50). The chemical composition of the alloy produced was determined using energy dispersive X-ray spectroscopy (EDAX). The hardness of the materials was measured on Tukon 2500 Vickers automated tester.

Table 1 **Chemical composition of the tested aluminium bronze according to EN 12163 standard / wt. % [10]**

Main alloy component		Admixtures – together max. 8,9						
Cu	Al	As	Bi	Cd	Fe	Mn	Ni	Zn
82,2	8,9	0,03	0,001	0,002	3,5	0,6	4,6	0,1

RESULTS AND DISCUSSION

Hardness

The HV3 hardness of the samples before and after annealing was measured. The results are shown in Table 2. The highest hardness was achieved for the material heat-treated at a temperature of 950 °C for 1 hour, then rapidly quenched in water, and subsequently aged at a temperature of 450 °C for 15 minutes. The average hardness reached 585 HV3, which is nearly three times higher than the hardness of the sample before heat treatment (206 HV3). It is also worth examining the results of samples that were annealed at 950 °C and then subjected to cooling in different mediums, namely water, oil, and air. Among this group of samples, the material rapidly quenched exhibited the highest hardness, while the sample slowly cooled in air showed the lowest hardness.

Table 2 **Hardness of CuAl10Ni5Fe4 alloy before and after heat treatment (annealing, quenching, aging)**

Sample	Hardness / HV3
Before heat treatment *	206
950 °C, 1 h + air quenched	227
950 °C, 1 h + oil quenched	278
950 °C, 1 h + water quenched *	370
950 °C, 1 h + water quenched + 350 °C, 15 min.	365
950 °C, 1 h + water quenched + 350 °C, 60 min.	465
950 °C, 1 h + water quenched + 350 °C, 120 min.	432
950 °C, 1 h + water quenched + 350 °C, 180 min.	429
950 °C, 1 h + water quenched + 400 °C, 15 min.	376
950 °C, 1 h + water quenched + 400 °C, 60 min.	395
950 °C, 1 h + water quenched + 400 °C, 120 min. *	484
950 °C, 1 h + water quenched + 400 °C, 180 min.	435
950 °C, 1 h + water quenched + 450 °C, 15 min. *	585
950 °C, 1 h + water quenched + 450 °C, 30 min.	399
950 °C, 1 h + water quenched + 450 °C, 60 min.	354
950 °C, 1 h + water quenched + 450 °C, 120 min. *	298
950 °C, 1 h + water quenched + 500 °C, 15 min.	375
950 °C, 1 h + water quenched + 500 °C, 30 min.	375
950 °C, 1 h + water quenched + 500 °C, 60 min.	262
950 °C, 1 h + water quenched + 500 °C, 120 min.	278

* samples selected for microstructural analysis

The graphical interpretation of the results is represented by a chart on Figure 2 illustrating the impact of the performed heat treatment on the hardness of the CuAl10Ni5Fe4 alloy. The hardness range covers values from 206 HV3 to 585 HV3. A decrease in hardness is also observed with the prolonged aging time at temperatures of 450 °C and 500 °C, indicating material overaging, as confirmed by light and scanning microscopy images that will be presented in next part (based on the hardness results, samples designated in Table 2 have been selected for further microstructural analysis).

Microstructural analysis

In the evident from the above discussion that the microstructure of aluminium bronze alloy is very complex depending upon the composition and thermal history. A typical microstructure of an alloy containing aluminium, nickel and iron and consisting of α matrix embedded with

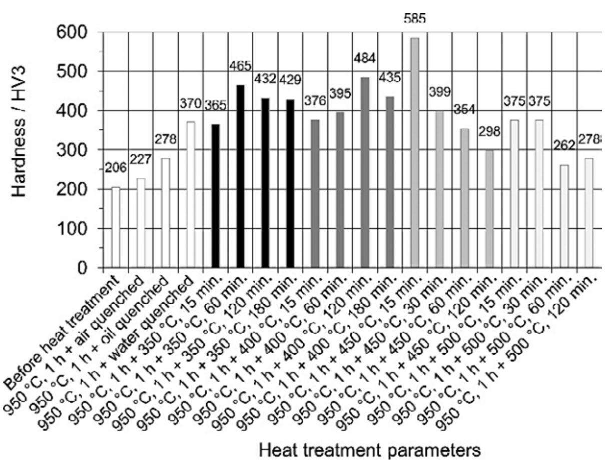

Figure 2 Effect of heat treatment (annealing, quenching, aging) on the hardness of CuAl10Ni5Fe4 alloy

particles of kappa, and an intimate mixture of $\alpha + \kappa + \gamma_2$ in the areas formerly occupied by the high-temperature β phase is shown in Figure 3a. At relatively high aluminium contents, the volume fraction of $\alpha + \kappa + \gamma_2$ increases significantly which is illustrated in Figure 3b.

Figure 4 shows the microstructures of CuAl10Ni5Fe4 nickel aluminum bronze after heat treatment (annealing, quenching and aging) observed on a light microscope.

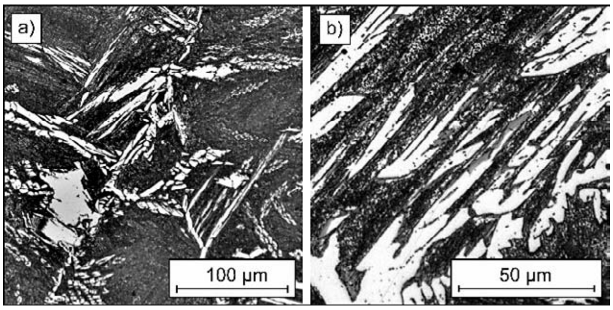

Figure 3 Microstructures of CuAl10Ni5Fe4 alloy before heat treatment (light microscope)

Figure 4a) shows the material annealing at 950 °C for 1 hour and rapidly quenching to water. As mentioned earlier, there was an increase in Vickers hardness, which is confirmed by a picture of the microstructure. Acicular

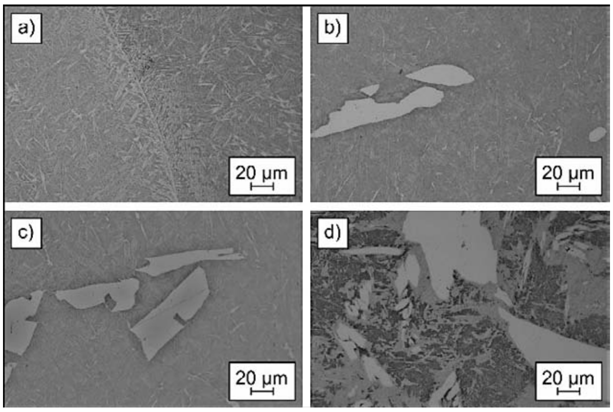

Figure 4 Microstructures of CuAl10Ni5Fe4 alloy after heat treatment: a) 950 °C / 1 h + water quenched, b) 950 °C / 1 h + water quenched + aged at 400 °C / 120 min., c) 950 °C / 1 h + water quenched + aged at 450 °C / 15 min., d) 950 °C / 1 h + water quenched + aged at 450 °C / 120 min. (light microscope)

precipitates of the beta phase resulting from martensitic transformation are visible. They have the form of elongated, densely arranged needle-shaped forks and grow from the grain boundaries. The sample shown in Figure 4b, i.e. heat treated at 950 °C / 1 h and aged at 400 °C / 120 minutes, does not show major differences in structure from the sample shown in Figure 4c). This is confirmed by light microscope images. The difference in microstructure is observed for bronze CuAl10Ni5Fe4 after heat treatment at 950 °C / 1h and aged at 450 °C / 15 minutes. This is a sample that, as previously mentioned, is characterized by the highest hardness. For this material, the presence of a martensitic strengthening beta phase is observed in the form of precipitates that appear throughout the entire volume of the material. The microstructure of the sample heat treated at 950 °C / 1 h + water quenched + 450 °C / 120 min. (Figure 4d) is definitely the most interesting in terms of observations. There are significant differences in the structure compared to the structures of the samples shown on the previous pictures. The acicular phases do not start only at the grain boundaries but appear throughout its entire volume. It can be assumed that these are no longer precipitates resulting from the martensitic transformation but a new phase with a lamellar structure. The above observations are confirmed by the Scanning Electron Microscope (SEM) shown in Figure 5a-d.

For samples of the CuAl10Ni5Fe4 alloy after heat treatment, the chemical composition of Energy Dispersive Spectroscopy (EDS) was also analyzed. It was made at various measurement points on lighter and

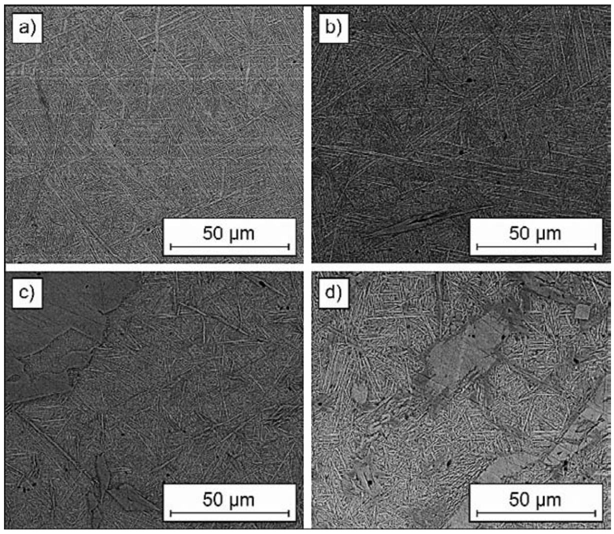

Figure 5 Microstructures of CuAl10Ni5Fe4 alloy after heat treatment: a) 950 °C / 1 h + water quenched, b) 950 °C / 1 h + water quenched + aged at 400 °C / 120 min., c) 950 °C / 1 h + water quenched + aged at 450 °C / 15 min., d) 950 °C / 1 h + water quenched + aged at 450 °C / 120 min. (SEM)

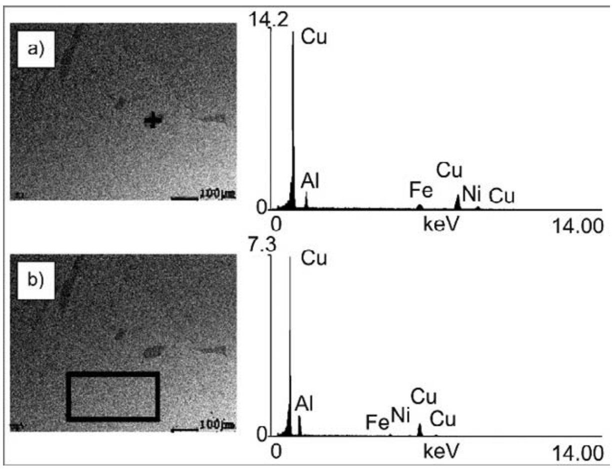

Figure 6 Energy Dispersive Spectroscopy (EDS) analysis of the chemical composition of the CuAl10Ni5Fe4 alloy after heat treatment at 950 °C / 1 h + water quenched

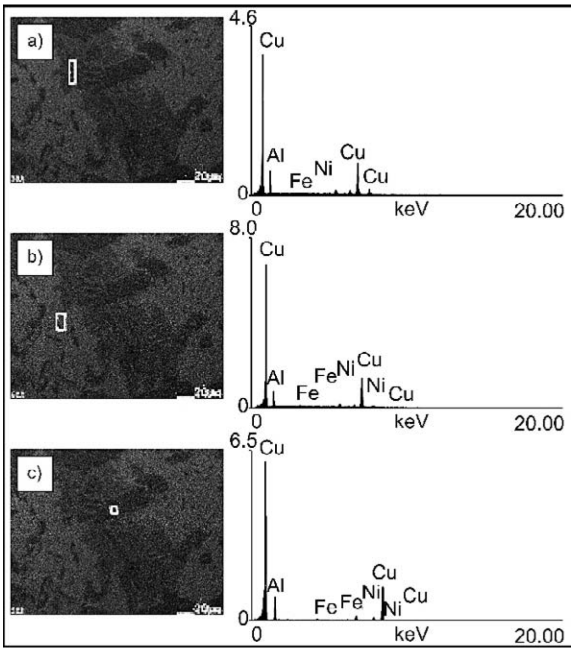

Figure 7 Energy Dispersive Spectroscopy (EDS) analysis of the chemical composition of the CuAl10Ni5Fe4 alloy after heat treatment at 950 °C / 1 h + water quenched + aged at 450 °C / 120 min.

darker areas of the material. The results showed that for the sample shown in Figure 6, the lighter areas are rich in aluminum, while the darker areas are rich in copper. Based on the EDS analysis in Figure 7, the same observations are observed.

CONCLUSIONS

On the basis of the research the following can be stated:

- A positive influence of heat treatment, specifically solution heat treatment, on the increase in Vickers hardness of CuAl10Ni5Fe4 aluminum bronze has been observed, confirmed by microstructure observations of the alloy.
- The highest increase in Vickers hardness, nearly threefold, for CuAl10Ni5Fe4 aluminum bronze compared to the untreated sample with a hardness of 206 HV3, was achieved through a two-stage annealing process: rapid quenching into water from a high temperature of 950 °C for 1 hour, followed by annealing (after the quenching process) at 450°C for 15 minutes. The alloy exhibited a hardness level of 585 HV3.
- Microstructure analysis of the CuAl10Ni5Fe4 alloy after the hardening process (950 °C / 1 h) and annealing (450 °C / 15 min.) indicates the presence of a martensitic strengthening phase β.
- The impact of cooling rate on the Vickers hardness of CuAl10Ni5Fe4 alloy has been observed.
- The greatest increase in Vickers hardness for CuAl10Ni5Fe4 aluminum bronze samples, quenched from a high temperature of 950 °C at different rates, was noted for rapidly quenched material into water (from 206 HV3 to 370 HV3), compared to the alloy quenched in oil (278 HV3) and in air (227 HV3).
- After the hardening process (950 °C / 1 h), annealing of CuAl10Ni5Fe4 aluminum bronze at 450 °C / 120 min. results in alloy overaging, confirmed by a decrease in Vickers hardness (278 HV3) and microstructure observations.

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REFERENCES

[1] J.R. Davis, ASM Specialty Handbook: Copper and copper alloys, ASM International, 2001.
[2] M. Maleta, J. Kulasa, Influence of the variable content of Al, Ni and Fe on the mechanical properties and susceptibility to cold working of aluminium bronze, Metalurgija 61 (2022) 3-4, 649-652.
[3] J. Maximov, G. Duncheva, A. Anchev, V. Dunchev, Y. Argirov, V. Todorov, T. Mechkarova, Effects of heat treatment and severe surface plastic deformation on mechanical characteristics, fatigue, and wear of Cu-10Al-5Fe bronze, 15 (2022) 24, 8905, DOI: 10.3390/ma15248905.
[4] K. Muhammad, M. Muhammad, A. Haider, H. Sajawal, K. Saheed, Effect of heat treatment on tribological characteristics of CuAl10Ni5Fe4 nickel aluminum bronze, Key Engineering Materials, 778 (2018), 61-67, DOI: 10.4028/www.scientific.net /KEM.778.61.
[5] G. Lin, Effects of heat treatments on microstructure and properties of nickel–aluminum bronze fabricated by centrifugal casting, Journal of Materials Research, 31 (2016) 24, 3832-3840, DOI: 10.1557/jmr. 2016.455.
[6] S. Thapliyal, D. Dwivedi, Study of the effect of friction stir processing of the sliding wear behavior of cast NiAl bronze: A statistical analysis, Tribology International, 97 (2016), 124-135,DOI: 10.1016/j.triboint.2016.01.008.
[7] K. Sadayappan, M. Sahoo, Aluminium bronze alloys, Casting copper-base alloys, AFS American Foundry Society, S.P. Thomas (ed), 2, American Foundry Society, Illinois, 2007, 231-248.
[8] W. Zhai, W. Lu, P. Zhang, M. Zhou, X. Liu, L. Zhou, Microstructure, mechanical and tribological properties of nickel-aluminium bronze alloys developed via gas-atomization and spark plasma sintering, Materials Science & Engineering A, 707 (2017), 325-336, DOI: 10.1016/j.msea. 2017.09.047.
[9] F. Hasan, J. Iqbal, N. Ridley, Microstructure of as-cast aluminium bronze containing iron, Materials Science and Technology, 1 (1985) 4, 312-315, DOI: 10.1179/mst.1985. 1.4.312.
[10] EN 12163 Copper and its alloys-Rod for general purposes.

Note: The translator responsible for English language: Małgorzata Zasadzińska, AGH University of Krakow, Faculty of Non-Ferrous Metals, Krakow, Poland