



CHANGES IN THE MARTENSITIC β' PHASE IN THE NICKEL ALUMINUM BRONZE DURING AGING

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Abstract

This paper presents the study of microstructural changes and microhardness of the martensitic β' phase during aging of the nickel-aluminum bronze (NAB) with the nominal composition CuAl9Ni3Fe3. After casting, the alloy was annealed at 900 °C for 2 h followed by a rapid cooling in cold water. The quenched samples were aged at 350 °C and 450 °C for 10 min, 60 min, 180 min, and 600 min. After each stage of heat treatment, the microhardness values of the martensitic β' phase were studied, and the microstructure was analyzed using the SEM microscopy with the EDS. The microhardness of β' martensite increased during the aging due to the precipitation of the nano κ phase rich in nickel.

Keywords: NAB, aging, microstructure, martensite

1. INTRODUCTION

The NABs are the copper-based alloys with the addition of aluminum, nickel, and iron which have a good combination of properties such as the high strength, toughness, wear, and corrosion properties, as well as good castability, machinability, and weldability [1]. Their properties can be modified further using the heat treatments that influence the complex multiphase microstructures [2]. Depending on the chemical compositions, the NABs usually possess the complex microstructures consisting of α and retained β solid solutions with intermetallic κ phases different in shape and composition [3]. These κ phases are: κ_i , κ_{ii} , κ_{iii} , and κ_{iv} . Some authors confirmed the κ_v phase. The κ_i , κ_{ii} , and κ_{iv} phases are rich in Fe, based on the Fe_3Al intermetallic, whereas κ_{iii} and κ_v are rich in Ni, based on NiAl [4,5]. The morphology and contribution of these κ phases are dependent on the content of alloying elements and the cooling rate during production, as well as the applied heat treatments [6,7]. Quenching from high temperatures leads to occurrence a brittle and hard martensitic structure of the β' phase. Additionally, aging can be used to produce an adequate microstructure with the desired combination of mechanical and corrosion properties [8,9]. Some research groups have studied the precipitation hardening due to the evaluation of κ phases during different heat treatments which contributed to the increment of mechanical properties of NABs [10-13]. The purpose of this paper is to study the changes in the β' phase of the low-alloyed NABs during the

low-temperature aging concerning microhardness, chemical composition, and morphology of this martensitic structure.

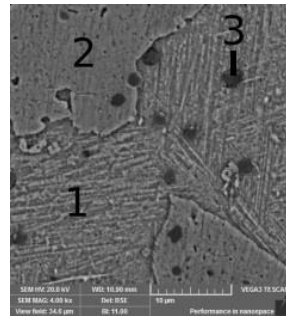
2. EXPERIMENTAL

After measuring the calculated amount of copper and alloying elements (aluminum, nickel, and iron), they were melted in a flame pot furnace with a silicon carbide pot. The melt was cast in a sand-clay mold. The obtained ingot with the nominal composition CuAl9Ni3Fe3 (in wt.%) was cut into samples, dimensions of 43 mm x 15 mm x 6 mm, which were subjected to further heat treatments. The cutting was done using the "Mesotom - Struers" device. Samples were the solid solution annealed using a "T 40/600" tube furnace in a reducing hydrogen atmosphere at 900°C for 2 h. After annealing, samples were quenched in cold water. The quenched samples were aged in an electro-resistant furnace "Heraeus K 1150/2", without a protective atmosphere at two different temperatures: 350°C and 450°C for 10 min, 60 min, 180 min, and 600 min. The microhardness of the martensitic phase was measured on the "PMT 3" device, at a load of 100 gf. Microstructural changes were analyzed using a scanning electron microscopy (SEM) on a "Tescan Vega 3LMU" microscope. For this purpose, the grinding, polishing, and etching with an alcoholic solution of ferric chloride were performed. The energy-dispersive spectrometer (EDS) "Oxford Instruments X-act" was used for the qualitative and quantitative chemical analyses of the martensitic phase.

3. RESULTS AND DISCUSSION

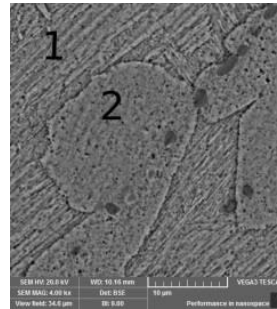
Figure 1 shows the microstructure of CuAl9Ni3Fe3 alloy after quenching (Figure 1a) and aging at 350°C and 450°C (Figures 1b and 1c, respectively), as well as the chemical composition of the existing phases obtained by the EDS. After quenching from 900°C, the high-temperature β phase was transformed into β' martensite. No eutectoid with the κ_{III} phase is observed, which follows the literature, because the κ_{III} phase dissolved at 800°C, and at 850°C the fine precipitates of the κ_{IV} phase also dissolved in the α solid solution [14]. Thus, after quenching, the α and β' phases and large spherical precipitates of the κ_I and κ_{II} phases are present in the microstructure. The β' phase (spectrum 1 in Figure 1a) has a higher Al content compared to the α phase (spectrum 2). Large spherical particles (spectrum 3) indicate the iron-rich phases, i.e., the κ_I or κ_{II} phases, which after quenching have the same morphology and do not differ.

After aging, the bright α phase and needles of β' martensite with the spherically shaped κ phases are still observed (Figures 1b and 1c). Based on the literature data, β' martensite does not transform into the α phase until above 550°C [15,16]. It is noted that the aluminum content in β' martensite is still higher compared to the α solid solution. Compared to the quenched state during aging, β' martensite is continuously enriched in Al and Ni, which is a confirmation that within β' martensite the intermetallic rich in Ni precipitated [17].



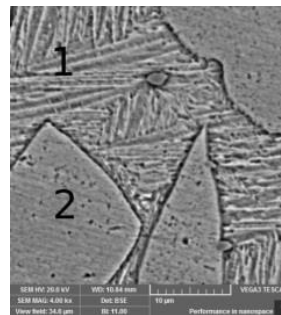
S	Al	Si	Fe	Ni	Cu
1 - β'	16.61		3.38	4.76	75.25
2 - α	12.09		3.37	4.28	80.26
3 - κ	10.71	5.41	64.50	4.92	14.45

a)



S	Al	Fe	Ni	Cu
1 - β'	17.43	3.82	6.62	72.14
2 - α	13.55	4.46		82.00

b)



S	Al	Fe	Ni	Cu
1 - β'	18.24	2.64	7.17	71.95
2 - α	13.92	4.27		81.81

c)

Figure 1. Microstructure of CuAl9Ni3Fe3 alloy after a) quenching from 900°C; b) quenching from 900°C and aging at 350°C; c) quenching from 900°C and aging at 450°C

Figure2 shows changes in the microhardness values of the martensitic β' phase during the aging at two temperatures - 350°C and 450°C.

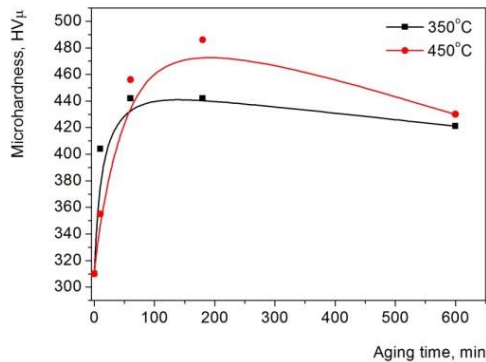


Figure 2. Microhardness of the martensitic β' phase during the aging at 350°C and 450°C

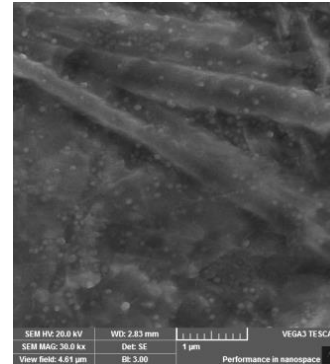


Figure 3. Nano κ phase rich in Ni within β' martensite after aging

It can be seen that the microhardness of the β' phase of the CuAl9Ni3Fe3 alloy during aging at 350°C increases with increasing aging time due to the precipitation of the hard intermetallic phase rich in Ni within β' martensite. The nano κ phase within β' martensite, appeared after aging, was shown in Figure 3. This phase is a barrier for moving the crystal imperfections, resulting in a hardening of this type of alloy [17]. The NiAl precipitates after heat treatment were designated as the κ_V phase in some literature [18]. But this phase has the same composition and crystal structure as the κ_{III} phase; some authors do not consider it as a separate phase and avoid using the κ_V terminology [9,19].

Compared to the quenched state (310 HV μ), the microhardness of the β' phase achieved the highest increase after aging at 350°C after 180 min (442 HV μ). This is an absolute increase in microhardness of the β' phase of 131 HV μ , or that is a relative increase in microhardness of 43% compared to the quenched state. A further increase in the aging time up to 600 min affected the decrease in the microhardness value of the β' phase, but its value is still above the value for the quenched state.

Aging at 450°C results in a higher increase in the microhardness values of the β' phase. The microhardness of the β' phase achieved the highest increase after aging for 180 min (486 HV μ). This is an absolute increase in the microhardness of the β' phase of 176 HV μ , i.e., a relative increase in hardness of 57%, compared to the quenched state.

4. CONCLUSION

In this paper, the cast NAB was produced with superior mechanical properties on the account of conducted heat treatment. The key conclusions of this paper are:

- The β phase undergoes martensitic transformation to the β' phase during the rapid cooling from high temperatures.



- After aging at 350°C and 450°C, the microhardness values of the martensitic β' phase achieved the peak values as the result of precipitation the nano κ precipitates rich in Ni within the metastable phase.

- The microhardness of the β' phase achieved the highest increase after aging for 180 min (486 HV μ) which is an increase of approximately 57% compared to the quenched NAB alloy.

- Longer lasting aging contributed to a decrease in the microhardness value of the β' phase due to the effect of over-aging.

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REFERENCES

- [1] S. Ozturk, S. E. Sunbul, A. Metoglu, K. Icin, Tribol. Int., 151 (2020) 106519.
- [2] T. Murray, S. Thomas, Y. Wu, W. Neil, C. Hutchinson, Addit. Manuf., 33 (2020) 101122.
- [3] P.J. Rivero, C. Berlanga, J.F. Palacio, M.V. Biezma-Moraleda, Mater. Res., 24 (2) (2021) e20200335.
- [4] M.K. Yaseen, M. Mansoor, H.A. Ansari, S. Hussain, S. Khan, Key Eng. Mater., 778 (2018) 61-67.
- [5] M.S. Nascimento, G.A. dos Santos, R. Teram, V.T. dos Santos, M.R. da Silva, A.A. Couto, Mater., 12 (2019) 1267.
- [6] Y. Tan, H. Xie, X. Feng, S. Huang, W. Zhang, L. Peng, W. Wang, Y. Zhao, Mater., 17 (2024) 1330.
- [7] Z.E. Doğan, F. Kahriman, Ş.H. Atapek, Koc. J. Sci. Eng., 1 (1) (2018) 6-10.
- [8] P. Jain, P. K. Nigam, IOSR-JMCE, 4 (6) (2013) 16-21.
- [9] S.M. Orzolek, J.K. Semple, C.R. Fisher, Addit. Manuf., 56 (2022) 102859.
- [10] R. Chen, Z. Liang, W. Zhang, D. Zhang, Z. Luo, Y. Li, Trans. Nonferrous Met. Soc. China, 17 (2007) 1254-1258.
- [11] M.M. Shirazabad, A. Karimi, A. Babakhani, 3rd International Conference on Materials Heat Treatments, 2012, p. 51.
- [12] P.K. Nigam, P. Jain, Arch. Appl. Sci. Res., 5(1) (2013) 224-230.
- [13] M.M. Sadawy, EIJEEST, 29 (2020) 43-50.
- [14] P. Sláma, J. Dlouhý, M. Kövér, Materials and Technology, 48 (2014) 599-604.



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- [15] M. Moradlou, N. Arab, R. Emadi, M. Meratian, *Am. J. Sci.*, 7(7) (2011) 717-722.
- [16] Y. Lv, M. Hu, L. Wang, X. Xu, Y. Han, W. Lu, *J. Mater. Res.*, 30 (20) (2015) 3041-3048.
- [17] J.M. da Silva, B.C.E.S. Kurelo, W.R. de Oliveira, A.G.M. Pukasiewicz, G.B. de Souza, S.F. Brunatto, *Surf. Topogr. Metrol. Prop.*, 10 (2022) 024007.
- [18] C. Dharmendra, K.P. Rice, B.S. Amirkhiz, M. Mohammadi, *Mater. Des.*, 202 (2021) 109541.
- [19] P. Brezina, *Int. Met. Rev.*, 27 (1) (1982) 77-120.