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Application of CALPHAD method for predicting of concentration range of amorphization of transition metals melts

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Metallic glasses are attractive due to a set of unique properties, such as mechanical, magnetic, chemical, etc. At present, information about amorphous alloys is available for individual point compositions in the form of data on conditions of production, structure, mechanical and some other physical properties. However, it is often necessary to search for a new alloy in a wider concentration region. Early, the efficiency of the CALPHAD (Calculation of Phase Diagrams) method to a targeted search for compositions of amorphous alloys has been shown. The method for predicting of amorphization ranges is based on the calculation of diagrams of metastable phase transformations between supercooled melts and boundary solid solutions. Within the framework of the CALPHAD method, the model parameters for thermodynamic properties of liquid alloys and boundary solid solutions were summarized in self-consistent database for the multicomponent Co–Cu–Fe–Ni–Ti–Zr–Hf system. Such database for the multicomponent system is based on a common set of model parameters for boundary binary and ternary systems. In this report the predicted ranges of amorphization for the quaternary Cu–Ni–Ti–Zr, Cu–Ni–Ti–Hf, and Fe–Ni–Ti–Hf systems are presented on concentration tetrahedrons. For the quinary Fe–Cu–Ni–Ti–Zr, Fe–Cu–Ni–Ti–Hf, and Cu–Ni–Ti–Zr–Hf systems the composition ranges are predicted along sections from four-component equiatomic alloys to pure metals. It was determined that the predicted composition ranges of amorphszation correspond to a certain total concentration of metals, which are donors (Ti, Zr, Hf) and acceptors (Fe, Ni, Cu) of electrons in the melt. For glass-forming melts of transition metals such a factor is the simultaneous fulfillment of the conditions of $xTi+xZr+xHf > 0.2$ and $xFe+xNi+xCu > 0.2$. This factor indicates the important role of the donor-acceptor interaction between components of the glass-forming liquid alloys and its influence on their ability to amorphization.

Acknowledgments

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Laboratory of Physico-Chemical Properties
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SYSTEMS AND COMPOSITIONS OF AMORPHOUS ALLOYS OF THE Cu–Fe–Ni–Ti–Zr–Hf SYSTEM

ternary amorphous alloys

Cu–Ti–Zr (127 compositions), Cu–Ni–Ti (33 compositions),
Cu–Ni–Zr (52 compositions), Cu–Ni–Hf (68 compositions),
Ni–Ti–Zr (26 compositions), Ni–Zr–Hf (11 compositions)

quaternary amorphous alloys

Cu–Ti–Zr–Hf ($Cu_{25}Hf_{25}Ti_{25}Zr_{25}$, $Cu_{60}Hf_{10}Ti_{10}Zr_{20}$),
Cu–Ni–Ti–Zr ($Cu_{47}Ni_{8}Ti_{34}Zr_{11}$),
Cu–Ni–Ti–Hf ($Cu_{25}Hf_{25}Ni_{25}Ti_{25}$),
Fe–Ti–Zr–Hf ($Fe_{25}Ni_{25}Ti_{25}Zr_{25}$),
Ni–Ti–Zr–Hf ($Ni_{25}Hf_{25}Ti_{25}Zr_{25}$),
$Al_8Ni_{45}Ti_{20}Zr_{27}$, $Al_{10}Ni_{45}Ti_{20}Zr_{25}$, $Ni_{57}Pd_5Ti_{18}Zr_{20}$, $Ni_{57}Pd_{10}Ti_{13}Zr_{20}$,
$Hf_5Nb_{20}Ni_{60}Ti_{15}$, $Hf_{10}Nb_{20}Ni_{60}Ti_{10}$, $Hf_5Nb_{10}Ni_{60}Ti_{25}$.

quinary amorphous alloys

CoCuTiZrHf ($Co_{20}Cu_{20}Hf_{20}Ti_{20}Zr_{20}$),
CuFeTiZrHf ($Cu_{20}Fe_{20}Hf_{20}Ti_{20}Zr_{20}$),
CuCrTiZrHf ($Cr_{20}Cu_{20}Hf_{20}Ti_{20}Zr_{20}$),
CuMnTiZrHf ($Cu_{20}Mn_{20}Hf_{20}Ti_{20}Zr_{20}$),
CuNiTiZrHf ($Cu_{20}Ni_{20}Hf_{20}Ti_{20}Zr_{20}$),
CuVTiZrHf ($Cu_{20}V_{20}Hf_{20}Ti_{20}Zr_{20}$),
FeNiTiZrHf ($Fe_{20}Ni_{20}Hf_{20}Ti_{20}Zr_{20}$),
$Cu_{47}Si_1Ti_{11}Zr_{11}Ni_8$, $B_{20}Co_7Fe_{56}Ni_7Zr_{10}$, $Al_{10}Cu_5Ti_{17}Ni_{40}Zr_{28}$, $Al_{10}Cu_{20}Ti_5Ni_8Zr_{57}$,
$Be_{25}Cu_{10}Ti_{11}Ni_{10}Zr_{44}$, $Be_{20}Cu_{20}Ti_{20}Ni_{20}Zr_{20}$.

six component amorphous alloys

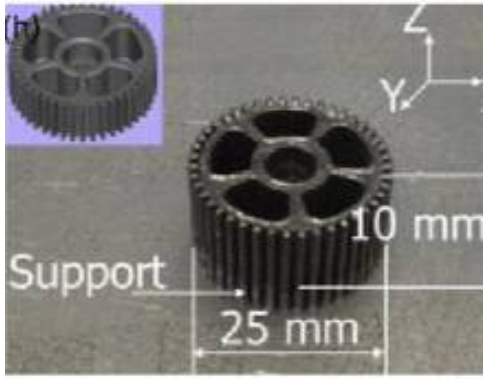
$B_{20}Co_7Fe_{56}Nb_2Ni_7Zr_8$, $B_{15}Co_7Fe_{61}Nb_2Ni_7Zr_8$, $B_{20}Co_7Fe_{56}Ni_7Ta_2Zr_8$,
$Al_{10}Cu_6Si_1Ti_{15}Ni_{39}Zr_{29}$.

OBJECTIVE AND TASKS OF THE WORK

Objective is to predict the concentration ranges of amorphization for the quinary Cu–Fe–Ni–Ti–Zr, Cu–Fe–Ni–Ti–Hf and boundary ternary and quaternary systems.

Tasks of the work are:

1. **Development of thermodynamic database for the Cu–Fe–Ni–Ti–Zr–Hf glass-forming system.**
2. **Usage of developed thermodynamic database for prediction in the framework of CALPHAD-method the concentration ranges of amorphization in the quinary Cu–Fe–Ni–Ti–Zr, Cu–Fe–Ni–Ti–Hf and boundary ternary and quaternary systems.**



MIXING GIBBS ENERGY OF MULTICOMPONENT LIQUID AND SOLID SOLUTIONS IN THE FRAMEWORK OF CALPHAD APPROACH

$$G_{\mathrm{m}}^{\phi}(x_{\mathrm{A}},\ldots,x_i,T) =$$

$$= \sum_{i=\mathrm{A},\ldots} x_i G_i^{\circ,\phi} + RT\sum_{i=\mathrm{A},\ldots} x_i \ln x_i + \Delta_{\mathrm{m}} G^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T) + \Delta_{\mathrm{m}} G^{\mathrm{mag},\phi}(x_{\mathrm{A}},\ldots,x_i,T)$$

Binary Assessment : $\Delta_{\mathrm{m}} G_{\mathrm{bin}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T)$

Ternary Assessment : $\Delta_{\mathrm{m}} G_{\mathrm{ter}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T$

+ Extrapolation : $\sum \Delta_{\mathrm{m}} G_{\mathrm{bin}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T)$

Quaternary Extrapolation $\left(\sum \Delta_{\mathrm{m}} G_{\mathrm{bin}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T) + \sum \Delta_{\mathrm{m}} G_{\mathrm{ter}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T)\right)$

Quinary Extrapolation $\left(\sum \Delta_{\mathrm{m}} G_{\mathrm{bin}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T) + \sum \Delta_{\mathrm{m}} G_{\mathrm{ter}}^{\mathrm{ex},\phi}(x_{\mathrm{A}},\ldots,x_i,T)\right)$

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EXCESS GIBBS ENERGY OF MIXING OF BINARY LIQUID AND SOLID SOLUTIONS

Excess Gibbs energy of mixing for the melts described in the framework of associate solution model (ASM)

$$\Delta_m G^{ex,\,L}(x_A, x_B, T) = f(\Delta_{assoc} H_n, \Delta_{assoc} S_n)$$

$\Delta_{assoc} H_n, \Delta_{assoc} S_n$ – enthalpy and entropy of formation of associate n

Excess Gibbs energy of mixing for liquid and solid solutions presented by Redlich-Kister polynomial

$$\Delta_m G^{ex,\,\phi}_{A-B}(x_A, x_B, T) = x_A x_B \sum_{i=0}^{v} {}^{i}L^{\phi}_{A-B}(x_A - x_B)^i$$

v – degree of Redlich-Kister polynomial;

${}^{i}L^{\phi}_{A-B} = {}^{i}A^{\phi}_{A-B} + {}^{i}B^{\phi}_{A-B}T + {}^{i}C^{\phi}_{A-B}T\ln T$ – polynomial describing the temperature dependence of the excess Gibbs energy, ${}^{i}A_{A\text{-}B}$, ${}^{i}B_{A\text{-}B}$ and ${}^{i}C_{A\text{-}B}$ are coefficients of the model

Contribution from ternary interaction of components to the excess Gibbs energy of mixing described using the Muggianu extension for the Relich-Kister polynomial (RKM)

$$\Delta_m G^{ex,\phi}_{A-B-C}(x_A, x_B, x_C, T) = x_A x_B x_C (x_A L^{\phi}_A + x_B L^{\phi}_B + x_C L^{\phi}_C)$$

$L^{\phi}_A, L^{\phi}_B, L^{\phi}_C$ – model parameters

STRUCTURE OF DATABASE FOR DIRECTED SEARCH FOR COMPOSITIONS OF AMORPHOUS ALLOYS OF THE Cu–Fe–Ni–Ti–Zr–Hf SYSTEM IN THE FRAMEWORK OF CALPHAD-METHOD

The database contains parameters describing the Gibbs energy of liquid alloys, BCC and FCC solutions based on pure metals for:

15 binary systems:

9 systems with attractive interaction of components:
Fe–Ti, Fe–Zr, Fe–Hf, Cu–Ti, Cu–Zr, Cu–Hf, Ni–Ti, Ni–Zr, Ni–Hf, presented by ASM parameters;

6 systems with repulsive(weak) interaction of components:
Fe–Ni, Cu–Fe, Cu–Ni, Hf–Ti, Hf–Zr, Ti–Zr, presented by Redlich-Kister polynomial

15 ternary systems:

13 systems with attractive interaction of components:
Fe–Ni–Ti, Fe–Ni–Zr, Fe–Ni–Hf, Cu–Fe–Ti, Cu–Fe–Zr, Cu–Fe–Hf, Cu–Ni–Ti, Cu–Ni–Zr, Cu–Ni–Hf, Cu–Ti–Zr, Cu–Ti–Hf, Ni–Ti–Zr, Ni–Ti–Hf, presented by ASM parameters;

2 systems with repulsive (weak) interaction of components:
Cu–Fe–Ni, Ti–Zr–Hf, presented by Redlich-Kister-Muggianu polynomial.

The excess Gibbs energy of liquid alloys and BCC and FCC solutions is described by the equation :

$$\Delta_m G^{ex,\phi}(x_A, x_B, x_C,\ldots,T) = \sum_i \sum_{j>i} \Delta_m G^{ex,\phi}_{i-j}(x_i,x_j,T) + \sum_i \sum_{j>i} \sum_{k>j} \Delta_m G^{ex,\phi}_{i-j-k}(x_i,x_j,x_k,T) + \Delta_m G^{mag,\phi}(x_i,x_j,\ldots,T)$$

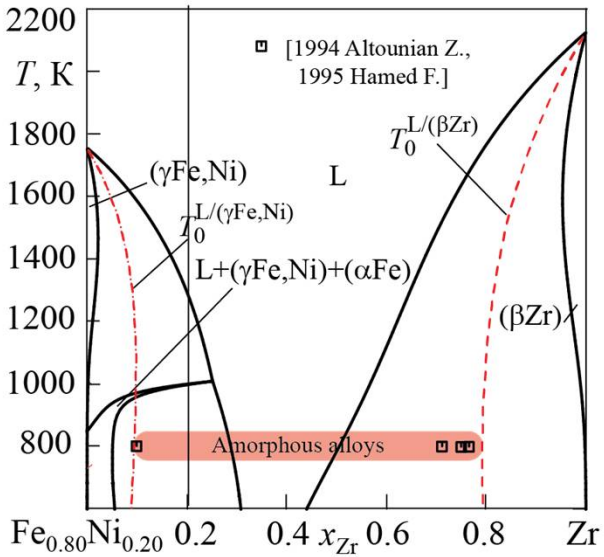
two-component interactions (parameters of ASM or Redlich-Kister polynomial)

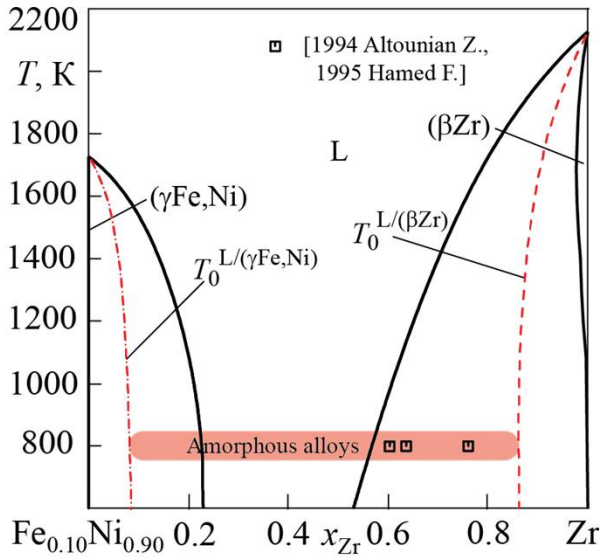
three-component interactions (parameters of ASM or RKM)

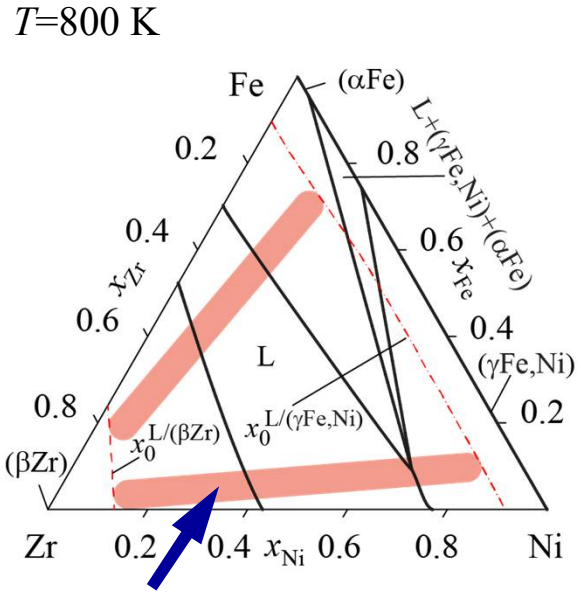
Gibbs energy from magnetic ordering (Inden-Hillert model parameters for FCC and BCC solutions)

All descriptions of ternary systems are related to a common dataset of parameters for boundary binary systems

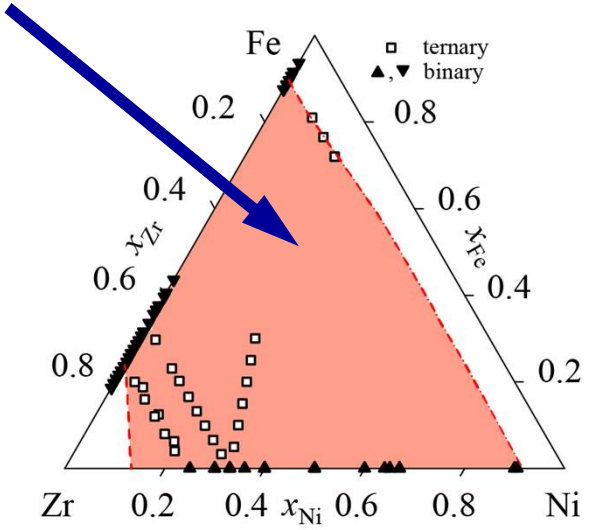
DIAGRAMS OF METASTABLE PHASE TRANSFORMATIONS, PREDICTED CONCENTRATION REGIONS OF AMORPHIZATION, AND LITERATURE DATA ON COMPOSITIONS OF AMORPHOUS ALLOYS OF TERNARY Fe–Ni–Zr SYSTEM





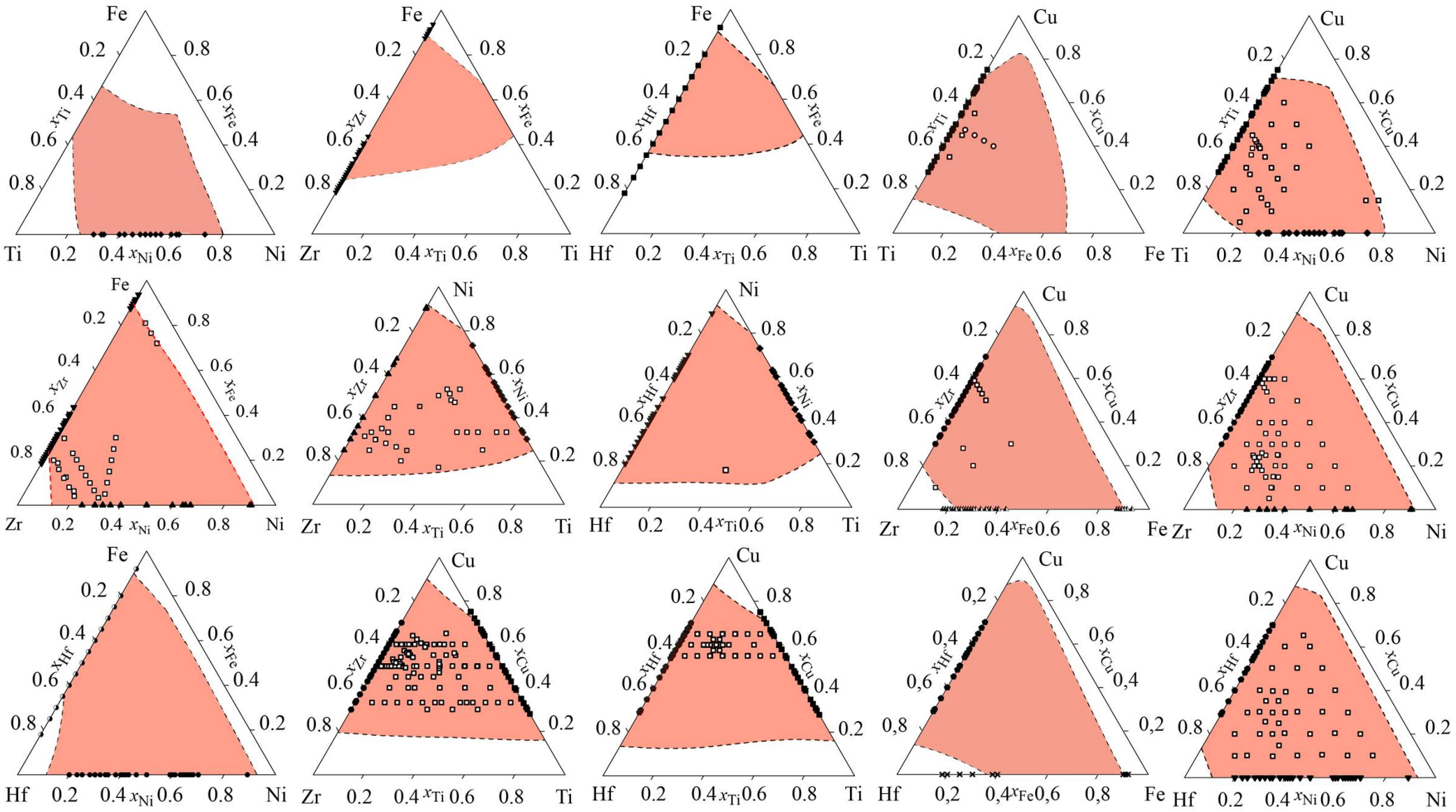


Predicted concentration region of amorphization



- At the diagrams of metastable phase transformations for $Fe_{0.8}Ni_{0.2}$–Zr and $Fe_{0.1}Ni_{0.9}$–Zr sections the $T_0^{L/(\gamma Fe,Ni)}$ and $T_0^{L/(\beta Zr)}$ lines bound the composition regions in which the supercooled liquid phase is thermodynamically stable with respect to the boundary solid solutions.
- At the isothermal section at 800 K the $x_0^{L/(\gamma Fe,Ni)}$ and $x_0^{L/(\beta Zr)}$ lines indicate compositions of alloys with equal Gibbs energies of the liquid and corresponding solid solutions, crystalline phases (γFe,Ni) and (βZr).
- The $x_0^{L/(\gamma Fe,Ni)}$ and $x_0^{L/(\beta)}$ lines bound the predicted glass-formation region of the Fe–Ni–Zr which is shown as a color area on the composition triangle.

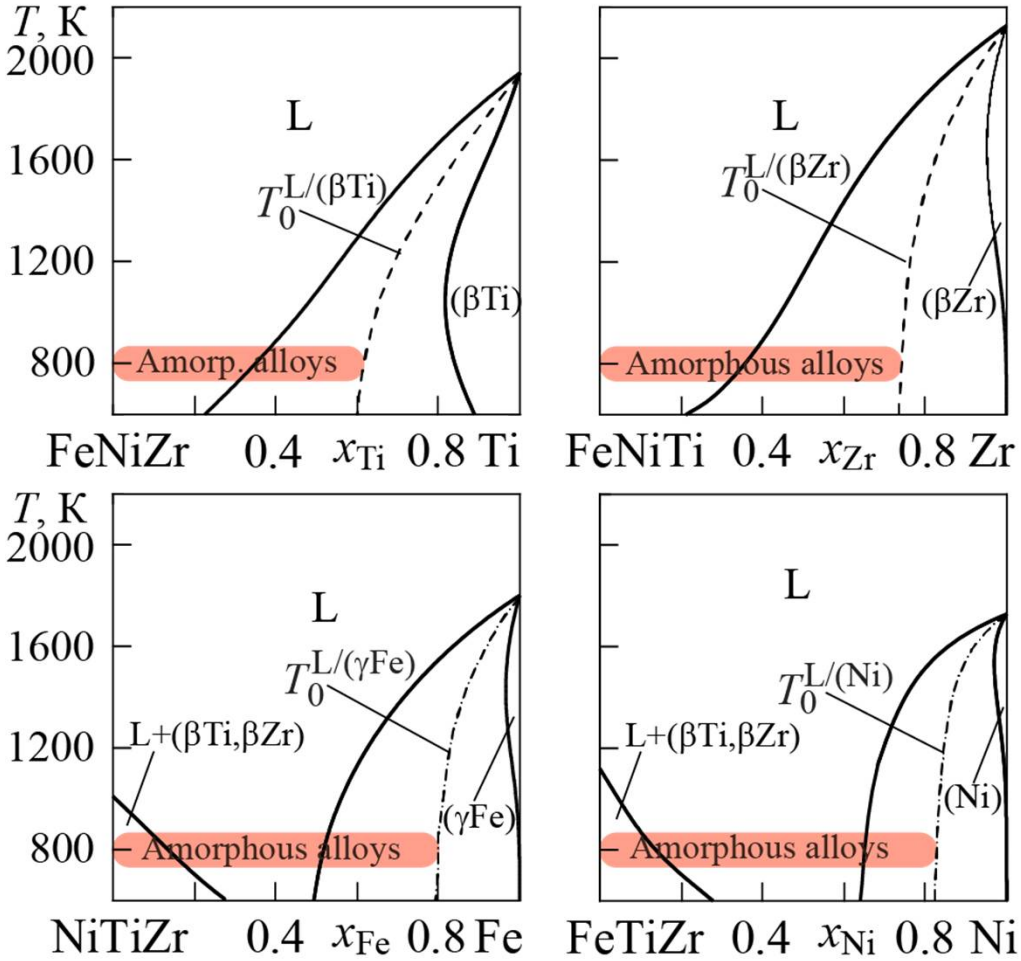
PREDICTED CONCENTRATION REGIONS OF AMORPHIZATION AND LITERATURE DATA ON COMPOSITIONS OF AMORPHOUS ALLOYS OF TERNARY SYSTEMS

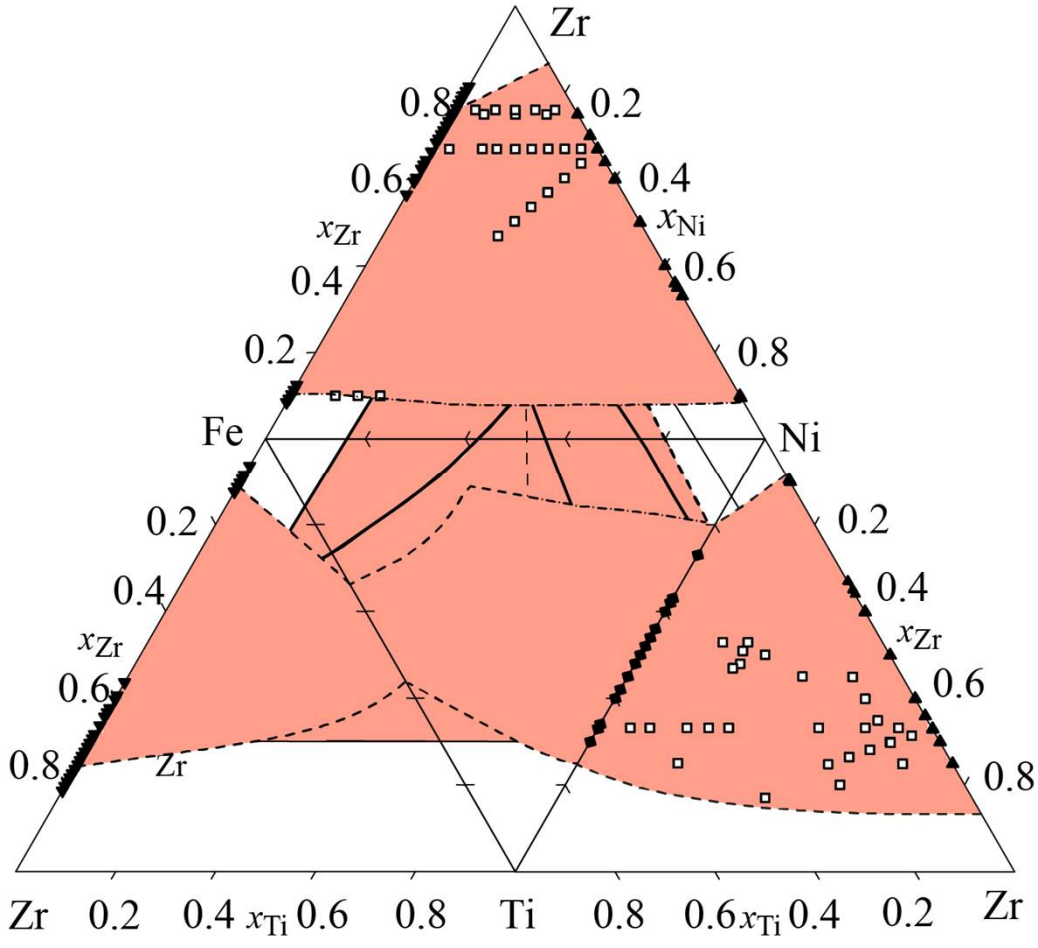


- predicted concentration region of amorphization

- **compositions of binary amorphous alloys**
- **compositions of ternary amorphous alloys**

DIAGRAMS OF METASTABLE PHASE TRANSFORMATIONS IN THE Fe–Ni–Ti–Zr SYSTEM, LITERATURE DATA ON COMPOSITIONS OF AMORPHOUS ALLOYS AND PREDICTED CONCENTRATION REGIONS OF AMORPHIZATION

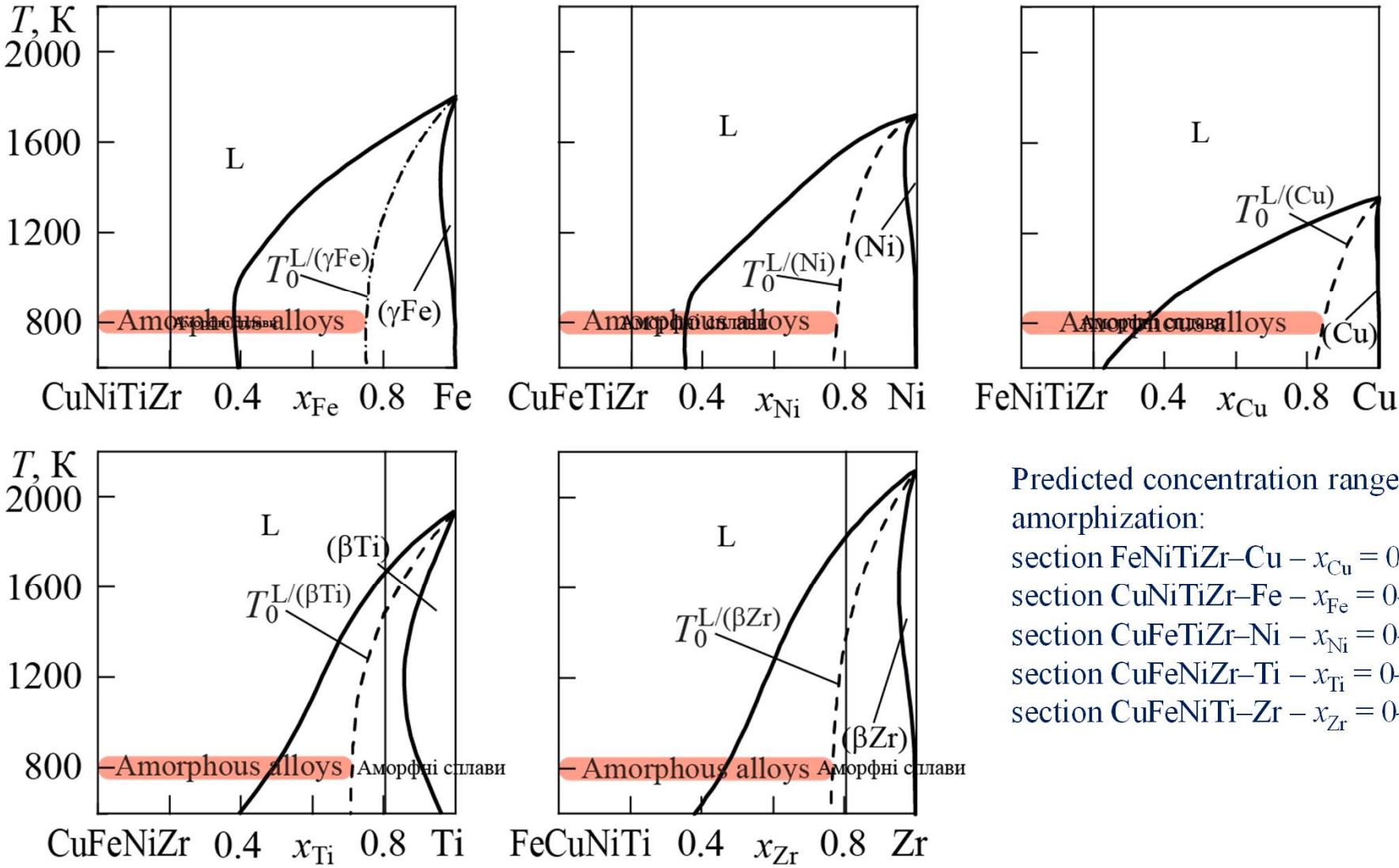




- predicted concentration region of amorphization

Predicted concentration ranges of amorphization:
section FeNiZr–Ti – x_{Ti} = 0–0.62;
section FeNiTi–Zr – x_{Zr} = 0–0.74;
section NiTiZr–Fe – x_{Fe} = 0–0.80;
section FeTiZr–Ni – x_{Ni} = 0–0.83

DIAGRAMS OF METASTABLE PHASE TRANSFORMATIONS IN THE Cu–Fe–Ni–Ti–Zr SYSTEM AND PREDICTED CONCENTRATION REGIONS OF AMORPHIZATION



Predicted concentration ranges of amorphization:
section FeNiTiZr–Cu – x_{Cu} = 0–0.84;
section CuNiTiZr–Fe – x_{Fe} = 0–0.75;
section CuFeTiZr–Ni – x_{Ni} = 0–0.78;
section CuFeNiZr–Ti – x_{Ti} = 0–0.71;
section CuFeNiTi–Zr – x_{Zr} = 0–0.77

A factor influencing the ability of liquid Cu–Fe–Ni–Ti–Zr–Hf alloys to amorphization is the simultaneous fulfillment of the conditions $x_{Fe} + x_{Ni} + x_{Cu} > 0.25$ and $x_{Ti} + x_{Zr} + x_{Hf} > 0.15$

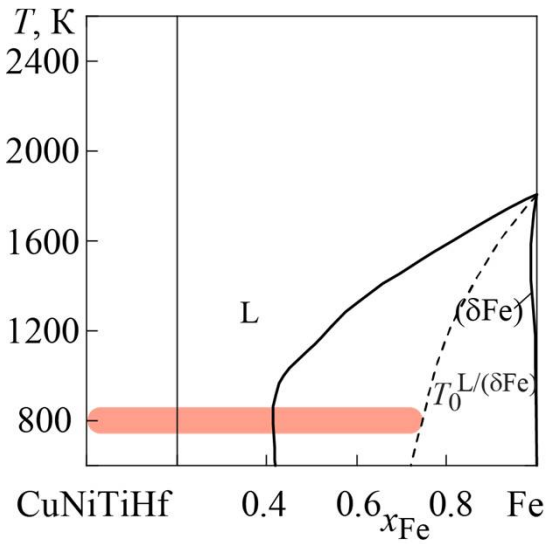
CONCLUSIONS

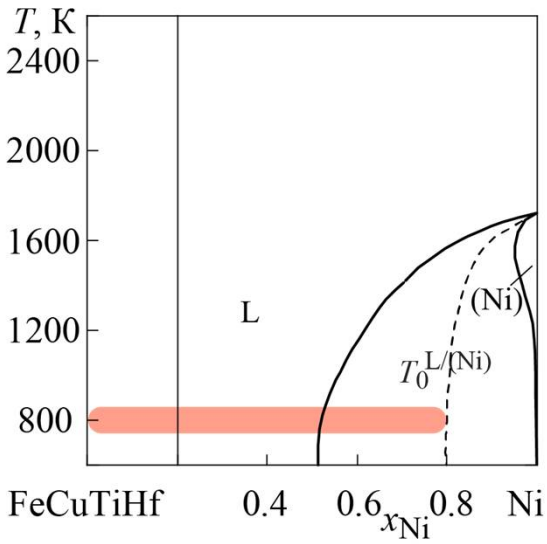
1. The thermodynamic database for targeted search of the concentration ranges of amorphization of transition metals melts by quenching was developed within the framework of the CALPHAD method. The database generalizes the thermodynamic descriptions of two- and three-component systems that are constituents for the quinary Cu–Fe–Ni–Ti–Zr and Cu–Fe–Ni–Ti–Hf systems and consist of the model parameters for the excess Gibbs energy of the liquid, bcc and fcc phases. New database complements the previously obtained one for the Cu–Ni–Ti–Zr–Hf system. The associate solution model is used to describe the thermodynamic properties of liquid glass-forming alloys. The Gibbs energy of solid solutions is described using the mathematical model based on Redlich-Kister polynomials with the Muggianu extension for ternary systems.
2. The database was used to calculate metastable phase diagrams involving supercooled liquid and boundary solid solutions. It was shown, the supercooled melts demonstrate in wide concentration ranges the thermodynamic stability in relation to solid solutions based on pure components. The concentration regions of amorphization by melts quenching were estimated by the relative location of the phase's Gibbs energy equality lines $T_0^{L/\phi}$ for vertical sections and $x_0^{L/\phi}$ for isothermal sections at the glass transition temperature T_g.
3. The generalization of the results of calculations for the Cu–Fe–Ni–Ti–Zr, Cu–Fe–Ni–Ti–Hf, and Cu–Ni–Ti–Zr–Hf systems and boundary quaternary systems demonstrated that the formation of amorphous alloys can be predicted in wide concentration ranges corresponding to the simultaneous fulfillment of the conditions $x_{Fe} + x_{Ni} + x_{Cu} > 0.25$ and $x_{Ti} + x_{Zr} + x_{Hf} > 0.15$. It is shown that equiatomic quaternary and high-entropy quinary alloys of the systems fall into the predicted concentration regions of amorphization.

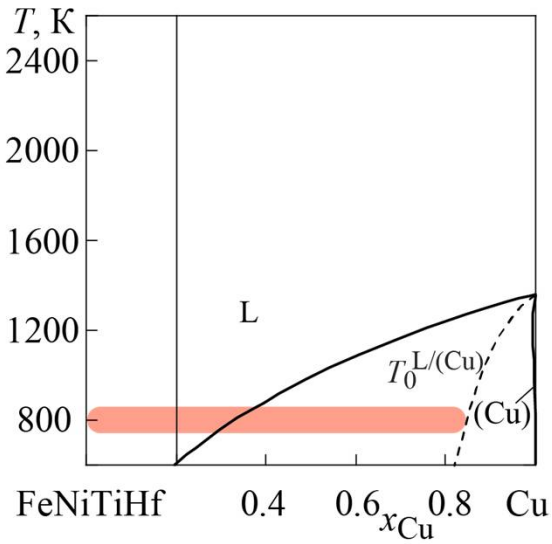
Thank You very much for Your attention

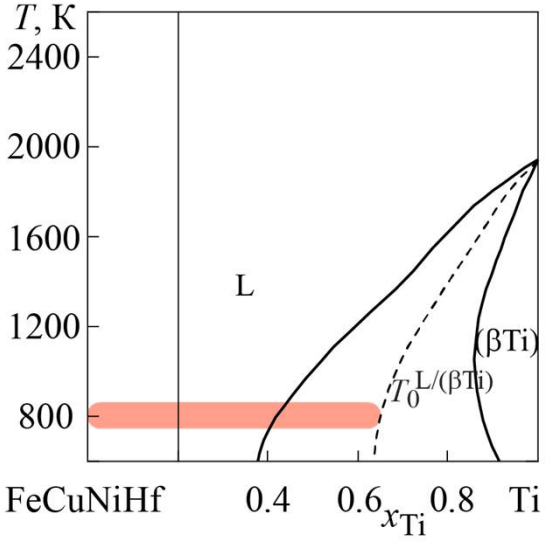
Acknowledgements
This work was supported by the Ministry of Education and Science of Ukraine under the grant 0122U000970.

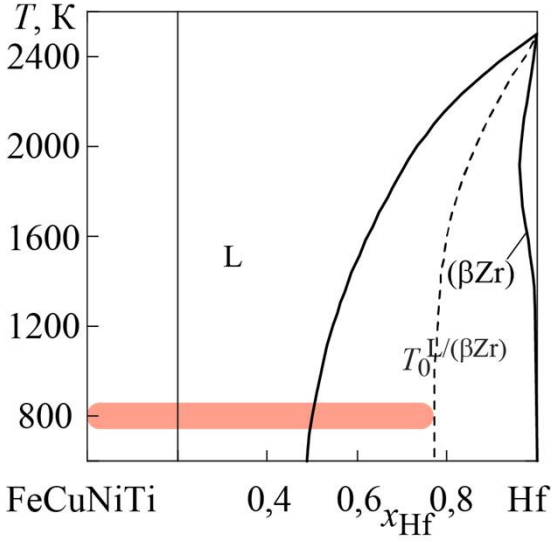
DIAGRAMS OF METASTABLE PHASE TRANSFORMATIONS IN THE Cu–Fe–Ni–Ti–Hf SYSTEM AND PREDICTED CONCENTRATION REGIONS OF AMORPHIZATION





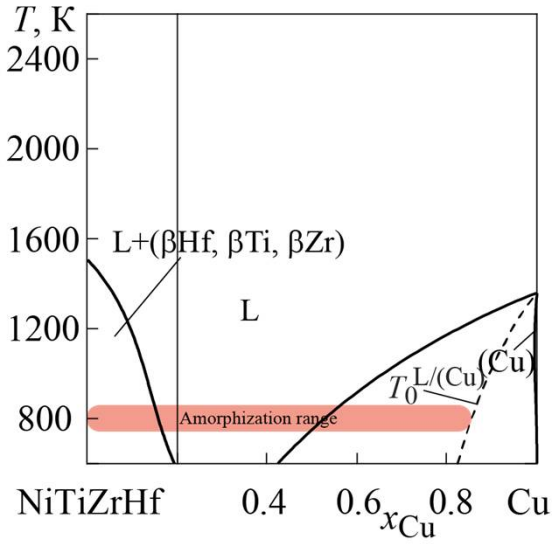


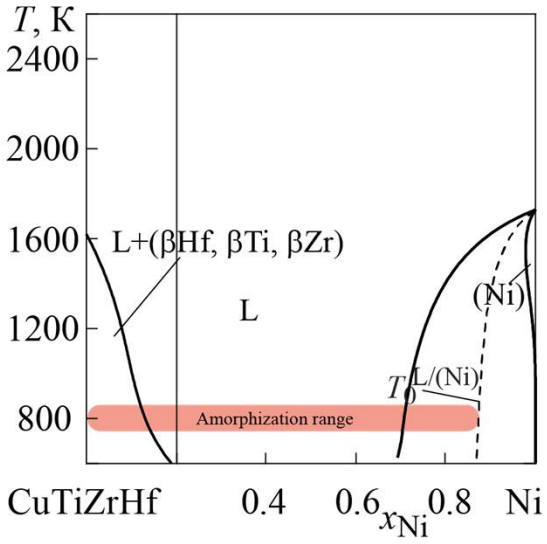


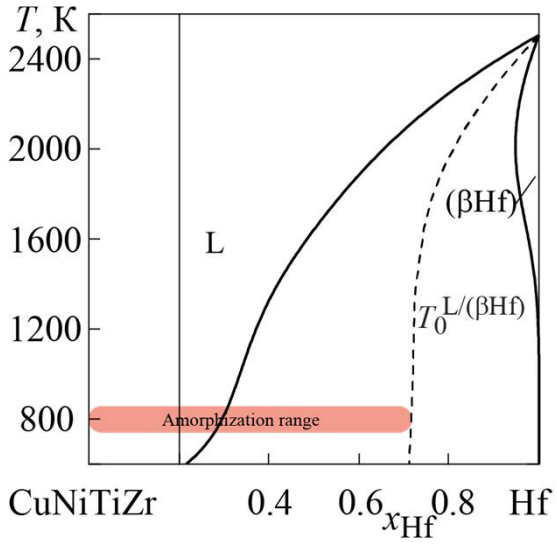


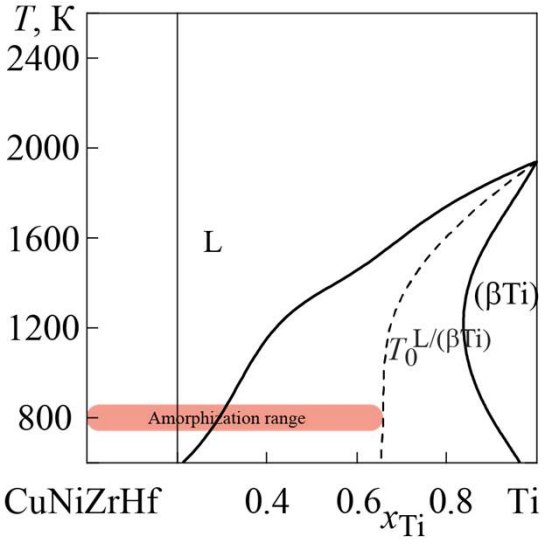
Predicted concentration ranges of amorphization:
section FeNiTiHf–Cu – x_{Cu} = 0–0.85;
section CuNiTiHf–Fe – x_{Fe} = 0–0.75;
section CuFeTiHf–Ni – x_{Ni} = 0–0.80;
section CuFeNiHf–Ti – x_{Ti} = 0–0.65;
section CuFeNiTi–Hf – x_{Hf} = 0–0.77

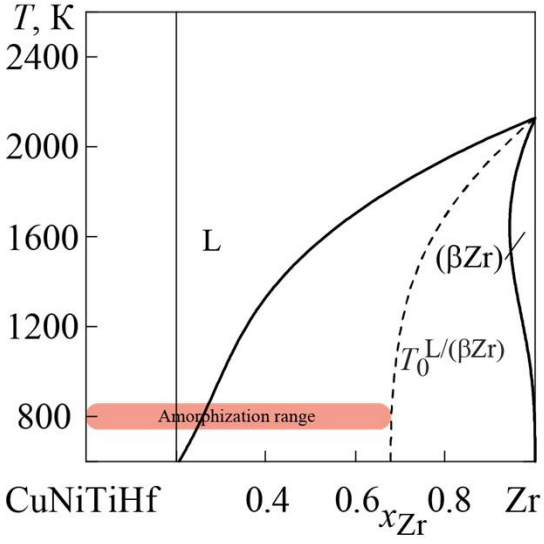
DIAGRAMS OF METASTABLE PHASE TRANSFORMATIONS IN THE Cu–Ni–Ti–Zr–Hf SYSTEM AND PREDICTED CONCENTRATION REGIONS OF AMORPHIZATION











Predicted concentration ranges of amorphization:
section NiTiZrHf–Cu – x_{Cu} = 0–0.85;
section CuTiZrHf–Ni – x_{Ni} = 0–0.87;
section CuNiZrHf–Ti – x_{Ti} = 0–0.65;
section CuNiTiHf–Zr – x_{Zr} = 0–0.69;
section CuNiTiZr–Hf – x_{Hf} = 0–0.72

HEA amorphous CuNiTiZrHf alloy is obtained by casting in copper form with the diameter of rods up to 2 mm [Ma, 2002]

Results of calculation are published in [M.A. Turchanin et al., Pow. Met. Met. Ceram. 57 (2018) 57]