Univerzita Komenského v Bratislave

Fakulta matematiky, fyziky a informatiky

Mgr. Juraj Zigo

Autoreferát dizertačnej práce

Local Structure in Rapidly-Quenched Al-Si Based Systems

(Lokálne usporiadanie v rýchlo chladených systémoch na báze Al-Si)

na získanie akademického titulu philosophiae doctor

v odbore doktorandského štúdia:
4.1.3 Fyzika kondenzovaných látok a akustika

Bratislava 10.6.2017

Dizertačná práca bola vypracovaná v dennej forme doktorandského štúdia

na Fyzikálnom ústave Slovenskej Akadémie vied

Predkladateľ: **Mgr. Juraj Zigo**
Oddelenie fyziky kovov
Fyzikálny ústav Slovenskej akadémie vied
Dúbravská cesta 9
Bratislava, 84511

Školiteľ: **Ing. Peter Švec DrSc.**
Oddelenie fyziky kovov
Fyzikálny ústav Slovenskej akadémie vied
Dúbravská cesta 9
Bratislava, 84511

Študijný odbor: 4.1.3 Fyzika kondenzovaných látok a akustika

Predseda odborovej komisie:

Prof. RNDr. Peter Kúš, DrSc.
Fakulta matematiky, fyziky a informatiky
Univerzity Komenského
Mlynská dolina F2
842 48 Bratislava

Abstrakt

Štruktúra rýchlo chladených zliatin $Al_{80-x}T_xSi_{20}$ (kde T = Fe, Co, Ni a x = 5, 10, 15) bola skúmaná v stavoch po príprave, po žíhaní a v roztavenom stave. Prítomnosť jednotlivých fáz a ich morfológia na mikroskopickej úrovni boli skúmané pomocou Röntgenovej difrakcie a transmisnej elektrónovej mikroskopie. Pozorované fázy sú zväčša v súlade s publikovanými fázovými diagramami. Výnimku tvorí napríklad neznáma Al-Ni-Si ternárna hexagonálna fáza ktorá precipituje z amorfnej fázy. Teplotná stabilita prítomných fáz bola skúmaná pomocou diferenciálnej skenovacej kalorimetrie. Lokálna atomárna štruktúra v amorfnom a roztavenom stave bola určená pomocou Röntgenovej difrakcie a simulácii molekulárnej dynamiky (MD). Chemické usporiadanie na krátku vzdialenosť podobné tomu v kryštalických fázach bolo pozorované v roztavených a amorfných systémoch. Koeficienty difúzie v tavenine vypočítané z MD simulácii súhlasia s publikovanými dátami. Výsledkom MD simulácii bola taktiež elektrónová hustota stavov v amorfných fázach. Depresia v okolí Fermiho energie ukazuje na dôležitosť elektrónového stabilizačného efektu.

Kľúčové slová: rýchle chladenie, planar-flow casting, kovové sklá, zliatiny Al, mikroštruktúra, transmisná elektrónová mikroskopia, Röntgenová difrakcia, simulácia molekulárnej dynamiky, elektrónová hustota stavov, difúzny koeficient , termická analýza

Abstract

The structure of rapidly-quenched $Al_{80-x}T_xSi_{20}$ alloys (where T = Fe, Co, Ni and x = 5, 10, 15) has been studied in as-cast, annealed and liquid states. Phase content and microstructure morphology have been determined using X-ray diffraction and transmission electron microscopy respectively. Phase content agrees approximately with phase diagrams, however, unknown ternary hexagonal Al-Ni-Si phase has been observed to precipitate from amorphous phase. Phase stability and reaction kinetics properties have been studied by differential scanning calorimetry. The local atomic structure of the amorphous and liquid states was determined using X-ray diffraction and molecular dynamics simulations (MD). The chemical short- range order which is similar to the one in crystalline phases has been found in the liquid and amorphous alloys. Diffusion coefficients in melt calculated from MD simulations show agreement with previously published data. Electronic density of states obtained from MD simulations in amorphous phase shows depression near Fermi energy indicating importance of electronic stabilization effect.

Keywords: rapid-quenching, planar-flow casting, metallic glasses, Al-based, microstructure, transmission electron microscopy, X-ray diffraction, molecular dynamics simulation, electronic DOS, diffusion coefficient, thermal analysis

Introduction

Disordered microstructure and other related physical properties of metallic glasses are what drives scientists' interest since first purposefully manufactured in 1959 at the California Institute of Technology [1]. Even after nearly 60 years of research of metallic glasses, there

are still many questions left. Mentioned disordered structure can be given as an example, as it is not really disordered. Even silica-based glasses contain some kind of short-range order [2] and situation is similar for metallic glasses. Diffraction experiments show presence of local ordering in metallic glasses [3], [4]. It is tempting to find a link of local ordering to macroscopic physical properties in way similar to linking crystallographic features of crystalline materials to their macroscopic properties. However, here lies one of the weak points of knowledge about metallic glasses. While in crystalline materials the structure-property relationship is well understood and describes link between for example crystal structure and mechanical properties [5], in metallic glasses this link is still mostly unresolved and under intensive investigation [6].

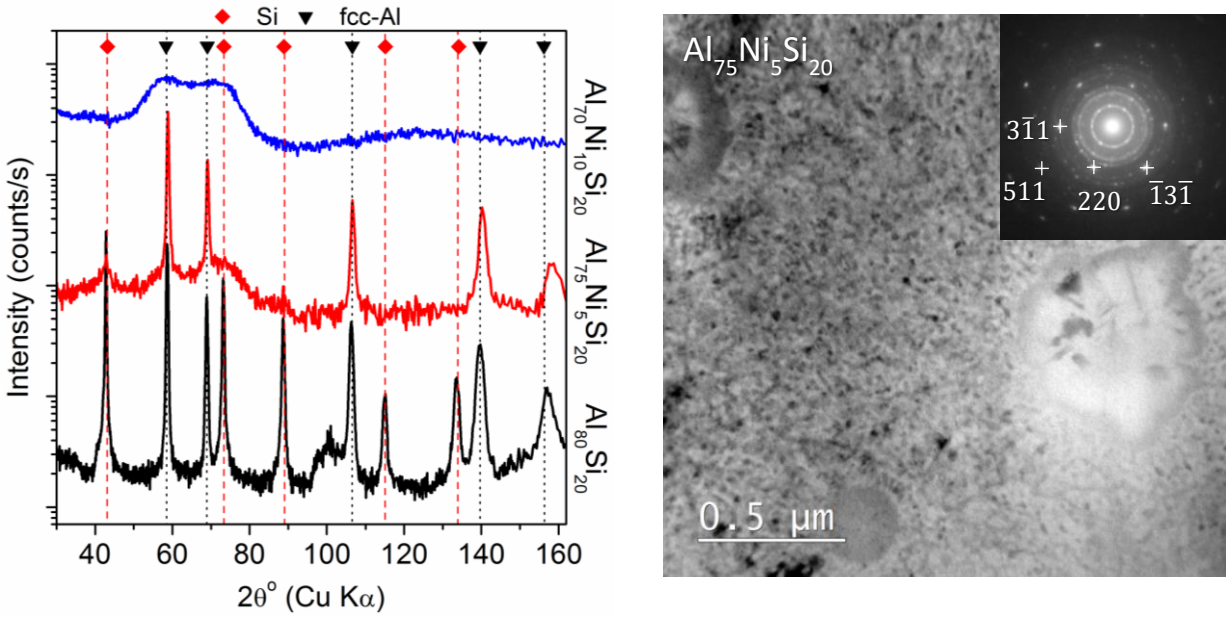

Figure 1: (left) X-ray diffraction of Al-TM-Si rapidly quenched alloy showing increasing content of amorphous phase with addition of transition metal. (right) microstructure of rapidly-quenched $Al_{75}Ni_5Si_{20}$ alloy containing mostly nanocrystalline fcc-Al and Si embedded in amorphous matrix

Aluminum alloys are one of the most widely used classes of light-weight construction materials. In metallic glass research field, Al-based alloys are also no novelty. It was shown, that Al-Ln (Ln stands for lanthanide metal) and Al-TM (TM stands for transition metal) alloys exhibit high ductility and high tensile strength [7]. Following previously established class of Al-Si alloys used in heavy duty applications [8], experiments with rapid quenching of Al-Si based alloys commenced, aiming to increasing of solid solubility of Si and refining Si crystals morphology [9]. It was found, that adding transition metal to Al-Si rapidly quenched alloy

extends Si solid solubility even more (see Figure 1) and improves mechanical properties of resulting alloy at higher temperatures, which were previously spoiled by coarse Si growth. It is done by precipitation strengthening by TM containing intermetallic particles [10].

Aluminum-based metallic glasses also attract attention from view point of fundamental research. Reports of highly ordered amorphous phase that grows through 1st order phase transformation from Al-Fe-Si melt can be taken as an example [11], [12].

It is clear, that Al-based metallic glasses offer at least as much potential as there is unresolved questions. With respect to the previously published data, the goal of this thesis was to prepare Al-TM-Si based rapidly-quenched materials and attempt to answer at least part of these questions by describing microstructure in as-cast and heat-treated states, determining thermal properties and local atomic structure in amorphous and liquid states.

Aims of the thesis

On the basis of our previously published work [13] and considering high application potential as well as interesting fundamental properties of rapidly-quenched Al-based alloys, the aims of this thesis have been set as follows:

- Prepare Al-Si based materials by planar-flow casting method. Optimize the preparation methods to produce ribbons with sufficient mechanical quality to perform structural and thermal investigations.
- Determine effect of transition metal addition to Al-Si rapidly-quenched material. Focus mainly on crystalline and amorphous phases content in as-cast state. Determine effect of transition metal content on glass-forming ability. Perform thermal analysis of the alloys to study thermal stability of amorphous and crystalline phases during heat-treatment.
- Perform XRD of systems upon heat treatment (annealed and/or in-situ). Perform phase content analysis according to these measurements. Determine effect of rapid-quenching and amorphous state as initial configuration with emphasis on similarities/differences with published phase diagrams.
- Determine microstructure morphology by transmission electron microscopy in as-cast state and analyze effect of heat treatment to microstructure.

- Verify hypothesis of amorphous phase (so called q-glass [12]) formation from melt by 1st order phase transformation.
- Optimize set-up for measurement of XRD of amorphous and liquid phases (use monochromated Mo Kα radiation). Use XRD data to calculate structure factors *S(Q)* and pair correlation functions *g(r)* to determine similarities in local atomic ordering of amorphous and liquid phases.
- Perform molecular dynamics simulations of amorphous and liquid phases. Extract local ordering information including partial pair correlation functions *g(r)* and compare to experimental data and data obtained from reverse Monte-Carlo simulations. Extract other possibly important data from MD simulations.
- Provide a broad set of information on this new material system based on Al with elevated content of Si and additional alloying element e.g. Fe, Co, Ni for potential targeted material research with specific applications in automotive, construction and recycling industry or for modern additive manufacturing technologies.

Summary of the results and discussion

The effect of the transition metal addition on Al-Si alloys phase content in as-cast state was determined by X-ray diffraction. X-ray diffraction experiments were performed on all rapidly-quenched ribbons with aim to qualitatively determine content of crystalline and amorphous phases. Figure 2a shows nearly pure amorphous nature of the as-cast samples with content of transition metals of 10 and 15 at. %. Small diffraction maxima on Figure 2a belong to Si, fcc-Al and tetragonal $FeAl_3Si_2$ (τ_4 phase in [14]). Rapidly-quenched systems containing 5 at.% of transition metal are mainly polycrystalline. XRD of these systems is displayed on Figure 2b. It is visible, that system with 5 at. % of Ni contains also amorphous phase.

It is apparent, that increasing content of transition metal increases glass-forming ability (GFA) of melt [15]. Particularly, alloys containing Ni have higher GFA as compared to those containing Fe and Co as 5 at. % of Ni is already sufficient to obtain partly amorphous system. Selecting alloying elements with low negative mixing enthalpy was proposed as one of the empirical rules to achieve high GFA [16]. Integral enthalpy of mixing of $Al_{60}Ni_{20}Si_{20}$ melt is strongly negative (-30,3 kJ/mol at 1770 K [17]) as compared to enthalpy of mixing of Al-Fe-Si melt with the same stoichiometry (-17,1 kJ/mol at 1750 K [18]). This is in agreement of our observation of higher GFA of Al-Ni-Si melts.

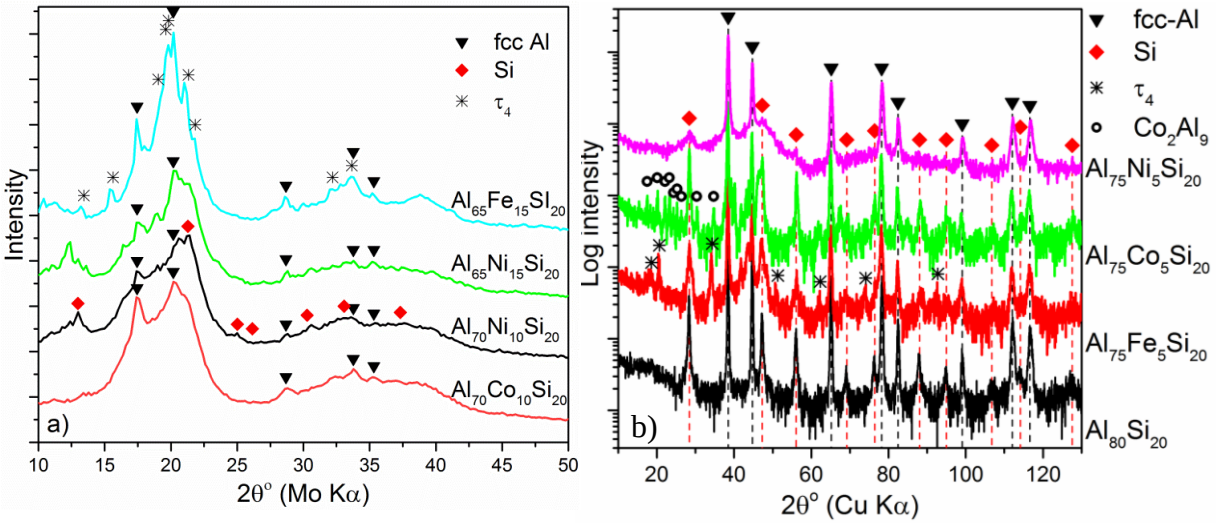

Figure 2: XRD patterns of as-quenched $Al_{80-x}T_xSi_{20}$ alloys. a) Alloys containing 10 or 15 at. % of T contain mainly amorphous phase. b) Alloys containing 5 at. % of T are mostly polycrystalline.

XRD measurements suggest, that microstructure differs significantly with varying content of transition metal. The microstructure of the rapidly-quenched alloys was determined by TEM and STEM in as-cast and annealed states. Selected samples were further analyzed by STEM using EDS and EELS giving insight to local chemical composition changes and atomic arrangement.

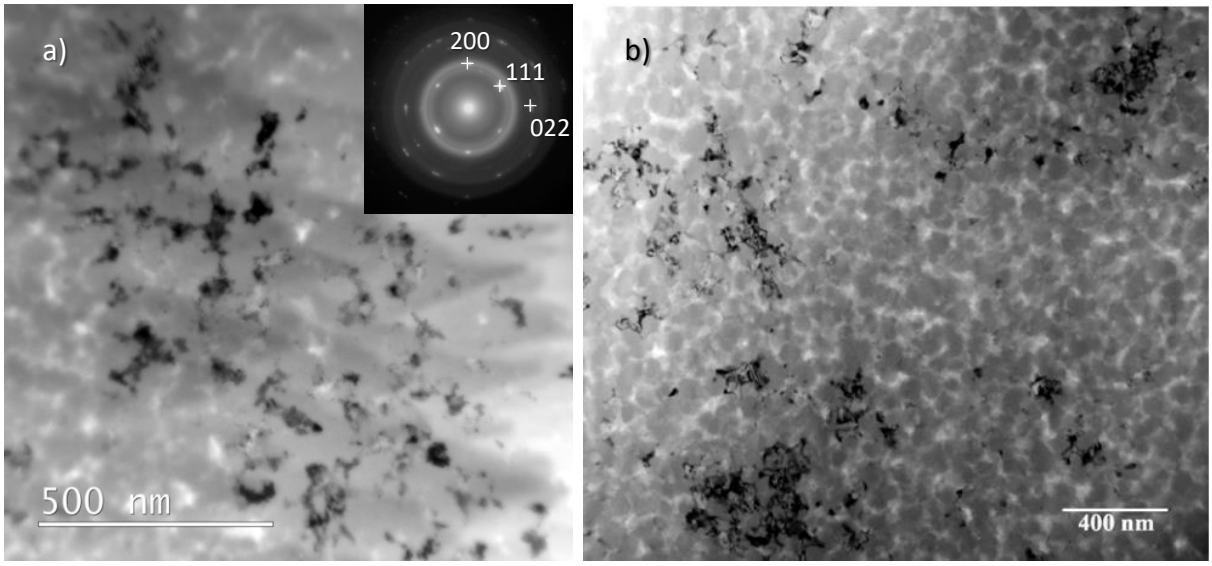

Figure 3: *a) Bright field TEM micrograph of the as-quenched $Al_{65}Fe_{15}Si_{20}$ showing grey amorphous nodules separated by bright or black fcc-Al crystalline areas. Inset SAD from whole displayed area shows diffraction pattern of fcc-Al in [011] orientation and amorphous background. b) Bright-field TEM of $Al_{70}Fe_{13}Si_{17}$ by Cahn and Bendersky* [12] *show similar morphology.*

TEM micrograph of the as-cast $Al_{65}Fe_{15}Si_{20}$ ribbon (Figure 3a) reveals two phase mixture containing thin bright or black layers separating the grey nodules (in bright-field) that is very similar to the microstructure of the as-quenched $Al_{70}Fe_{13}Si_{17}$ on Figure 3b obtained by Cahn and Bendersky [12]. The selected-area diffraction obtained from the nodule (not shown here) reveals its mainly amorphous structure. On the other hand the bright area separating nodules has crystalline structure that is confirmed by selected area diffraction (SAD) showing fcc-Al [0 1 1] zone axis pattern and amorphous background. The SAD obtained from areas > 10 μm apart shows similar orientation of fcc-Al crystals. It suggests that these areas are interconnected and may belong to a one single crystal or have been formed under the same conditions e.g. during solidification by rapid quenching.

The observed separation into two components is explained in [12] by nucleation and growth of the amorphous nodules (of so called q-glass) from the undercooled melt. According to this theory, layers of crystalline Al are originated from the melt depleted of Fe and Si left between the growing nodules of the q-glass. However, this explanation does not agree well with our experimental data that revealed that the fcc-Al layers over a large area have the same orientation.

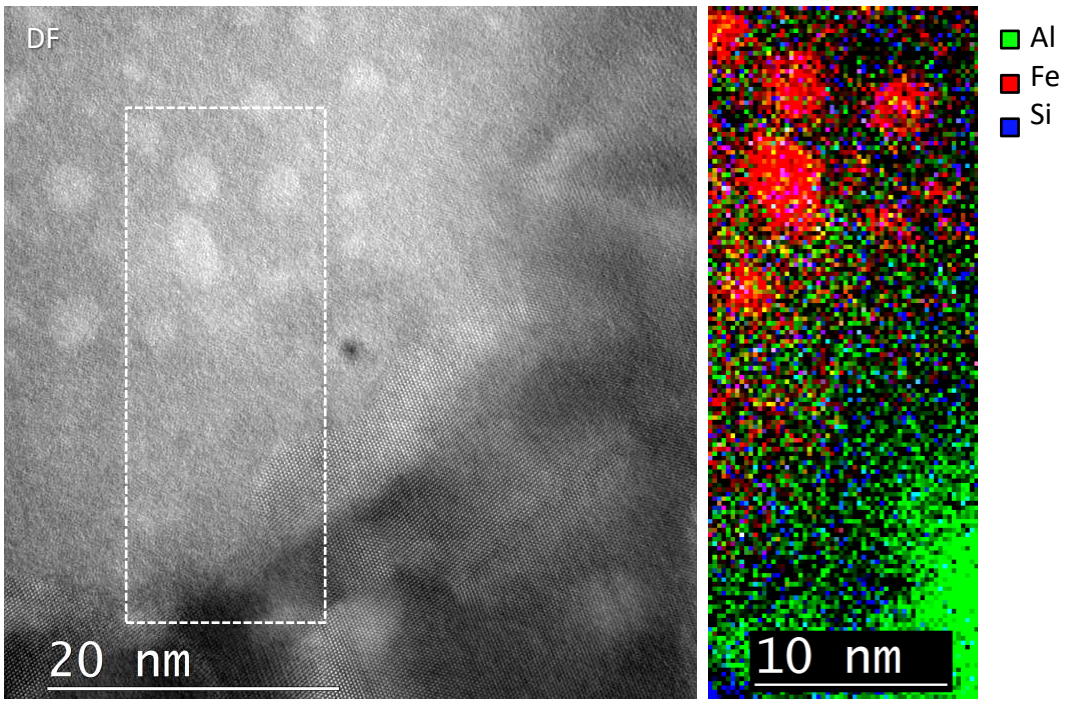

Figure 4: STEM DF image (left) of the crystalline-amorphous interface with EELS elemental map (right) obtained from indicated area.

The same type of nodules which are appearing in amorphous part of structure displayed on Figure 3 was further analyzed by EELS elemental mapping. Figure 4 shows

dark-field STEM image with indicated area for elemental mapping. Elemental map shows Al-rich area on the bottom which can be assigned to fcc-Al. Upper part of the elemental map shows amorphous phase containing Al, Fe and Si with embedded Fe-rich amorphous nodules.

Annealing of $Al_{65}Fe_{15}Si_{20}$ up to 623 K results in microstructure (Figure 5) with several particle types embedded in amorphous matrix. The particles according to morphology can be divided to three classes. The smallest crystalline nanoparticles are of size ≈ 5 nm, bigger ones are of size ≈ 70 nm. Particles as big as 1 – 1,5 μm are marked on Figure 5. Morphology of the biggest particle reminds of eutectic colony found in $Fe_{40}Ni_{40}B_{20}$ glass as referred to in [19]. This article describes type of eutectic crystallization in which two phases grow cooperatively. SAD from the area of particle indicates presence of several crystallites with similar orientation. In our case, SAD (Figure 5 top) points out that this particles contain fcc-Al and either τ_4 or τ_6 (Al_3FeSi_2 and $Al_{4,5}FeSi$ respectively in [14]). SAD from area containing small particles show mainly bimodal amorphous halo as was observed by XRD in as-cast state and several diffraction spots originating probably small crystalline particles of fcc-Al and Si.

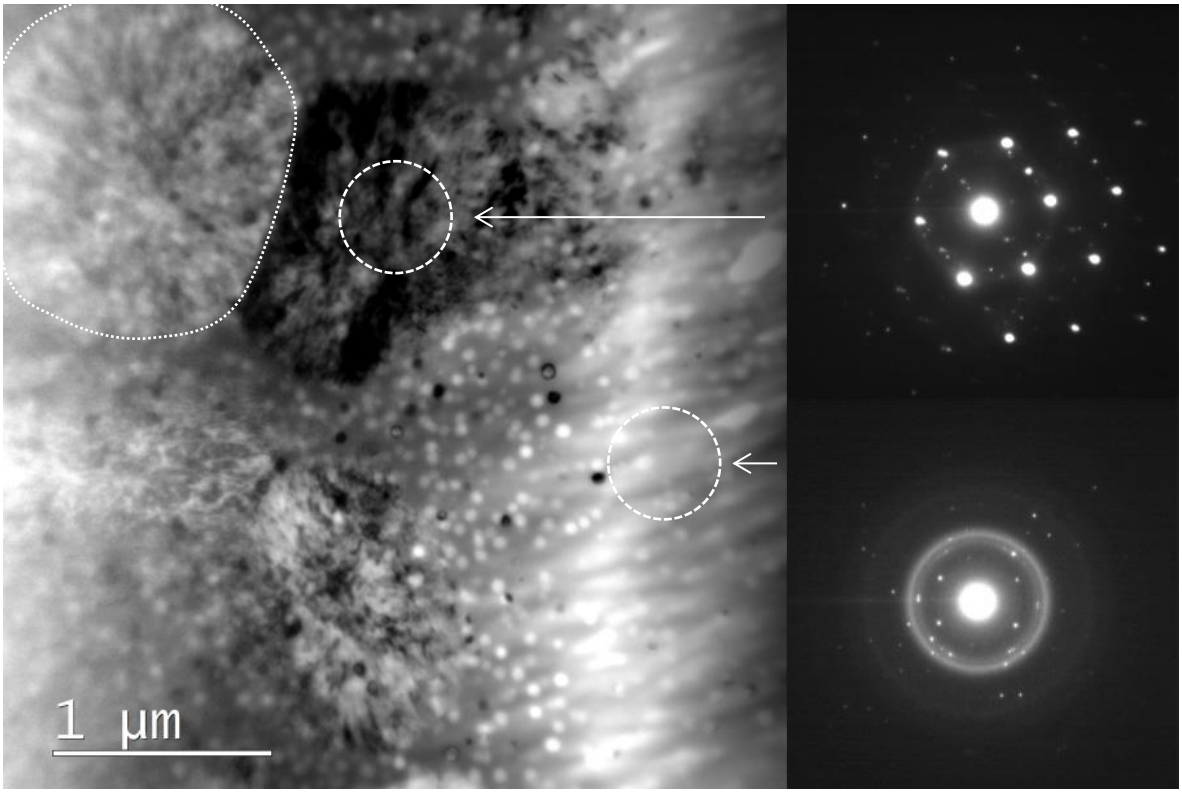

Figure 5: Bright-field TEM micrograph of annealed $Al_{65}Fe_{15}Si_{20}$ at 623 K showing three types of particles distinguished by morphology. SAD from indicated areas is shown on right-hand side. Top SAD shows mainly fcc-Al diffraction pattern and minor diffraction peaks of τ_4 or τ_6 phase. Lower SAD shows amorphous background with diffraction spots from fcc-Al and Si.

Evolution of phase content during heat-treatment was investigated in two regimes. First, samples were annealed in Ar according to DSC measurements and XRD was obtained at room temperature. Second, XRD was obtained in-situ at high temperature in He atmosphere using custom-made XRD instrument at Taras Schevchenko National University of Kiev, enabling measurements at temperatures as high as 1300K. XRD investigation temperatures were selected according to DSC/SDT measurement to obtain structure before and after each phase transformation. Example of DSC measurement of $Al_{65}Fe_{15}Si_{20}$ on Figure 6 shows at least three exothermic events and selection of annealing temperatures.

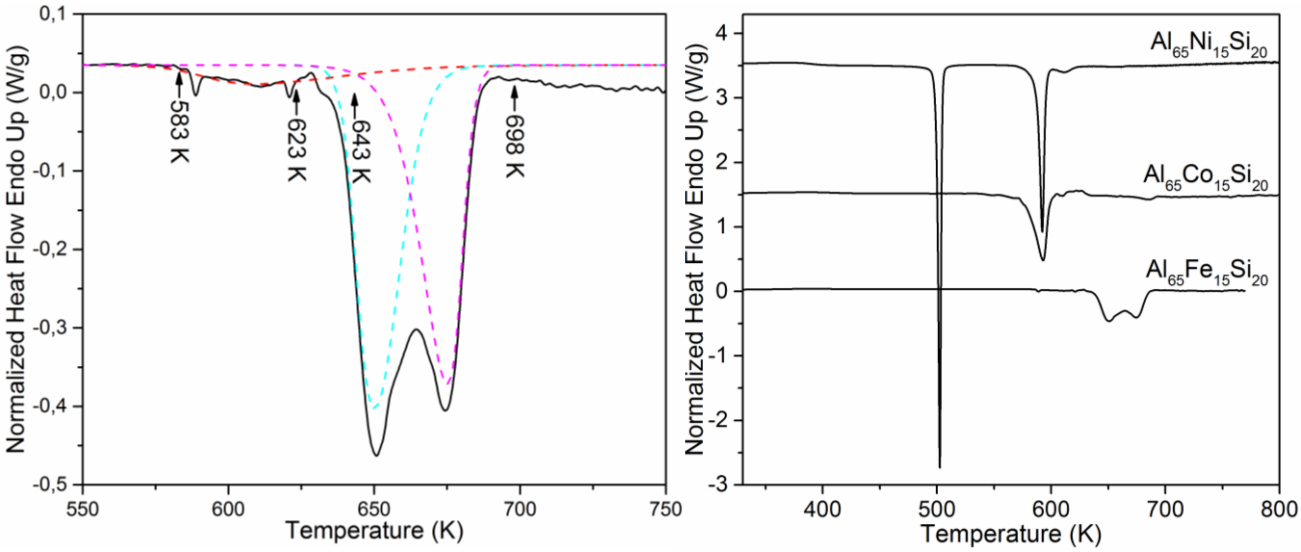

Figure 6: (left) Selection of annealing temperatures illustrated on example of $Al_{65}Fe_{15}Si_{20}$ DSC measurement. Small bumps around 583 K and 623 K are instrument effects. (right) DSC measurements of $Al_{65}TM_{15}Si_{20}$ rapidly-quenched alloys show crystallizations from initially amorphous state.

XRD of annealed $Al_{65}Ni_{15}Si_{20}$ (Figure 7) shows the presence of unknown hexagonal phase after annealing to 518 K. This hexagonal phase has been previously observed by Legresy [20]. Formation of the hexagonal phase can be assigned to first crystallization peak on DSC curve (Figure 6 right). Activation energy of transformation from initially amorphous phase to this hexagonal phase has been calculated as 233 ± 10 kJ/mol according to DSC kinetic analysis. During further heating to 598 K the hexagonal phase disappears, which suggests about its metastable nature. XRD pattern shows the presence of the fcc-Al, Si and orthorhombic Al_3Ni phases. We may suggest that second exothermic peak in DSC corresponds to disappearance of the metastable ternary (ternary according to STEM XEDS) hexagonal phase and formation of the Al, Si and Al_3Ni phases. After heating to 623 K and

763 K, no new phase in the XRD patterns were observed and the intensities of diffraction peaks for Al, Si and Al_3Ni phases increased.

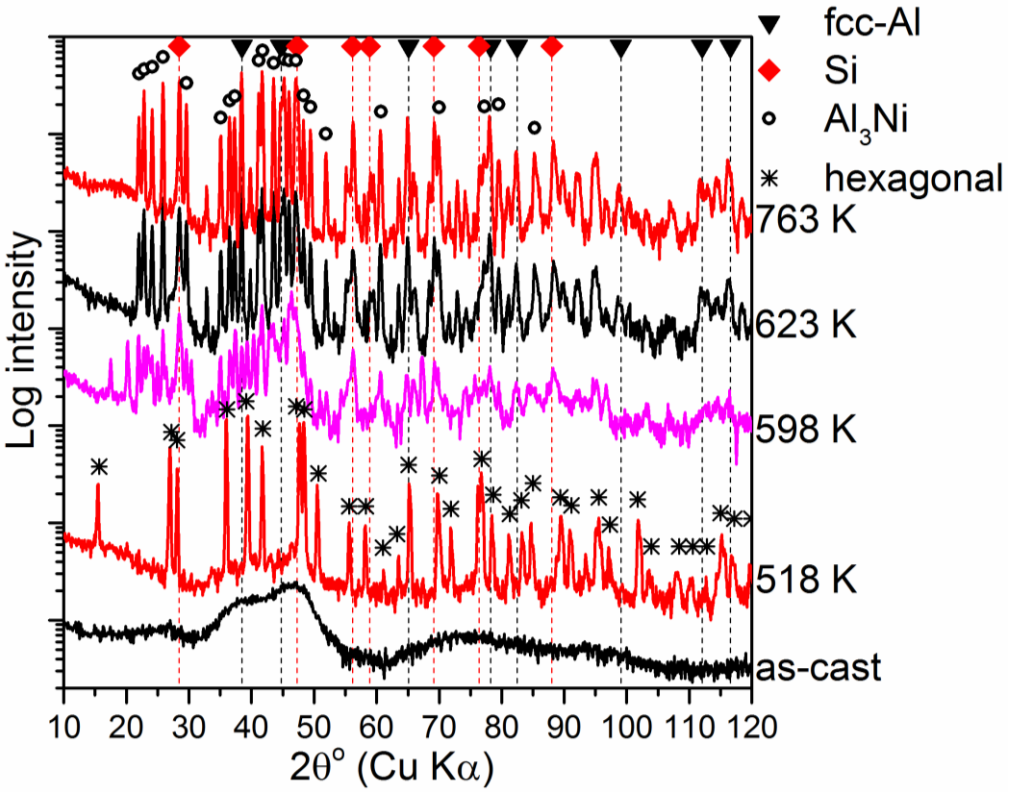

Figure 7: XRD of $Al_{65}Ni_{15}Si_{20}$ at room temperature and annealed to different temperatures. Unknown hexagonal phase appears at 518 K and transforms to fcc-Al, Si and Al_3Ni at 598 K. Resulting structure contains fcc-Al, Si and Al_3Ni.

The unknown phase that was observed by XRD in $Al_{65}Ni_{15}Si_{20}$ alloy annealed at 518 K was also observed by TEM and STEM. Bright-field TEM micrograph on Figure 8 top left reveals hexagonal phase crystals with sizes 200 – 700 nm. Inset precession nano-beam electron diffraction shows [0 0 0 1] zone axis electron diffraction pattern from indicated area. From this area STEM HAADF (Figure 8 top right) image was obtained that shows clearly distinguishable atomic columns. Color circles show estimated elemental composition of the columns according to XEDS elemental maps shown below.

By combining preliminary information about this phase (mainly XRD and STEM), phase was identified as hexagonal ternary with cell parameter specified as a = 6,6 Å, c = 3,8 Å and a/c = 1,74. According to this, number of atoms in unit cell was approximated as 9,48. Known phases with Pearson symbol hP9 and similar a/c ratio to our phase were searched resulting in fundamental structure candidate Fe_2P. This structure together with XRD data were used for Rietveld refinement. The best result (with goodness of fit = 3,95) has been achieved

assuming that the unknown ternary phase has space group 189 (P-62m), a = b = 0,66216 nm, c = 0,37987 nm.

This phase was already reported, microstructure morphology is very similar, however the structure was not completely solved [20]. According to XRD analysis described in US patent[21], the phase is identified as hexagonal with a = 0,6611 nm and c = 0,3780 nm.

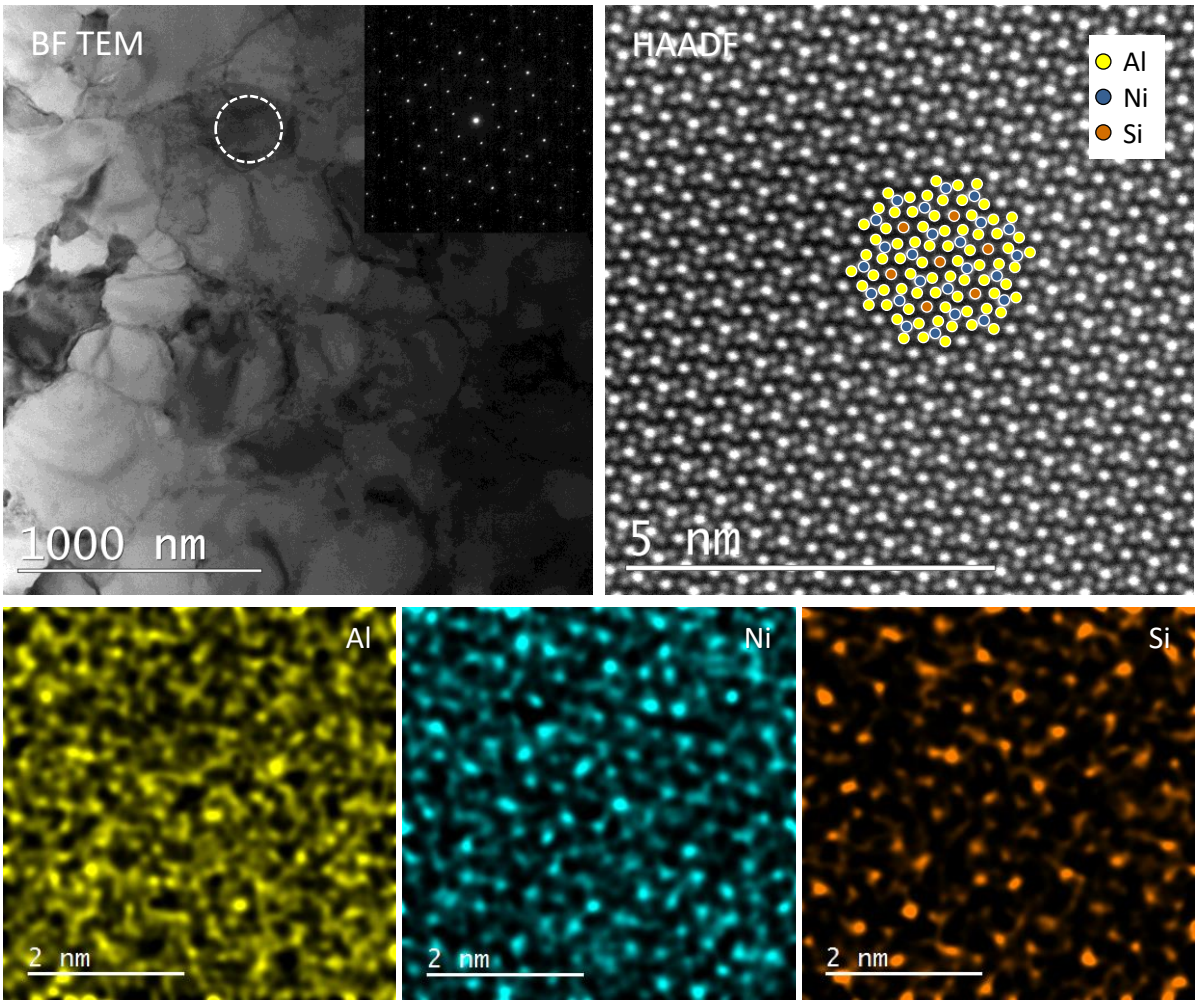

Figure 8: The same structure and electron diffraction (top left). STEM image of atomic structure of marked hexagonal crystal in [0 0 0 1] orientation (top right). Color circles mark positions of Al, Ni and Si atomic columns obtained by XEDS. Below are STEM XEDS elemental maps from the same area and orientation.

The phase evolution analysis of heat-treated systems is summarized on Figure 9. This figure shows DSC/SDT measurements obtained for Al-TM-Si systems combined with phase content at various temperatures. Generally, it is shown that the diamond-cubic Si starts to form during heat-treatment at 500 – 600 K. Annealing of the Al-Co-Si alloys caused formation of the fcc-Al, Al_9Co_2 and Si. In case of the Al-Fe-Si systems the ternary τ_4 and τ_6

phase precipitate beside Al and Si phase. Already discussed ternary hexagonal phase forms from amorphous phase in $Al_{70}Ni_{10}Si_{20}$ and $Al_{65}Ni_{15}Si_{20}$.

The temperature evolution in the Al-TM-Si systems in range from 800 K up to melting point mostly agrees with phase diagrams. However the in-situ XRD measurements point to existence of unknown phases in the $Al_{65}Ni_{15}Si_{20}$ and $Al_{70}Ni_{10}Si_{20}$ at high temperature. It was established that during heating of the quenched Al-TM-Si alloys the most prominent peaks on the in-situ XRD patterns close to melting point of fcc-Al belong to the $Fe_2Al_9Si_2$ (τ_6), Al_9Co_2, Al_3Ni phases. On the other hand after cooling from the liquid state the main phases are Al and Si.

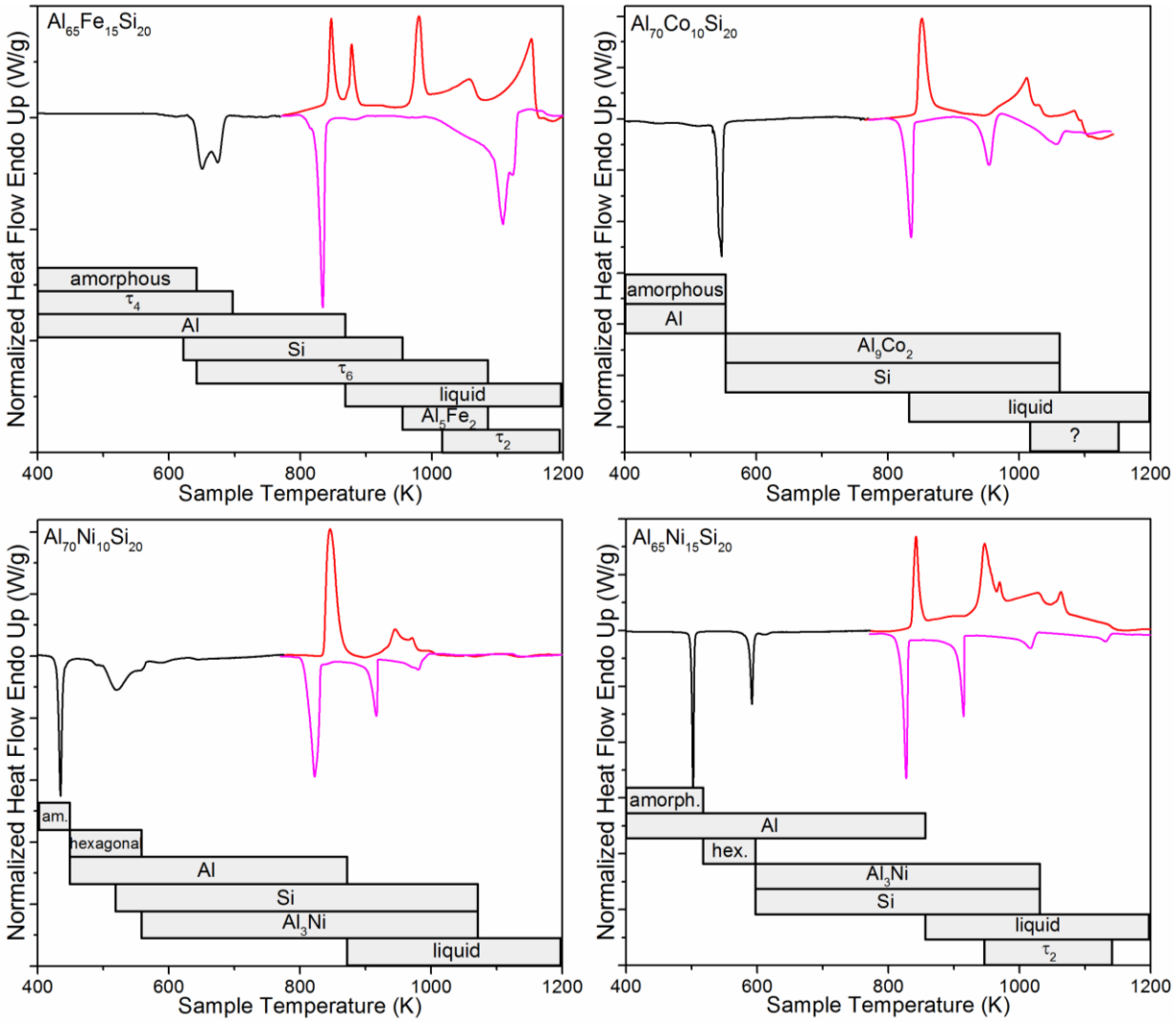

Figure 9: DSC and SDT measurements of the $Al_{80-x}TM_xSi_{20}$ alloys during linear heating/cooling (10 K/min). Below each measurement is the schematic drawing of temperature dependent phase content.

Short-range order in amorphous and liquid Al-TM-Si alloys was studied by X-ray diffraction, MD and RMC simulations. Obtained results suggest that there are atomic clusters in melts with local structure that is similar to the corresponding clusters in amorphous state. The size of these clusters and ordering between them increase during glass-formation. Both RMC and MD give partial pair correlation functions which are distinct for amorphous and melted systems. Further, according to the simulations the prepeak in the S(Q) originates from the ordering in TM–TM pair at a distance of ~ 0.45 nm. The MD simulations show that the local atomic ordering in the amorphous and liquid $Al_{65}Ni_{15}Si_{20}$, $Al_{76}Fe_{15}Si_{20}$ alloys has much in common with the crystalline $Al_9Fe_2Si_2$ (see Figure 10) and Al_3Ni phases correspondingly, which is consistent with precipitation of these phases from amorphous phase during annealing.

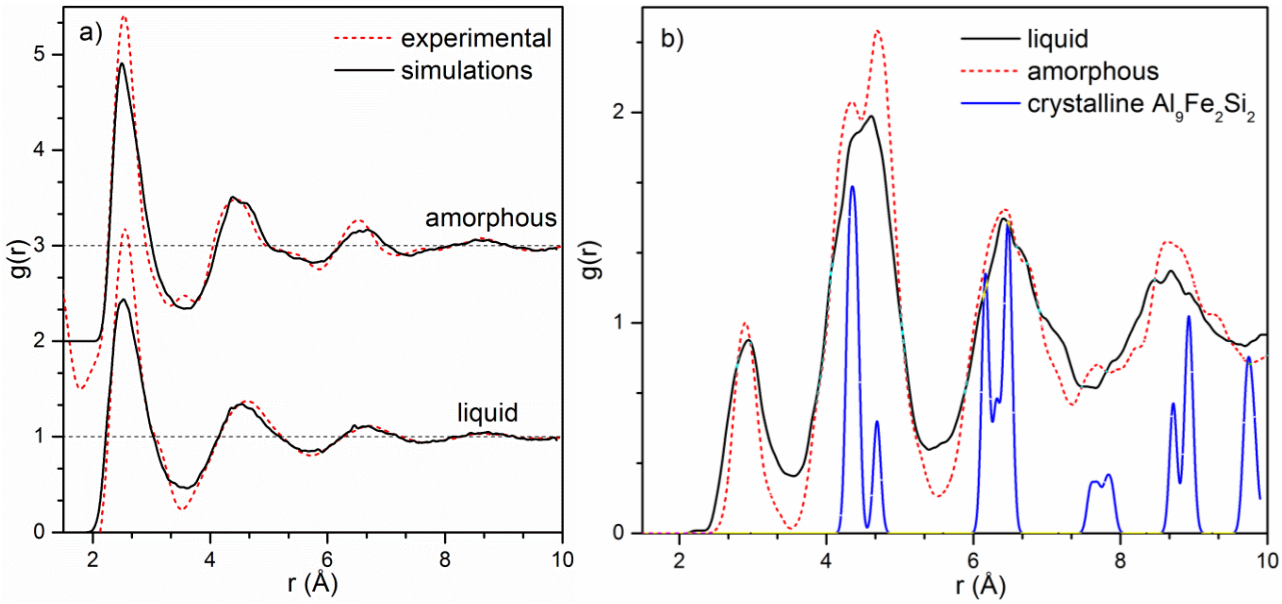

Figure 10: The experimental and calculated from MD simulations total PCF (a) and partial PCF $g_{FeFe}(r)$ calculated from MD simulations of the liquid and amorphous $Al_{65}Fe_{15}Si_{20}$. There is $g_{FeFe}(r)$ of τ_6 ($Al_9Fe_2Si_2$) phase, which scale is reduced for clarity.

The diffusion coefficients (D_i) of Al, Si, Fe/Ni atoms in liquid $Al_{65}Fe_{15}Si_{20}$ and $Al_{65}Ni_{15}Si_{20}$ were calculated using MD models at different temperatures (Figure 11). Obtained results point out that all D_i values are higher for $Al_{65}Ni_{15}Si_{20}$ alloy compared to the ones of $Al_{65}Fe_{15}Si_{20}$. If we compare D_i within a particular MD model, one can see that the lowest value of D_i is assigned to transition metal atoms. Our results are in agreement with previously published diffusion coefficients for binary liquids ($Al_{80}Ni_{20}$ [22], [23] and $Al_{95}Fe_5$ [24]) within order of magnitude.

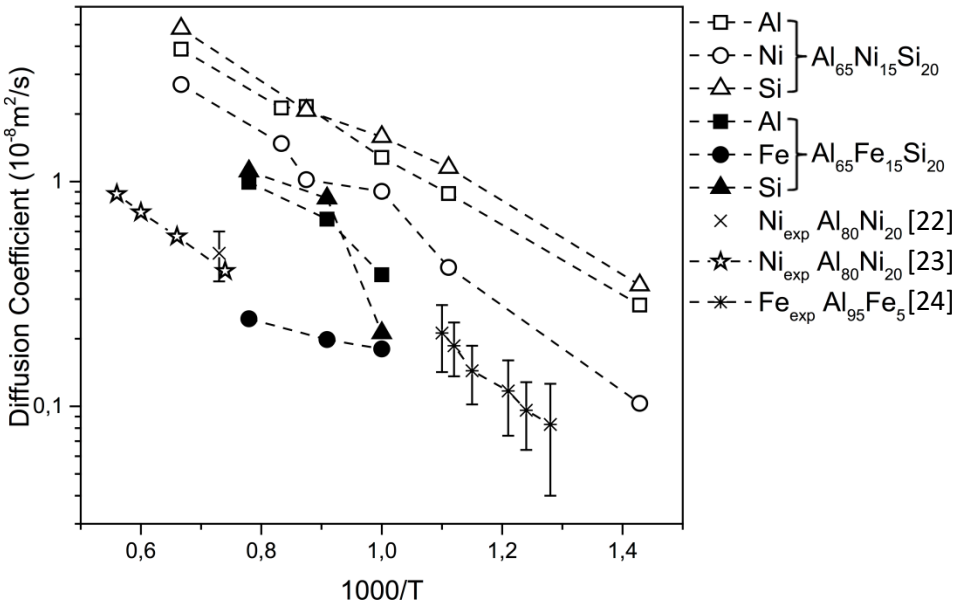

Figure 11: Diffusion coefficients of Al, Fe and Si in $Al_{65}Fe_{15}Si_{20}$ and $Al_{65}Ni_{15}Si_{20}$ calculated from MD models at different temperatures in comparison with experimental data for some binary melts.

It was shown that rapidly-quenched Al-based systems with high content of Si and addition of Fe, Co or Ni belong to class of materials with high application potential mainly in aerospace industry. With suitable composition ratio of Si and transition metals, it is possible to obtain (besides nanocrystalline Al and intermetallic phases) so far unidentified or unobserved crystalline or disordered phases with supposedly unique structure and formation mechanism. Using state-of-the-art techniques (thermal analysis, atomic-resolution transmission electron microscopy, in-situ x-ray diffraction, molecular dynamics simulations and reverse Monte-Carlo algorithm), we have described formation and local ordering of these structures. We obtained detailed information about phase evolution in three of the systems in temperature range from ambient up to and above the melting point. The structural information of amorphous and melted systems was obtained (partial/total pair correlation functions) experimentally and from MD simulations and compared against each other. Phase formation and stability was described as well, containing so-far unidentified crystalline phase which was subject of detailed analysis. Valuable information was also provided about formation and morphology of so called q-glass phase. Obtained results are extending knowledge in field of Si rich Al systems with addition of Fe, Co or Ni which can be prepared only by rapid quenching of the melt.

References

[1] W. Klement, R. H. Willens, and P. O. L. Duwez, 'Non-crystalline Structure in Solidified Gold-Silicon Alloys', *Nature*, vol. 187, no. 4740, pp. 869–870, Sep. 1960.

[2] A. C. Wright, 'Neutron scattering from vitreous silica. V. The structure of vitreous silica: What have we learned from 60 years of diffraction studies?', *J. Non. Cryst. Solids*, vol. 179, no. C, pp. 84–115, 1994.

[3] K. Saksl *et al.*, 'Evidence of icosahedral short-range order in Zr70Cu30 and Zr70Cu29Pd1 metallic glasses', *Appl. Phys. Lett.*, vol. 83, no. 19, pp. 3924–3926, 2003.

[4] A. Hirata and M. Chen, 'Angstrom-beam electron diffraction of amorphous materials', *J. Non. Cryst. Solids*, vol. 383, pp. 52–58, 2014.

[5] J. W. Morris, Jr., Z. Guo, C. R. Krenn, and Y.-H. Kim, 'Advances in Physical Metallurgy and Processing of Steels. The Limits of Strength and Toughness in Steel.', *ISIJ Int.*, vol. 41, no. 6, pp. 599–611, 2001.

[6] Y. Q. Cheng and E. Ma, 'Atomic-level structure and structure-property relationship in metallic glasses', *Prog. Mater. Sci.*, vol. 56, no. 4, pp. 379–473, 2011.

[7] K. Ohtera, A. Inoue, T. Terabayashi, H. Nagahama, and T. Masumoto, 'Mechanical-Properties of an Al88.5ni8mm3.5 (Mm, Misch Metal) Alloy Produced by Extrusion of Atomized Amorphous Plus Fcc-Al Phase Powders', *Mater. Trans. Jim*, vol. 33, no. 8, pp. 775–781, 1992.

[8] J. Jorstad and D. Apelian, 'Hypereutectic al-si alloys: Practical casting considerations', *Int. J. Met.*, vol. 3, no. 3, pp. 13–36, 2009.

[9] C. L. Xu, H. Y. Wang, F. Qiu, Y. F. Yang, and Q. C. Jiang, 'Cooling rate and microstructure of rapidly solidified Al-20 wt.% Si alloy', *Mater. Sci. Eng. A*, vol. 417, no. 1–2, pp. 275–280, 2006.

[10] M. Rajabi, M. Vahidi, A. Simchi, and P. Davami, 'Effect of rapid solidification on the microstructure and mechanical properties of hot-pressed Al-20Si-5Fe alloys', *Mater. Charact.*, vol. 60, no. 11, pp. 1370–1381, 2009.

[11] G. G. Long *et al.*, 'Highly ordered noncrystalline metallic phase', *Phys. Rev. Lett.*, vol. 111, no. July, pp. 1–4, 2013.

[12] J. W. Cahn and L. A. Bendersky, 'An isotropic glass phase in Al-Fe-Si formed by a first order transition', *Proc. Amorph. Nanocrystalline Met.*, vol. 806, no. MM2.7.1, 2004.

[13] J. Zigo *et al.*, 'Evolution of Complex Phases in Al-Fe-Si Systems', *Mater. Res.*, vol. 18, pp. 141–145, Nov. 2015.

[14] V. Raghavan, 'Al-Fe-Si (Aluminum-Iron-Silicon)', *J. Phase Equilibria Diffus.*, vol. 30, no. 2, pp. 184–188, 2009.

[15] A. Inoue, K. Ohtera, and T. Masumoto, 'Recent progress on aluminum base amorphous alloys', *Sci. Reports Res. Institutes, Tohoku Univ. Ser. A (Physics, Chem. Metall.*, vol. 35, no. 1, pp. 115–164, 1990.

[16] H. Wang, H. M. Fu, H. F. Zhang, and Z. Q. Hu, 'A practical thermodynamic method to calculate the best glass-forming composition for bulk metallic glasses', *Int. J. Nonlinear Sci. Numer. Simul.*, vol. 8, no. 2, pp. 171–178, 2007.

[17] V. Sudavtsova, L. Romanova, N. Kotova, and T. Zinevich, 'Thermochemical properties of ternary Si-Ni-Al liquid alloys', *Powder Metall. Met. Ceram.*, vol. 46, no. 3, pp. 169–174, 2007.

[18] D. S. Kanibolotsky, O. A. Bieloborodova, N. V. Kotova, and V. V. Lisnyaka, 'Enthalpy of mixing in liquid Al-Fe-Si alloys at 1750 K', *Thermochim. Acta*, vol. 408, no. 1–2, pp. 1–7, 2003.

[19] A. L. Greer, *4 Metallic Glasses*, Fifth Edit. Elsevier B.V., 2014.
[20] J. M. Legresy, M. Audier, and P. Guyot, 'Characterization and kinetics of the crystallization of AlNiSi amorphous alloys', *Mater. Sci. Eng.*, vol. 97, no. C, pp. 385–390, 1988.
[21] S. Dermarkar, 'Amorphous Al-based alloys essentially containing Ni and/or Fe and Si and process for the production thereof', U.S. patent no: 4731133, 1988.
[22] J. Horbach, S. K. Das, A. Griesche, M.-P. Macht, G. Frohberg, and A. Meyer, 'Self-diffusion and interdiffusion in Al80Ni20 melts: Simulation and experiment', *Phys. Rev. B*, vol. 75, no. 17, p. 174304, Apr. 2007.
[23] N. Jakse and A. Pasturel, 'Dynamic properties and local order in liquid Al-Ni alloys', *Appl. Phys. Lett.*, vol. 105, no. 13, 2014.
[24] N. Isono, P. M. Smith, D. Turnbull, and M. J. Aziz, 'Anomalous diffusion of Fe in liquid Al measured by the pulsed laser technique', *Metall. Mater. Trans. a-Physical Metall. Mater. Sci.*, vol. 27, no. 3, pp. 725–730, 1996.

List of relevant publications

2017

ZIGO, Juraj - ROIK, Oleksandr - ŠVEC, Peter - MIHALKOVIČ, Marek - ŠVEC Jr., Peter – MAŤKO, Igor. Study of the Al-T-Si (T = Fe, Co, Ni) alloys in the solid, liquid and as-quenched states, In: Journal of Alloys and Compounds, (currently under review)

2016

JANOTOVÁ, Irena - ŠVEC, Peter - ŠVEC, Peter Jr. - MAŤKO, Igor - JANIČKOVIČ, Dušan -**ZIGO, Juraj**. The comparison of rapidly quenched Co-Sn-B and Fe-Sn-B alloys. In C-MAC Days 2016 : Program and Abstracts. - Bratislava : VEDA, 2016, p. P-07. ISBN 978-80-224-1540-8. Typ: **AFL**

ROIK, O. - **ZIGO, Juraj** - ŠVEC, Peter. What is difference in local atomic ordering of liquid and amorphous Al-Fe(Co, Ni)-Si alloys. In C-MAC Days 2016 : Program and Abstracts. - Bratislava : VEDA, 2016, p. C-12. ISBN 978-80-224-1540-8. Typ: **AFH**

ŠVEC, Peter Jr. - JANOTOVÁ, Irena - **ZIGO, Juraj** - MAŤKO, Igor - JANIČKOVIČ, Dušan - MARCIN, Jozef - ŠKORVÁNEK, Ivan - ŠVEC, Peter. Development of selected amorphous and nanocrystalline soft magnetic systems with enhanced functional properties. In 16th Czech and Slovak Conference on Magnetism : Book of Abstracts. Košice, 13.-17.6.2016. Ed. P. Sovák et al. - Košice : UPJŠ and ÚEF SAV, 2016, p. 85. ISBN 978-80-971450-9-5.(Czech and Slovak conference on magnetism). Typ: **AFB**

ZIGO, Juraj - ROIK, O. - ŠVEC, Peter. Phase transformations up to melting point in Al-(Fe, Co, Ni)-Si alloys. In C-MAC Days 2016 : Program and Abstracts. - Bratislava : VEDA, 2016, p. P-16. ISBN 978-80-224-1540-8. Typ: **AFL**

2015

ČAVOJSKÝ, Miroslav - ŠVEC, Peter - ŠVEC, Peter Jr. - **ZIGO, Juraj** - MAŤKO, Igor - SIMANČÍK, František. The annealing behaviour of rapid solidification processed Al-Mo-Fe alloys. In ISMANAM 2015 : 22nd International Symposium on Metastable, Amorphous and

Nanostructured Materials, July 13-17, 2015, Paris, France. Book of Abstracts. - Paris, 2015, p. 294. Typ: **AFK**

JANIČKOVIČ, Dušan - ŠVEC, Peter Jr. - MAŤKO, Igor - NOSKO, Martin - JANOTOVÁ, Irena - **ZIGO, Juraj** - ŠVEC, Peter. Amorphous Ni-based composite prepared by direct melt-spinning. In ISMANAM 2015 : 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials, July 13-17, 2015, Paris, France. Book of Abstracts. - Paris, 2015, p. 295. Typ: **AFK**

JANOTOVÁ, Irena - **ZIGO, Juraj** - ŠVEC, Peter Jr. - MAŤKO, Igor - JANIČKOVIČ, Dušan - ŠVEC, Peter. Analysis of phase transformations in Fe-(Co)-B-Si-(P). In Journal of Alloys and Compounds, 2015, vol. 643, s265-S269. (2.999 - IF2014). (2015 - Current Contents, WOS, SCOPUS). ISSN 0925-8388. Typ: **ADCA**

JANOTOVÁ, Irena - **ZIGO, Juraj** - ŠVEC, Peter Jr. - MAŤKO, Igor - JANIČKOVIČ, Dušan - ŠVEC, Peter. Crystallization in rapidly quenched Fe-B-Si system with additions of C and Cu. In Materials Research, 2015, vol. 18, suppl, p. 136-140. (0.793 - IF2014). ISSN 1516-1439. Typ: **ADMA**

JANOTOVÁ, Irena - **ZIGO, Juraj** - ŠVEC, Peter Jr. - MAŤKO, Igor - JANIČKOVIČ, Dušan - ŠVEC, Peter. Crystallization in rapidly quenched Fe-B-Si system with additions of C and Cu. In C-MAC Euroschool 2015. Materials Synthesis and Characterization Applied to Complex Metallic Alloys, June 1-5, 2015, Bratislava, Slovakia : Program and Abstracts. - Bratislava : VEDA, 2015, p-10. ISBN 978-80-224-1441-8. Typ: **AFK**

JANOTOVÁ, Irena - MAŤKO, Igor - ŠVEC, Peter Jr. - **ZIGO, Juraj** - JANIČKOVIČ, Dušan - ŠVEC, Peter. Structure of rapidly quenched Fe-CO-SN-B systems with varying Fe/CO ratio. In APCOM 2015 : Proceedings of the 21st International Conference on Applied Physics of Condensed Matter, June 24-26, 2015, Štrbské Pleso, Slovak Republic. Eds. J. Vajda, I. Jamnický ; rev. J. Sitek, P. Ballo et al. - Bratislava : STU, 2015, p. 164-169. ISBN 978-80-227-4373-0. Typ: **AFD**

JANOTOVÁ, Irena - ŠVEC, Peter - MAŤKO, Igor - ŠVEC, Peter Jr. - JANIČKOVIČ, Dušan - **ZIGO, Juraj.** Structure of rapidly quenched Fe-Co-Sn-B systems with varying Fe/Co ratio. In Journal of Electrical Engineering, 2015, vol. 66, no. 5, p. 297-300. (0.378 - IF2014). (2015 - INSPEC, SCOPUS, WOS). ISSN 1335-3632. Typ: **ADNA**

JANOTOVÁ, Irena - MAŤKO, Igor - ŠVEC, Peter Jr. - **ZIGO, Juraj** - JANIČKOVIČ, Dušan - MARCIN, Jozef - ŠKORVÁNEK, Ivan - ŠVEC, Peter. The influence of Fe/Co ratio on structure and magnetic properties in Fe-Co-Sn-B based RQ systems. In ISMANAM 2015 : 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials, July 13-17, 2015, Paris, France. Book of Abstracts. - Paris, 2015, p. 322. Typ: **AFK**

MAŤKO, Igor - JANOTOVÁ, Irena - ŠVEC, Peter Jr. - **ZIGO, Juraj** - ŠVEC, Peter - JANIČKOVIČ, Dušan - ŠKORVÁNEK, Ivan. Investigation of phases eleborated by thermally activated crystallization of amorphous Fe/Co-Sn-B ribbons. In ISMANAM 2015 : 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials, July 13-17, 2015, Paris, France. Book of Abstracts. - Paris, 2015, p. 233. Typ: **AFK**

ŠVEC, Peter Jr. - **ZIGO, Juraj** - JANOTOVÁ, Irena - MAŤKO, Igor - ČAVOJSKÝ, Miroslav - JANIČKOVIČ, Dušan - MARCIN, Jozef - ŠKORVÁNEK, Ivan - ŠVEC, Peter. New rapidly quenched alloy systems and their processing. In ISMANAM 2015 : 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials, July 13-17, 2015, Paris, France. Book of Abstracts. - Paris, 2015, p. 93. Typ: **AFK**

ŠVEC, Peter Jr. - **ZIGO, J**. - NOWICKI, M. - JACKIEWICZ, D. - FRANKO, M. - HAMELA, M. - WINIARSKI, W. - SZEWCZYK, R. - ŠKORVÁNEK, Ivan - ŠVEC, Peter. Preparation, processing and selected properties of modern melt- quenched alloys. In Mechatronics- Ideas for Industrial Application : Advances in Intelligent Systems and Computing. Vol. 317. - Springer International Publishing, 2015, p. 381- 396. ISBN 978-3-319-10990-9. Typ: **AECA**

ŠVEC, Peter Jr. - **ZIGO, Juraj** - JANOTOVÁ, Irena - JANIČKOVIČ, Dušan - MARCIN, Jozef - ŠKORVÁNEK, Ivan - ŠVEC, Peter. Structure and properties of equiatomic Fe-M-Nb-B (M=Co, Ni) and M-rich metallic glasses. In C-MAC Euroschool 2015. Materials Synthesis and Characterization Applied to Complex Metallic Alloys, June 1-5, 2015, Bratislava, Slovakia : Program and Abstracts. - Bratislava : VEDA, 2015, p-14. ISBN 978-80-224-1441-8. Typ: **AFK**

ZIGO, Juraj - ŠVEC, Peter Jr. - JANOTOVÁ, Irena - MAŤKO, Igor - ČAVOJSKÝ, Miroslav - JANIČKOVIČ, Dušan - ŠVEC, Peter. Enhancement of Si content in rapidly quenched Al-Si based systems containin transition elements. In ISMANAM 2015 : 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials, July 13-17, 2015, Paris, France. Book of Abstracts. - Paris, 2015, p. 240. Typ: **AFK**

ZIGO, Juraj - ŠVEC, Peter Jr. - JANIČKOVIČ, Dušan - JANOTOVÁ, Irena - MAŤKO, Igor - MIHALKOVIČ, Marek - ŠVEC, Peter. Evolution of complex phases in Al-Fe-Si systems. In Materials Research, 2015, vol. 18, suppl, p. 141-145. (0.793 - IF2014). ISSN 1516-1439. Typ: **ADMA**

2014

JANOTOVÁ, Irena - **ZIGO, J**. - ŠVEC, Peter Jr. - MAŤKO, Igor - JANIČKOVIČ, Dušan - ŠVEC, Peter. Phase transformation in Fe-B(Si)-C-(Cu) soft magnetic systems. In Proceedings of the 20th International Conference on Applied Physics of Condensed Matter (APCOM 2014), June 25-27, 2014, Štrbské Pleso. Eds. J.Vajda, I.Jamnický. - Bratislava : FEI STU, 2014, p. 219-223. Typ: **AFD**

SZEWCZYK, R. - ŠVEC, Peter - SALACH, J. - JACKIEWICZ, D. - ŠVEC, Peter Jr. - BIEŃKOWSKI, A. - **ZIGO, J**. - WINIARSKI, W. Modelling the anisotropy of magnetic field annealed Fe61Co19Si5B15 amorphous alloy. In Proceedings of the 20th International Conference on Applied Physics of Condensed Matter (APCOM 2014), June 25-27, 2014 Štrbské Pleso. Eds. J.Vajda, I.Jamnický. - Bratislava : FEI STU, 2014, p. 35-38. Typ: **AFD**

ŠVEC, Peter Jr. - **ZIGO, Juraj** - JANOTOVÁ, Irena - MAŤKO, Igor - JANIČKOVIČ, Dušan - KOVÁČ, Jozef - ŠKORVÁNEK, Ivan - ŠVEC, Peter. Preparation, stability and post-preparation processing of rapidly quenched monolayer, bilayer and trilayer ribbons : Abstract-5. In 15th International Conference on Rapidly Quenched and Metastable Materials (RQ15), August 24-28, 2014, Shanghai, China : RQ15 Conference Proceedings, p. 58. Typ: **AFE**

ZIGO, J. - ŠVEC, Peter Jr. - JANIČKOVIČ, Dušan - JANOTOVÁ, Irena - MAŤKO, Igor - ŠVEC, Peter. Structure of new Al-Si based RQ systems with potentially enhanced stiffness. In Proceedings of the 20th International Conference on Applied Physics of Condensed Matter (APCOM 2014), June 25-27, 2014, Štrbské Pleso. Eds. J.Vajda, I.Jamnický. - Bratislava : FEI STU, 2014, p. 308-311. Typ: **AFD**

2013

JANIČKOVIČ, Dušan - **ZIGO, J.** - ŠVEC, Peter Jr. - MAŤKO, Igor - ŠVEC, Peter. On the structure evolution in q-phase rapidly solidified Al65Fe15Si20 composite. In NANOVED 2013 & NANO INFO DAY : 6th International Conference on Nanosciences, Nanotechnologies, Nanomaterials and NANO INFO DAY of the Nanoforce Project. - Brno : TRIBUN EU, 2013, p-13. ISBN 978-80-263-0511-8. Typ: **AFH**

ŠVEC, Peter Jr. - **ZIGO, Juraj** - PINČÍK, Emil - BALOG, M. - ŠVEC, Peter. Phase and orientation mapping of fine-grained structures by procession electron diffraction. In Proceedings of 8th Solid State Surfaces and Interfaces : Extended Abstract Book. - Bratislava : Comenius University, 2013, p. 181. ISBN 978-80-223-3501-0. Typ: **AFB**