



	<b>Experiment title:</b> <b>Kinetics of diamond crystallization from carbon - metal melts: <i>in situ</i> studies</b>	<b>Experiment number:</b> CH 985
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## Report:

Phase relations and kinetics of diamond crystallization from melt have been studied to 5.2 GPa and 1700 K in the Fe-Ni-C system using *in situ* energy-dispersive X-ray diffraction with synchrotron radiation. The experiments have been done using large-volume Paris-Edinburgh press and Canberra Ge solid state detector at beamline ID30. The results obtained are briefly described below.

At 4.1, 4.5 and 5.0 GPa, diamond crystallization from the Fe-Ni-C melt is not observed because the liquid phase appears in the system only in the region of thermodynamic stability of graphite (4.1 and 4.5 GPa), or just 10-20 K below the graphite-diamond equilibrium line (5.0 GPa).

In view of these data, it appears that literature data on the melting of the  $\gamma$ +Fe<sub>3</sub>C+C<sup>1</sup> ternary eutectic in the Fe-Ni-C system at high pressures and temperatures are rather contradictory. According to Kocherzhinsky *et al.* [1], the melting temperature of the ternary eutectic ( $T_e$ ) at 6 GPa is 1400 K, while according to Pavel *et al.* [2]  $T_e = 1665$  K at 5.7 GPa. From our experimental data it follows that in the 4.1-5.2 GPa range the pressure dependence of the melting temperature of the ternary eutectic is described by the  $T_e$  (K) = 1346(27) + 29.8(18)· $p$  (GPa) equation.

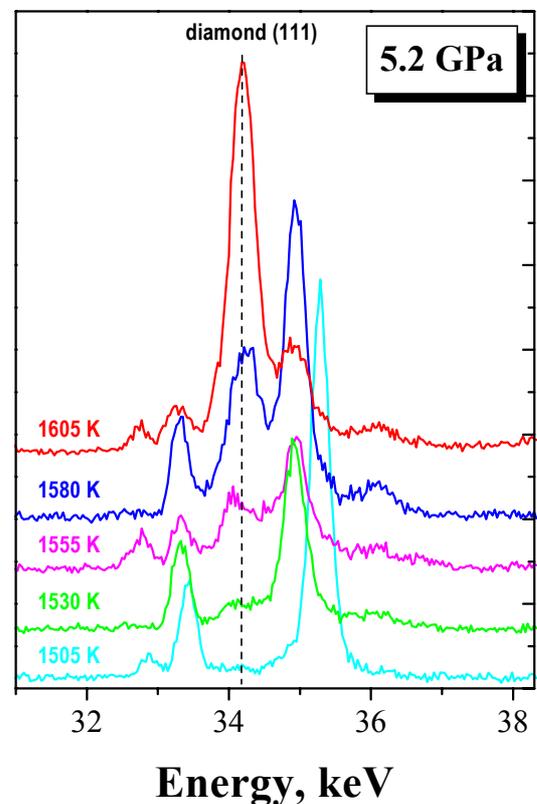


Figure 1

<sup>1</sup>  $\gamma$  - fcc Fe-Ni-C solid solution

Experiments in [2] were conducted by the quenching method, therefore the errors in temperature determination were very serious. As to the paper [1], the authors have not evidently managed to avoid the interaction between the samples and a thermocouple when conducted the DTA experiments under pressure. They have attributed the thermal effect observed at 1400 K to the melting of eutectics, which has resulted in an understated (by more than 100 K) evaluation of the position of the melting line of the  $\gamma$ +Fe<sub>3</sub>C+C ternary eutectic.

At 5.2 GPa and the heating rate of 25 K/min, the diamond spontaneous crystallization in the Fe-Ni-C system starts at 1510 K immediately after the halo of the liquid phase appears, and is fully completed at 1605 K (Fig. 1). We note that despite the presence of a liquid in the system over the whole temperature range of diamond crystallization, all diffraction patterns exhibit lines of the solid phase that can be ascribed to the fcc Fe-Ni-C solid solution. This fact indicates that in accordance with  $p,T$ -phase diagram of the Fe-Ni-C system [1], under experimental conditions the  $L = C + \gamma$  monovariant eutectic reaction takes place. In this case, the melt is in equilibrium with both diamond and  $\gamma$ -phase.

Diamond crystallization in the system under study is very fast and proceeds in a narrow temperature range that plagues essentially isothermal kinetics studies. Because of this, the present work describes a non-isothermal approach. As all the diffraction patterns exhibited diffraction lines of graphite, we state that diamond crystallization from the Fe-Ni-C melt occurs at the constant carbon supersaturation with respect to diamond, which is ensured by dissolution of the initial graphite. Based on this, the degrees of the graphite-to-diamond conversion proceeding via melt has been calculated by normalizing integral intensities of the (111) reflection of diamond at various temperatures to the appropriate value at 1605 K ( $\alpha = 1$ ).

The results obtained at 5.2 GPa and the heating rate of 25 K/min are shown in Fig. 2 as the degree of the graphite-to-diamond conversion ( $\alpha$ ) vs temperature. The kinetic data were further processed in the framework of Avrami's approach [3,4] after generalization for non-isothermal conditions.

Kinetic data might be best fitted by the model with  $m = 2.5$ ,<sup>2</sup> that assumes a constant nucleation rate and three-dimensional growth of the resulting nuclei under the conditions where the limiting stage of the diamond crystallization is the carbon diffusion in the melt to the surface of a growing crystal.

From the temperature dependence of conversion rate constant ( $k$ ) in the 1505-1605 K range at 5.2 GPa, the activation energy of diamond crystallization from the Fe-Ni-C melt being in equilibrium with graphite was calculated to be 148(64) kJ/mole.

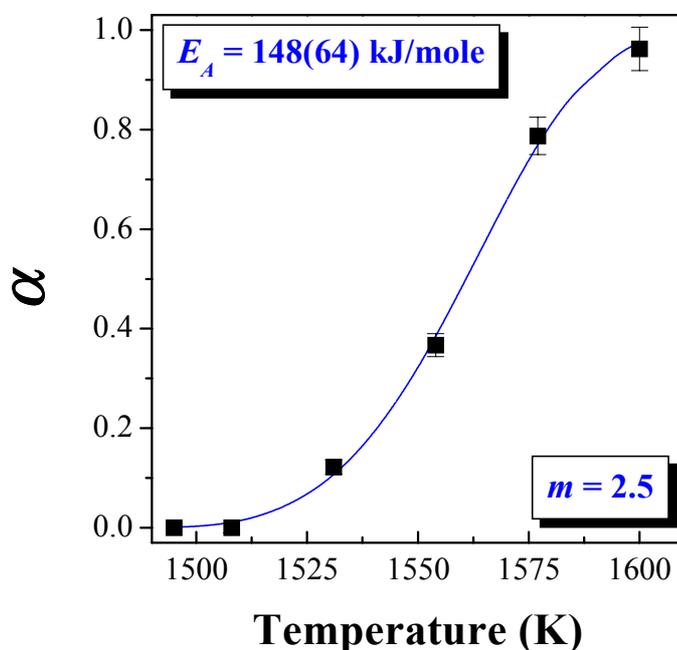


Figure 2

## References

- [1] Yu.A. Kocherzhinsky, O.G. Kulik, and V.Z. Turkevich, Phase equilibria in the Fe-Ni-C and Fe-Co-C systems under high temperatures and high pressures. *High Temp. - High Pres.* **25** (1993) 113-116.
- [2] E. Pavel, L. Pintiliescu, Gh. Baluta *et al.* The ternary constitution diagrams for the Fe-Ni-C and Fe-Co-C systems at 5.7 GPa. *Physica B* **175** (1991) 354-360.
- [3] M. Avrami, Kinetics of phase change. I. *J. Chem. Phys.* **7** (1939) 1103-1112.
- [4] M. Avrami, Kinetics of phase change. II. *J. Chem. Phys.* **8** (1940) 212-224.

<sup>2</sup>  $m$  is the order of kinetic equation