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Crystal structure and electrical resistance of Ni–W alloys

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The purpose of the paper is to establish the correlation between chemical composition, phase content and magnetic ordering of $Ni_{(1-x)}W_x$ alloys and behavior of their electronic properties in a wide range of temperatures. Alloys $Ni_{(1-x)}W_x$ of different composition ($0 < x < 0.5$) are synthesized. It is studied the crystal structure and the nature of the temperature dependence of electrical resistivity. It is shown, that in the range of concentrations of tungsten $0 < x < \sim 0.15$ there is only face centered cubic (FCC) lattice, whereas, at the higher values of x, the Ni–W alloy is two-phase system consisting of the face centered and body centered cubic (BCC) crystal structures. The strong drop in residual resistivity ratio (*RRR*) with increasing of x in the ferromagnetic area of single-phase FCC alloy, the weak dependence of *RRR* in the paramagnetic area of the FCC alloy, and growth of *RRR* in the two-phase region (FCC + BCC) of Ni–W are observed. It is established, that in the two-phase region of the alloy at concentrations of $\sim 0.15 < x < 0.3$ the electric current flows through the matrix of FCC Ni–W. At the higher concentrations of tungsten ($x \geq \sim 0.3$) the mechanism of charge transfer changes: electric current flows through percolation channels, formed by BCC phase of Ni–W system.

Keywords: Ni–W, phase composition, magnetic ordering, resistivity, percolation.

Целью статьи является установление корреляции между химическим составом, содержанием фаз и магнитным упорядочением сплавов $Ni_{(1-x)}W_x$ и поведением их электронных свойств в широком диапазоне температур. Синтезированы сплавы $Ni_{(1-x)}W_x$ различного состава ($0 < x < 0,5$). Исследована кристаллическая структура и характер температурной зависимости электросопротивления. Показано, что в диапазоне концентраций вольфрама $0 < x < \sim 0,15$ в сплаве существует только гранецентрированная кубическая (ГЦК) кристаллическая структура, тогда как при более высоких значениях x, сплав Ni–W представляет собой двухфазную систему, состоящую из гранецентрированной кубической и объемно-центрированной кубической (ОЦК) кристаллических структур. Наблюдалось сильное падение остаточного удельного сопротивления (*RRR*) с увеличением концентрации x в ферромагнитной области однофазного ГЦК-сплава, слабая зависимость *RRR* в парамагнитной области ГЦК-сплава и рост *RRR* в двухфазной области (ГЦК + ОЦК) Ni–W. Установлено, что в двухфазной области при концентрациях $\sim 0,15 < x < 0,3$ электрический ток протекает по зернам ГЦК подсистемы сплава Ni–W. При более высоких концентрациях вольфрама ($x \geq \sim 0,3$) происходит изменение механизма переноса заряда: электрический ток протекает по перколяционным каналам, образованным ОЦК-фазой системы Ni–W с более низким удельным электросопротивлением.

Кристалічна структура та електричний опір сплавів Ni–W. *В.В.Дерев'янко, М.С.Сунгуров, Т.В.Сухарева, В.О.Фінкель, Ю.М.Шахов.*

Метою статті є встановлення кореляції між хімічним складом, фазовим вмістом і магнітним упорядкуванням сплавів $Ni_{(1-x)}W_x$ і поведінкою їх електронних властивостей у широкому діапазоні температур. Синтезовано сплави $Ni_{(1-x)}W_x$ різного складу ($0 < x < 0,5$). Досліджено кристалічну структуру та характер температурної залежності електроопору. Показано, що у діапазоні концентрацій вольфраму $0 < x < \sim 0,15$ у сплаві існує тільки гранецентрована кубічна (ГЦК) кристалічна структура, тоді як при більш високих значеннях x сплав Ni–W являє собою двофазну систему, що складається з гранецентрованої кубічної і об'ємноцентрованої кубічної (ОЦК) кристалічних структур. Спостерігалося сильне падіння залишкового питомого опору (*RRR*) зі збільшенням концентрації x у феромагнітній області однофазного ГЦК-сплаву, слабка залежність *RRR* у парамагнитній області однофазного ГЦК-сплаву і зростання *RRR* у двофазної області (ГЦК + ОЦК) Ni–W. Встановлено, що в двофазній області при концентраціях $\sim 0,15 < x < 0,3$ електричний струм протікає зернами ГЦК підсистеми сплаву Ni–W. При більш високих концентраціях вольфраму ($x \geq \sim 0,3$) відбувається зміна механізму переносу заряду: електричний струм протікає перколяційними каналами, утвореними ОЦК-фазою системи Ni–W з більш низьким коефіцієнтом електроопору.

1. Introduction

Nickel-tungsten alloys are of great interest because of their unique combination of magnetic, electrical, mechanical, chemical and other properties. Ni–W alloys may be applicable in a large number of applied areas as the functional materials for ultra-large-scale integration (ULSI) devices, micro-electromechanical systems (MEMS), mold inserts, relays, bearings, etc. [1–4].

By the way nickel based alloys, especially Ni–W, are currently the most widely used for substrates in the second generation high temperature superconductors (2G HTS) architectures. The Ni–W alloys may develop a strong and resilient up cube texture, suitable for epitaxial growth of buffer and HTS films [5–9].

Investigating the physical properties of the nickel-tungsten binary systems started since the end of 19th century [10]. Considerable attention also has been paid to construction of phase diagrams for such systems. The phase diagram of Ni–W looks quite unusual [11]. Eutectoid decomposition results in forming of two main regions on the diagram. There appear solid solutions of Ni(W) with face centered cubic (FCC) structure existing at concentrations up to 16.4 at. % at $T \sim 1000–1400$°C; and mixed region of Ni(W) and W(Ni) solid solutions spacious to almost 99.7 at. % W at 1455°C, where W(Ni) possess the body centered cubic structure (BCC).

In the fcc region of Ni–W system the ferromagnetic ordering [12] takes place at rather low concentrations of tungsten in the alloy. The ferromagnetic Curie temperature of pure nickel $T_c = 631$ K falls to $T_c = 0$ K in the case ~ 10 at. % W.

The main purpose of this research is to establish nature and mechanisms of influence of the chemical and phase composition of model systems $Ni_{(1-x)}W_x$ on the electron properties behavior.

The following comprehensive research program was implemented:

— synthesis of $Ni_{(1-x)}W_x$ alloys in a wide range of concentrations x;

— examination of crystal structure of the obtained samples;

— examining the temperature and concentration dependences of electrical resistivity.

The final result of the study should be determination of the nature of the mechanisms of temperature, chemical and phase composition influence on electrical resistivity of the research objects.

2. Experimental

For conducting the research a series of $Ni_{(1-x)}W_x$ samples was obtained in the wide range of tungsten concentrations: $x = 0$; 0.025; 0.05; 0.075; 0.085; 0.095; 0.11; 0.13; 0.15; 0.2; 0.25; 0.3; 0.4; 0.5.

The initial materials for synthesis of Ni–W alloys were Ni and W powders with 99.98–99.99 % purity (by metallic impurities). The following methods were used for purification from gaseous impurities: 1) heat treatment at temperatures ~ 850°C for the purification of Ni powder; 2) for refinement of W powder was applied the high-temperature treatment (1000–1200°C) in reducing Ar + 4 % H_2 gaseous mixture flow.

After the refinement from impurities, the Ni and W powders were thoroughly mixed in necessary proportions using mill-

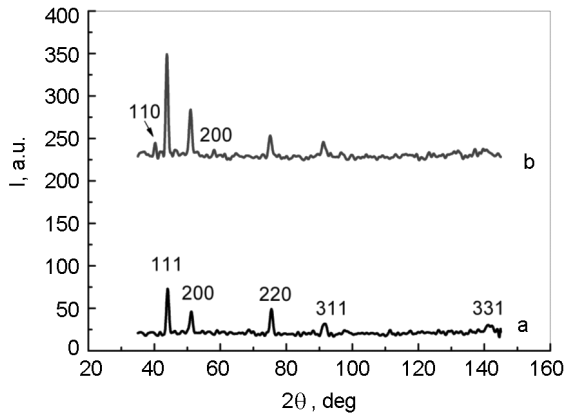

Fig. 1. X-ray diffraciton patterns of some $Ni_{(1-x)}W_x$ alloys: a) single-phase FCC alloy $Ni_{0.85}W_{0.15}$; b) biphasic (FCC + BCC) alloy $Ni_{0.8}W_{0.2}$.

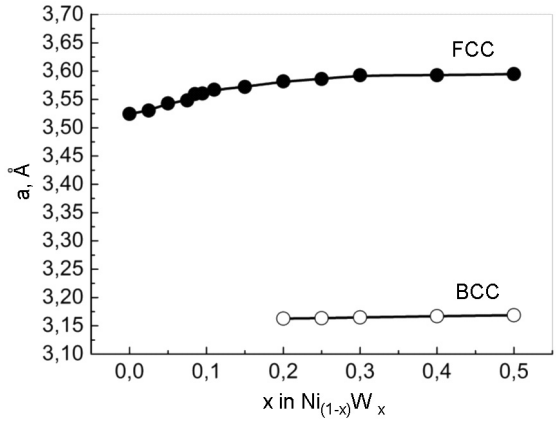

Fig. 2. Lattice parameters of both FCC and BCC subsystems of $Ni_{(1-x)}W_x$ alloys in a wide range of concentrations x.

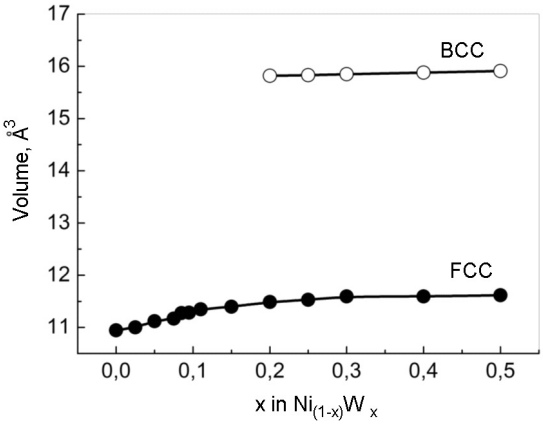

Fig. 3. Atomic volumes of $Ni_{(1-x)}W_x$ alloys for FCC ($V_{fcc} = a^3/4$) and BCC ($V_{bcc} = a^3/2$) subsystems.

mortar "Pulverizette". Then the powder mixtures were pressed for subsequent thermal treatment.

The synthesis was carried out by means of powder metallurgy in deep vacuum ($p \sim 10^{-6}$–10^{-5} Torr) at $T = 1150$°C during $t = 4$ h [13]. Typical sample sizes for the electrical studies were 2×2×15 mm^3. For attestation of the obtained samples the X-ray phase analysis and resistometric measurements were applied.

Structural studies were performed on X-ray diffractometer DRON UM-1 using Cu Kα-irradiation.

To carry out the electrical measurements at low temperatures, special apparatus based on cryostat was used. The conditions of the measurement process were strictly standardized [14]. Electrical resistivity was measured by means of four-probe potentiometric method. All measurements were performed in the range of temperatures $T = 50$–270 K at constant electric current density $j = 500$ mA/cm^2 for all concentration x values.

3. Results

3.1. Structural studies

In Fig. 1, as example there are shown XRD patterns similar in chemical, but different in phase composition. On XRD curve (a) there are only diffraction peaks, which belong to solid solution of Ni(W) with the FCC crystal structure. On XRD curve (b) there are observed two systems of diffraction lines, indicating presence of the W(Ni) BCC phase together with the Ni(W) FCC phase.

Fig. 2, shows concentration dependences of lattice constants. At concentration $x \sim 0.15$ the strong growth of the FCC phase lattice parameter slows down and at $x \sim 0.3$ the dependence $a_{fcc}(x)$ is going to saturation. The dependence of lattice constant $a_{bcc}(x)$ is almost linear.

Based on the data presented in Fig. 2, the dependences (Fig. 3) of atomic volumes for FCC ($V_{fcc} = a_{fcc}{}^3/4$) and BCC ($V_{bcc} = a_{bcc}{}^3/2$) solid solutions of $Ni_{(1-x)}W_x$ alloys are established. In the range of $0 \le x \le 0.15$ the curve V_{fcc} qualitatively corresponds to behavior of a_{fcc}. It should be emphasized, that in the two-phase region at concentrations $x \ge 0.2$, the values of V_{bcc} are much larger than values of V_{fcc}.

3.2. Electrophysical studies

Fig. 4 shows a set of some curves for temperature dependences of electrical resis-

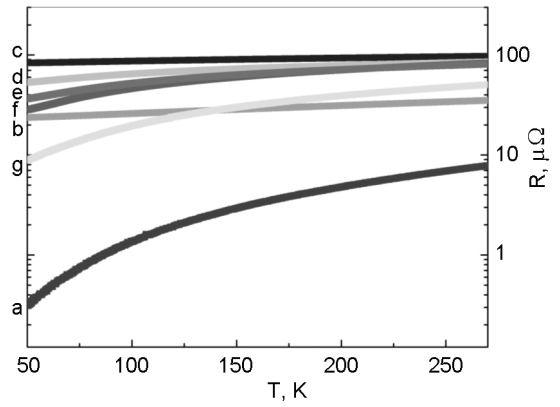

Fig. 4. Experimental curves for temperature dependences of resistivity ρ(*T*) of Ni–W alloys in a wide range of tungsten concentrations: a) Ni–0 at.% W; b) Ni–5 at.% W; c) Ni–13 at.% W; d) Ni–20 at.% W; e) Ni–25 at.% W; f) Ni–30 at.% W; g) Ni–50 at.% W.

tivity ρ(*T*) obtained at the low temperatures. As is seen from the pattern in the single-phase region of $x \leq 0.15$ the curves ρ(*T*) are shifted to the region of the higher values of ρ with an increase of tungsten concentration.

In the region of coexistence both the FCC and the BCC phases at concentrations $x >$ ~0.15 the curves ρ(*T*) have explicitly expressed the non-linear character: correlation between the chemical composition in the two-phase region and the electrical resistivity is violated. For certain values of *R*(*T*), the curves can intersect.

4. Discussion

Below the nature of the evolution of electrophysical properties, depending on the composition and external influences, i.e. temperature, is considered. The methodology of the discussion is based on establishing the correlation between the behavior of the crystal lattice parameters and the electrical resistance of Ni–W alloys.

Based on the results presented in Fig. 4, the character of the dependence of residual-resistivity ratio (*RRR*) on concentration *x* is determined (Fig. 5). Three distinct regions on the dependence *RRR*(x) are revealed: 1) sharp decrease in *RRR* in the ferromagnetic single-phase FCC region as *x* increases from 0 to 0.1; 2) weak dependence of *RRR* in the narrow paramagnetic state in the FCC crystal structure of $Ni_{(1-x)}W_x$ at $0.1 < x <$ ~0.15; 3) growth of *RRR* over transition to the two-phase region (FCC + BCC).

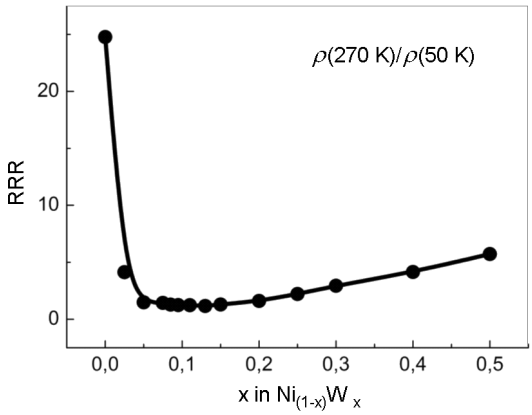

Fig. 5. Residual resistivity ratio ρ(270 K)/ρ(50 K) for samples of $Ni_{(1-x)}W_x$ alloys in a wide range of concentrations.

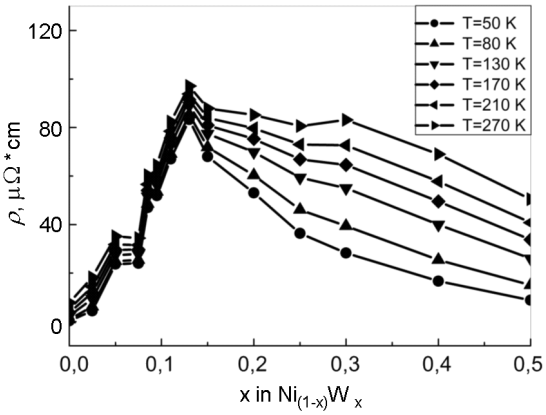

Fig. 6. Dependences of electical resistivity ρ(*x*) on tungsten concentration in $Ni_{(1-x)}W_x$ alloys in temperatures range of T = 50–270 K.

The behavior of the *RRR*(*x*) dependence in the ferromagnetic region is related to the electron-magnon scattering mechanism. Sharp falling in the residual resistivity with increasing of tungsten content in the FCC alloy $Ni_{(1-x)}W_x$ ($x < 0.1$), as well as decrease in the value of the ferromagnetic Curie point T_c with increase in *x*, correlates with a significant growth of the lattice constant a_{fcc} in the single-phase FCC region of the Ni–W alloy.

Obviously, a small value of the *RRR* parameter in the paramagnetic area of the single-phase close-packed FCC solid solution is determined solely by mechanism of the electron scattering by lattice vibrations.

In the two-phase region (FCC + BCC) at $x >$ ~0.15, the amount of BCC phase with larger formula volume ($V_{bcc} > V_{fcc}$) is growing, the amplitude of the crystal lattice vibrations increases. So it can be assumed, that the reason of the strong growth of the

residual resistivity ratio in the two-phase region of Ni–W system can be strengthening the contribution of the electron-phonon scattering mechanism.

For establishing the nature of influence of $Ni_{(1-x)}W_x$ alloys composition on the electrical resistivity in the wide range of temperatures the data of direct measurements of temperature dependences of electrical resistivity $\rho(T)$ were transformed into a set of concentration dependences $\rho(x)$. For this, matrix $\rho(T)_{x=const}$ was transposed into the matrix $\rho(x)_{T=const}$.

In this connection, the values of $\rho(T)_{x=const}$ were interpolated with a "step" of 5 K, and some curves are presented in Fig. 6.

All curves $\rho(x)$ are of complex character.

It is established that at the comparatively high temperature T = 270 K, the concentration dependence of the electrical resistivity $\rho(x)$ reveals three distinct regions:

1. There is an almost linear growth of $\rho(x)$ in the range of concentrations x from 0 to 0.15.

2. At concentrations of $0.13 < x < 0.3$, the value of the resistivity is weakly dependent on the concentration of tungsten in the alloy.

3. At concentrations $0.3 < x < 0.5$, there is a strong drop in the resistivity.

Observed growth of resistivity in the FCC region corresponds to the characteristic behavior of the electrical resistivity in single-phase dilute alloys based on transition metals. The nature of the $\rho(x)$ behavior in the given region is conserved with temperature decreasing.

Changes in the character of the concentration dependence $\rho(x)$ in the two phase region at $\sim 0.15 < x < 0.3$ corresponds to the scenario of the electric current in the FCC subsystem, the lattice parameter a_{fcc} of which practically does not change during transition to the two-phase region, i.e. composition of which varies very little with the chemical content change, (see Fig. 2).

The resistivity strong decrease in the two phase region corresponds to the beginning of electric current percolation through continuous channels formed by the BCC subsystem. The value of $x = \sim 0.3$ obviously corresponds to the value of percolation threshold [15], that equals to ~ 17 % of BCC phase in the two phase system.

When the temperature is lowered to about 210 K, three sections on the dependence $\rho(x)$ are realized, but there is a tendency to blur the curves in the two phase region (FCC + BCC). Further lowering of temperature leads to the disappearance of the pronounced percolation effect. At temperatures below 80 K, the concentration dependence $\rho(x)$ has a monotonic character, which is well described by the concentration exponential dependence.

The observed dynamics of changes in the electrical resistivity behavior with decrease in temperature indicates the change in scenario of the electrical charge transfer through the two-phase region. Despite the fact that at relatively high temperatures, the electrical resistance of the FCC phase exceeds the resistance of the BCC phase, with decreasing temperature the differences between electrical resistivity in the both phases of Ni–W solid solution are blurred, consequently the mechanism of charge transferring along the percolation paths changes to the transfer over the main phase with the lower resistivity, i. e. the BCC subsystem.

5. Conclusions

In the present work, the crystal structure and the character of temperature dependences of the electrical resistivity at the low temperatures were investigated for 14 different alloys of system $Ni_{(1-x)}W_x$ ($0 \le x \le 0.5$) with face centered cubic and body centered cubic crystal structures.

In the concentration range of $x = 0$–0.15, the Ni–W alloy is in a single-phase state. At $x > \sim 0.15$ the alloy is a biphasic system, consisting of the face centered and body centered cubic solid solutions.

It is determined that the character of the temperature dependence of the electric resistance of Ni–W alloys essentially depends on the chemical composition, the phase composition and the type of the magnetic ordering of the alloys. In the ferromagnetic single-phase FCC region of the Ni–W alloy, the main contribution to the resistivity is made by scattering of electrons by magnons. In the two-phase region as the content of the BCC phase increases, the effect of scattering of electrons on the lattice vibrations is greatly enhanced.

The charge transfer features in the two-phase region (FCC + BCC) of the Ni–W phase diagram were described for the first time. At relatively high temperatures at tungsten concentrations below the value corresponding to the percolation threshold, the electric current flows through the grains of the FCC phase with a large electri-

cal resistivity. At the vicinity of the percolation threshold, strong decrease of the electrical resistivity is observed on the concentration dependence $\rho(x)$: the transfer of electric charge takes place mainly through the percolation channels formed by the grains of the BCC phase of $Ni_{(1-x)}W_x$ with the lower electrical resistance. At the low temperatures, the role of the percolation effect in the behavior of the electrical resistivity substantially decreases.

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