

MEASURING TRANSDUCERS

ELECTRICAL PROPERTIES OF *TI-CU-CO-SI* HIGH-ENTROPY ALLOY

Svyatoslav Yatsyshyn, Dr. Sc., prof; Pylyp Skoropad, Dr. Sc., prof.,

Lviv Polytechnic National University, Ukraine;

e-mail: pylyp.i.skoropad@lpnu.ua

Mikolaj Karpinski, Dr. Sc., prof., University of Bielsko-Biala, Poland;

Abstract. To study the metrological characteristics, there were studied manufactured based on the *Ti-Cu-Co-Si* alloy, obtained by quenching from the melt, the sensitive element of the resistance thermotransducer. The instability of its metrological characteristics as a function of temperature up to 350 °C and operation time up to 3000 hours was investigated; it does not exceed 0.025% under the worst operating conditions. In addition, the methodological error of measurement caused by heating of the sensitive element by the measuring current was examined. It was shown that the recorded changes in electrical resistance were outside the value of the methodological error. They may be due to the presence of nanostructured fields of mechanical stresses and the formation of nanoprecipitates as a consequence of manufacturing.

Key words. High-entropy alloy, Temperature, Measurement error, Drift of metrological characteristics.

1. Introduction

Some studies of high-entropy alloys (HEAs) [1-3] for the needs of various branches of science and technology have demonstrated the following. The HEAs are characterized “as a superb specific strength, excellent mechanical performance at high temperature, exceptional ductility and fracture toughness at cryogenic temperatures, superparamagnetism, and superconductivity” [3]. Some properties can be promising for particular applications in high temperatures. The focus of research on the study of certain materials to ensure specific properties and their nominal values makes it possible to assess the possibility of attracting certain alloys for the especially necessary areas, in particular for thermometry.

2. Drawbacks

Unfortunately, a certain part of the research has been carried out [3] on samples by destroying them - these are mainly mechanical properties. The other part [4] required preparation for conducting research by forming special samples. Another [5] aimed to compile the data obtained by various scientists and studied in non-standard conditions. In addition, the involved modern equipment is mainly characterized by insufficiently established metrological characteristics, which could not ensure unambiguously qualify the obtained results of research of the latest materials. The experiment itself suffered from the lack of measurement approaches and processing of the results based on current metrological concepts [6-8].

3. Aim of the Work

The work aims to study several electrical characteristics and their changes depending on the temperature and duration of annealing the *Ti-Cu-Co-Si* high-entropy alloy as a possible sensitive element of resistance thermotransducers.

4. Study of Metrological Characteristics of Sensitive Elements Made from the HEAs

Due to the substantial potentials of HEAs, they seem to be the promising candidates for specific applications one of which may be the contact thermometry the main demand for which is the maximal stability of electric properties of the sensitive elements of thermotransducers in time. Simultaneously not less interest is the reverse effect of such studies. It consists of the most exact and precise studies of materials based on the foundation pillars of contemporary technologies [9] among which can be attributed the metrology. The latter is inherent in the developed and high-precision tools, procedures, and techniques [10]. Therefore, conducting research in this regard can be considered promising.

4.1. Materials and their preparation for research

To study the metrological characteristics, a sensitive element of the thermotransducer was manufactured based on an alloy obtained by quenching from the melt. The sensitive element itself was made bifilarly wound from a thin plate of the *Ti-Cu-Co-Si* alloy. It was connected to the measuring instrument according to a 4-wire circuit through a switching pad.

4.2. Characterization of the samples for research

The main electrophysical properties of the *Ti-Cu-Co-Si* system as material for producing the sensitive elements that are the HEAs are given in Table 1. These data relate to known electrophysical characteristics such as the temperature coefficient of electrical resistance *TCER*, which was studied at room temperature; the ratio of the values of electrical resistance $R_{273}/R_{4.2}$ of the same sample at temperatures of 273 K (temperature of the water-ice mixture) and 4.2 K (boiling point of liquid helium); the ratio of the values of electrical resistance R_A/R_{cr} of the same sample at temperatures of 273 K,

which was previously in the amorphous state (R_A), and then transferred to the crystalline state - R_{cr} - by heating to a temperature of T_{cr} ; while the specific electrical

resistance of the sample r_{273} exceeded $160 \text{ k}\Omega\text{sm}$ or its specific conductivity σ_{273} was less than $0.61 \cdot 10^6 \text{ S/m}$.

Table 1

The major electrophysical properties of Ti-Cu-Co-Si HEA

Alloy	$TCER, 10^4 \text{ K}^{-1}$	$R_{273}/R_{4.2}$	R_A/R_{cr}	T_{cr}, K	$\rho_{293}, \text{k}\Omega\text{sm}$	$\sigma_{293}, 10^6 \text{ S/m}$
Ti-Cu-Co-Si	-2.167	0.943	1.53	≈ 700	>160	<0.61

4.3. Studies and Consideration

As a result of conducted studies, it was found that increasing operating time and temperature of heating, decreases the resistivity of its sensitive element. This drift does not exceed 0.025% after 3000 hours of operation at 350^0C (Fig. 1). It is probably caused by certain ordering processes occurring in the

structure of the Ti-Cu-Co-Si alloy, studied by the X-ray structural method. The experimental results of the resistivity changes were processed using the CurveExpert Basic. Approximation dependences in the form of algebraic expressions $y = a + bx + cx^2$ were obtained (see Table 2, which describes the dependences of Fig.1).

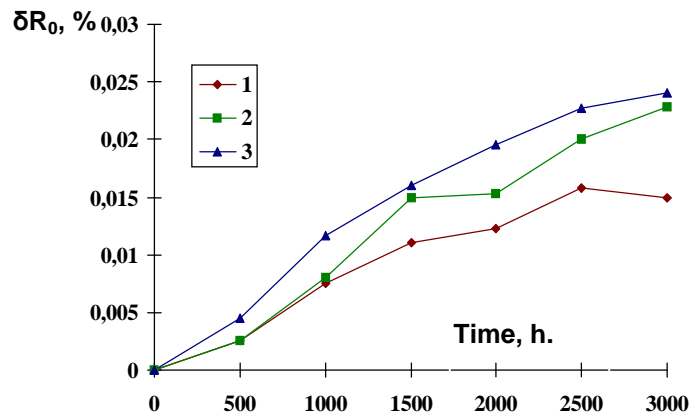


Figure 1. Dependence of electric resistivity changes δR_0 on operating time at: 1 - 250^0C ; 2 - 300^0C ; 3 - 350^0C .

Table 2

Approximating by dependences of electric resistivity changes on operating time at different temperatures: 1 - 250^0C ; 2 - 300^0C ; 3 - 350^0C

Temperature	Approximation dependence		
	$y = a + bx + cx^2$		
	Coefficient Data	Standard Error	Correlation Coefficient
250^0C	a = -0.00040810811 b = 9.1353282e-006 c = -1.2552124e-009	0.00096807	0.99232170
300^0C	a = -0.00086428571 b = 1.0178571e-005 c = -7.5714286e-010	0.00158801	0.98874758
350^0C	a = -0.00063809524 b = 1.3635714e-005 c = -1.7761905e-009	0.00076056	0.99769246

The data obtained above were transformed to identify patterns of changes in metrological characteristics over time for the studied thermotransducers by deviations of their R_0 in the calculated values of the instrumental error (Fig.2). They do not exceed 0.8 K. Studies (obtained results and their

subsequent analysis) show that the individual calibration characteristics of the considered transducer are described by the dependence: $R_t = A + Bt + Ct^2$ for sensitive elements made from Ti-Cu-Co-Si HEAs.

It should be noted that while measuring the temperature utilizing resistance thermotransducers, an

important factor is the choice of the maximum allowable value of the measuring current and minimization of the error caused by additional heating of the sensitive element. This error depends on the measuring current, the thermophysical characteristics of the structural materials of the thermotransducer, and the heat transfer

conditions. Therefore, errors from heating by measuring current in conditions close to industrial were studied (Fig.3). It is shown that the error from heating by measuring current up to 10 mA (this value corresponds to the value of the measuring current of most secondary measuring devices) does not exceed 0.05 K.

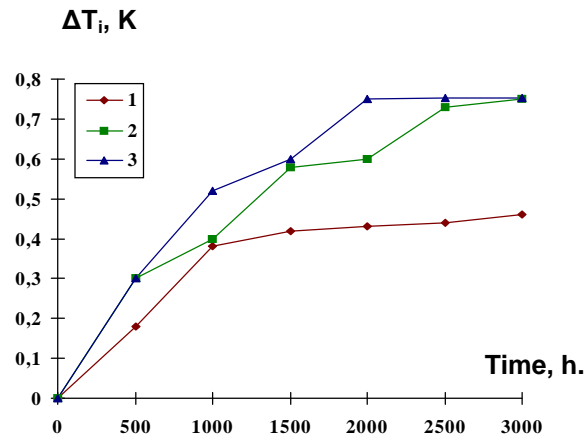


Figure 2. The drift of characteristics of resistance thermometers with sensitive elements made from Ti-Cu-Co-Si HEAs at 1- 250⁰C; 2 - 300⁰C; 3 - 350⁰C.

Table 3 shows the approximation dependences, which describe obtained values of the measurement error

(Fig.3) caused by heating of the sensitive element by the measuring current.

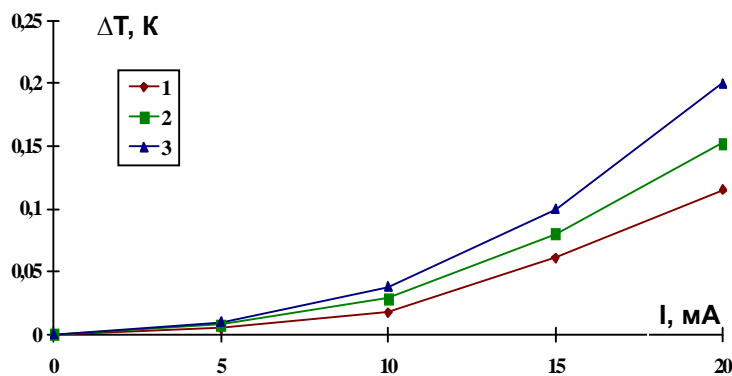


Figure 3. The methodic error ΔT of resistance thermotransducer due to heating by the measuring current I .

Table 3

Approximation dependences of methodic error of resistance thermotransducers due to heating by the measuring current

Temperature	Approximation dependence		
	Quadratic Fit: $y=a+bx+cx^2$		
	Coefficient Data	Standard Error	Correlation Coefficient
250 ⁰ C	a = 0.00088571429 b = -0.0015942857 c = 0.00036571429	0.00352947	0.99867033
300 ⁰ C	a = 0.0011714286 b = -0.0015085714 c = 0.00045142857	0.00283347	0.99949610
350 ⁰ C	a = 0.0021714286 b = -0.0024285714 c = 0.00061142857	0.00458569	0.99923008

4.4. Consideration of mechanisms and identification of possible reasons for the exceptional long-term stability of the electrical characteristics of HEAs

Comparison of the high-researched drift for 3000 hours at 350°C with studying in [1] the same alloy, held out at 500°C for much less time 0.5 hour, showed the following: our material is inherent in the low specific conductivity $<0.61 \cdot 10^6$ Sim / m or 1.3% IACS [11-12]; and for the material of [1] the high conductivity 41.7% IACS was recorded.

Such a state of the first one compared to the second underlines the exceptional importance of internal mechanical stresses [13] and nanoprecipitants [14], more precisely Co-Si precipitates [2], in the evolving of mechanisms of nanoscale stabilization of the HEAs. It manifests itself in the exceptional stability of specific electrical conductivity, as structurally-sensitive characteristics. The latter seems to be especially important in thermometry. We have previously established [15] a similar conclusion for sensitive elements of thermoelectric thermotransducers.

5. Conclusions

1. High-precision studies of the specific electrical conductivity of *Ti-Cu-Co-Si* high-entropy alloys in the range of medium-high temperatures 250... 350 °C and the duration of up to 3000 hours, have been carried out. This confirms the prospects of these alloys for the manufacture of sensitive elements of resistance thermometers.

2. It is shown that the drift of electrical conductivity does not exceed 0.14% or 0.8 K at 350 °C, which is due to the stability of their disordered structural state according to X-ray diffraction studies. In this case, the specific electric conductivity was measured and was equal to 1.05% of IACS ($58 \cdot 10^6$ S/m at 20°C [11]), or $0.61 \cdot 10^6$ S/m. In [1] there was obtained value of 41.7% IACS for the same property of quite a similar alloy.

3. Methodical error due to heating of the sensitive element by the measuring current does not exceed 0.2 K or is 4 times less than the fixed drift value. That is, it was found that the values of the drift of specific electric conductivity due to structural changes are insignificant (for contact thermometry) and cannot be caused by to annealing material of the sensitive element during measurement.

4. The main reason for the exceptional stability of the specific electrical conductivity of *Ti-Cu-Co-Si* alloys, in the range of middle-high temperatures 250... 350 °C with annealing time of 3000 hours, is recorded while manufacturing materials internal mechanical stresses. The latter has arisen due to evolving Co₂Si or Cu₄Ti nanoprecipitates according to [1].

6. Gratitude

The authors express their gratitude to the Staff of the Department of Information and Measuring Technologies of Lviv Polytechnic National University.

7. Conflict of Interest

The authors state that there are no financial or other potential conflicts regarding this work.

References

- [1] Y. Geng, Y. Ban, Xu Li, S. Tang, Excellent mechanical properties and high electrical conductivity of Cu-Co-Si-Ti alloy due to multiple strengthening, *Materials Science and Engineering*, Vol. A821, Is.5 : 141639, June 2021, https://www.researchgate.net/publication/352717779_Excellent_mechanical_properties_and_high_electrical_conductivity_of_Cu-Co-Si-Ti_alloy_due_to_multiple_strengthening. DOI: 10.1016/j.msea.2021.141639.
- [2] Chenhui Lei, Huiya Yang, Feng Zhao, Xiaoyang Fang, Youtong Fang and Liang Meng, Effect of Co addition on hardness and electrical conductivity of Cu-Si alloys. *Journal of Materials Science*, Vol. 56, Issue 26, Sept. 2021, Springer. <http://www.springer.com/materials/journal/10853>.
- [3] Y.F.Ye, Q.Wang, J.Lu, C.T.Liu, Y.Yang, High-entropy alloy: challenges and prospects, *Materialstoday*, Volume 19, Issue 6, July–August 2016, Pages 349-362, <https://doi.org/10.1016/j.mattod.2015.11.026> <https://www.sciencedirect.com/science/article/pii/S1369702115004010?via%3Dihub>
- [4] Sh. McCombes, Research Design. *A Step-by-Step Guide with Examples*. Publ. June 7, 2021. <https://www.scribbr.com/methodology/research-design/>
- [5] S. Elo, M. Käriäinen, O. Kanste, T. Pölkki, K. Utriainen, H. Kyngäs, Qualitative Content Analysis: A Focus on Trustworthiness, *Sage Journals, Research Article*. Publ. Febr. 11, 2014, <https://doi.org/10.1177/2158244014522633>
- [6] N.Raghavendra, L.Krishnamurthy, *Engineering Metrology and Measurements*, Oxford university press, 2014. <https://www.google.com/url?sa>
- [7] L. Pendrill, Man as a Measurement Instrument, *NCSLI Measure J. Meas. Sci.*, Vol. 9 No. 4, Dec. 2014, pp.24-35, <https://www.diva-portal.org/smash/get/diva2:964486/FULLTEXT01.pdf>
- [8] *Introduction to Measurements & Error Analysis*, University of North Carolina, Department of Physics and Astronomy, pp.1-18, 2012, <https://physics.unc.edu/wp-content/uploads/sites/218/2012/10/uncertainty.pdf>
- [9] European Metrology Research Program for Innovation and Research, EURAMET, 2022, <https://msu.euramet.org/>
- [10] A. Goel, *Metrology & Quality Control : Science of Measurement*, 2020, <https://www.amazon.com/Metrology-Quality-Control-Science-Measurement/dp/B08KT4PRMP>
- [11] International Annealed Copper Standard (IACS). <https://archive.org/stream/copperwiretables31unituoft#page/n0/mode/1up>
- [12] Eddy Current Conductivity Meter for Metals, Model 12Z. 2018, Zappitec. <http://www.zappitec.com/en/products>.
- [13] Ju Li, Z. Shan, E. Ma, Elastic strain engineering for unprecedented materials properties, *MRS Bull.*, Vol. 39, Issue 2, 2014, pp. 108-114.
- [14] H. Hofmann, *Advanced nanomaterials*, Course support, Powder Technology Laboratory, IMX, EPFL, Version 1, Sept 2009.
- [15] S. Yatsyshyn, B. Stadnyk. Accuracy and metrological reliability enhancing of thermoelectric transducers, *Sensors and Transducers*, Vol. 123, Issue 12, 2010, pp. 69-75. <https://www.proquest.com/openview/86ba8e8135e87f4a6ab54cff313e866c/1?pq->