

INVESTIGATION OF THE INFLUENCE OF Mo, W AND V MODIFICATION ON THE STRUCTURE AND HARDNESS OF IRON-DOPED CuAl9 BRONZE IN THE CAST STATE

Maria Krasteva¹, Vladimir Petkov¹

University of Chemical Technology and Metallurgy
8 Kliment Ohridski Blvd., Sofia 1797, Bulgaria
mariqkrasteva@uctm.edu (M.K.); fenikspak@abv.bg (V.P.)

Received 15 July 2025

Accepted 19 September 2025

DOI: 10.59957/jctm.v60.i6.2025.22

ABSTRACT

Of the group of tin-free bronzes, the most widespread in foundry production is the use of so-called “aluminium” bronze, or bronze type CuAl9. Double bronzes of this type tend to “self-anneal”, resulting in a coarse-grained cast structure. To suppress this tendency, aluminium bronzes are most alloyed with iron, manganese and nickel, but are also further modified with various modifiers. The aim of this development is to investigate the influence of Mo, W and V modification on the structure and hardness of iron alloyed CuAl9 type in the cast state.

Keywords: aluminium bronze, CuAl9 bronze, modifiers, cast state.

INTRODUCTION

The refinement of the primary grains in copper alloys containing Al is achieved by the addition of the difficult-to-melt elements V, W, Mo, etc. [1, 2].

The addition of the difficult-to-melt modifiers causes a change in the microstructure of the alloys (a change in the shape and grain size of the alloy). In some cases, these changes are particularly evident after heat treatment. A difficult-to-melt modifier is introduced into the alloy using an Al-V(50 %) ligature, or FeW, FeV alloys, at an alloy temperature of 1200 - 1250°C. Overheating of the modified alloy can lead to complete combustion of the modifying element and obtain a coarse-grained structure. The optimum concentration of the listed modifiers is in the range between 0.05 - 0.5 % [1 - 3].

The sample bodies are moulded with a standard sand-bentonite moulding mix (4 % bentonite, 96 % OPK25 silica moulding sand and 4 % water) according to a plan designed and developed specifically for this purpose. The specimens obtained for the study were cylindrical 25 mm diameter specimens with a cooling modulus of 6.25. Melting of the alloys was carried out in a laboratory induction furnace with a graphite crucible.

The alloys were melted at a temperature of 1230 - 1250°C. The sample bodies were machined by cutting, grinding and polishing. A hydrochloric acid solution of ferric chloride was used to develop the structure.

The microstructure of the alloys was examined using an Epitep-2 metallographic microscope. Metallographic photographs were taken at ×63 magnification using a digital camera. The hardness of the sample bodies was also investigated using the Brinell method (BS ISO 6506). The measurement was carried out with a sphere (ball) with a diameter of 2.5mm and a load of 187.5 kgf (1875N) [4 - 6].

EXPERIMENTAL

The calculation of the charge was carried out based on bronze grade CuAl9Fe3 according to standard methodology; the permissible deviations in the chemical composition of the alloys according to the standard were considered and a 10 % set-aside of aluminium was provided. For all alloys the same amount of copper was used at 500 g. For the preparation of the alloys the following blast furnace materials were used:

- electrolytic copper - 500 g - 88 %.

- aluminium - 9% - 51 g 10% set aside ~5 g;
- armco iron - 3% - 17 g;
- 0.3 % modifier Al-V (50 %) - 1.7 g;
- FeW - 80 % W- 2.125 g;
- FeV - 50 % V- 3.4 g;
- Mo - 100 % - 1.7 g.

A graphite crucible was used to prepare the alloys. The sequence of the smelting process is as follows: copper is first charged and smelted; the modifier and iron are added, after their dissolution, aluminium is introduced. The alloy is cast at a temperature of 1230 - 1250°C in a pre-prepared casting mould. After cooling, the sample bodies are knocked out of the mould and machined by turning. From the sample bodies so prepared, grinding and polishing are used to produce the cut for metallographic analysis. The structure is developed using a reagent consisting of 5 g FeCl_3 , 20 mL concentrated hydrochloric acid and distilled water to 100 mL. The reagent stains the α -phase dark, and the second phase (β or eutectoid) remains light [7].

The microstructure of the CuAl9 base alloy in the cast state is shown in Fig. 1.

Alloying the aluminium bronze with iron results in a noticeable fabrication of the structure. Dual-composition aluminium bronzes, and CuAl9 in particular, tend to form a coarse, ladder-like primary structure, with its dispersity strongly dependent on the cooling regime (rate). This mode also determines the course of the eutectoid decomposition of the β -phase and hence the final hardness of the alloy shown in Fig. 2. This is the reason why aluminium bronze is alloyed with Fe which affects the progress of both primary crystallization and eutectoid decomposition.

Modification with molybdenum causes a noticeable rounding of the eutectoid crystals and minimal nucleation of the structure (Fig. 3).

Modification with W results in a significantly (about four times) smaller structure than the baseline and a significantly larger structure with more elongated eutectoid crystals relative to the iron-doped cast alloy. The eutectoid crystals are more elongated compared to the Mo-modified one (Fig. 4).

Modification with V contributes to a much finer-grained structure than the base alloy and a coarser structure than the iron-doped alloy, as well as to a change in shape and an uneven distribution of eutectoid crystals (Fig. 5). The resulting microstructure is the



Fig.1. Base alloy microstructure CuAl9.



Fig.2. Base alloy microstructure CuAl9Fe3.



Fig. 3. Alloy microstructure CuAl9Fe3Mo.



Fig. 4. Alloy microstructure CuAl9Fe3W.



Fig. 5. Alloy microstructure CuAl9Fe3V.

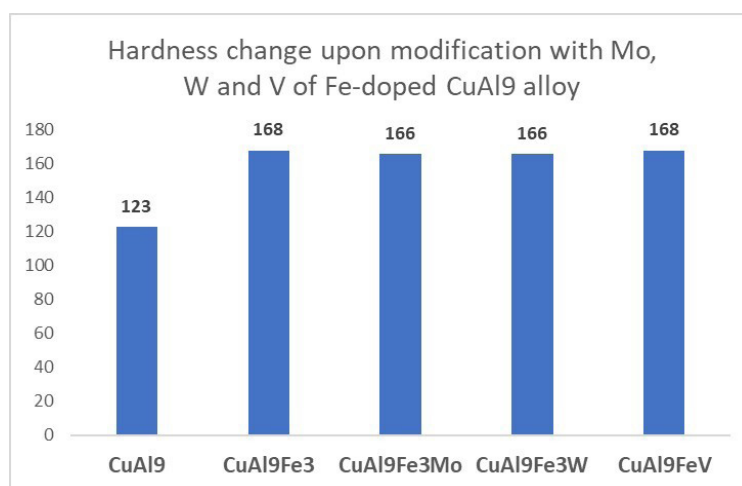


Fig. 6. Hardness change upon modification with Mo, W and V of Fe-doped CuAl9 alloy.

larger structure in the Mo-modified alloy. The tendency towards elongation of grains is maintained. The shape of the grains resembles CuAl9Mn3 alloy.

RESULTS AND DISCUSSION

The results of the measured Brinell hardnesses of CuAl9 alloy in the cast state alloyed with Fe and modified with the difficult-to-melt modifiers Mo, W and V are shown in Fig. 6.

The results obtained from the measured HBS hardnesses clearly show that CuAl9 alloy has a hardness

of 123 HBS, which is increased to 168 HBS upon alloying with Fe as well.

When the alloy is modified with W, the measured hardness is 166 HBS, which is a decrease in hardness relative to the Fe-doped base alloy by about two HBS units and an increase in hardness by about 43 units relative to the base cast alloy.

After modifying the alloy with V the measured hardness was 168 HBS, which resulted in no change in hardness relative to the iron-doped base alloy, but resulted in a hardness increase of about 45 units relative to the cast base alloy.

CONCLUSIONS

As a result of the research and the results obtained, the following conclusions can be drawn:

- The modification with hard-to-melt modifiers W and V of CuAl9 alloy doped with Fe in the cast state leads to the structure refinement after the modification with respect to the base alloy.
- When modifying with Mo of CuAl9Fe3 alloy, a minimal coarsening of the structure and rounding of the eutectoid crystals is observed.
- The hardness of alloys modified with Mo, W and V relative to the base alloy CuAl9 increases significantly.
- The measured hardnesses of the alloys modified with Mo, W, and V relative to the hardness of the CuAl9Fe3 alloy are maintained in close or equal order.
- Suppression of coarse-grained cast structure formation and retention of increased hardness of aluminum bronzes can be achieved by iron alloying and further modification with Mo, W and V.

Acknowledgments

This research is supported by the Bulgarian Ministry of Education and Science under the National Program "Young Scientists and Postdoctoral Students-2.

Authors' contributions: *M.K.: conceptualization, methodology, experimental research, analysis of results*

and writing the article; V.P.: experimental research, contribution to the analysis of results and advice.

REFERENCES

1. A. Kurdymov, M. Pikunov, V. Chursin, Foundry production of non-ferrous metals and alloys, Moscow, Metallurgy, 1982.
2. R. Petkpv, R. Gavrilova, S. Krasteva, Investigation of effect of dual alloyed with fe, mn, ni on the structure and the hardness of aluminum bronze, Scientific proceedings XXII international scientific technical conference "Foundry 2015", 16-18, ISSN 1310-3946.
3. R. Smallman, R. Bishop, Modern Physical Metallurgy and Materials Engineering, Science, process, applications, Sixth Edition, ButterworthHeinemann, Linacre House, Jordan Hill, Oxford OX2 8DP, 225 Wildwood Avenue, Woburn, MA 01801-2041, 1999.
4. H. Schumann, Metallography, VEB DVG, Leipzig, 1997.
5. R. Gavrilova, R. Petkov, Researches on the structure and properties of heat treated, nickel alloyed, molybdenum modified aluminum bronze, Bulgarian Chemical Communications, 45, 4, 2013, 644-648.
6. B. Kolachev, V. Elagin, B.A. Livanov, Metal science and heat treatment of non-ferrous metals and alloys, Moscow, MISIS, 2005.
7. H. Meigh, Cast and wrought aluminum bronzes - properties, processes and structure, Institute of Materials, London, 2000.