PHASE TRANSISIONS

1 THEORETICAL INTRODUCTION

1.1. Single and multiphase systems

A phase is a macroscopic part of a system that has the same physical properties everywhere and is separated from other parts of the system by an interface called a phase boundary. A distinction is made between single-phase and multi-phase systems.

A single-phase system is a system consisting of only one phase (solid, liquid or gas) of a substance. Ice is an example of a single-phase and single-component system.

A polyphase system is a system composed of more than one phase. An example of a multiphase system may be a system composed of water and steam containing only one component, i.e. water. An example of a multi-phase and multi-component system may be a vessel with water to which we have added mercury. Since mercury does not mix with water, in this case we have two liquid phases (water and mercury) and one gaseous phase (water vapor, mercury vapor and air), and two components: water and mercury. Coexistence of phases is possible under precisely defined conditions. The condition of equilibrium is, for example, equality of temperatures of all phases. If the equilibrium conditions are not met, one phase transforms into another.

1.2. First order phase transitions

Changes in the phase of the system, during which density (ρ) and such thermodynamic functions as: internal energy (U), free energy (F), enthalpy (H) and entropy (S) undergo sudden changes. For the first order phase transitions the heat of transformation is different from zero ($Q_{trans} \neq 0$) The first order phase transitions are: melting, solidification, evaporation and, in addition to changes in the state of matter, these transitions also include some changes in the crystal structure in solids (Fig.1).
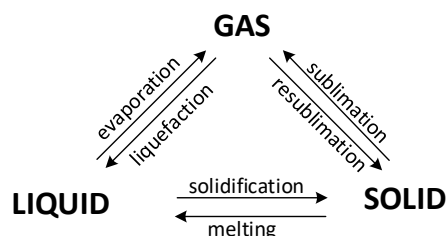

Fig.1 First order phase transisions
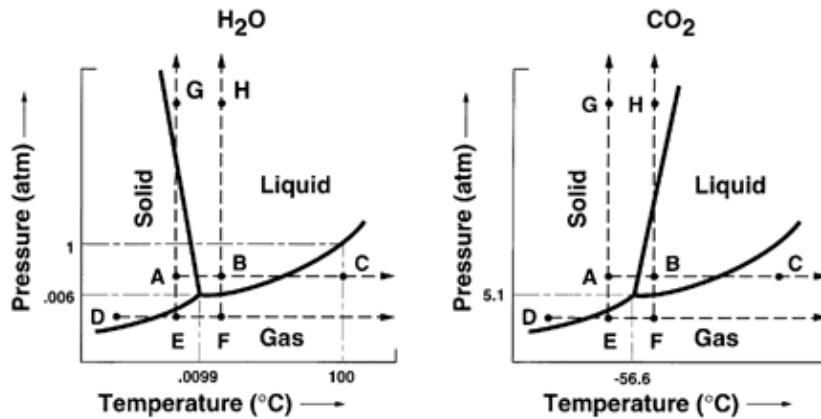
The Phase Diagrams of H₂O and CO₂

Fig.2 First order phase transitions - the diagram of water and carbon dioxide

1.3. Crystallization and melting

Crystallization (solidification of crystalline bodies) is a first order phase transition that cannot occur without heat exchange. It involves the transformation of an amorphous substance into a crystalline form. Crystallization is an exothermic process - it produces heat in amounts characteristic of a given substance. For pure compounds and at constant pressure, crystallization occurs at a precisely defined temperature and with the release of a constant amount of heat.

Melting is an endothermic process, opposite to crystallization, and for its implementation it is necessary to provide a certain amount of energy.

It should be noted that for a given substance, the amount of heat that must be supplied to melt it is equal to the amount of heat given off by this substance in the crystallization process.

$$C_t = C_k$$

where: C_t - heat of melting, C_k - heat of crystallization

Due to intramolecular ordering (formation of a crystal lattice), crystallization occurs at a slightly lower temperature than melting. In the case of amorphous bodies, solidification and melting occur at the same temperature.

Crystallization stages:

- nucleation: formation of crystal nuclei
- propagation: growth of single crystals
- reorganization of the crystal microstructure and agglomeration of crystals

Solidification of crystalline bodies may occur spontaneously when the temperature is lowered. It may also be caused by chemical factors (introduction of substances that initiate or accelerate nucleation) or physical factors (mechanical or sound stimuli).

1.4. Second-order phase transition:

Second-order phase transitions are also called "continuous phase transitions". In such transformations the heat of transformation is zero ($Q_{trans} = 0$) and they occur without changing density. In these transformations, the specific heat, isothermal compressibility coefficient and volume expansion coefficient change abruptly. Phase transitions of the second type include, for example, ferromagnetic-paramagnetic transitions. An example here is iron, which at a temperature below the so-called Curie point (T$_C$=768°C) is ferromagnetic and has an α-type crystal lattice. At a temperature of 768°C, the density of iron does not change, but the coefficient of thermal expansion changes abruptly and becomes negative at higher temperatures (the length decreases when heated). In this transformation of iron, the type of crystal lattice changes from α to β. β-iron is paramagnetic.

2. METHOD AND LABORATORY STAND FOR TESTING FIRST ORDER PHASE TRANSITIONS ON THE EXAMPLE OF SUPERSATURATED SOLUTIONS

Samples of supersaturated solutions were used to study the phenomenon of first order phase transition. The tests will be carried out at a measuring stand, the diagram of which is shown in Figure 3. Measurements carried out at laboratory stand will enable the determination of the specific heat of the material of the tested sample and the heat of phase transformation. A vessel (1) with walls made of insulating material contains a certain amount of water (2) with a mass of m$_W$. The tested sample (3) with mass m$_P$ is placed in water. The water temperature is measured using a type K thermocouple (4). The reference junctions of the thermocouple are located in the thermos (5) and are immersed in an ice-water environment. Compensation cables are attached to the millivoltage meter (6) - KEITHLEY 2000 multimeter. The voltage value is displayed on the multimeter screen with a resolution of 0.01mV. The measured voltage value can be converted into a temperature value in the range from 0°C to 100°C with sufficient accuracy using the proportionality coefficient k = 4.019mV / 100°C.
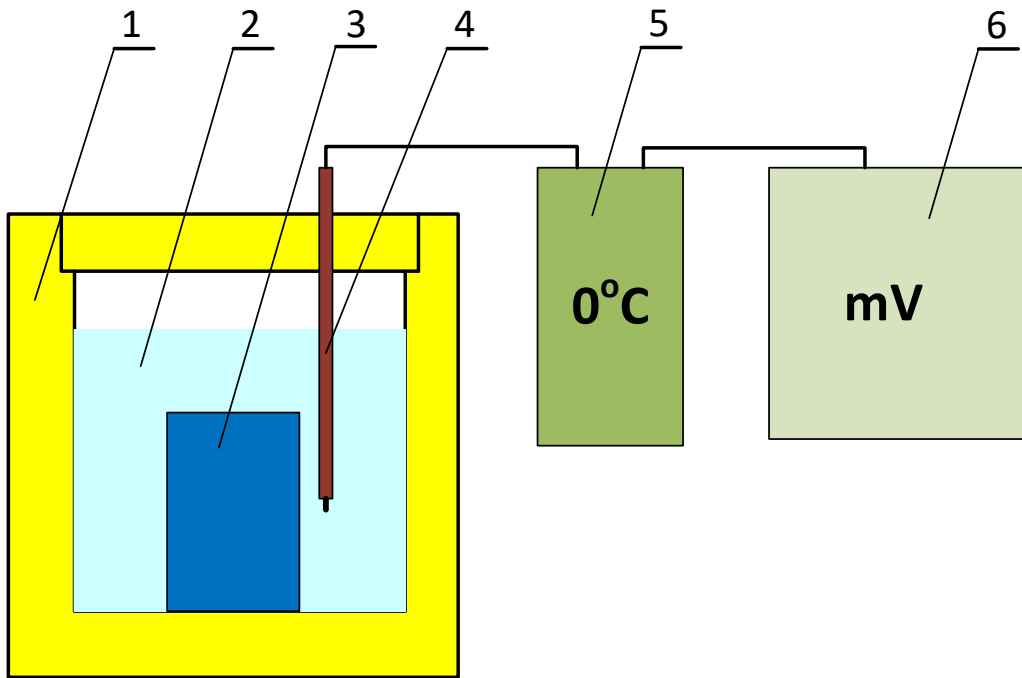
Fig.3 The laboratory stand

The research involves carrying out sequential crystallization processes for two prepared samples. The tested sample was previously heated in boiling water for 10 minutes and then cooled to room temperature. The internal structure of the sample is a liquid created by melting a crystallized hydrated sodium acetate.

Before measurements, determine the mass of each sample using a scale. Pour 750ml of water into the vessel, measuring the water volume using a measuring cup. Measure the initial temperature of the water in the tank.

Measurements for the first sample

- We produce an acoustic signal by bending a plate located inside the sample. The generated pulse initiates the crystallization of the substance, i.e. the first order phase transition, which occurs with heat exchange. The amorphous transformation of a substance is an exothermic process releasing a specific amount of heat. When the crystallization process of all the material is completed, the sample is placed in a vessel with water. We record the measured voltage value every time step, designated by the instructor, until a constant value is reached. The measured voltage values are converted into temperature values. We determine the initial and final temperature of water and sample material. An example of the course of sample temperature changes is shown in Figure 4 - curve in blue.

- Based on the measurements performed, the specific heat of the measured substance is determined by equating the heat Q_P transferred from the sample to the water with the heat Q_W absorbed by the water from the sample.

$$Q_p = Q_w \tag{1}$$

$$Q_p = m_p * c_p * (\Delta T)_p$$

$$Q_w = m_w * c_w * (\Delta T)_w$$

where:

T_W, T_K – initial and final water temperature,

T_{PF} – initial temperature of the sample material (crystallization temperature),

$(\Delta T)_P = T_{PF} - T_K$, $(\Delta T)_W = T_K - T_W$ - appropriate temperature differences,

c_P – specific heat of the sample material,

c_W – specific heat of water

Equation 1 after substitution will take the form:

$$m_p * c_p * (\Delta T)_p = m_w * c_w * (\Delta T)_w$$

from which the specific heat value c_P of the sample material is determined.

Measurements for the second sample

The measurement cycle for the second sample differs in that the sample is placed in water immediately after initiating the crystallization process. We perform voltage measurements as for the first sample. Particular attention, in this part of the experiment, should be placed on the first 10 seconds when the phase change heat is released, which generates a faster increase in water temperature.

An example of water and sample temperature changes is shown in Figure 4 - curve   in red.

$$Q_p^* = Q_w^* \tag{2}$$
$$Q_p^* = m_p * L + m_p * c_p * (\Delta T)_p^*$$
$$Q_w^* = m_w * c_w * (\Delta T)_w^*$$

where: L – heat of phase transformation of the sample material,

   c_P – specific heat of the sample material determined for the first cycle   measurement.

After transformations we get:
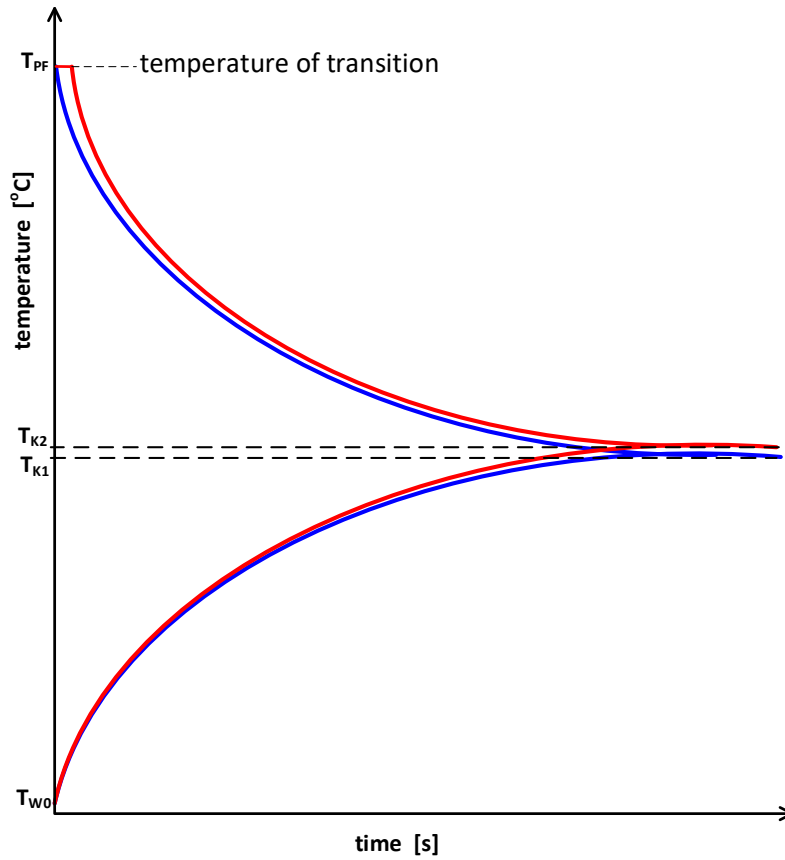
$$L = \frac{Q_w^* - Q_p^*}{m_p} \tag{3}$$

Fig.4 Temperature changes during both of the measuring cycles

Figure 5 shows changes in the physical state of the tested sample depending on the initial temperature and the input or removal of heat
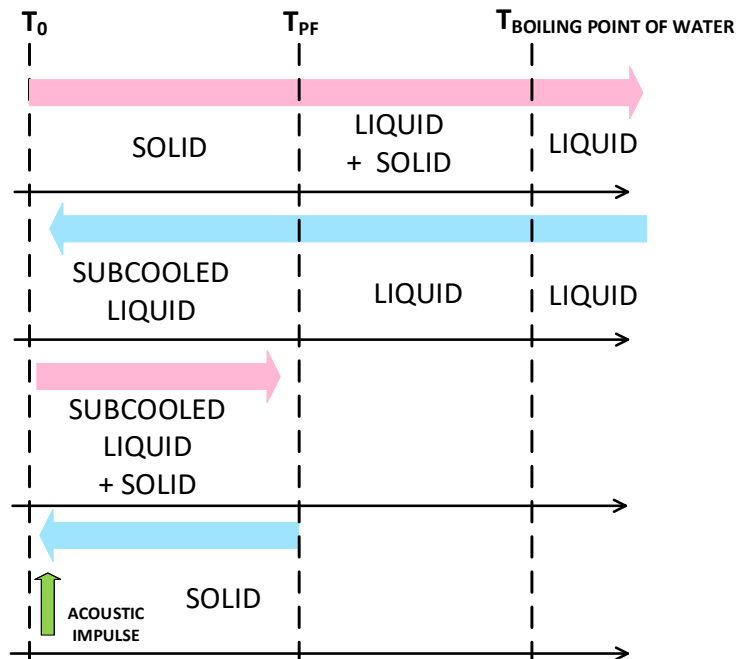

Fig.5 Changes in the physical state of the tested sample depending on the initial temperature

3. METHOD AND STAND FOR TESTING SECOND-ORDER PHASE TRANSITIONS IN FERROMAGNETICS

Iron-nickel alloys are double alloys. A characteristic feature of double alloys is, among other things, the occurrence of a second-order phase transition at the Curie point T_C (Curie temperature). In general, it is characterized by a sudden change in physical properties at the T_C temperature, such as: linear expansion coefficient ⬚, specific heat, compressibility coefficient, thermal diffusivity and magnetic susceptibility.

As part of the scientific activities of the Department of Aerodynamics and Thermodynamics, the temperature characteristics of thermal diffusivity of selected Fe-Ni alloys were determined. Six iron-nickel double alloys were selected for thermal diffusivity tests. Thermal diffusivity tests of these alloys were carried out in the temperature range from 300K to 900K. From the results obtained, the Curie point temperature values were determined for each of the alloys. The summary results are shown in Figure 6.
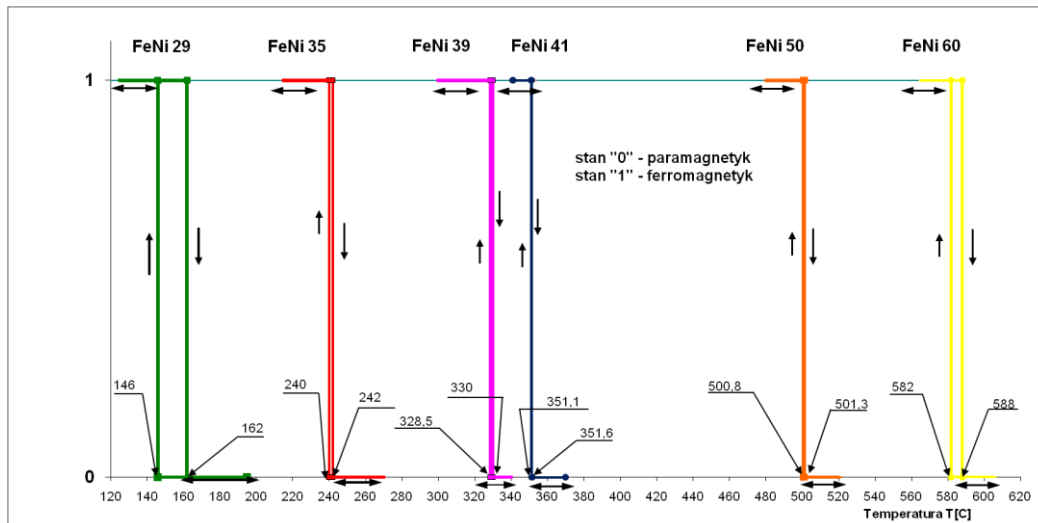

Fig. 6 Experimentally determined Curie point values for Fe-Ni alloys

The phase equilibrium diagram of Fe-Ni alloys (Fig. 7) shows that in each of these alloys there is a phase transition from the ferromagnetic state to the paramagnetic state at the Curie point.

Laboratory tests of the location of the Curie point as a function of temperature TC(T) were carried out at the measurement station as in Fig. 8.a. Samples with a diameter of ϕ12 mm and a thickness of approximately 1.5 mm were used for testing. The temperature of the tested samples was measured with NiCr-NiAl thermocouples (chromel-alumel, type "K").
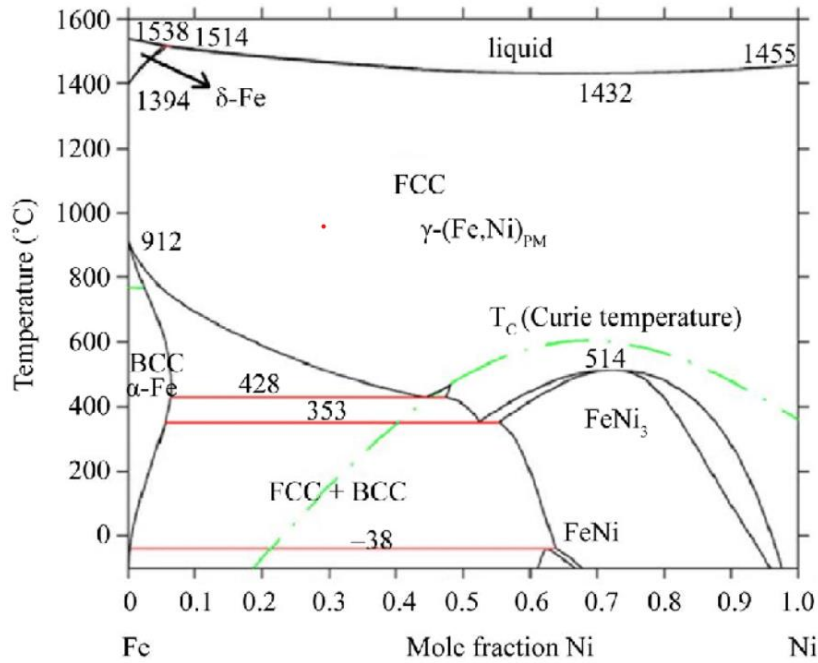
Fig.7 The Fe-Ni phase diagram

The thermoelectrodes were electrically welded to the side surface of the tested sample (Fig. 8.b).
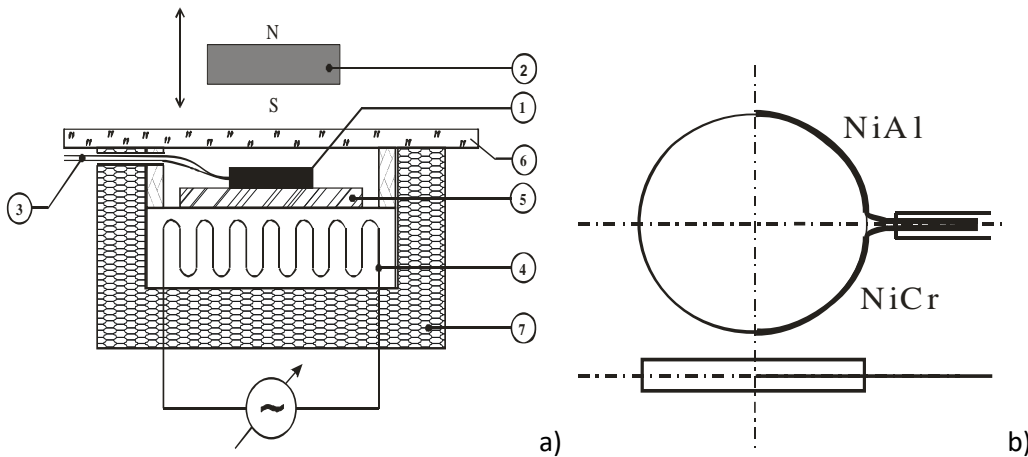

a)   b)

Fig. 8 a) Laboratory stand for testing the Curie point temperature TC of magnetic alloys (Fe-Ni): 1 - tested
sample, 2 - magnet, 3 - thermocouple, 4 - radiator, 5 - copper plate (1.3 mm), 6 - plate glass
(1 mm), 7 – insulation.
b) material sample with thermocouple wires attached

The experiment, aimed at determining the temperature of the Curie point and the hysteresis loop of the tested materials, was as follows:

- tested samples (1) were placed centrally on a copper plate (5) and the heater (4) was turned on;

- in the temperature range $T<T_C$, the tested samples are ferromagnetic and therefore the presence of an external magnetic field [bringing the magnet (2) closer to the glass plate (6)] causes it to detach from the Cu plate and stick to the glass plate (6). Reducing the magnetic field [moving the magnet (2) away from the glass plate (6)] causes the sample (1) to fall back onto the copper plate (5) and its temperature further increases;

- after a series of such samplings, with the constantly increasing temperature of the tested sample, its temperature $T=T_C$ value is finally reached at which it loses its ferromagnetic properties, becoming paramagnetic. The magnet no longer causes it to be detached from the surface of the copper plate;

- after exceeding the temperature $T=T_{C,1}$ by approximately 20 K, we start to slowly cool the sample;

- while the sample is cooling, we constantly check, by moving the magnet closer and further away, whether it is still paramagnetic. The temperature at which the tested sample responds again to the external magnetic field $T=T_{C,2}$ is also the Curie temperature. Typically $T_{C,1} > T_{C,2}$ (hysteresis loop).

Table 1 lists frequently used Fe-Ni alloys, their basic properties and applications.

Table 1. Typical alloy compositions in practical applications

Alloy name	Weight composition	Typical properties	Area of application
Permalloy	FeNi 79	High magnetic susceptibility (easily magnetized and demagnetized).	Transformer and rectifier cores, computer memory chips, amplifiers, magne-tic screens and magnetic recording heads.
"Balco" "Hytemco" Resistive Detectors (RTD).	FeNi 70	Thermal conductivity is almost that of nickel, but much higher electrical resistivity, mechanically strong and moderately resistant to corrosion.	Resistive Detectors (RTD).
Alloy 52	FeNi 52	Expansion coefficient similar to non-porous glass (K-Na-Pb).	Sealing of passages of electric cables through glass (electric lamps).
Alloy 48.	FeNi 48	Expansion coefficient similar to Na-Pb glass and lime glass	Application in electronics.
Alloy 42	FeNi 42	Low expansion coefficient up to 300oC, similar to aluminum oxide and non-porous glass.	Sealing of electrical cable passages through glass (electric lamps).
Invar.	FeNi 36	Expansion coefficient close to zero in the range of 20÷100oC. Low eddy current losses.	Used in precision measuring instruments and thermostats. Cores of teletransmission transformers

REVIEW QUESTIONS:

1. Single and multiphase systems.

2. First order phase transition.

3. First order phase transition on the example of water or carbon dioxide.

4. Crystallization and melting.

5. Diagram of the laboratory station (first order phase transition).

6. Graph of temperature change during the first order phase transition

7. Second-order phase transition.

8. What is Curie point.

9. Diagram of the laboratory stand (second-order phase transition).

REPORT

The laboratory report should include:

- a brief description of the measurements performed,

- graph of measured temperature changes,

- data for calculations and obtained results - values of specific heat and heat of transformation of the sample material.