Particle morphology of energetic materials to a great extent defines their sensitivity and reactivity properties. The morphology in its turn strongly depends on the crystallization process. In the present research the thermal crystallization of pentaerythrol tetranitrate (PETN) explosive and ammonium perchlorate (AP) was studied by differential scanning calorimetry (DSC) and FT-IR spectroscopy. DSC test usually included the heating of the sample with the constant rate of 5°C/min to the temperature which was several degrees higher than the melting temperature and then the cooling of the sample with the different cooling rates. The cooling led to the crystallization. The crystallization temperature, heat and rate were measured. The newly crystallized samples were then subjected to microscopic inspection and FT-IR spectroscopy.

It was found that the crystallization of AP takes place in two stages. The first high temperature stage proceeds at temperatures higher than the melting temperature and starts just after beginning of cooling. The second low temperature stage occurs at temperature significantly less than the melting temperature, e.g. the crystallization is realized from the overcooled liquid. The relative contributions of these types of crystallization strongly depend on the cooling rate. At low cooling rate (0.2°C/min) the crystallization takes place through the high temperature mechanism solely whereas at high cooling rate (15°C/min) only low temperature process is realized. At intermediate cooling rates both types of crystallization exist. The ratio of the heat of low temperature crystallization to the high temperature one ($H_{lowtemp}/H_{hightemp}$) increases exponentially with the cooling rate. FT-IR spectroscopy showed that the AP sample crystallized through the high temperature mechanism has strictly the same spectrum as the initial material. The spectrum of AP crystallized from the overcooled melt demonstrates certain differences (line shapes and frequencies) in the range of NH_4^+ stretching (≈ 3200 cm^{-1}) and bending (≈ 1400 cm^{-1}) vibrations and ClO_4^- stretching (≈ 1100 cm^{-1}) vibrations. These facts testify perhaps that the different mechanisms of crystallization result in formation of different crystal structures.

Crystallization of PETN in all experiments takes place from the overcooled melt and proceeds in one stage. The value of the overcooling depends on the cooling rate. At low cooling rates (up to 4°C/min) the crystallization temperature is approximately constant and concentrates near 120 °C (T_{melt}=141 °C). The further rise of the cooling rate (from 5°C/min and up to 15°C/min) results in the sharp increase of the overcooling ($T_{cryst}\approx 100$ °C). It was found that the rate of crystallization has the same step like dependence upon the cooling rate. The high overcooling leads to the significant increase of the crystallization rate. FT-IR spectra do not show any differences between initial and newly crystallized samples. However visual and microscopic inspection show that in the case of low rate crystallization (low overcooling) the newly formed crystals have a regular needle like shape, while the high rate crystallization (high overcooling) results in formation of irregular mainly small-sized particles.

Keywords: crystallization, energetic, DTA

MS35.P24

Growth decorations on facets of Al-Cu-Fe single quasicrystals

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The contribution reports on investigations of facet decorations formed during crystallization of polygonal single quasicrystalline ψ phase occurring in Al-Cu-Fe alloy. The perfectly stable icosahedral

single quasicrystals of ψ phase are formed in the range of compositional triangle Al$_{62.4}$ Cu$_{24.4}$ Fe$_{13.2}$, Al$_{65}$ Cu$_{23}$ Fe$_{12}$ and Al$_{61}$ Cu$_{28.4}$ Fe$_{10.6}$ [1-4].

Polyhedral equilibrium single grains of the ψ phase were obtained inside of ingots of an Al-Cu-Fe alloy, for which the nominal composition was 65 at. % Al, 20 at.% Cu and 15 at.% Fe. The specimens were synthesized in a helium atmosphere using the Bridgman-Czochralski-Growth (BCG) apparatus equipped with an induction furnace. The growth morphology was investigated by the scanning electron microscopy (SEM) using primary and secondary electrons. The selected area diffraction (SAD) as well as X-ray powder diffraction were applied [5].

Single quasicrystals of ψ phase Al$_6$Cu$_2$Fe exhibit icosahedral symmetry with pentagonal dodecahedral growth forms - 12 faces perpendicular to the 5-fold axes (Fig. 1 (a)). The dodecahedra have irregularities and different dimensions of edges extending up to 160 μm. The faces of dodecahedra are not perfectly smooth and show residual flux. Some of the dodecahedra are uniformly covered by primary cellular decorations gradually covering almost all facets. During the next stage of crystallization, the secondary fractal like decorations appeared on the quasicrystals surfaces (Fig. 1(b)). There was no evident difference in chemical composition between the inner dodecahedra, primary cellular decorations as well as the secondary fractal like decorations.

The facets of dodecahedra are decorated in similar way as fivefold facets of quasicrystals units of Al-Pd-Mn found by Beeli and Nissen [6]. Contrary to their conclusion we don't found a relationship between facet symmetry and the symmetry of dendrites. The decorations can be formed during the last stage of crystallization, when residual flux crystallizes on the quasicrystal facet in a form of solid dendrites.
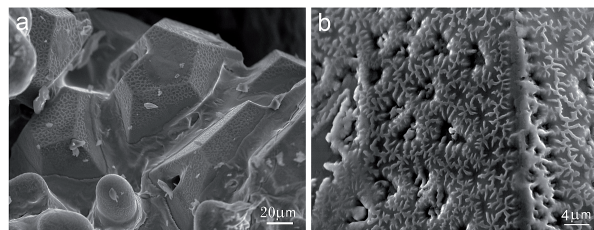

Fig. 1. Decorations on pentagonal faces of the ψ phase. Primary cellular decoration (a) and secondary fractal like decoration (b).

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Keywords: Al-Cu-Fe system, quasicrystal growth morphology, decoration of facets.

MS35.P25

Uncoupling nucleation and protein crystal growth using microfluidic chips

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Microfluidic devices reduce protein consumption required for identifying crystallization conditions and obtaining well ordered crystals. This nanoliter volumes approach has nevertheless some inconvenient, generally involving higher levels of supersaturation than equivalent experiments at the microliter or milliliter scales.

As the influence of channel depth of the PDMS microcircuits has not yet been evaluated, we have undertaken a comparison of the nucleation depending of this parameter. We observed that it is indeed correlated with the supersaturation needed to get crystals [1]. When the depth of the microchannels is decreasing the number of lysozyme crystals is dramatically reducing whereas their mean size is increasing.

Consequently, in order to uncouple nucleation and crystal growth, we propose original microfluidic chips which can be used to initiate nucleation in its deepest section and facilitate crystal growth in its shallow end.

The data presented in this work can contribute to a better control of the crystallization in microfluidics and shed light for the design of new microcircuits uncoupling nucleation and crystal growth that should facilitate the appearance of single crystals suitable for X-ray diffraction. They can also be used for macroseeding and microseeding experiments to improve the quality and size of crystals obtained after a first random screening.

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Keywords: crystallization, microfluidics, nucleation

MS35.P26

Cubic growth of natural diamond

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Natural diamond grows by at least three different modes: (a) Faceted growth on {111} planes giving octahedra; (b) Fibrous growth in <111> directions giving cubes [1]; and (c) Cuboid growth on crinkly surfaces approximating to {100}, which also produces cubes [1]. Combinations may also occur: growth by (a) followed by (b) gives coated stones [2]; and (a) and (c) growth modes may occur together to give combined morphologies. Twinning of (a) gives spinel-type contact twins (called 'macles') [3] and twinning of (b) gives fluorite-type interpenetrant cubes [4]. Subsequent dissolution may greatly modify the morphology: for example, octahedral diamonds grown by mode (a) may dissolve into rounded rhombic dodecahedra [5].

Here we report the existence of a fourth mode of growth: (d) Faceted growth on {100} planes. Flat cube facets are a common occurrence for *synthetic* diamonds grown by high-pressure high-temperature techniques, especially at the lower range of temperatures at which diamonds are formed; but cube facets are so rare in nature that some have denied that they are a true growth form. It is true that they have been seen only on small diamonds (< 1 mm). Their absence from larger diamonds may simply be the result of their growth rate being much larger than that for octahedral facets and thus they grow out.

We also report another finding [6]: a diamond which has grown by fibrous mode (b), followed by octahedral growth (a): an unusual

occurrence, whereas (a) followed by (b) is quite common.

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Keywords: diamond, morphology, X-ray topography

MS35.P27

Calculating the interaction energy between 1-D hydrogen bond motifs using semi-empirical methods

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One dimensional hydrogen bond motifs often, but not always, tend to display needle-like morphologies which extend in the motif direction. Perhydropyrimidin-2-one and a highly substituted derivative display identical 1-D hydrogen bonding motifs. However, the former displays a block morphology while the latter grows exclusively as needles. These observations have been investigated by calculating the interaction energy between a motif and its surroundings.

A 7 motif pack was constructed. Each motif was 6 molecules long and the central one was surrounded by its 6 nearest neighbours. MOPAC2009 [1] was used to optimize this pack using the AM1 method. The pack was then split into a core and a shell and these energies were also computed. The difference in the energy of the core + shell and the energy of the pack is taken to be the interaction energy. The interaction energy per 100 $Å^2$ of core surface (Connolly) was calculated. There is a significantly lower interaction energy calculated for the substituted system. This suggests that in nucleation and crystal growth the structure will advance slower normal to the 1-D motif direction.

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Keywords: 1D, hydrogen_bonding, morphology

MS35.P28

Morphology of synthetic tourmaline crystals

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Single crystals of colored Co-, Ni-, Fe-, (Ni,Cr)-, (Ni,Fe)-, and (Co,Ni,Cr)-bearing tourmalines have been grown on a seed in boric, boric–alkaline, boric–fluoride, boric–chloride–fluoride, and boric–chloride hydrothermal solutions at 400–750°C and 100 MPa [1]. The morphology of spontaneous tourmaline crystals formed in experiments in solutions of different composition has been studied.

Crystals synthesized in boric-chloride solutions, are characterized by the long prismatic habit (needles) formed by the trigonal pyramid {10-11} and the hexagonal prism {11-20} faces. Long prismatic