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STRUCTURAL AND MECHANICAL PROPERTIES OF HOT ROLLED CuAlBe NON-SPARK ALLOY

Explosion protection is of particular importance for safety as explosions also endanger the health of workers due to the uncontrolled effects of flames and pressure, the presence of harmful reaction products and the consumption of oxygen in the ambient air breathed by workers. CuAlBe alloy is proposed as a solution for mechanical actuators such as gears that work in environments with possible explosive atmosphere. Made of CuBe master alloy and pure aluminum in a induction furnace the material present large grains in melted state. After the hot rolling (heated 600s at 900°C) of the ingots small variation of chemical composition was observed based on the oxidation of the material, appearance of small cracks on the edges and a preferential orientation of the grains along the lamination direction. Scanning electron microscopy (SEM) was used to characterize the microstructural states of CuAlBe as laminated and heat treated states.

Keywords: Anti-spark material; SEM; EDS; cold rolling; indentation

1. Introduction

Copper, one of the most important metals used in technology, is widely used both in its pure state and in the form of an alloy. Its value has increased mainly due to the special physico-chemical properties that its various combinations with other metals have, but also due to the fact that it is irreplaceable in some practical applications. Aluminum bronzes are the most widespread and the most valuable special bronzes due to their superior properties. Bronzes with aluminum can be binary (simple) alloys, when copper is alloyed only with aluminum, or complex bronzes, when in addition to aluminum they also contain other alloying elements such as: iron, manganese, or nickel [1].

Beryllium bronze belongs to the group of so-called dispersion hardening compositions. Their distinctive feature is the dependence of the degree of solubility of the alloying ingredients on heating. One of the usages of beryllium bronzes (Cu-Be) is as non-spark materials for usage in possible explosive environments (natural gaseous or mining) [2]. When quenching is carried out from a single-phase section in a solid, an excessive number of atoms of the main alloying component is formed compared to the equilibrium state of such a system. The resulting concentrated solid solution is characterized by thermodynamic instability and

a tendency to decompose; this process is activated when increasing the temperature. The effect of compaction is explained by the dispersion of precipitates obtained as a result of the decomposition of the components.

All bronze alloys, the structure of which includes beryllium, are characterized by high heat resistance. The bronze alloys products don't change their properties at temperatures up to 340°C in working conditions. And when heated to 500 degrees, the mechanical properties and density of any beryllium bronzes become completely identical to aluminum in their performance to aluminum, as well as tin-phosphorite compositions at a standard operating temperature of about +20 degrees. This property allows beryllium bronze to be used to produce the highest quality molded castings. Beryllium alloys are easily adapted to any mechanical processing (cutting, soldering and welding). Although there are some limitations on performing the listed manipulations. Thus, any beryllium alloys should be soldered immediately after finishing the mechanical pickling. In this case, use of silver solders and flux are recommended. It is important that fluoride salts are always present in the flux itself. In recent years, the so-called vacuum soldering has become widespread – it is carried out under a thick layer of flux. Thus, the unique quality of the product is ensured. More recently, innovative processing

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approaches have been proposed to fabricate various types of Cu-based alloys with improved functionality and/or mechanical properties [3,4]. CuAlBe alloys present a solid state transformation from austenite to martensite type structure at cooling and reverse at heating [5,6].

In this article two CuAlBe alloys with customized chemical compositions were hot-rolled (HR) and the structure and mechanical properties analyzed after HR and after HR+ water quenching heat treatment (WQ).

2. Experimental details

CuAlBe alloys were obtained by melting of CuBe master alloy (4%wt Be) and high purity Al (99,99%) using an electric furnace at 1000°C. The alloys named Alloy 1 respectively Alloy 2 have the chemical composition: Cu: 89.0, Al: 10.4 and Be: 0.6 wt% and Standard Deviation (calculated from ten determinations): ± 1.5 for Cu, ± 0.5 for Al and ± 0.1 for Be [7]. The ingots (diameter 10 mm and length 100 mm) were hot rolled, diagram from Fig. 1a), using an electric resistance laboratory furnace for heating and a rolling mill equipment. Bands with 3 mm thickness and 160 mm length were obtained, Fig. 1b). No longitudinal cracks were observed; the material integrity was not affected by the thermo-mechanical process applied.

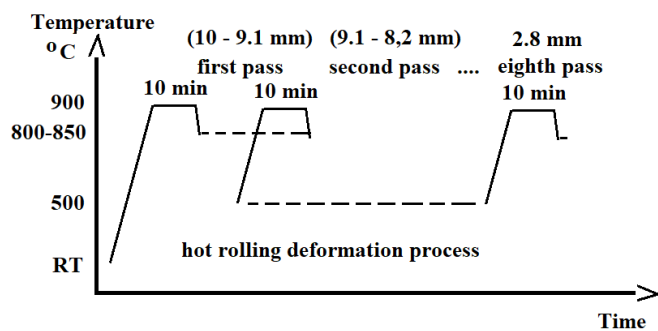
After the hot rolling the materials were heat treated by water + ice quenching, Fig. 1c) – schematic. The role of the subsequent heat treatment (solution quenching) is to form the martensitic phase and sometimes an aging heat treatment can be performed

at a lower temperature in order to stabilize the martensite-like phase. Since copper-based alloys are mostly applied in sheet or wire form, they were also hot or cold worked by forging, rolling or extrusion. The structure and the surface state was identified using a scanning electron microscope type Vega-Tescan model: LMH-II (SEM) with a Secondary Electrons detector and 30 kV filament power supplied [8]. The materials, as plates, mechanical properties were determined using a Tribometer: CETR-UMT2 [9-10]. The tests were performed on samples with parallel faces having $90 \times 18 \times 8$ mm dimensions. The microhardness tests (five on every sample at 0.30 mm distance between them) were made using a Rockwell diamond tip (120°). Main characteristics of the Rockwell's tip indenter were: radius: $210 \pm 7 \mu\text{m}$; angle $120^\circ \pm 0.25^\circ$. The scratch tests were realized in order to observe the behaviour of the structure (grains and grain limits) at a mechanical force. The experiment was made through applying an increasing force from 1 to 25 N over a distance of 70 mm with 1 mm/s rate on the etched sample surface. The results were interpreted using Test Viewer software.

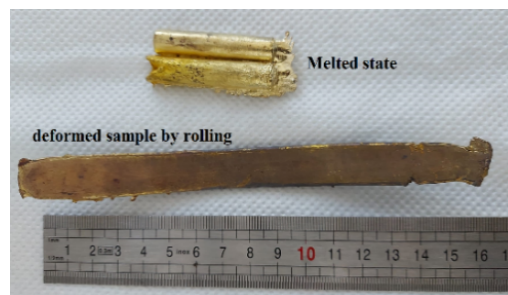
3. Results and discussion

3.1. Structural analysis

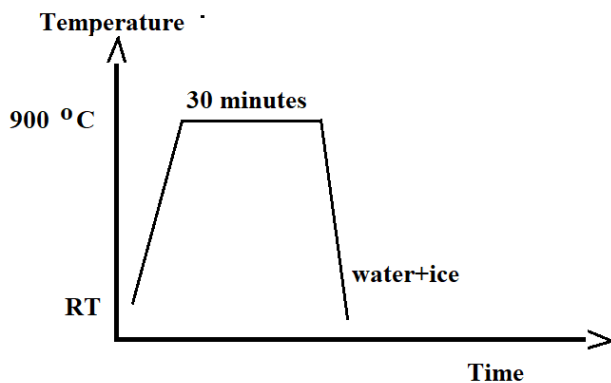
The materials were mechanical grinded and chemical etched with H_3NO_4 with ethyl alcohol solution (60-40%) in order to reveal the structure. Mechanical tests were made on clean samples surfaces.



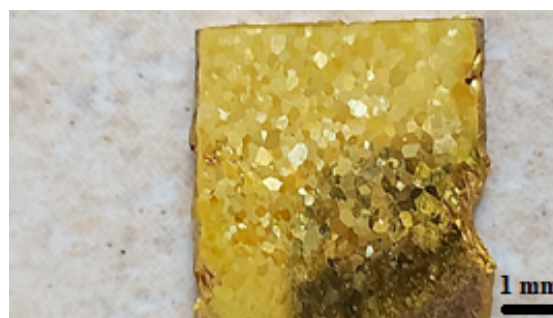
a)



b)



c)



d)

Fig. 1. Hot rolling diagram of melted ingot in a), image of the material before – as ingot and after the hot rolling as plate in b) and final heat treatment diagram of the rolled material

On Fig. 2 the microstructure of the samples is presented and can be observed that the predominant phase in all micrographs, at room temperature, is the austenite phase [11]. Structural evaluation by optical microscopy (OM) and scanning electron microscopy (SEM) of the microstructure reveal large grains typically for Cu-based alloy for all states, Fig. 2a)-c) with an orientation on rolling direction for HR+WQ structure. An abnormal grain dimension growth (AGG) happened after the hot rolling process (Fig. 1a) compared with b) and c)) occurred for both states of the material (HR and HR+WQ). This phenomenon was reported by da Mota Candido et al [12] in a previous study, for a hot-rolled poly-crystalline Cu-Al-Be alloy. The induces plastic deformation of the material during the hot-rolling (the sample pass from an ingot with 8.5 mm diameter and 100 mm length in a plate with thickness of 2.5 mm, 15 mm width and 140 mm length through 6 passes) represent the reason of the dynamic recrystallization process [13]. Based on Oliveira et. al. [14] findings during the heat treatment + deformation recrystallization process, an entire new grains group is growth and take place for big energy contribution during the deformation of the as-cast structure, for example the grains intersections, deformation lines sliding or self-blocking, similar paths crossed of slip process and in some cases near the areas of the grain limits. The abnormal growth of the grains stage caused by the deformation in hot-rolling process is connected to the relocation procedure of the grain limits which transform (ingest) the sub-grains formed during the heating stage. Furthermore, the rate of expansion of the grains increases with the degree of disorientation of the small grains [15].

The main reason for AGG is the movement of grain limits that transform the sub-grains that appear during the heating (850°C) from each step of the hot-rolling process, Fig. 1b). In this case, of plastic deformation of CuAlBe alloy, exist a limit of reproving deformation for the active stage of the recrystallization stage to occur and at this limit when deformation pass the critical value, the recrystallized grains are moderately restructured with the deformation [16]. The austenite to martensite transformation and reverse is influenced by the low energy of straight grain boundary and by the nonappearance of triple grain boundary junctions in polycrystalline materials [17].

3.2. Mechanical properties

The elastic modulus (E) was estimated from loaded displacement curves (Fig. 3) using the Oliver and Pharr method. Mechanical properties present variations between hot-rolled and water quenched state based on partially austenite to martensite transformation. Compared to melted state the mechanical properties vary based on the report between the abnormal grain growth phenomena and the elimination of some as-cast typical defects.

From loading curves, Fig. 3, the mechanical properties of the materials are given in TABLE 1. In order to establish the homogeneity of the properties on the entire material five determinations were made in different areas (point 1-5).

The differences between the HR and WQ state of the mechanical properties, especially indentation Young Modulus (GPa)

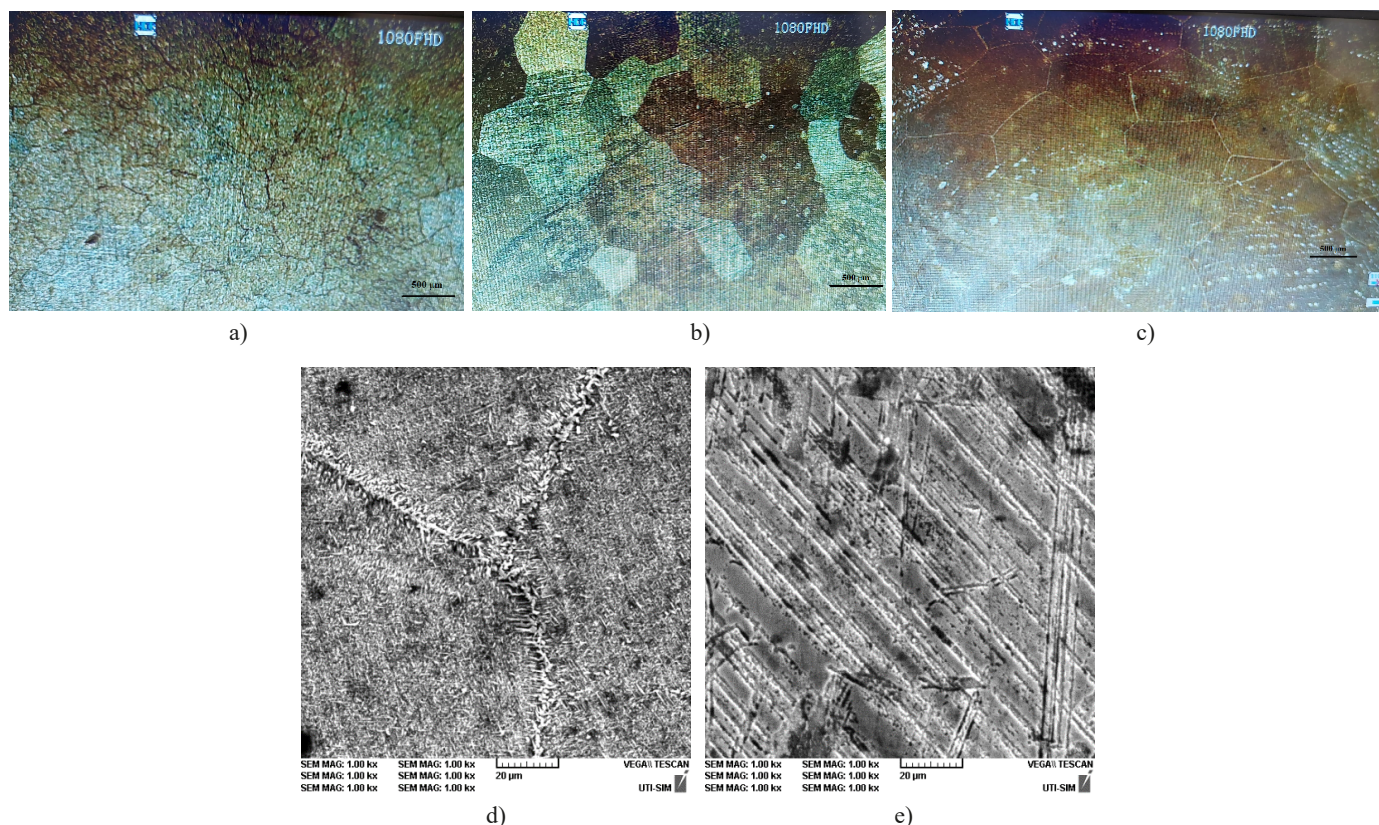


Fig. 2. Optical (a-c) and scanning electron (d-e) microstructure of CuAlBe a) melted state of alloy 1, b) hot rolling state of alloy 1, c) hot rolling + water-quenched structure of alloy 1, d) detail of alloy 1 after hot-rolling and in e) of alloy 2 after hot-rolling and water quenching

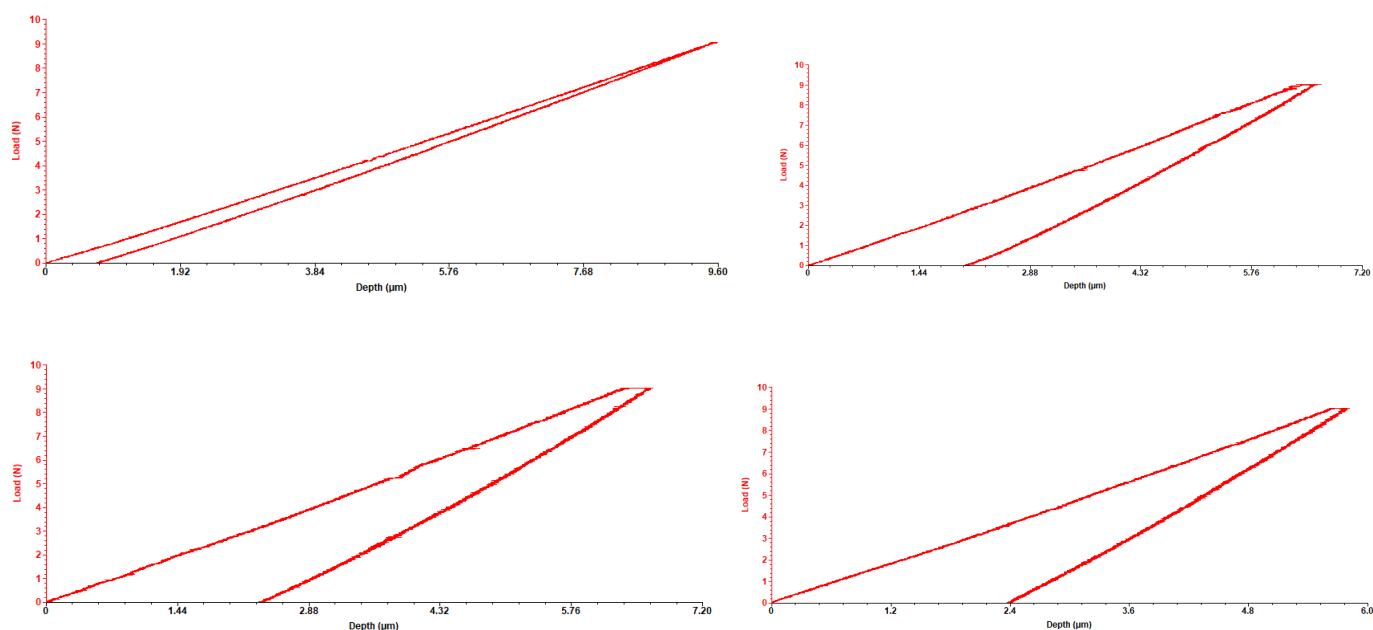


Fig. 3. Indentation graphs for CuAlBe samples (1 and 2) a) sample 1 hot rolled, b) sample 2 hot-rolled, c) sample 1 hot rolled heat treated (water quenched) and d) sample 2 hot-rolled and heat treated (water quenched)

TABLE 1

Mechanical properties of CuAlBe experimental alloys in hot-rolled and heat treated state obtained from indentation tests

Material	Crt. no	Indentation Modulus Young [GPa]	Hardness [GPa]	Contact stiffness [N/ μm]	Maximum Load [N]	Maximum Displacement [μm]	Contact depth [μm]	Contact area [μm^2]
CuAlBe_WQ 1	Point 1	13.96	2.13	1.1	9.05	9.58	3.41	4248.61
	Point 2	14.21	2.16	1.11	9.03	9.46	3.36	4183.68
	Point 3	14.06	2.15	1.10	9.03	9.52	3.38	4207.26
	Point 4	14.06	2.15	1.10	8.98	9.49	3.35	4171.78
	Point 5	13.82	2.11	1.09	9.02	9.63	3.44	4279.40
	Average	14.02	2.14	1.10	9.02	9.53	3.38	4218.15
CuAlBe_WQ2	Point 1	27.75	2.01	2.22	9.02	6.66	3.61	4495.87
	Point 2	25.42	2.16	1.97	9.02	6.79	3.38	4183.62
	Point 3	23.47	2.21	1.79	9.03	7.05	3.27	4079.49
	Point 4	20.58	2.18	1.58	8.99	7.56	3.30	4112.85
	Point 5	17.41	2.16	1.41	9.02	8.43	3.65	4539.79
	Average	22.92	2.14	1.79	9.02	7.29	3.44	4282.32
CuAlBe_HR 1	Point 1	30.65	1.90	2.38	9.02	6.65	3.81	4743.19
	Point 2	30.12	2.15	2.33	9.03	6.29	3.38	4205.28
	Point 3	29.60	2.12	2.30	9.04	6.36	3.42	4260.12
	Point 4	28.49	2.05	2.26	9.04	6.55	3.55	4416.16
	Point 5	28.40	2.14	2.20	9.01	6.45	3.37	4202.27
	Average	29.450	2.07	2.29	9.024	6.46	3.50	4365.40
CuAlBe_HR2	Point 1	37.16	2.09	2.89	9.03	5.81	3.47	4321.45
	Point 2	37.44	2.29	2.78	9.04	5.60	3.16	3934.70
	Point 3	40.1	2.341	2.95	9.01	5.380	3.086	3847.94
	Point 4	40.22	2.48	2.87	9.05	5.29	2.93	3652.13
	Point 5	42.16	2.48	2.87	9.02	5.27	2.911	3631.16
	Average	39.42	2.34	2.87	9.03	5.47	3.11	3877.47

is given by the presence of more martensite state in WQ samples. It is known that the elastic modulus of the A-austenite and M-martensite phase for a CuAlBe alloy are 75,000 MPa and respectively 35,000 MPa [18]. Compared to melted state an increase of Young Modulus is observed (values for melted

state are: Young modulus [GPa]: 23,9 respectively 17,2) for both state (especially for hot rolled and less for water quenched samples). An increase of the hardness, through hot rolling process was also highlighted. Hardness of the second alloy present a decrease with the heat treatment (a higher percentage of martensite

phase being transformed by water quenching). Contact stiffness present also an important modification based on the phase transformation from austenite in martensite based on the known fact that martensite phase is softer and the austenite phase is stiffer.

The scratch test on both samples present the friction properties of the materials. In Fig. 4, for sample 1, are given the variations of F_x (resistance force of the material to scratch force), COF (friction coefficient) and AE (acoustic emission: represent the occurrence of propagation of acoustic (elastic) ripples in solid materials – like alloys that take place when a material presents irreversible changes in its micro-structure, especially at the surface and near inside the material like a consequence of a fissure start and grow or like plastic deformation of the material due to aging, temperature gradients or outer sollicitations [19,20])

on 10 mm distance. On the heat treated alloy a difference in F_x force can be observed between 4 and 7 mm of the test were the equipment tip meet a different phase, martensite area, and after returns to initial behavior.

Friction coefficient behavior is similar for both samples (alloy states), Fig. 4b). COF presents different variations and peaks that can correspond to grain limits or different metallic compounds with a higher COF [21]. Martensite (M) state of materials with austenite to martensite transformation is a softer state compared to stiffer austenite. This fact influences their friction coefficient. In case of sample 1 the water quenching heat treatment promote the austenite to martensite transformation and a higher M percentage contribute to the increase of COF value.

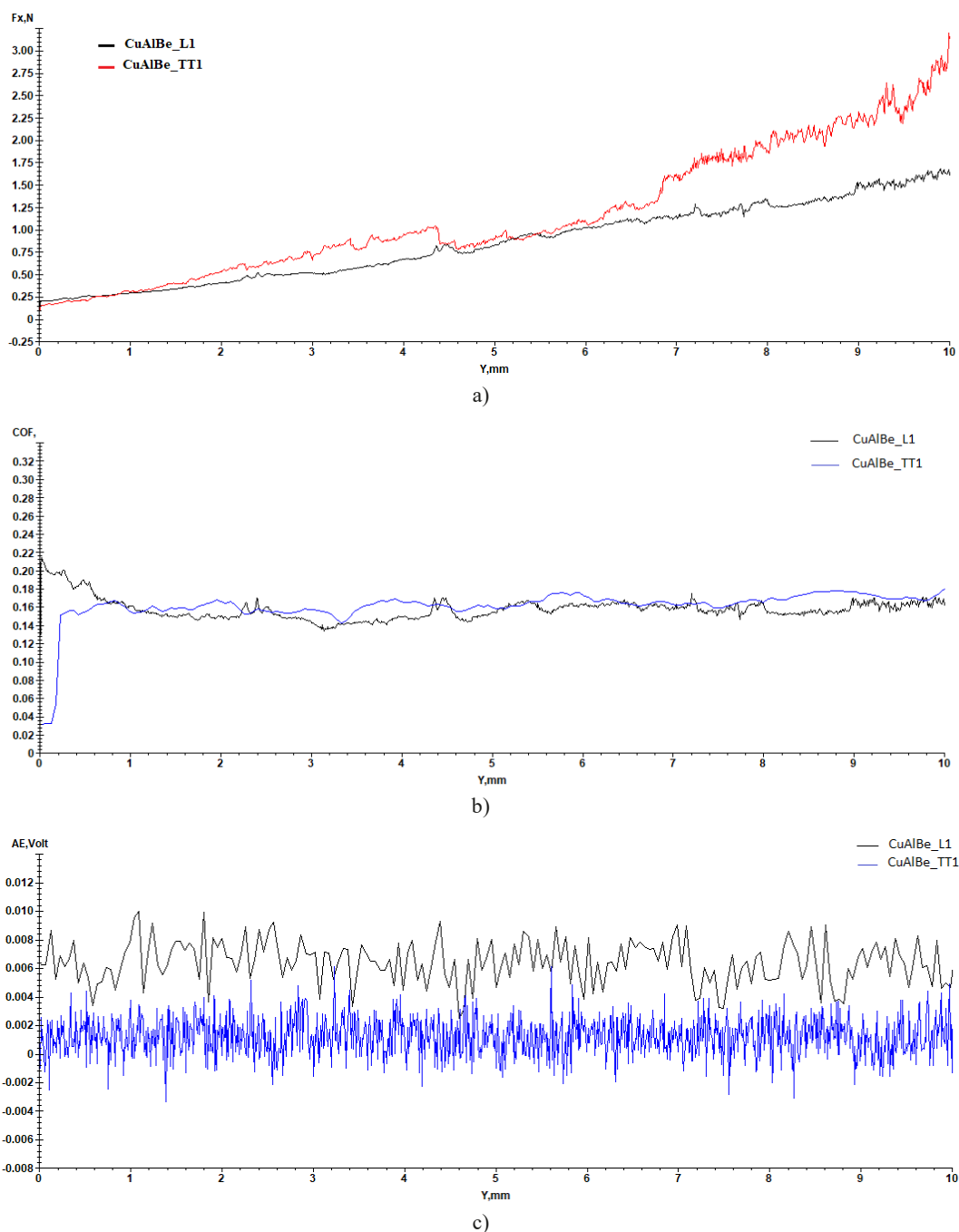


Fig. 4. Scratch test results variations of a) F_x , b) COF and c) AE on a 10 mm length

TABLE 2

Mechanical properties of CuAlBe experimental alloys in hot-rolled and heat treated state obtained from scratch tests

Material	F _x [N] Average	A _e [Volt] Average	COF Average	F _f [N] Average
CuAlBe_HR1	0.85	0.005	0.16	0.85
CuAlBe_HR2	0.94	0.005	0.17	0.94
CuAlBe_WQ1	1.16	0.001	0.21	1.16
CuAlBe_WQ2	0.98	0.001	0.18	0.97

Compared with melted state the friction coefficient presents a modification only in case of the second alloy (a decrease from 0.27 to 0.17) and no influence of hot rolled on the COF for first sample. The average values of friction coefficients present an increase with the heat treatment in case of the first alloy based on the martensite phase appearance. The acoustic emission present similar values for hot-rolled samples and respectively for water quenched materials.

4. Conclusions

A new alloy, based on Cu-Al-Be, is proposed for non-spark materials with improved corrosion resistance and mechanical properties compared to classical Cu-Be materials. The possible application of the new alloys is in the production of mechanical parts for devices used in possible explosive environments. Further investigations on the non-sparking character of these alloys will be made and the mechanical and physical advantages of M or A structure will be considered.

Based on the obtained results can be concluded that:

- structurally an abnormal grain growth was observed after hot rolling,
- CuAlBe alloys improve their mechanical properties through hot rolling (850°C) and water quenching heat treatment,
- the mechanical properties modifications are based on the partial transformation of austenite phase to martensite through water quenched heat treatment.

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