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CONTEMPORARY HEAT-RESISTANT COPPER CONDUCTOR ALLOYS

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by

M. V. Zakharov

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CONTEMPORARY HEAT-RESISTANT COPPER CONDUCTOR ALLOYS

M. V. Zakharov

In the last decade conductor copper alloys with various combinations of strength and electrical properties have found wide application in connection with the development of new areas of engineering. In particular, copper conductor alloys capable of prolonged resistance to plastic deformations at elevated and high temperatures have turned out to be irreplaceable. Under these conditions the use of pure copper is impossible because of its low softening temperature and excessive creep. Beginning at a temperature on the order of 200-250°C worked copper softens noticeably and creeps intensively under prolonged loading, since the temperature at the beginning of recrystallization lies in the 140-160°C region for pure worked copper. Such copper cannot be hardened by cold working, since the recrystallization and softening temperatures of the carbon are reduced with an increase in the degree of deformation. The only choice is to use the copper conductor alloys which possess a higher softening temperature and adequately high strength and heat resistance.

Practice shows that only by the introduction of hundredths of a percent of zirconium (0.05-0.08 wt%) into copper is it possible to raise the temperature of the beginning of softening to a level around 550-560°C, to increase ultimate strength to 36-40 kgf/mm^2, while reducing electrical conductivity by only 10-15% in all. Addition of 0.2% Zr to copper increases the softening temperature of heat-treated Cu-Zr alloy to 575°C, increases ultimate strength 45 kgf/mm^2, and reduces electrical conductivity to a level about 80% of electrically conducting copper. The heat-resistance characteristics σ_{100} and $\sigma_{0.1/100}$ are retained at an adequately high level in the copper-zirconium alloy. Thus, the creep limit $\sigma_{0.1/100}$ for hardened copper-zirconium alloy with 0.2% Zr is retained at a level of 32 kgf/mm^2 at 200°C, while the creep limit for pure copper comprises only 5 kgf/mm^2. Unfortunately, not every additive will harden copper so substantially as zirconium while reducing its electrical conductivity insignificantly. In practice alloying additions which sharply reduce electrical conductivity of copper and give little increase in its strength and heat resistance predominate.

If we consider the influence of the additive on the cost and technological properties of the alloys - weldability, soldering quality and ease of other operations - the number of promising additives for copper is sharply reduced and the development of new conductor high-strength and heat-resistant alloys becomes extremely difficult.

The minimum requirements which must be met by a copper conductor alloy should include the following: 1) adequately high strength at normal and elevated temperatures; 2) required ductility at normal temperature and in the temperature zone in which ductility shows a dip (300-600°C); 3) the necessary electrical conductivity, depending on the intended function of the alloy; 4) satisfactory qualities during smelting in open conditions or under minimum rarefaction, good resistance to the formation of hot cracks during semicontinuous casting (technological effectiveness); 5) moderate cost and reasonable availability.

Besides this, it is sometimes necessary that copper conductor alloys be capable of undergoing various types of welding, soldering; minimum oxidation at elevated temperatures and high corrosion resistance during prolonged storage of finished articles are needed.

Usually copper alloys are broken down into groups according to electrical conductivity, chemical composition, suitability for hardening heat treatment, properties, and function.

In terms of the value of electrical conductivity, conductor alloys can be tentatively broken down into four groups:

1) alloys with very high electrical conductivity (greater than 90% of the conductivity of pure annealed copper);

2) alloys with high electrical conductivity (conductivity on the order of 70-90% of that of copper);

3) alloys with medium electrical conductivity (50-70% of copper);

4) alloys with moderate electrical conductivity (30-50% of the value for copper).

Since conductivity and strength depend primarily on the degree of alloying of the alloys, it is possible to maintain the strength characteristics of copper alloys in wide limits at the expense of a reduction in electrical conductivity.

The most promising heat-resistant copper conductor alloys of the <u>first group</u> must include the low-alloy chromium-zirconium alloy type Mts-5A, containing 0.15-0.35%, Cr, 0.08-0.25% Zr, with the remainder being pure copper, grade MO. The electrical conductivity of this alloy with optimum thermomechanical treatment (TMO) conditions there noticeably a function of the content of chromium and zirconium; in alloys in which the alloying elements are at the lower limit (0.15 wt% Cr and 0.08 wt% Zr) it reaches 93-94% of the electrical conductivity of pure copper, while with the maximum addition (0.35% Cr and 0.25% Zr) its value is 88-90% of copper, while with medium contents (0.25% Cr and 0.16% Zr) it amounts to 92% of the conductivity of copper. When grade M1 copper is used the electrical conductivity is reduced by a respective 6-7% from the indicated values, while when approximately 0.02% boron is present in the alloy it is increased by 5-6% with other characteristics being retained.

Similar regular behavior is observed during comparison of strength characteristics. The higher the content of additives in the alloys, the stronger the alloys. In particular, an alloy with approximately the maximum limit of alloying additions (0.28% Cr and 0.24%Zr) and subjected to quenching from 930-950°C (hold -1.5 h) in cold water, cold deformation by 50-60% and aging at 460-470° for 4-3 h, respectively, will give HB = 130 kgf/mm^2 and $\sigma_b \geq 46$ kgf/mm^2 with adequate relative elongation (15-20%).

A characteristic feature of alloys in the Cu-Cr-Zr system is their high level of strength and heat-resistance characteristics. Thus, an alloy with 0.28% Cr and 0.24% Zr which is treated by the regime indicated above will have ultimate tensile strength of 43, 30 and 15 kgf/mm^2 at temperatures of 300, 500, and 700°C respectively. Stress-rupture strength (σ_{100}), which characterizes the heat resistance of the alloys, comprises 38-40 kgf/mm^2 at 300°C and no less than 18-20 kgf/mm^2 at 500°C; other copper conductor alloys do not possess such high stress-rupture strength.

Table 1. One hundred hour strength of copper alloys (after TMO) at 300° and 500°.

Designation of alloy	Content of alloying element, %	Electrical conductivity as % of Cu	σ_{100}, kgf/mm^2	
			300°	500°
Copper	—	100	10	—
Copper (MK)	0.9 Cd	95	7-8	0.6
Br. Kh 0.4	0.4 Cr	90	20	4
Br. Kh 0.6	0.6 Cr	85	21	4
Br. Tsr 0.18	0.18 Zr	92	26	10
Br. Tsr 0.37	0.37 Zr	90	31	12
Mts-4A 0.2-0.13	0.2 Cr and 0.13 Mg	88	30	7
Mts-4A 0.2-0.2	0.2 Cr and 0.2 Mg	86	32	8
Mts-5 0.44-0.25	0.44 Cr and 0.25 Zr	85	—	20
Mts-5A 0.34-0.26	0.34 Cr and 0.26 Zr	85	38*	20
Mts-5B 0.5-0.43	0.5 Cr and 0.43 Cd	88	26	6
Br. NBT	1.56 Ni; 0.4 Be; 0.05 Ti	45	45	14*

*Specimens were not destroyed.

From the data given in Table 1 it is clear that the alloys with high and very high electrical conductivity most widely used in practice differ widely from one another in terms of stress-rupture strength and are noticeably inferior to the alloy of the type Mts-5A at temperatures of 300-500°C.

In terms of ultimate stress-rupture strength (σ_{100}) at 500°C, all of the alloys can be arranged in descending order: Mts-5A(Mts-5A) → Br. Tsr. 0.37 → Br. Tsr. 0.18 → Mts-4A → Mts-5B → → BrKh 0.6 → MK → copper.

In terms of short-time ultimate strength (σ_b) at 500°C the alloys fall into a somewhat different series: Mts-5A (34 kgf/mm^2)→ → Mts-4A (29 kgf/mm^2) → Br.Kh 0.6 (29 kgf/mm^2) → Br. Tsr. 0.37 (28 kgf/mm^2) → Mts-5B (27 kgf/mm^2) → copper (11 kgf/mm^2), although in this case the Cu-Cr-Zr alloys turned out to be stronger.

Under conditions of lower temperatures (20-300°C) and with somewhat different treatment conditions (Table 2) the low-alloy Cu-Cr-Zr alloy type Mts-5A turned out to be once again in first place.

Working temperatures in the 20-300° limits are the most widely encountered for copper conductor alloys, in particular if we are considering collector materials. Therefore not only the absolute values of strength characteristics, but also their stability with a change in temperature and hold time at a given temperature are important for such materials.

From the data in Table 2 (compare treatment regimes 1 and 3) it is clear that the low-alloy material (0.15% Cr and 0.15% Zr) behaves very stably under conditions of prolonged heating (1000 h) at 200° after hardening heat treatment (quenching and aging). Prolonged heating at 200°C of aged binary alloys Cu-Cr and Cu-Zr reduced their ultimate strength and yield point at normal test temperature by approximately 1-2 kgf/mm^2 with an insignificant increase in electrical conductivity (σ_b was reduced to 27 kgf/mm^2 from 28 kgf/mm^2 and the electrical conductivity was increased from 92-94% to 93-95%), while the strength characteristics and electrical conductivity remained unchanged in the alloy of type Mts-5A (0.15% Cr and 0.15% Zr) (σ_b = 35 kgf/mm^2); this is connected with the retention of a stable structure.

Treatment by regime 2, including cold working after quenching, showed higher strength properties than the other methods. Thermomechanical treatment had a positive influence on elongation characteristics (σ_{100} and $\sigma_{0.1/100}$), if we bear in mind the test temperature, which did not exceed 600°C for the given alloys. Only at a temperature of 650° and above is there a negative, instead of positive, influence of TMO on the heat resistance of the given alloys.

Multiple tests of alloy Mts-5A as electrode material showed very high stability. Thus, according to data from S. I. Kutkovskiy [1], during spot-welding of low-carbon steel the alloy Mts-5A showed the highest stability, exceeding that of existing foreign Cu-Zr alloys with 0.2% Zr - Br. Kh 0.8, etc. This agrees with the very prolonged creep tests of certain copper conductor alloys carried out very recently [2]. It is clear from these tests that the Mts-5A Cu-Cr-Zr alloy containing 0.28% Cr, 0.14% Zr, and 0.05% Mg has a higher creep limit ($\sigma_{1/10000}$) at 300-400°C then does the Br. Kh 0.86 and the Cu-Zr alloy with 0.16% Zr. As a substitute for the alloy Mts-5A we can recommend for this type of welding the Cu-Cr-Mg alloy type Mts-4A [3], occupying second place after the alloy Cu-Cr-Zr; this is in agreement with short-term and prolonged strength characteristics (see Tables 1 and 2) of this alloy. During comparative tests with the alloys Mts-5B (0.2% Cr and 0.3% Cd) and Br. Tsr 0.3 (0.3% Zr) the alloy Mts-5A (0.2% Cr and 0.2% Zr) showed the best results during spot welding of the aluminum alloy AMg6, where not only stability but also the absence of transfer of copper (expressed in darkening of the welded spots) is important.

Table 2. Mechanical properties and electrical conductivity of copper alloys at 20-300°C after various treatment regimes.

Content of alloying element in copper, %	Electrical conductivity as % of Cu	20°			200°			300°		
		σ_b, кГ/мм²	σ_0, кГ/мм²	δ, %	σ_b, кГ/мм²	σ_0, кГ/мм²	δ, %	σ_b, кГ/мм²	σ_0, кГ/мм²	δ, %
Regime 1 (quenching + aging)										
0.15% Cr	94	28	18	21	22	16	22	17	14	15
0.2% Zr	92	28	16	26	25	15	25	22	13	16
0.15% Cr и 0.15% Zr	90	35	23	24	30	18	20	25	—	24
0.14% Cr и 0.15% Mg	90	34	20	20	28	—	26	23	—	26
0.2% Cr и 0.16% Cd	91	30	17	28	22	15	26	26	—	22
Regime 2 (quenching + cold working to 50% deformation)										
0.3 % Cr и 0.14% Zr	88	48	45	13	—	—	—	40	38	10
0.3 % Cr и 0.11% Mg	88	42	33	8	—	—	—	35	32	14
Regime 3 (holding 1000 h at 200° after quenching and aging)										
0.15% Cr	95	27	17	22	—	—	—	—	—	—
0.2% Zr	93	27	14	25	—	—	—	—	—	—
0.15 Cr и 0.15% Zr	90	35	23	19	—	—	—	—	—	—

Designations: кГ/мм² = kgf/mm²; и = and.

As is known, besides high physicomechanical and heat-resistant characteristics, commutation stability is of major significance for collector materials. Alloys of the Mts-5A type show good results in this case also. Thus, according to data from VNIIEM [All-Union Scientific Research Institute of Electromechanics], resource tests of Cu-Cr-Zr alloys as collector materials showed good wear resistance and good commutation properties for these alloys, which can be used for d-c electric motors with EG-47K brushes at a working temperature of 200°C.

The most promising alloys in the second group, i.e., those possessing electrical conductivity of 70-90% of that of copper, are alloys of the same Cu-Cr-Zr system, type Mts-5, containing 0.35-0.6% Cr and 0.2-0.35% Zr. As compared with alloy Mts-5A, the alloy Mts-5 shows a higher effect of hardening heat treatment, since it contains more chromium and zirconium. Unfortunately, as compared with Mts-5A the technological properties of alloy Mts-5 are somewhat lower; owing to its high content of chemically active zirconium this alloy must be smelted and poured in the vacuum or under protective media, while the alloy Mts-5A with a zirconium content up to 0.15%, can be smelted and cast successfully using a salt (CaF_2 + MgF_2) or, up to 0.06% Zr, a carbon cover. The higher chromium content in alloy Mts-5 also requires a higher heat during smelting, since dissolution of the chromium is also hampered even in copper which is liquid but not extremely highly heated. However, since it possesses higher mechanical properties and better long-term characteristics at elevated temperatures, alloy Mts-5 is the most heat-resistant material, and, in addition, has an electrical conductivity on the level 85-87% if copper of grade M0 is used as its base. After quenching in water from 950°, additional cold working to 60-70% deformation, and annealing at 460° for four hours, alloy Mts-5 (0.36% Cr and 0.26% Zr) provides σ_b of 52, 44, 34, 26, and 15 kgf/mm^2 at temperatures of 20, 300, 500, 600, and 700°C, respectively, with a relative elongation of no less than 10%. The stress-rupture strength (σ_{100}) of alloy Mts-5 (0.44% Cr and 0.2% Zr), manufactured under factory conditions and then heat treated, is maintained at levels of 38-42 and 20-25 kgf/mm^2 at temperatures of 300 and 500°C, respectively, with electrical conductivity 84% of that of copper. A content of hundredths of a percent of boron (0.01-0.02%) in Mts-5 makes it possible to raise its electrical conductivity to 86-87% with a simultaneous increase in the reserve of ductility, required for the semicontinuous casting method and for all forms of pressure working.

Whereas fifty years ago [4] we regarded Cu-Cr-Zr alloys as experimental, since at that time our industries had no factory-scale vacuum furnaces, at present we possess the entire base required to carry out centralized introduction of these Soviet alloys. It was no accident that beginning in 1962-1963 the Western countries not only began extensive studies of Cu-Cr-Zr alloys, but also began their wide introduction, carrying out long (1000 h) and extremely long (10,000 h and more) tests at high temperatures [2]. The addition of only hundredths of a percent (0.05-0.07%) of zirconium to the alloy Br. Kh 0.6 noticeably increased the mechanical properties of chrome bronze and mainly made it possible to manufacture this alloy under exposed conditions of smelting and casting. Bronze Br. KhTsr 0.6-0.06 has already been mastered by our industry and has been widely used (for example, the Volga Auto Plant) as an electrode alloy. Unfortunately, we cannot recommend Br. KhTsr 0.6-0.06 for welding aluminum alloys, since by comparison with the low-alloy Mts-5A alloy it provides but half the number of spot welds on alloy AMg6 before they become darkened.

Very promising alloys in the <u>third group</u> include Br. NBT, containing on the average 1.6% Ni, 0.3% Be, and 0.1% Ti (this is a variant of alloy Mts-3). A very important feature of this bronze is, in addition to high stability, the possibility of industrial manufacture of the material from inexpensive wastes from production of Br. B2, Br. B2.5, Br. BNT1.9.

Since we cannot examine in detail the extremely high physico-mechanical properties of Br. NBT, we will refer the reader to literature sources [5, 6] and we will present here data on its industrial use in welding various steels and heat-resistant alloys. Thus, for example, during seam welding of stainless steel using rollers of Br. NBT, it has proved possible to weld 472 running meters under factory conditions, while only 347 running meters could be welded using rollers made of existing and expensive English alloy (Cu + 2.5% Co + 0.5% Be); with rollers of Mts-5B the total is 187 running meters, and for rollers of Br. Kh 0.6 it is 125 running meters. During spot welding of stainless and other steels and heat-resistant alloys the stability of Br. NBT is, on the average, 5-8 times higher than that of Br. Kh 0.8. The annual economic savings from the introduction of welding electrodes made from bronze Br. NBT in cold-rolling shops on only four of our largest ferrous metallurgy plants amounts to 900,000 rubles.

The elastic properties of Br. NBT are quite high ($\sigma_{0.05} \geq 60$ kgf/mm^2) and in a number of cases it can replace extensive high-beryllium bronzes. Bronze NBT has been produced industrially since 1962, being cast into ingots by the modern semicontinuous plant method in any required quantity.

The Soviet conductor alloys Mts-5A and Br. NBT were named the finest electrode alloys at the International Congress on Welding held in Warsaw in 1968.

Finally, promising alloys in the fourth group, with electrical conductivity 30-50% of copper and high heat resistance, include Br. ZhNBT, containing 1-2.5% Fe, 2-3% Ni, 0.2-0.5% Be, 0.2-0.4% Ti, and impurities of Si, B, and other elements. This electrode alloy is intended for spot and roll welding of alloys with various thermophysical properties and different thicknesses (greater than 2:1).

In foreign practice such specialized materials are welded with electrodes of pure molybdenum, which has electrical conductivity on the order of 30-35% of that of copper. Together with F. V. Korolev and P. L. Chuloshnikov, we tested spot welding of sheets of high-strength steel (VNS-2) and the heat-resistant alloy VZh-98 using electrodes of Br. ZhNBT, with high heat resistance (σ_{100} with 500° more than 20 kgf/mm^2) and electrical conductivity 30-35% of copper. In terms of depth of fusion and stability of electrodes the results were 1.5-2 times higher than with the application of the existing electrode alloys Br. Kh and Br. NBT.

All of the prospective conductor heat-resistant copper alloys examined above were developed using the principles of alloying whose basis was laid in the works by A. A. Bochvar and his school [7, 8].

Conclusion

1. The alloy type Mts-5A, containing 0.15-0.35% Cr, 0.08-0.25% Zr, (remainder copper of high purity) and possessing the required combination of heat-resistance and electrical conductivity, is recommended for spot and roller welding of aluminum alloys of the AMg6 type and low-carbon steel. At the same time this alloy can be used as a collector material.

2. Bronze Br. NBT, containing 1.4-1.6% Ni, 0.2-0.4% Be, and 0.05-0.15% Ti (remainder grade M1 copper), provides very excellent results during butt welding of stainless steels and heat-resistant alloys. Manufactured from inexpensive waste products from the production of high-beryllium bronzes, Br. NBT can in a number of places substitute for expensive beryllium bronzes.

3. Bronze Br. ZhNBT, containing 1-2.5% Fe, 2-3% Ni, 0.2-0.5% Be, 0.2-0.4% Ti (remainder grade M1 copper), possesses high heat resistance and moderate electrical conductivity; it is recommended for welding high strength steels with different thermophysical properties (sheets of different thicknesses).

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