MEASURING TRANSDUCERS

ELECTROKINETIC CHARACTERISTICS OF STRUCTURALLY DISORDERED BINARY ALLOY $Ni_{1-x}P_x$

Bohdan Stadnyk, *Dr. Sc., Prof.,* ***Pylyp Skoropad,*** *Dr. Sc., Prof.,* ***Svyoslav Yatsyshyn,*** *Dr. Sc., Prof.;*
Lviv Polytechnic National University, Ukraine;
e-mail: pylyp.i.skoropad@lpnu.ua

Abstract. The paper presents the results of studies of the temperature dependences of the resistivity ρ(T) and the Seebeck coefficient S(T) of binary structurally disordered alloys of the $Ni_{1-x}P_x$ system. It was found that at $0.10 < x < 0.25$ the absolute value of S(T) increases with phosphorus concentration and changes the sign, becoming positive at $x > 0.18$. The resistivity ρ increases with x, the temperature coefficient of electrical resistance α decreases and becomes negative, and S also increases and becomes positive near x=0.18. These results agree with the Mooij correlation and the r -S correlation for the studied samples, namely for samples with high resistivity S> 0 and for samples with low resistivity - S <0, which is observed in some non-magnetic structurally disordered alloys. Thus, the $Ni_{1-x}P_x$ system covers the range and behavior of electrokinetic characteristics that are characteristic of a few structurally disordered alloys. For x <0.175 dependencies r (T) and S(T) of the studied samples are similar to those observed in ferromagnetic structurally disordered iron-based alloys.

Key words: Metrological support, Risks, Product quality, Metrological instruments, RMS deviations

1. Introduction

Metallic glasses to which belong the binary alloys of $Ni_{1-x}P_x$ system are inherent in high strengths and extra-elastic properties. Some barriers prevent their applications as engineering materials for ndustry. That are the insufficient knowledge about the plasticity mechanisms for deformation beyond the elastic limit as well as the peculiarities of atomic structure which are manifested in the structure-to-property relationships, etc. [1-2].

The higher the electrical resistance of the metallic structurally disordered alloys (SDA), the lower in absolute value and negative in a sign its temperature factor a. The resistance of mono- or polycrystalline metals is much smaller and increases rapidly with temperature. This dependence in metallic SDAs (referred to a and r) is an example of the general trend of Mooij correlation: a is lower in systems with higher resistance. Thus, most systems with r <150 μΩ temperature factor a is positive, and with r >150 μΩ - factor is negative. A correlation was also found between the signs of S and a in nonmagnetic metallic SDAs with r >150 μΩ ×cm; here a<0 and S>0.

2. The Goal of the Study

The aim of the current work is the complex study of the electron transport phenomenon in binary metallic structurally disordered alloys on the example of a typical $Ni_{1-x}P_x$ system for further application of research results in the creation of new types of primary thermotransducers.

3. Materials for Investigation

Nowadays, the high-entropy alloys (HEAs) are of great interest in materials science. Unlike binary alloys, which contain one or two base elements, HEAs comprise multiple principal elements, with the possible number of HEA compositions extending considerably more than the mentioned alloys. Due to their considerable structural and functional potential as well as richness of design, HEAs are promising candidates for new applications, which warrants further studies [3]. Such properties of HEAs as excellent specific strength, superior mechanical performance at high temperatures, exceptional ductility and fracture toughness at cryogenic temperatures, superparamagnetism, and superconductivity require the issues of the high-mentioned properties performed on the simple binary alloys. Then we can develop a learning-based approach to predict the vast compositional space of multi-element alloys (binary, ternary, and high-entropy alloys), involving the binary alloy dataset as the training set. Using a learning-based approach, to design of the proper features is crucial, since it determines the accuracy of the prediction [4].

The choice of $Ni_{1-x}P_x$ system for research is explained by the fact that changing the phosphorus content in it, it is possible to obtain alloys with electrical resistivity in the range from 100 to 170 μΩ ×cm covering the value of 150 μΩ ×cm, which is a characteristic point in the Mooij correlation. At the same time, at the lowest electrical resistance the coefficient a>0, but decreases and becomes negative

with increasing electrical resistance. Thus, it is an opportunity to observe thermo emf in one system covering the range of behavior of electrical resistance in non-magnetic metallic SDAs.

There are a number of ways in which disorder can arise. For instance, *interstitial* disorder occurs when an impurity atom is placed in the vacant space between two substrate atoms. It exists a *structural* disorder, where the substrate atoms move away from their positions on the perfect lattice. The situation of interest is also the *substitutional* disorder [5]. They affect the electronic properties of the binary alloys [6]. Selected electronic properties of these materials are considered below.

4. Scattering Mechanisms and Properties

The work considers the foundations of several scattering mechanisms to explain the negative values of coefficient a in the certain temperature range for the studied SDAs.

· Within theory of free electrons, the resistance of the metallic SDAs, as a function of temperature, is approximated by the dependence:

$$\rho(T) = \frac{30\pi^3\hbar^3}{m e^2 k_F^2 E_F \Omega}\sin^2\left[\eta_2\left(E_F\right)\right]\left[1+\frac{S_0(2k_F)}{2k_F}-1\right]e^{-2[W(T)-W(0)]} \quad (1)$$

Here k_F and E_F are the Fermi wave vector and energy, Ω is the atomic volume, $\eta_2(E_F)$ is the phase wave factor, $S_0(k)$ is the static structural factor at T = 0, and W(T) is the Debye-Waller function at a temperature T.

· Mott's theory of s-d scattering suggests that electrons near the Fermi surface can be divided into two groups with very different mobilities.

More mobile s or p carriers are constantly scattered in less mobile *d* holes of the Fermi surface. The electrical resistance determined by this scattering process is proportional to the number of such holes, i.e.: $N_d(E_F)$ and the density of d levels in Fermi energy. In metals with partially filled d levels, $N_d(E)$ changes rapidly nearby E_F and the resistance decreases with temperature due to thermal expansion of the electronic distribution and changes in chemical potential. Using a simplified model, where $\rho(E)\sim N_d(E)$ and the density of levels does not change with temperature, the electrical resistance is determined by:

$$\rho(T) = \rho(0)\left\{1-\frac{\pi^2}{6}\left(k_B T\right)^2\left[\left(\frac{1}{N_d}\frac{dN_d}{dE}\right)^2-\frac{1}{N_d}\frac{d^2N_d}{dE^2}\right]_{E_F}\right\} \quad (2)$$

Assuming for simplicity that the d level is almost full and that $N_d(E) = C\sqrt{(E_0 - E)}$, the electrical resistance is written as follows:

$$\rho(T) = \rho(0)\left[1-\frac{\pi^2}{6}\left(k_B T\right)^2\left(E_0 - E_F\right)^{-2}\right] \quad (3)$$

It was considered the case when $N_d(E)$ depends on temperature and found that there is a significant deviation outside $N_d(E)$ with temperature. In addition to the effect of thermal expansion of the electronic distribution, this modification of $N_d(E)$ and changes in E_F cause an additional component of electrical resistance, which can either increase or decrease with temperature according to the Mooij correlation.

Each of these models can predict a decrease in electrical resistance with increasing temperature. To be able to distinguish them, it is necessary to study another transport property. It is advisable to choose the thermo emf S since it is quite sensitive to the scattering mechanism. The simplified relationship between thermo emf and electrical resistance is described by Mott's formula:

$$S(T) = \frac{\pi^2 k_B^2 T}{3|e|}\left(\frac{d\ln\rho}{dE}\right)_{E_F} \quad (4)$$

Below we briefly present the forecast of thermo emf for each of the scattering mechanisms discussed above. Thermo emf S(T) in Ziman's theory [7] is the following:

$$S(T) = -\frac{\pi^2 k_B^2 T}{3|e|E_F}\left[3-2q-\frac{1}{2}\rho\right] \quad (5)$$

Here kB is the Boltzmann constant, T is the absolute temperature.

$$q = \frac{S(2k_F)\left|t(2k_F)\right|^2}{\int_0^{2k_F}\left[4(2k_F)^{-4}k^3 S(k)\left|t(k)\right|^2\right]dk} \quad (6)$$

Here t(k) is the matrix. r is the energy dependence of the t matrix:

$$r = \frac{\int_0^{2k_F} \left[4\left(2k_F\right)^{-4} k^3 S(k)\, k_F\, d\left|t(k)\right|^2 \left(d\, k_F\right)^{-1}\right] dk}{\int_0^{2k_F} \left[4\left(2k_F\right)^{-4} k^3 S(k)\left|t(k)\right|^2\right] dk} \qquad (7)$$

Characteristically, S(T) is linear with temperature and can be either positive or negative, depending on the value of q. When 2kF»kp , and S(2kF) is large, then q is large and thermo emf is positive. The condition 2kF»kp also determines the negative temperature coefficient of electrical resistance and high electrical resistance.

5. Methods and Obtained Results

The resistance of the test samples was measured by the four-probe method. The measurement error was not more than ±0.01%. The temperature dependence of the resistance was studied in the range of 4.2K to 300K. The error in determining the reduced electrical resistance R(T)/R(4.2K) did not precede ±0.01%. Thermo emf of the samples was studied relative to the lead standard in the range of 4.2 ... 500K. An integrated method was used: one end of the sample was thermostated, and the temperature of the other was changed. Its value in the investigated range was measured by the type T thermocouple. Here is a derivative of the measured voltage – differential thermo emf of thermocouple formed by the test sample and the lead standard. Then an absolute thermo emf of the studied sample was counted as the difference between the absolute thermo emf of the lead standard and differential thermo emf of the high mentioned thermocouple. The error of determination of S(T) does not precede ±0.075 μV/K.

The dependence of the resistivity at room temperature as a function of the content of phosphorus (x, at.% P) is shown in Fig. 1. Here the specific electrical resistance increases with the phosphorus content.

The temperature dependence of the reduced electrical resistance R(T)/R(4.2K) for the alloys of the studied system is shown in Fig. 2. With increasing phosphorus content, the temperature coefficient of resistance a of the studied feet decreases and changes sign, becoming negative near x=0.23. Temperature dependence of a is also interesting. In Fig. 3, the dependence a(T) for three pairs of samples of similar composition is shown, however, the first ones are obtained by the method of chemical precipitation, and the second one - by the method of tempering.

For each chemically precipitated sample a(T) decreases above 80 K, but inversely increases for the sample obtained by tempering. This phenomenon can be explained by the fact that the amorphous structure of the alloys is determined by either chemical or structural disposition, and thus by one or another mechanism of scattering.

The temperature dependence of thermo emf of the mentioned alloys is shown in Fig. 4.

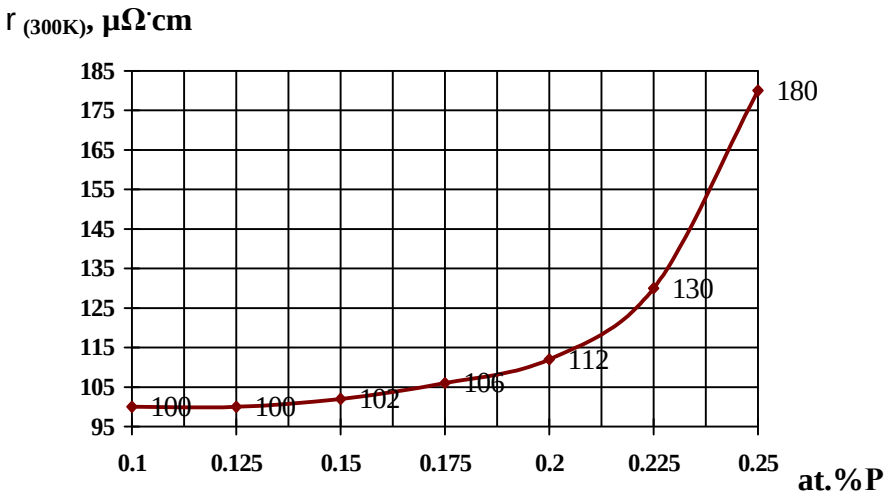

Fig. 1. Dependence of specific electrical resistance of the alloys of the studied system on the content of phosphorus.

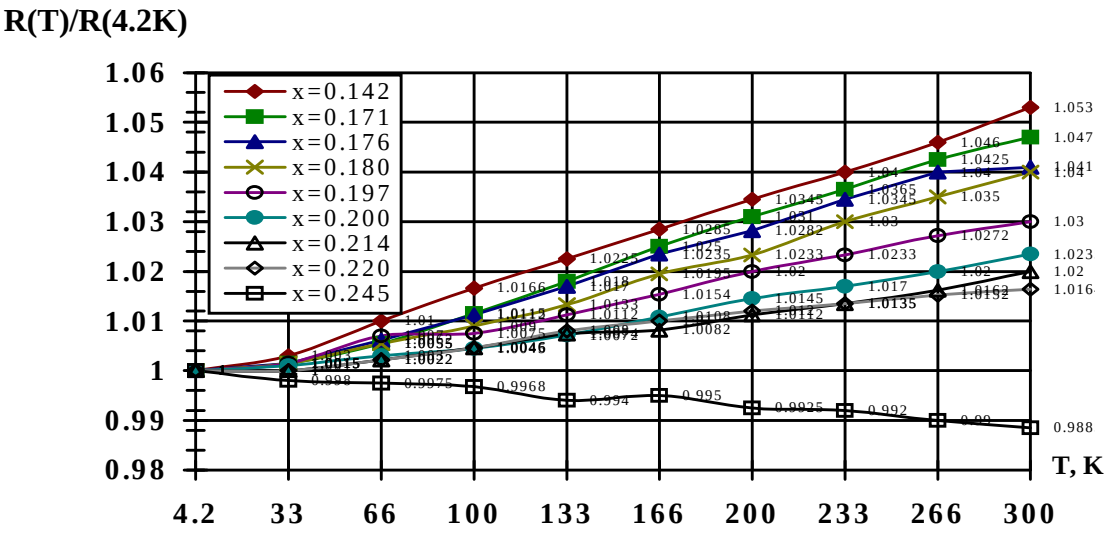

Fig. 2. Dependence of the reduced electric resistance on the temperature of the alloys of the studied system

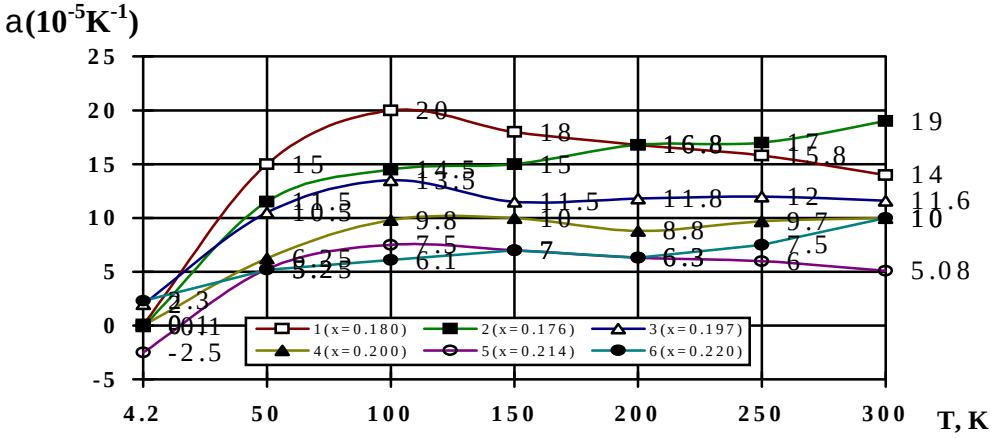

Fig. 3. Temperature dependence a *of the alloys of the studied system (1, 3, 5 - chemically precipitated samples; 2, 4, 6 - samples obtained by melts quenching).*

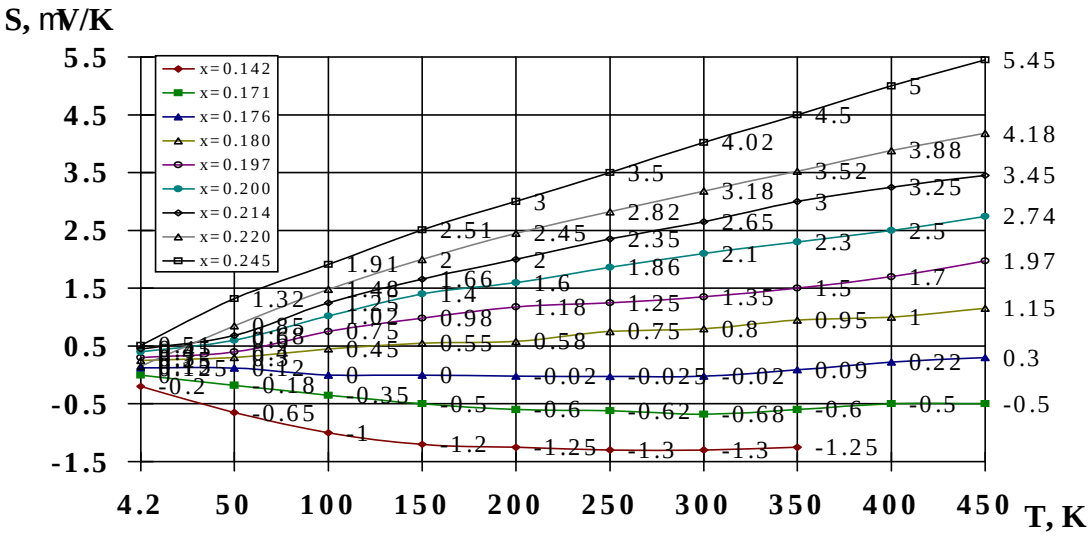

Fig. 4. Temperature dependence of thermo emf of the alloys

Thus, S(T) increases with phosphorus concentration and changes sign, becoming positive above x=0.18. The dependence S(T) is nonlinear in the measured temperature range. Samples with the lowest content of P that is the ferromagnetic range (x=0.142; 0.171) are inherent in the Seebeck coefficient. Samples with an intermediate content of P (x = 0.176; 0.180) differ by an insignificant value of the coefficient, both less than and greater than zero depending on the temperature. These are alloys with both ferro- and paramagnetic properties. Samples with a high content of P (x = 0.197; 0.200; 0.214; 0.220; 0.245) are inherent in the positive Seebeck coefficient. In the mentioned range of phosphorus content S(T) is described by a typical power dependence: $S(T) = C \cdot T^B$.

The obtained results can be used to determine a new multi-element alloys with further experiment by training result from binary-alloy data. For this purpose, we try to develop the deep machine-learning in the prediction of the particular properties of multi-element alloys (ternary and high entropy alloys) [8].

6. Conclusions

1. Studies of the temperature dependences of the resistivity and the Seebeck coefficient of binary structurally disordered $Ni_{1-x}P_x$ alloys revealed that there exists a link between these properties and ferromagnetic/ paramagnetic state of the samples.

2. At $0.10 < x < 0.25$ the absolute value of the Seebeck coefficient increases with phosphorus concentration and changes the sign, becoming positive at $x > 0.18$. Samples with phosphorus content x = 0.142; 0.171 (this is the ferromagnetic range of content) are characterized by negative absolute values of S (T) with a large positive curvature and wide minima depending on S(T). Samples with an intermediate phosphorus content x = 0.176; 0.180 inherent in a small absolute S(T) with both positive and negative curvatures in different temperature ranges. These compositions are close to the transition from ferromagnetic to paramagnetic. Samples with large values of x (x = 0.197; 0.200; 0.214; 0.220; 0.245) are characterized by positive S(T) with negative curvature.

3. We suggest that this work can be used to define new multi-element/high-entropy alloy with further experiment. In further work, we expect the approach can be expanded to find unknown HEAs by developing the deep machine-learning in the prediction of their particular properties of multi-element alloys with training result from binary-alloy data.

References

[1] D. Zh. Chen, “Atomic - Level Structure and Deformation in Metallic Glasses”, Dissertation (Ph.D.), California Institute of Technology, 2016. [Online]. Available: doi:10.7907/Z95Q4T2B.

[2] P. Swain, S. K. Srivastava, “Exploring quantum Griffiths phase in Ni1−xVx nanoalloys”, Scientific Reports, Vol.7, no.1223, 2017. [Online]. Available: https://www.nature.com/articles/s41598-017-01423-x

[3] Y. F. Ye, Q. Wang, J. Lu, C.T.Liu, Y. Yang, “High-entropy alloy: challenges and prospects”, Materials today, Vol.19, Iss.6, pp.349-362, 2016. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1369702115004010

[4] T. Jin, I. Park, T. Park, J. Park, J. H. Shim, “Accelerated crystal structure prediction of multi-elements random alloy using expandable features”, Sc. Reports, 2021. [Online]. Available: https://www.nature.com/articles/s41598-021-84544-8.pdf?proof=t

[5] S. G. Davison, K.W. Sulston, *Disordered Binary Alloys, in Green-Function Theory of Chemisorption*. pp.91-116, Springer, 2006. [Online]. Available: https://link.springer.com/chapter/10.1007/1-4020-4405-4_6.

[6] E. Belin-Ferré, *Basics of Thermodynamics and Phase Transitions in Complex Intermetallics*. Université Pierre et Marie Curie, France, 2008. [Online]. Available: https://doi.org/10.1142/6718

[7] N. Wetta, J. C. Pain, “Consistent approach for electrical resistivity within Ziman's theory from solid state to hot dense plasma: Application to aluminum”, Phys. Rev. E102,053209, 2020. [Online]. Available: https://journals.aps.org/pre/abstract/10.1103/PhysRevE.102.053209

[8] N. S. Punn, S. K. Sonbhadram, S. Agarwal, “COVID-19 Epidemic Analysis using Machine Learning and Deep Learning”, 2020. [Online]. Available: https://www.medrxiv.org/content/medrxiv/early/2020/04/11/2020.04.08.20057679.full.pdf