

Report to APDIC, May 2022

Activities of Members of Ukrainian Phase Diagrams and Thermodynamics Commission, Ukraine

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Short Information about the Meetings held in 2021

7th International Samsonov Conference "Materials Science of Refractory Compounds" (MSRC-2021) was held from 25th to 28th May, 2021 in Kyiv.

The Conference was organized by Frantsevich Institute for Problems of Materials Science of NASU (FIPMS; Kyiv, Ukraine) and National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" under patronage of Ukrainian Materials Research Society (UMRS).

The main topics of the Conference were:

- The electronic structure and properties of refractory compounds.
- Synthesis of refractory compounds, chemical properties, phase diagrams.
- Low-dimensional nanostructures of refractory compounds.
- Films and coatings based on refractory compounds.
- Ceramics and composites based on refractory compounds.

VIII International Scientific and Technical Conference "Advanced technologies, materials and equipment in the foundry" was held from 21st to 24th September, 2021 in Kramatorsk.

The Conference was organized by Donbas State Engineering Academy (Kramatorsk, Ukraine).

Section 2. "Physico-chemical fundamentals of production of metals and alloys" worked as a part of the conference. The main topics of the Section 2 were:

- Fundamental principles of advanced materials science;
- Metallic materials and technologies of their production;
- Thermodynamics of liquid alloys;

- Phase equilibria and thermodynamic properties of phases;
- Oxide-based materials.

The Seventh International Materials Science Conference “HighMatTech” was held from 5th to 7th October, 2021 in Kyiv.

The Conference was organized by Frantsevich Institute for Problems of Materials Science of NASU (FIPMS; Kyiv, Ukraine), the Ukrainian Materials Research Society and National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”.

The main topics of the Conference were:

- Fundamental principles of advanced materials science. Modelling of the technological processes for material production and treatment and the properties of modern multifunctional materials for various applications.
- Metallic materials and technologies of their production, including high-entropy alloys, dispersion hardened metals and etc.
- Oxide based materials, including multiferroics, materials for optical applications.
- Non-oxide materials, including ultrahigh temperature ceramics, MAX phases, ceramic-based composites.
- Powder metallurgy: science and industry; modern materials, technologies and properties.
- Low-dimensional materials for various applications.
- Composite materials, including multifunctional ones: special properties and ways of their practical use.
- Surface engineering, methods of coating production, properties, applications.
- Modern technologies of material joining.
- Equipments and methods for material characterization.
- Materials for nanoelectronics and nanophotonics.
- Materials for energy applications, including materials for batteries, supercapacitors, solar cells and etc.
- Advanced technologies for recycling of industrial wastes.

Short Information about the defended theses for academic degree of Doctor of Chemistry in 2021

Specialized Academic Council D26.207.02 works in Frantsevich Institute for Problems of Materials Science (National Academy of Sciences of Ukraine, Kyiv). It was established by decree of Ministry of Education and Science, Youth and Sports of Ukraine № 1528 from 22.12.2014.

In 2021 three theses for academic degree of Doctor of Sciences for speciality 02.00.04 “Physical chemistry” were defended:

1. Fartushna Iulia Viktorivna. *Phase Equilibria, Structure and Properties of Alloys of Titanium and Iron Systems with d–metals, p–elements and REM.* I.M. Frantsevich Institute for Problems of Material Science, NAS of Ukraine, Kyiv.

The thesis is devoted to the construction of phase diagrams of ternary systems Ti–{V, Zr, Co, Ni, Ga}–Sn, Zr–Co–Sn, Ti–{V, Cr}–Si, Fe–R–{C, Co, Ni} and some boundary binaries in wide concentration and temperature ranges. The intermetallic compounds and miscibility gap in liquid phase in the La–Fe system were not confirmed. Most remarkable feature of La–Fe–C system involves isolated miscibility gap in liquid phase $L_1 + L_2$ and formation of ternary compound $\text{La}_{3,67}\text{FeC}_6$ (τ) ($\text{La}_{3,67}\text{FeC}_6$, *hP24-P6₃/m*). It is shown that τ is formed by peritectic reaction at 1250 °C. An expert evaluation of the published data on phase equilibria was performed for Fe–Ce–C and Fe–Nd–C systems.

A new binary compound $\text{Ce}_5\text{Ni}_{19}$ was found. Its crystal structure was determined ($\text{Ce}_5\text{Co}_{19}$, *hR72-R-3m*). $\text{Ce}_5\text{Ni}_{19}$ is formed by a peritectic reaction at 1123 °C. New ternary compounds Ti_5GaSn_2 (Nb_5SiSn_2 , *tI32-I4/mcm*) and $\text{Ti}_2\text{Ni}_2\text{Sn}$ ($\text{U}_2\text{Pt}_2\text{Sn}$, *tP20-P4₂/mmm*) were found and their crystal structure was established. The crystal structure of the ternary compound $\text{Zr}_5\text{Co}_6\text{Sn}_{18}$ was determined for the first time. The thermodynamic description of the Ti–Ni–Sn system is carried out. The enthalpies of formation of ternary compounds Ti_5GaSn_2 , TiNi_2Sn , TiNiSn , $\text{Ti}_2\text{Ni}_2\text{Sn}$ and Ti_5NiSn_3 have been calculated. It is shown that ternary compound $(\text{Co,Fe})_{17}\text{La}_2$ (τ) ($\text{Th}_2\text{Zn}_{17}$, *R-3m*) is formed by peritectic reaction at 978 °C and has a wide homogeneity range from 46 to ~78 at.% Co at solidus temperature. It was found that compounds $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Co}_{17}$ and Laves phases Fe_2Ce and Co_2Ce continuous solid solutions $\text{Ce}_2(\text{Co,Fe})_{17}$ and $\text{Ce}(\text{Co,Fe})_2$. The Laves phases Fe_2Ce and Ni_2Ce also form a continuous solid solution $\text{Ce}(\text{Ni,Fe})_2$.

An expert evaluation of the published data on phase equilibria was performed for the Fe–Mn–Ce system. There are two ternary compounds $\text{Fe}_{11}\text{Mn}_6\text{Ce}_2$ (τ_1) ($\text{Th}_2\text{Ni}_{17}$, *hP38-P6₃/mmc*) and $\text{Fe}_5\text{Mn}_7\text{Ce}$ (τ_2) (ThMn_{12} , *tI26-I4/mmm*), which are formed by peritectic reactions and have wide homogeneity regions.

A comparative analysis of the studied and related systems was performed. All systems are divided into two groups: systems with weak ternary interaction and systems with strong or middle ternary interaction.

The most typical ternary compounds in the $M^{IV-VI}-M^{VII-VIII, lb}-Sn$ and $Ti-M^{VII-VIII, lb}-Sn$ systems are Heusler phases M_1M_2Sn (for titanium systems – $TiMSn$, half-Heusler phase, HH) and M_1M_2Sn (for titanium systems — TiM_2Sn , Heusler phase, H). The temperature formation of H phases is higher than HH phases. This is due to order and occupation of crystallographic positions in structure of H phases, while structure of HH phases is subtraction phase with respect to H.

2. Agraval Pavlo Gyanovych. *Thermodynamics and Phase Transformations in Multicomponent Glass-forming Systems of Transition Metals*. Donbas State Engineering Academy, Ministry of Education and Science of Ukraine, Kramatorsk.

The mixing enthalpies of the components in the binary Fe–Ti, Fe–Zr, Fe–Hf and in the ternary Co–Cu–Ti, Co–Cu–Zr, Cu–Fe–Ti, Cu–Fe–Zr, Cu–Fe–Hf, Cu–Ni–Ti, Cu–Ni–Hf, Cu–Ti–Zr, Cu–Ti–Hf, Ni–Ti–Zr i Ni–Ti–Hf systems were determined by high temperature calorimetry. It is shown that there is an intense chemical interaction between the components of the melts, which is expressed in the mostly negative values of the mixing enthalpies. The pair interactions of components play a significant role in the considered ternary systems. The role of electron acceptor in the interaction belongs to the Fe, Co, Ni, Cu, and the role of electron donor belongs to the Ti, Zr, Hf.

Within the framework of the associated solution model (ASM), the thermodynamic mixing functions of melts of the investigated systems were described, and it was shown that the inherent for them mostly negative deviations from ideality increase with decreasing temperature. A thermodynamic database that describes the functions of glass-forming melts of the Co–Cu–Fe–Ni–Ti–Zr–Hf system is created. The database has been used for modeling of the temperature and concentration dependences of the thermodynamic mixing functions of liquid alloys of the quaternary Cu–Ni–Ti–Zr, Cu–Ni–Ti–Hf, Cu–Ni–Zr–Hf, Cu–Ti–Zr–Hf, Ni–Ti–Zr–Hf and the quinary Cu–Ni–Ti–Zr–Hf systems and for calculation of thermodynamic functions of mixing of 21 equiatomic quinary liquid alloys of the Co–Cu–Fe–Ni–Ti–Zr–Hf system. The relative contributions of the ideal and excess components to the Gibbs mixing energy were determined by the calculation. It was shown that when the temperature decreases from 1873 K to 800 K, the contribution of the ideal component decreases from 65 ... 85% to 20 ... 45%.

A thermodynamic description of the Cu–Ti–Hf system has been performed for the first time, and new thermodynamic descriptions of the Ti–Zr and Cu–Ti–Zr systems have been developed.

Within the framework of the CALPHAD method, a database of parameters of models of thermodynamic properties of melts and boundary solid solutions based on pure components for the multicomponent Co–Cu–Fe–Ni–Ti–Zr–Hf system was developed. The parameters of the models of excess Gibbs energy presented in the database were used for the calculation of metastable phase transformations with the participation of supercooled liquid alloys and boundary solid solutions of the binary Fe–(Ti, Zr, Hf) systems and of the ternary Co–Cu–(Ti, Zr, Hf), Cu–Fe–(Ti, Zr, Hf), Cu–Ni–(Ti, Zr, Hf), Cu–Ti–(Zr, Hf),

Cu–Zr–Hf, Ni–Ti–(Zr, Hf), Ni–Zr–Hf systems. Also, the concentration regions of amorphization of the quinary Cu–Ni–Ti–Zr–Hf system and of the corresponding boundary quaternary systems were predicted. The results of the calculations are generalized with the known experimental information about the compositions of amorphous alloys.

3. Kornienko Oksana Anatoliivna. *Phase Equilibria in the Systems Oxides of the IV Group d-elements and Rare Earths*. I.M. Francevich Institute for Problems of Material Science, NAS of Ukraine, Kyiv.

Firstly the comprehensive study of phase equilibria in ternary systems $\text{CeO}_2(\text{ZrO}_2)\text{--La}_2\text{O}_3\text{--Ln}_2\text{O}_3$ ($\text{Ln}=\text{Sm, Eu, Gd, Er}$) and $\text{ZrO}_2\text{--CeO}_2\text{--Ln}_2\text{O}_3$ ($\text{Ln}=\text{Eu, Gd, Yb}$) has been carried out in the whole concentration range using conventional XRD technique, petrography, SEM and X-ray microprobe analyses. The isothermal sections for the systems $\text{ZrO}_2\text{--La}_2\text{O}_3\text{--Sm}_2\text{O}_3$ at 1100, 1500 °C and $\text{ZrO}_2\text{--La}_2\text{O}_3\text{--Eu}_2\text{O}_3$ at 1250, 1500 °C, $\text{ZrO}_2\text{--La}_2\text{O}_3\text{--Gd}_2\text{O}_3$ at 1500 and 1600 °C, $\text{CeO}_2\text{--La}_2\text{O}_3\text{--Ln}_2\text{O}_3$ ($\text{Ln}=\text{Sm, Eu, Gd, Er}$) at 1250, 1500 °C and $\text{ZrO}_2\text{--CeO}_2\text{--Eu}_2\text{O}_3$ at 1500 °C, $\text{ZrO}_2\text{--CeO}_2\text{--Dy}_2\text{O}_3(\text{Yb}_2\text{O}_3)$ at 1500, 1100 °C were constructed. The phase equilibria in the boundary binary systems $\text{La}_2\text{O}_3\text{--Ln}_2\text{O}_3$ and $\text{CeO}_2\text{--Ln}_2\text{O}_3$ have been studied for the first time in the temperature range 600–1500 °C. The fragments of the 5 binary phase diagrams of the $\text{CeO}_2\text{--Eu}_2\text{O}_3$ ($\text{Dy}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Yb}_2\text{O}_3$), $\text{ZrO}_2\text{--Yb}_2\text{O}_3$ systems and complete phase diagrams of the $\text{La}_2\text{O}_3\text{--Sm}_2\text{O}_3$ ($\text{Eu}_2\text{O}_3, \text{Gd}_2\text{O}_3, \text{Er}_2\text{O}_3$), $\text{ZrO}_2\text{--Dy}_2\text{O}_3$ systems were developed.

The main regularities of the phase reactions in the solid state have been revealed depending on lanthanide ionic radius. The topology of isothermal sections were forecasted the unknown ternary systems $\text{CeO}_2\text{--La}_2\text{O}_3\text{--Ln}_2\text{O}_3$ ($\text{Ln} = \text{Nd, Dy, Yb, Lu}$) at 1500 °C and $\text{HfO}_2\text{--La}_2\text{O}_3\text{--Ln}_2\text{O}_3$ ($\text{Ln} = \text{Nd, Sm, Eu, Gd, Dy, Yb}$) at 2100, 1900, 1600, 1250 °C grounding on the aforementioned regularities of the binary systems studied in this research.

Presented data are scientific background for desing of novel prospective ceramic materials of both structural and functional applications in energy engineering, medicine, nuclar power engineering, thermal barrier coatings and solid oxide fuel cells.

**The Organizations and Investigators in the Field of Phase Diagrams,
Thermodynamics and Crystal Structures in Ukraine
Presented their Results in the 2022 year Report
of Ukrainian Phase Diagrams and Thermodynamics Commission**

Organization	Persons	Field of Interests
<i>Frantsevich Institute for Problems of Materials Science (National Academy of Sciences of Ukraine, Kyiv)</i> <i>Department of Physical Chemistry of Inorganic Materials</i> <i>Physical Chemistry and Refractory Oxides Technology Department</i> <i>Department of Functional Ceramics Based on Rare Earths</i>	Team Leader Dr.Sc. A. Bondar Prof. Dr.Sc. T. Velikanova Prof. Dr.Sc. V. Sudavtsova Dr.Sc. M. Bulanova Dr.Sc. J. Fartushna Ph.D. O. Dovbenko Ph.D. M. Ivanov Ph.D. K. Korniyenko Ph.D. O. Myslyvchenko Ph.D. O. Semenova	Alloy phase diagrams and thermodynamics of the metallic alloys
	Team Leader Dr.Sc. E. Dudnik Dr.Sc. S. Lakiza	Phase diagrams of the ceramic systems
	Team Leader Dr.Sc. O. Kornienko Ph.D. O. Chudinovych	Phase diagrams of the ceramic systems based on rare earths
<i>Donbas State Engineering Academy (Ministry of Education and Science of Ukraine, Kramatorsk)</i> <i>Laboratory of Physico-chemical Properties of Metallic Liquid Alloys</i>	Team Leader Prof. Dr.Sc. M. Turchanin Dr.Sc. P. Agraval Ph.D. L. Dreval Ph.D. A. Vodopyanova	Thermodynamics of phases and phase diagrams

Organization	Persons	Field of Interests
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<p><i>Taras Shevchenko National University of Kyiv (Ministry of Education and Science of Ukraine, Kyiv)</i></p> <p><i>Department of Physical Chemistry</i></p>	<p>Team Leader Prof. Dr.Sc. O. Roik</p> <p>Prof. Dr.Sc. V. Kazimirov Dr.Sc. V. Sokol'skii Ph.D. N. Usenko Ph.D. N. Kotova Ph.D. N. Golovataya Ph.D. O.Yakovenko</p>	<p>Structure and thermodynamics of metallic alloys</p>
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System	EP	ET	CA	CT	ICE	Contributor	Comment
Ag-Au-Bi					F	[21Dre1]	Ph.D. L. Dreval in collaboration with MSI
Ag-Au-Sb					F	[21Dre2]	Ph.D. L. Dreval in collaboration with MSI
Ag-Cu-In					F	[21Dre3]	Ph.D. L. Dreval in collaboration with MSI
Ag-Cu-P					F	[21Kub1]	Ph.D. O. Semenova in collaboration with MSI
Al-Ca-Ge		F				[21Iva2]	Ph.D. N. Usenko in collaboration with M. Ivanov and N. Kotova isoperibolic calorimetry
Al-Ce-O-Y-Zr	X					[21Smy, 22Smy]	Dr.Sc. E. Dudnik phase composition, specific surface area and morphology of the nanosized $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3\text{-CeO}_2$ powders
Al-Co-Cr	X					[21Kor2]	Ph.D. K. Korniyenko phase composition of the alloys in the range 0–70 at. % Al
Al-Cu-Eu		F				[21Iva1]	Ph.D. N. Usenko in collaboration with M. Ivanov and N. Kotova isoperibolic calorimetry
Al-Gd-Mn		F				[21Iva3]	Ph.D. N. Usenko in collaboration with M. Ivanov and N. Kotova isoperibolic calorimetry
Al-Ge-Fe			F			[21Roi2]	Dr.Sc O. Roik in collaboration with V. Kazimirov, V. Sokol'skii, O. Yakovenko, and N. Golovataya Reverse Monte Carlo simulations
Al-Ge-Ni			F			[21Roi2]	Dr.Sc O. Roik in collaboration with V. Kazimirov, V. Sokol'skii, O. Yakovenko, and N. Golovataya Reverse Monte Carlo simulations

System	EP	ET	CA	CT	ICE	Reference	Comment
Al-Sn	F		F			[21Roi1]	Dr.Sc O. Roik in collaboration with V. Kazimirov, V. Sokol'skii, O. Yakovenko, N. Golovataya, and Ya. Kashirina high-temperature X-ray diffraction
B-Cr-Ni					F	[20Bon]	Dr.Sc. A. Bondar in collaboration with MSI
B-Fe-Mo	F			F		[21Wit]	Dr.Sc. A. Bondar in collaboration with Dr.Sc. V. Witusiewicz phase composition of the alloys
B-Mo-Ni	X					[21Kub2]	Dr.Sc. A. Bondar phase composition of the alloys in the range Ni-MoNi-Mo ₂ NiB ₂ -Ni ₂ B
Bi-Cu-Ni					F	[21Far]	Dr.Sc. J. Fartushna in collaboration with MSI
Bi-In-Sb					F	[21Vel1]	Prof. Dr.Sc. T. Velikanova Prof. Dr.Sc. M. Turchanin in collaboration with MSI
Ce-La-O-Sm	X					[21Kor]	Dr.Sc. O. Kornienko isothermal sections of the CeO ₂ -La ₂ O ₃ -Sm ₂ O ₃ system at 1250°C
Ce-O-Y-Zr	X					[21Mar]	Dr.Sc. E. Dudnik phase composition, specific surface area and morphology of the nanosized ZrO ₂ -Y ₂ O ₃ -CeO ₂ powders
Co-Cr-Cu-Fe-Ni		F				[21Agr]	Dr.Sc. P. Agraval Temperature- composition dependence of thermodynamic mixing functions of liquid alloys
Co-Cu-Mn					F	[21Rok]	Dr.Sc. A. Bondar in collaboration with MSI
Co-Ni-Zr	X					[21Sem2, 21Sem3]	Ph.D. O. Semenova phase composition of the alloys in the range 50–100 at. % Zr

System	EP	ET	CA	CT	ICE	Reference	Comment
Cu-Eu		F				[21Iva1]	Ph.D. N. Usenko in collaboration with M. Ivanov and N. Kotova isoperibolic calorimetry
Cu-Hf-Ni-Ti		F		F		[20Tur]	Prof. Dr.Sc. M. Turchanin Temperature- composition dependence of thermodynamic mixing functions and chemical ordering in liquid alloys
Cu-Hf-Ni-Ti-Zr		F		F		[21Tur]	Prof. Dr.Sc. M. Turchanin Temperature- composition dependence of thermodynamic mixing functions and chemical ordering in liquid alloys
Cu-In-Sn					F	[21Vel2]	Prof. Dr.Sc. T. Velikanova Prof. Dr.Sc. M. Turchanin in collaboration with MSI
Cu-Mn-Ni					F	[21Wat]	Ph.D. L. Dreval in collaboration with MSI
Cu-P-Sn					F	[21Dre4]	Ph.D. L. Dreval Ph.D. O. Dovbenko in collaboration with MSI
Cu-Ti-Zr					F	[21Vel3]	Prof. Dr.Sc. T. Velikanova Prof. Dr.Sc. M. Turchanin Dr.Sc. P. Agraval in collaboration with MSI
Fe-Hf-Ni		F				[22Tur]	Prof. Dr.Sc. M. Turchanin Mixing enthalpy of liquid alloys at 1873 K
Fe-Ni-Ti		F				[22Tur]	Prof. Dr.Sc. M. Turchanin Mixing enthalpy of liquid alloys at 1873 K
Fe-Ni-Zr		F				[22Tur]	Prof. Dr.Sc. M. Turchanin Mixing enthalpy of liquid alloys at 1873 K
Gd-Ni-Sn		F				[21Sud2]	Prof. Dr.Sc. V. Sudavtsova isoperibolic calorimetry
Gd-Sn		F				[21Sud1, 21Sud2]	Prof. Dr.Sc. V. Sudavtsova isoperibolic calorimetry
Hf-Ni-Ti		F				[20Tur]	Prof. Dr.Sc. M. Turchanin Dr.Sc. P. Agraval Ph.D. L. Dreval isoperibolic calorimetry

System	EP	ET	CA	CT	ICE	Reference	Comment
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In-Ni-Sn					F	[21Dre5]	Ph.D. L. Dreval in collaboration with MSI
In-Sr		F				[21Sud4]	Prof. Dr.Sc. V. Sudavtsova isoperibolic calorimetry
La-Lu-O-Yb	X					[21Chu]	Ph.D. O. Chudinovych isothermal section of the La ₂ O ₃ –Lu ₂ O ₃ –Yb ₂ O ₃ system at 1600°C
Mo-Nb-Ti	X					[21Mys1, 21Mys2]	Ph.D. O. Myslyvchenko phase composition
Ni-Pd-Si					F	[21Sem1]	Ph.D. O. Semenova in collaboration with MSI
Ni-Pr		F				[21Sud3]	Prof. Dr.Sc. V. Sudavtsova isoperibolic calorimetry
Sn-Ti-Zr	F					[22Far]	Dr.Sc. J. Fartushna Dr.Sc. M. Bulanova in collaboration with Prof. Dr.Sc. J. Tedenac phase composition

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