Anomalies were found in the ferritic solution of cobalt in iron on the curve of dependence of the saturated magnetisation, electrical resistivity, thermoelectric power and dilatation on composition [1]. On a basis of heat and X-ray structural measurements Ellis and Greiner [2] explained these anomalies in 1941 as a formation of ordered FeCo structure. Besides the superstructure FeCo with critical ordering temperature 730 °C Yokoyama et al. [3] when evaluating measurements of density, hardness, electrical resistivity and its temperature coefficient and thermal conductivity quoted superstructures Fe₃Co and FeCo₃ with critical temperatures 565 °C and 475 °C. Viting [4] has made the same conclusion from his measurements of hardness, electrical resistivity and from microstructures. Masumoto et al. [5] confirm the anomalous behaviour of various physical quantities in a wide concentration range. They found in alloys with composition Fe₃Co and FeCo₃ that the change of specific heat is small and that its shape is not characteristic for the ordering processes. It appears even in alloys with the component ratio 1 : 1 at the temperature 550 °C. Asano et al. [6] measured this "550 °C anomaly" of specific heat on powdered specimens, prepared by reduction of the oxalates of respective metals in the concentration range 20—50 at% of Co; at higher cobalt concentration the temperature of this anomaly abruptly decreases. Neither the results of the neutron diffraction and of Mössbauer effect measurements, quoted in this paper, proved the existence of the superstructure of the type Fe₃Co.

A direct evidence of superlattice Fe₃Co and FeCo₃ was not given and is difficult since X-ray diffraction lines of the superlattice can not be observed because both elements have nearly the same structural factors. As both components have almost similar physical and chemical properties the ordering causes only a slight difference in the properties of alloys, which makes an indirect evidence of the superstructure difficult. Moreover at low critical temperatures of above mentioned superstructures, when the diffusion is slow it is difficult to achieve the equilibrium state. In these cases, the thermophysical methods, recording the changes in the crystal lattice heat energy, seems very useful for the investigation of ordering processes. It is necessary to draw special attention to the heat treatment of alloys.

Fig. 1.
Letters to the editor

In a high-temperature twin calorimeter, described in another paper [7] the heat-temperature spectra of three iron-cobalt specimens with the component ratio 1 : 1, 3 : 1 and 1 : 3 were measured at a non-stationary heating conditions at the rate about 6 deg/min. The differences of temperature between examined specimen and dummy (nickel) measured with chromel-alumel thermocouples were recorded with 100 μV per scale (28 cm) recorder against temperature under reproducible conditions. The results after different heat treatments of alloys are given in Fig. 1.

The curve No 1 corresponds to the specimen of FeCo alloys quenched from the temperature of about 800 °C into water. The maximum at 530 °C is the exothermal transition of the alloy from the disordered to the ordered state. The thermal effect varies from 300 to 400 cal/g at according to the quenching rate. The dependence of the temperature maximum of the thermal effect on the heating rate could not be determined in the interval 2.8—13.5 deg/min. At 730 °C a characteristic maximum for disordering processes was proved connected with the increase of specific heat. The curve No 2 corresponds to the specimen of the same composition, which was quenched in the same way, but before being measured it was annealed for 1 hour at 550—600 °C. The maximum caused by transition into ordered state decreased but did not disappear completely and it can be seen on the curve No 3, corresponding to the quenched specimen which was annealed for 5 hours at the same temperature (550—600 °C). It is obvious that by cooling down from temperature higher than 550 °C the specimen remains in quenched state to which higher heat content corresponds then to a slowly cooled down specimen, which has a heat-temperature spectrum shown by curve No 4. On this curve it can be seen that within the temperature range 550—600 °C the specific heat increases, the so-called “550° anomaly” takes place, which can be already seen on curves No 2 and No 3. Further ordering can occur in the temperature range 550—730 °C, which is accompanied with the heat evolution.

The curve No 5 corresponds to the specimen of FeCo alloys quenched from the temperature of 800 °C into water. The maximum at 540 °C is the exothermal transition of the alloy from the disordered to the ordered state. The thermal effect varies from 300 to 400 cal/g at according to the quenching rate. The dependence of the temperature maximum of the thermal effect on the heating rate could not be determined in the interval 2.8—13.5 deg/min. At 730 °C a characteristic maximum for disordering processes was proved connected with the increase of specific heat. The curve No 2 corresponds to the specimen of the same composition, which was quenched in the same way, but before being measured it was annealed for 1 hour at 550—600 °C. The maximum caused by transition into ordered state decreased but did not disappear completely and it can be seen on the curve No 3, corresponding to the quenched specimen which was annealed for 5 hours at the same temperature (550—600 °C). It is obvious that by cooling down from temperature higher than 550 °C the specimen remains in quenched state to which higher heat content corresponds then to a slowly cooled down specimen, which has a heat-temperature spectrum shown by curve No 4. On this curve it can be seen that within the temperature range 550—600 °C the specific heat increases, the so-called “550° anomaly” takes place, which can be already seen on curves No 2 and No 3. Further ordering can occur in the temperature range 550—730 °C, which is accompanied with the heat evolution.

A different situation is with the specimen Fe3Co. By a long time anneal (about 24 hours) at 500 °C with a slow cooling down from this temperature we did not succeed to prepare a specimen which heat-temperature spectrum would have a maximum characteristic for the transition from ordered to disordered state as illustrated on the curve No 6. This fact is an evidence against the existence of the superstructure [3, 4]. The heat-temperature spectrum of the specimen quenched from 800 °C has a peak at 540 °C (curve No 5).

By any heat treatment of the specimen of FeCo3 composition could not be achieved on heat temperature spectrum the characteristic maximum for ordering process. Nevertheless in the quenched specimen (curve No 7) and even in the long time annealed one (curve No 8) a flat maximum appeared within the temperature range 500—700 °C, that was more expressed in the quenched specimen. This fact is in disagreement with [6]. In this cobalt rich specimen the existence of the superstructure, can not be assumed either, which is against conclusions in [4].

The ordering processes in Ni-Co [8] and Co–Fe alloys are considerably different. In f.c.c. solution of cobalt in nickel ordering occurs probably near Ni3Co while in b.c.c. solution of iron in cobalt superstructure occurs at the ratio of components 1 : 1. The speeds of both ordering processes are different. The long distance ordering in Ni3Co specimen needs annealing times of tens hours just below the critical temperature of disordering. The non-stationary heating process of tens degrees per minute in disordered solution of Fe-Co is sufficient for transition to ordered state and at higher