

Short Lectures - B, Monday, June 11

SL - B1

CRYSTALLIZATION IN SANDWICH NANOCOMPOSITES OF PE, PP AND POM POLYMERS**M. Šlouf, T. Vacková, H. Vlková, N. H. Vu, A. Sikora, J. Kratochvíl, H. Šandová, M. Steinhart***Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic; slouf@imc.cas.cz*

Polymer nanocomposites are modern materials, formed usually by a matrix of synthetic polymer (such as polyethylene, PE, polypropylene, PP, polyoxymethylene POM...), which is filled with inorganic nanoparticles (such as oxides, metallic nanoparticles...). The inorganic fillers may influence mechanical, rheological, barrier and other properties of the final nanocomposite. In this study, we focus our attention on nucleation of polymer matrix crystallization: some nanoparticles act as nucleating agents, which means that the polymer spherulites start to grow on their surface. The nucleation effect impacts on the supermolecular structure of polymer matrix (spherulite size, overall crystallinity...) and on the crystallinity-related mechanical properties (modulus, yield strength...).

In this work, we introduce the improvements in our recently developed sandwich method [1, 2]. We also summarize the results achieved for PE, PP and POM sandwich nanocomposites. The sandwich nanocomposites consist of thin (ca 100 micrometers) polymer plates, between which a thin homogeneous layer of nanoparticles is deposited (Fig. 1a). The nucleating activity of the nanoparticles can be studied by a number of methods, such as polarized-light microscopy (PLM; Fig. 1b), differential scanning calorimetry (DSC) and two-dimensional wide angle X-ray scattering (2D-WAXS; Fig. 1c). By means of model sandwich nanocomposites PP/Au and PP/TiX, where Au stands for several types of gold nanoparticles with different morphologies and TiX stands for various TiO₂-based nanoparticles we proved that the nucleation activity is connected not only with the size, but also with the morphology

and the agglomeration of the filler. The impact of filler morphology on its nucleation activity was observed also in PE/Au, PE/TiX, POM/Au and POM/TiX nanocomposites.

The sandwich method exhibits several advantages as far as the study of nucleating activity of micro- and/or nanoparticles in polymer nanocomposites is concerned: (i) The sandwich nanocomposites are small microscopic samples and, consequently, they are suitable for testing of small amounts of special nanoculcants. (ii) The preparation of sandwich nanocomposites, if performed carefully, is highly reproducible. (iii) The nanoparticles in sandwich nanocomposites do not suffer from agglomeration, which usually leads to not-very-well reproducible results in case of bulk-prepared nanocomposites. (iv) The combination of microscopic (PLM), thermal (DSC) and scattering (2D-WAXS) methods for characterization of crystal structure of polymer matrix in sandwich nanocomposites yields detailed insight into the nucleation activity of the studied nanoparticles.

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1. E. Pavlova, M. Slouf, H. Sandova, J. Baldrian, A. Sikora, F. Lednický, R. Masírek, E. Piorkowska, *J. Macromol. Sci. Phys.*, **49**, (2010) 392.
2. M. Slouf, A. Sikora, E. Pavlova, H. Vlkova, J. Baldrian, T. Base T, E. Piorkowska, *J. Appl. Pol. Sci.*, (2012), in press, DOI 10.1002/app.36589.

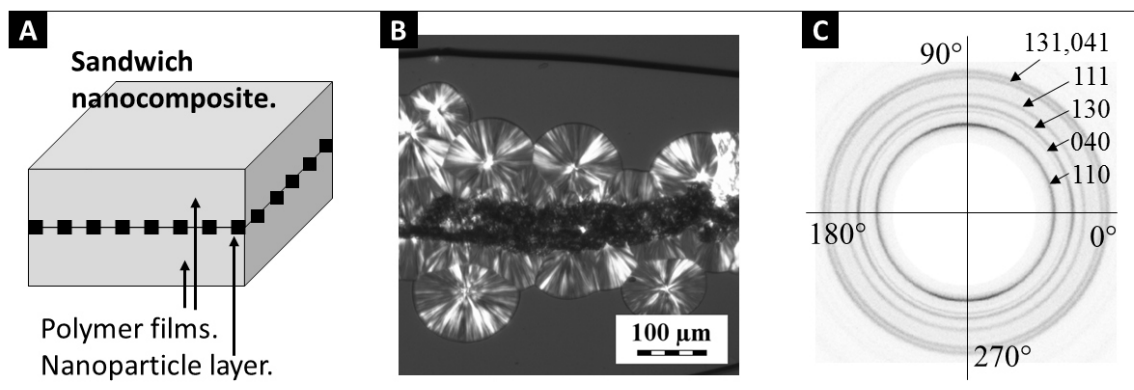


Figure 1. Principle of sandwich method: (a) Scheme of the sandwich nanocomposite. (b) PLM micrograph of the cross-section of PP/TiNT (where TiNT = titanium nanotubes) sandwich nanocomposite showing the PP spherulites growing from the central TiNT layer. (c) 2D-WAXS diffraction pattern of a sandwich nanocomposite, recorded with the beam going through the sandwich along the nanoparticle layer; the anisotropy in polymer crystallization due to nucleated crystallization demonstrates itself in the anisotropy of diffraction intensities.



SL - B2

CRYSTALLOGRAPHIC STUDY OF TERNARY SYSTEMS WITH PLATINUM-GROUP METALS

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Within the research of phase relations of the Pd-Hg-Se and Ag-Pd-Se systems, two new ternary phases Pd₅HgSe and (Ag,Pd)₂₂Se₆ were discovered. Several phases from these systems are known as minerals or as poorly characterized naturally occurring phases. Pd₅HgSe and (Ag,Pd)₂₂Se₆ phases have not yet been described as minerals. However they can be expected to be found in nature, probable in association with palladium selenides or another platinum-group minerals.

Both phases were synthesized from elements by conventional solid-state reactions. Stoichiometric amounts of individual elements were sealed in silica glass tubes and resultant mixtures were heated at selected temperatures. Samples with Pd₅HgSe and (Ag,Pd)₂₂Se₆ were heated at 400 °C. After long-term annealing, the samples were quenched in a cold-water bath. All attempts to prepare single crystals suitable for single-crystal examinations failed; consequently the crystal structures of Pd₅HgSe and (Ag,Pd)₂₂Se₆ were determined from powder X-ray diffraction data. The Rietveld refinements were performed with the FullProf program.

Pd₅HgSe: Space group *P4/mmm*, $a = 4.01 \text{ \AA}$, $c = 7.04 \text{ \AA}$, $V = 113 \text{ \AA}^3$ and $Z = 1$. The crystal structure of this compound is composed of alternating layers of the AuCu₃-type [HgPd₁₂] cuboctahedra and the PtHg₂-type [SePd₈] rectangular prism. These rectangular prisms share the four Pd-Pd

edges running parallel to *c* direction, with four adjacent rectangular prisms forming a layer parallel to (001) plane. The layers of [SePd₈] rectangular prism and [HgPd₁₂] cuboctahedra are connected by the common edges formed by the Pd atoms. This phase represents the structural antitype to the HoCoGa₅ structure type [1].

(Ag,Pd)₂₂Se₆: Space group *Fm3m*, $a = 12.31 \text{ \AA}$, $V = 1868 \text{ \AA}^3$ and $Z = 4$. This structure can be viewed as a $3a.3a.3a$ superstructure of cubic Pd ($a = 3.89 \text{ \AA}$), where only 4 from 108 octahedral holes are occupied. The Ag and Pd atoms are expected to substitute each other and form mixed sites. The main structural building unit are the [Pd/Ag]₁₂ cuboctahedra and [Pd/Ag]₈ cubes, which alternate in the NaCl fashion. Both polyhedra are centred by (Pd/Ag) atoms. The (Ag,Pd)₂₂Se₆ crystal structure shows close structural relation to the Cr₂₃C₆ and Mn₂₃Th₆ type structures, nevertheless it represents a distinct structural type.

1. F. Laufek, A. Vymazalová, M. Drábek, J. Navrátil, T. Plecháček, J. Drahokoupil, *S. State Chemistry*, (submitted) (2012).

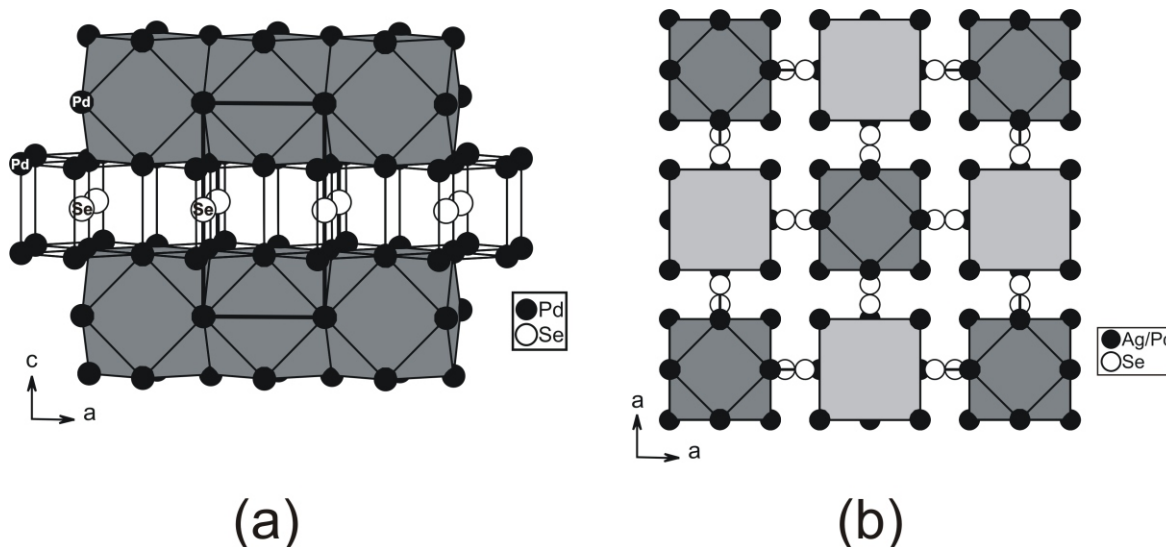


Figure 1. (a) Polyhedral representation of Pd₅HgSe structure emphasizing the [HgPd₁₂] cuboctahedra and [SePd₈] rectangular prisms. Unit cell edges are highlighted. (b) Schematical view of the (Ag,Pd)₂₂Se₆ crystal structure showing the [Pd/Ag]₁₂ cuboctahedra and [Pd/Ag]₈ cubes.

SL - B3

STUDIUM ATOMOVÉHO USPOŘÁDÁNÍ Ni-Mn-Ga POMOCÍ RENGENOVÉ DIFRAKCE**K. RichtEROVÁ, J. DRAHOKOUPIL, O. HE CZKO***Institute of Physics of the ASCR, v.v.i.; Na Slovance 2, 18221 Prague 8, Czech Republic
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Single crystals of stoichiometric Ni₂MnGa were studied using the X-ray powder diffractometer. The crystal at room temperature is in cubic state called austenite. Diffraction spectra of quenched and annealed states of the austenite were compared. The extinction of 200 lines of the diffraction spectrum was observed in the quenched sample. The extinction is likely caused by a disordered structure.

Úvod

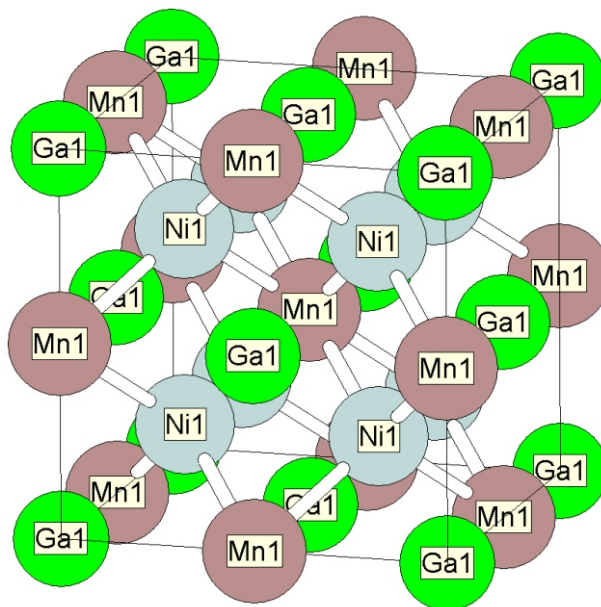
Nedávno bylo objeveno, že některé slitiny typu Ni-Mn-Ga vykazují obří deformaci v magnetickém poli [1]. Tento nový jev, fundamentálně odlišný od magnetostrikce, se nazývá jev magnetické tvarové paměti. Obří deformace je výsledkem reorientace nekubické atomové mřížky, ke které dochází pohybem hranic dvojčatění v magnetickém poli [1-2]. Slitiny Ni-Mn-Ga vykazují i další zajímavé fyzikální jevy jako je magnetokalorický a elastokalorický jev a tvarová paměť [3]. Proto jsou tyto slitiny v současné době intenzivně studovány. Ni-Mn-Ga patří do rodiny Heuslerových slitin, které vykazují atomové uspořádání na dlouhou vzdálenost. Očekává se, že uspořádání má vliv na martensitickou transformaci z vysokoteplotní kubické fáze zvané austenit na fázi s nižší symetrií zvanou martensit. V práci jsme studovali vliv žhání a rychlosti chlazení na atomové uspořádání v austenitu.

Krystalografická struktura

Předmětem studia byl monokrystal Ni₅₀Mn₂₅Ga₂₅ (at.%) od firmy AdaptMat Ltd. Při daném složení má NiMnGa za pokojové teploty kubickou mříž s prostorovou grupou $Fm\bar{3}m$ a mřížkovými parametry $a = 5,832$ nm a $\alpha = 90^\circ$. Při teplotách nad 1100 K jsou atomy Mn a Ga náhodně uspořádány v základní buňce (uspořádání B2'), zatímco při pokojové teplotě se usazují na pozicích s frakčními souřadnicemi Ga: 0 0 0; Mn: 0,5 0,5 0,5; Ni: 0,25 0,25 0,25 a 0,75 0,75 0,75 [4-5]. Základní buňka je znázorněna na obrázku 1.

Experimentální část

RTG měření proběhlo na horizontálním práškovém diffraktometru X'Pert PRO PANalytical. Zdrojem záření byla kobaltová anoda ($\lambda = 1,78901$ Å) s bodovým ohniskem. Ozářený objem byl vymezen monokapilárou s vnitřním poloměrem 0,1 mm. Vzorek byl upevněn na texturní nástavec ATC-3, který umožňuje rotaci, náklon a posuv vzorku ve směru osy x. Současný pohyb zdroje a detektoru umožňuje jemnou a přesnou změnu úhlu (2θ) dopadajícího záření. Nejdříve byl vzorek zorientován ve směru laboratorního systému. Provedli jsme několik θ -skenů pro různé



Obrázek 1. Základní buňka uspořádaného kubického austenitu Ni₂MnGa.

úhly 2θ , dokud jsme nenalezli orientaci maximum silné difrakce (400). Linie (400) je fundamentální a proto nezávisí na stupni uspořádání. Poté bylo proměřeno celé spektrum.

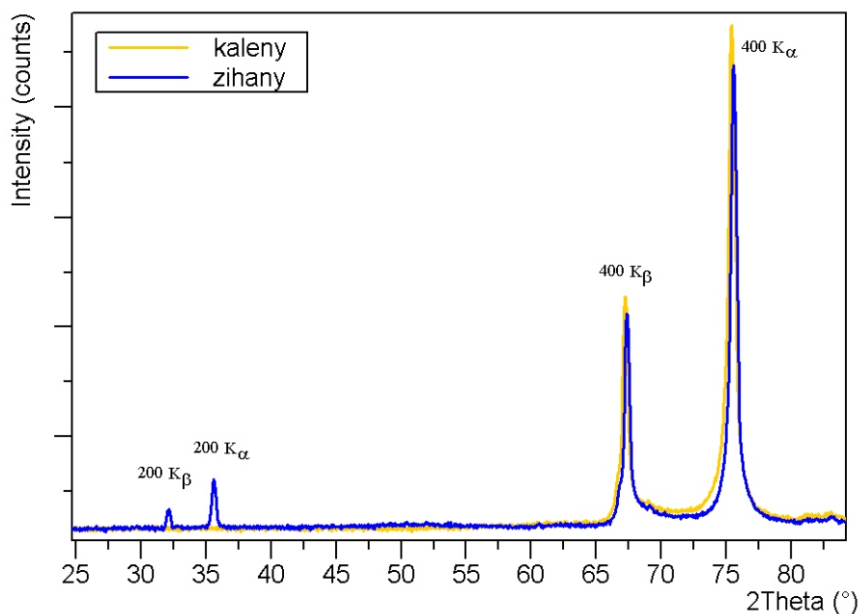
Výsledky a diskuse

Byly měřeny dva monokrystalické vzorky: jeden po žhání a chlazení v peci a druhý v zakaleném stavu. Na obrázku 2 vidíme jejich difrakční záznam (θ -sken) pro orientaci vzorků vzorku ve směru [100].

Z obrázku je patrné úplné vyhasínání linie (200) kaleného vzorku. Linie (200) je superstrukturní linie příslušná uspořádání L2₁. Vyhasínání je proto možné interpretovat jako neuspořádanost kalené struktury. Dále jsme hledali přítomnost další superstrukturní linie (111). V presentace budeme diskutovat i jiné možné interpretace vyhasínání reflexí.

Poděkování

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Obrázek 2. Žiháný vzorek (tmavá čára) a vzorek v zakaleném stavu (světlá čára).

Reference

1. K. Ullakko et al. Appl. Phys. Lett. **69** (1996) 1966.
2. O. Heczko, A. Sozinov, K. Ullakko, IEEE Trans Mag **36** (2000) 3266.
3. O. Söderberg, I. Aaltio, Y. Ge, O. Heczko and S.-P. Hannula, Mat. Sci. Eng. A **481–482** (2008), 80–85.
4. K. H. J. Buschov, P.G. van Engen, R. Jongebreu thesiss, *J. Magn. Magn. Mat.*, **38**, 1 (1983), 1-22.
5. R. W. Overholser, M. Wuttig, and D. A. Neumann, Scripta Mater. **40**, 1095 (1999).

SL - B4

STRUCTURE OF QUASICRYSTALLINE MATERIAL

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Quasicrystals are studied for their possibilities of practical applications. The most interesting are properties such as low friction coefficient, high hardness, wear resistance, and oxidation; and low electrical and thermal conductivity [1]. This efficiency is limited by high brittleness and low deformability at the room temperature. These drawbacks are decreased in applications using quasicrystalline materials like composite or coating material. Quasicrystalline materials based on Al-Cu-Fe are becoming the most researched materials in this field.

This study determined the structure of quasicrystalline powder based on Al-Cr-Fe. The same material will be ap-

plied on the coating of Al-alloy surface by means cold plasma spray coating or thermal spraying [2].

The X-ray diffraction phase analysis of the powder exhibited the presence of majority of hexagonal $\text{Al}_{49.74}\text{Cr}_{21.41}\text{Fe}_{5.35}$, and rest of -Fe and Al_5Fe_2 phases.

1. H.S. Jeevan and S. Ranganathan. *J. Non-Cryst. Solids*, **184** (2004) 334.
2. J. Cizek, K.A. Khor, *Surf Coat Tech*, **206 (8-9)** (2012) 2181.