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BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 13, no. 1, 2019

Physical Chemistry

Thermal Anomalies at Structural and Magnetic Transformations of Iron Subgroup Metals

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(Presented by Academy Member Givi Tsintsadze)

ABSTRACT. **The structural and magnetic phase transformations of Fe, Co, and Ni was studied by thermogravimetric (TGA) and calorimetric methods in the range 300-1000K. By TGA the temperature domains of transformations were detected and the effect of oxidation on thermal properties of these metals at heating in air was shown. The calorimetric studies were conducted in argon using the high temperature calorimeter HT-1500 ("Seteram"). The temperature of transformations and the values of thermal effects: for Fe Curie temperature is Tc = 1143K, enthalpy ΔHm = 454 J/mole; structural transformation temperature Tst = 1183K, ΔH = 623 J/mole; for Co Tc = 1400K, ΔHm = 430 J/mole; Tst = 700K, ΔH = 269 J/mole; for Ni Tc = 631K, ΔHm = 373 J/mole. To characterize the ferromagnetic disordering process, the heat capacity Cp(T) of nickel in the region of 300–1000 K was studied by differential scanning calorimeter (DSC-111). The excess magnetic heat capacity ΔC_m was separated from experimental Cp (T) by using the special method. The ΔC_m (T) has the λ-type curve with Curie temperature at 625K. Above Tc it has a tail over 150K which corresponds to short-range magnetic interactions. The full magnetic enthalpy H_m and entropy S_m are evaluated to be 1100 J/mole and 2.3 J/K.mole, respectively. The share of short-range energy is ~15-20 per cent of this value. The relationship between the enthalpy of magnetic transformation and of magnetic moment of saturation of metallic and oxide ferromagnets is illustrated** *© 2019 Bull. Georg. Natl. Acad. Sci.*

Key words: transition metals, enthalpy, thermogravimetry

The study of the various physical properties of compounds in the region of phase transitions is of significant importance for solid-state physics and chemical thermodynamics. Transition metals of iron subgroup from this point of view are quite successful objects for research, since they are characterized by various types of structural and magnetic transformations occurring at temperature and pressure change. For classical ferromagnets (iron, cobalt, nickel) in the region of high temperatures (above room temperature) various structural transformations and magnetic disordering processes are elucidated and reported [1-5]. The study of thermal behavior of these processes, especially in the nearest region of phase transitions, is a significant task for modeling and predicting the properties of numerous new compositions developed on the basis of transition metals.

The nature of phase transformations of transition metals at high temperatures has been studied quite well (with the exception of high-temperature transitions in rare-earth metals). In most cases, there is detailed information about magnetic characteristics, as well as the change in the parameters of the crystal lattices and other structural characteristics of these metals during phase transformations of the first kind [5]. However, the question of the behavior of the thermophysical properties of transition metals near points of phase transformations of the first and second kind in many cases remains poorly understood and controversial. Experimental data on temperature and heat conductivity, as well as information on the heat capacity and electrical conductivity of transition metals during high-temperature phase transformations were studied by the authors in [1-5].

According to the existing literature data [5] polymorphic and magnetic transformations for iron, nickel and cobalt have the following temperature characteristics: iron has a volume-centered cubic lattice (bcc) of α-Fe at T <1184K, and face-centered – fcc γ-Fe at T> 1184K. At 1665K the reverse transformation of fcc-bcc γ-α (δ) occurs. Ferromagnetic transformation take place at T_c = 1041K. The standard state of cobalt in the interval of 0–718 K is assumed to be hexagonal modification – α – Co and in the interval 718–1768 K – the cubic modification, β - Co (fcc). Cobalt is ferromagnetic with Curie temperature at 1394 K. Nickel has a ferromagnetic transformation with Curie point at T_c - 631K.

The aim of this work is an experimental study of transition metals – iron, cobalt, nickel – in the high-temperature region near the points of structural and magnetic phase transformations, and evaluation of enthalpy of the corresponding thermal anomalies.

Experiments and Results

Investigations of high-temperature transformations of Fe, Co and Ni were carried out on an HT-I500 calorimeter manufactured by "Seteram" (France). High-purity metals (<99.9%) were used as research objects.

A preliminary thermos-gravimetric study (at the facility by NETZSCH, STA-2500 Regulus) in the temperature range 300-1300K showed that conducting experiments in the atmosphere of air is associated with a change in the weight of the samples as a result of oxidative processes. As an example, Fig. 1 shows the thermal behavior of iron during heating. It is obvious that the oxidation process gradually increases above 800K and sharply increases in the region above 1100K. Oxidation processes at temperatures T>300 K are also expected for cobalt and nickel. The corresponding exothermic effects prevent the unequivocal identification and evaluation of both structural and magnetic transformations occurring in the same temperature range.

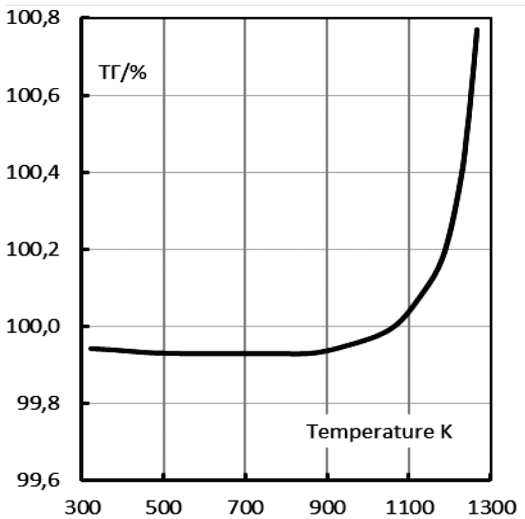

Fig. 1. Process of oxidation of iron.

In order to avoid oxidative processes, calorimetric studies on HT-1500 were carried out in an argon atmosphere. The samples weighed with an accuracy of 0.00005 g were loaded into a crucible, which was then placed in the calorimeter. After careful assembly and degassing of the calorimeter, argon was injected into the furnace and into the muffle to a certain pressure (1.1 atm.). Then the required mode of operation of the calorimeter was set.

The studies were carried out on a calorimetric detector with differential thermal battery Rt /Pt/Rd 60% /Pt Pt/Rd 30%. Experimental conditions (sample heating rate, instrument sensitivity, sample size, etc.) were selected empirically depending on the nature of the studied process in such a way that the configuration of the thermal anomaly provided a minimum error in its evaluation. The constant of the calorimeter K at a given temperature was determined by the enthalpy of melting of the reference substances – indium, tin, lead, zinc, aluminum, silver, and gold as:

$$K = \Delta H\ G/A\ M, \qquad (1)$$

where:

ΔH – the heat of melting of reference substance (j / mol) [6];

A – the area corresponding to the calorimetric peak of melting;

G – the sample weight in g.;

M – the molecular weight.

In our studies the heating rate of the samples was 200 K / hour (~ 3 K/ min.), the sensitivity of the galvanometer -500 mv, the number of measurements for each substance was 5-8.

In case of the samples of metallic ferromagnets Fe, Co, Ni experiments were carried out under analogous conditions. The heats correspondent to the anomalies in the region of transition points were calculated using the formula:

$$\Delta H = K \cdot A \cdot M / G \quad \text{(J/mole)}, \qquad (2)$$

where:

K – the calorimeter constant taken from the calibration graph (Fig. 2);

A – experimental calorimetric thermal anomaly;

M – the molecular weight of the metal;

G – the weight of the metal sample in grams.

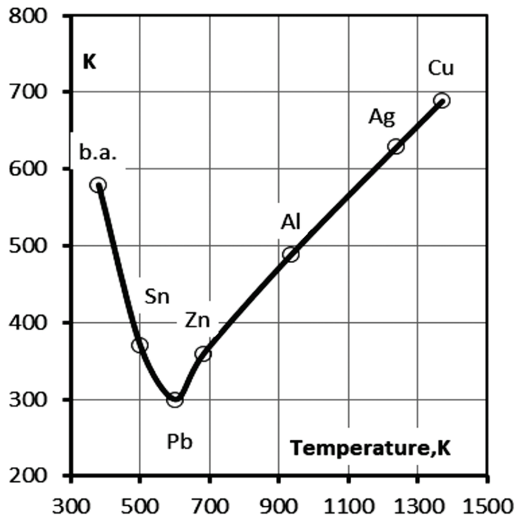

Fig. 2. Calibration curve of calorimeter.

Standard deviation of enthalpy S =±2.5%. The results are shown in Table 1 and in (Figs. 3,4).

Table 1. Characteristics of structural and magnetic phase transitions

	ΔH ferromag. (J/mole)	ΔH structural (J/mole)	T_c K	T_{st} K
Fe	454	955	1143	1259
Co	430	269	1400	700
Ni	372		631	

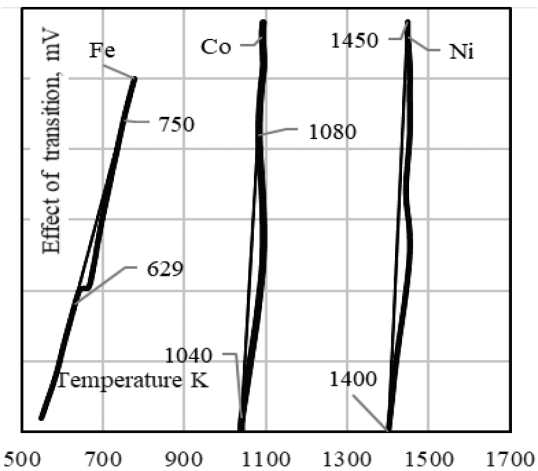

Fig. 3. Enthalpy of magnetic transition of iron, cobalt, nickel.

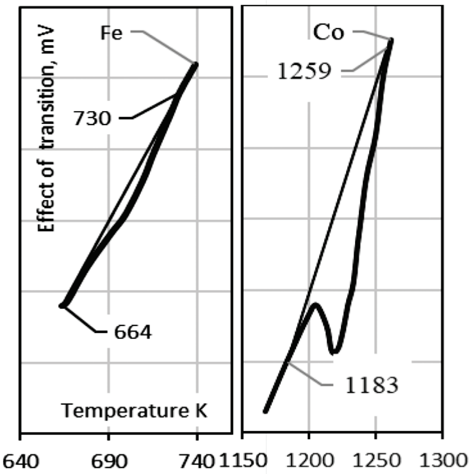

Fig. 4. Enthalpy of structural transition of iron and cobalt.

It is known that in most cases the ferromagnetic disordering process is realized in the form of second-order transformations with the λ-shaped form of heat capacity function. Based on the temperature dependence of magnetization (magnetic moment M) as an order parameter, we can conclude that the process of magnetic disordering occurs most intensely in the immediate vicinity of the critical temperature – Curie point T_c, making this area most interesting for detailed study. Therefore, the magnetic part of the enthalpy (H_m) and the excess magnetic part of the heat capacity (C_m) in classical ferromagnets are determined by the value of magnetic moment of saturation M, as [7]:

$$H_m = -0.5nM^2 \quad \text{and}$$

$$C_m = dH_m/dT = 0.5n\,(dM^2/dT) \qquad (3)$$

Consequently, a complete decreasing (jump) of the heat capacity at the transition temperature ΔC_m correlates with the magnetic moment of saturation M_s as well. A detailed study of the thermal characteristics in the critical region makes it possible to clarify the type and nature of the transformation, to determine the temperature boundaries and other critical indexes and parameters of transformation. All this information is necessary for further improvement of theoretical models of ferromagnetic phase transformations.

From this point of view, the study of the temperature function of heat capacity, the reliable determination of its excess magnetic component, and estimation of a heat capacity jump at the Curie point (T_c) are especially informative for characterization of ferromagnetic disordering process. For this purpose, as an example, we investigated the heat capacity of nickel in the region of 300–1000 K on the differential scanning calorimeter DSC-111 (Setaram). Accuracy of measurements, determined by the standard substance – alumina was 1.5%.

The obtained data are presented in Fig. 5 (curve 1) and in Table 2. A comparison with the most reliable literature values is given also. The critical point of the singularity on the λ – curve of heat capacity at 625K corresponds to the Curie point of nickel, which agrees well with the existing literature data and also with the values given in Table 2.

Table 2. Heat capacity of Nickel Cp(J/K.mole)

T K	$C_{p(Exp)}$	C_p [8,9]	T.K	$C_{p(Exp)}$	C_p [8,9]
298.15	25.83	25.79	600.00	34.88	34.75
310.00	26.50	26.08	610.00	35.50	35.38
330.00	27.05	26.67	620.00	36.89	36.22
350.00	27.51	27.26	624.00	37.89	37.05
370.00	28.01	27.84	625.00	36.63	-
390.00	28.51	28.43	630.00	33.41	-
410.00	28.72	29.01	640.00	32.24	32.87
430.00	29.48	29.60	650.00	31.69	31.82
450.00	29.73	29.64	670.00	31.44	31.61
470.00	29.98	30.35	690.00	30.98	31.19
490.00	30.48	30.94	710.00	30.98	30.98
510.00	30.98	31.40	750.00	30.73	31.07
530.00	31.82	32.24	800.00	31.19	31.15
550.00	32.45	32.70	850.00	31.40	31.53
570.00	33.16	33.70	900.00	31.74	31.40
590.00	34.42	34.29			

Evaluation of the magnetic part of enthalpy is associated with a very sensitive task of separating the excess magnetic heat capacity from the full experimental function Cp (T). To estimate the magnetic excess heat capacity C_m, we used the method described in our previous work [10], and also by extrapolating the heat capacity equation of Mayer and Kelly type [11] from the paramagnetic region to the standard temperature.

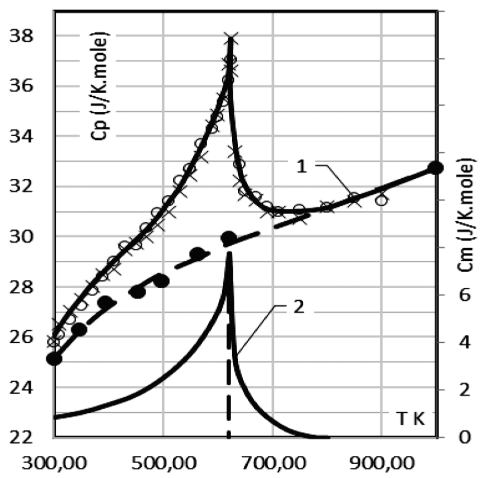

Fig. 5. Heat capacity of nickel
1. experimental Cp
2. magnetic part Cm.

The obtained magnetic heat capacity is shown in Fig. 5 curve 2. It is obvious that at the point of ferromagnetic transformation the heat capacity decreases sharply, but above T_c has a tail over 150K. It is assumed that in the region of $T<T_c$, the destruction of the long-range magnetic order occurs, and the region above Tc corresponds to the destruction energy of the nearest magnetic interactions. The full magnetic enthalpy H_m and entropy S_m are found to be 1100 J/mole and 2.3 J/K.mole, respectively. Despite the fact that the energy of short-range magnetic order (H_{sh}) is a small part of the total energy of magnetic exchange interactions (~15–20%), still the values of H_{sh}. S_{sh}, and ΔC_m are an additional and important information when developing model representations of ferromagnetic transitions, and at estimating corresponding critical parameters.

Based on calorimetric measurements, the relationship between the enthalpy of magnetic transformation and of magnetic moment of saturation of metallic ferromagnets is illustrated on Fig. 6a which reveals the rectilinear correlation. It should be said that the similar type of relationship was received in our earlier work (Fig. 6b) [11] for antiferromagnetic individual ferrites and their solid solutions, which has magnetic moments higher than 2 nB.

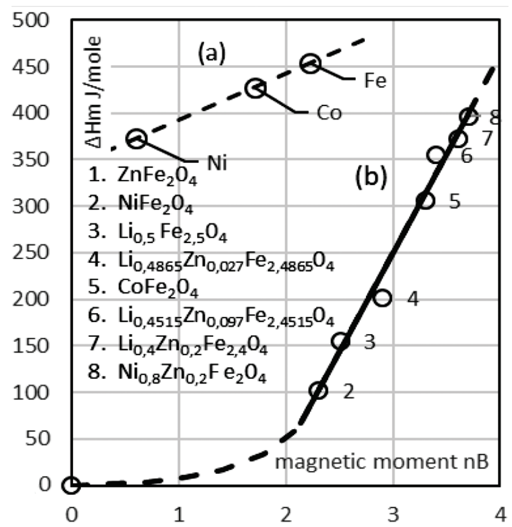

Fig. 6(a,b). Correlation between magnetic enthalpy ΔHm and magnetic moment nB:
(a) – Ni, Co, Fe
(b) – ferrites.

ფიზიკური ქიმია

სტრუქტურული და მაგნიტური ფაზური გარდაქმნების თერმული ანომალიები რკინის ქვეჯგუფის მეტალებში

მ. ხუნდაძე*, ვ. ვარაზაშვილი*, თ. მაჩალაძე*, მ. ცარახოვი*, რ. ჯორბენაძე*

**ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, რ. აგლაძის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

წარმოდგენილ ნაშრომში ექსპერიმენტულად შესწავლილია Fe, Co, და Ni-ის სტრუქტურული და მაგნიტური ფაზური გარდაქმნები. კვლევები ჩატარებულია ფირმა „Seteram"-ის (საფრანგეთი) მაღალტემპერატურულ კალორიმეტრ HT-1500-ზე. დადგენილია ამ გარდაქმნების შესაბამისი ტემპერატურული ზღვრები და თბური ეფექტების ენთალპია. 300-1500 K-ის ფარგლებში: Fe-ს კიურის ტემპერატურაა T_c = 1143K, ენთალპია ΔH_m = 454 J/mole; სტრუქტურული გარდაქმნის ტემპერატურა T_{st} = 1183 K , ენთალპია ΔH = 623 J/mole: Co-ის T_c = 1400 K, ΔH_m = 430 J/mole; T_{st} = 700 K, ΔH= 269J/mole; Ni-ს T_c =631 K, ΔH_m=373 J/mole; გამოვლენილია კორელაციის ხასიათი მაგნიტურ მომენტსა და ფერომაგნიტური გარდაქმნის ენთალპიას შორის. წინასწარმა თერმოგრავიმეტრულმა კვლევამ გვიჩვენა, რომ მაღალტემპერატურული კვლევები ჰაერის ატმოსფეროში დაკავშირებულია მნიშვნელოვან ცდომილებებთან მეტალების ჟანგვის პროცესებით გამოწვეული გავლენის გამო. ამიტომ ჟანგვითი პროცესების თავიდან აცილების მიზნით კალორიმეტრული გაზომვები ჩავატარეთ არგონის ატმოსფეროში. ვინაიდან ფერომაგნიტური გარდაქმნების დახასიათებისათვის განსაკუთრებით ინფორმაციულია ჭეშმარიტი თბოტევადობის ტემპერატურული ფუნქციის ექსპერიმენტული კვლევა, ამიტომ წარმოდგენილ ნაშრომში მაგალითის სახით შესწავლილია ნიკელის თბოტევადობა 300–900K ფარგლებში დიფერენციალური სკანირების კალორიმეტრის (DSC-111) გამოყენებით. სპეციალური მეთოდის საშუალებით საერთო ექსპერიმენტული თბოტევადობიდან გამოყოფილი და შეფასებულია მისი ფერომაგნიტური მდგენელი და ამის საფუძველზე განისაზღვრა ნიკელის ფერომაგნიტური გარდაქმნის შემდეგი ძირითადი მახასიათებლები: მაგნიტური ენთალპია, ენტროპია, თბოტევადობის ვარდნა კიურის ტემპერატურასთან, ახლო და შორი მაგნიტური გაცვლითი ურთიერთქმედების შესატყვისი ენერგეტიკული მაჩვენებლები.

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Received January, 2019