HEAT OF DISSOCIATION* OF KURNAKOV COMPOUNDS

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HEAT OF DISSOCIATION* OF KURNAKOV COMPOUNDS

Ni_3Fe, Ni_3Mn, Ni_3Cr, and Ni_3V

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In 1914 N. S. Kurnakov, for the first time using the copper—gold system as an example, established the formation of metallic compounds from solid solutions (1). Subsequent investigations of metallic systems by methods of physicochemical analysis made it possible to discover similar phenomena in many solid solutions of metals. These compounds, formed from solid solutions, were named Kurnakov compounds in honor of their discoverer (2). However, in the literature, mainly foreign (3,4), the formation of compounds from solid solutions is often regarded as a simple atomic rearrangement associated with ordering of the structure in a homogeneous medium, without a phase transformation.

In the nickel—iron, nickel—manganese, and nickel—chromium systems, the formation of metallic compounds of composition Ni_3Me from solid solutions takes place; but on the equilibrium diagrams of these systems in the region of 75% nickel, usually only a dashed line of the critical temperatures of ordering of the solid solutions is drawn (5).

At the same time, phase transformations with the formation of metallic compounds must be accompanied by a considerable change in energy, and on the phase diagram of the system there must exist an independent region of extension of these compounds, including a two-phase region.

Determination of the heats of phase transformations of alloys of composition Ni_3Me in the systems nickel—iron, nickel—manganese, nickel—chromium, and comparison of them with the heats of formation of the compounds Ni_3V and Ni_3Ti can provide additional information on the nature of the transformations in these systems.

In work (6), the influence of the disordering process on the temperature dependence of the heat capacity of an alloy of composition Ni_3Fe, previously annealed for 500 h in the temperature interval from 490° to 370°, was studied. By integrating the heat capacity in the temperature range from 325° to 625°, the magnitude of the disordering energy of the alloy was calculated, amounting to 0.8 kcal/g-at. Data on the corresponding heats in the systems nickel—manganese, nickel—

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

chromium, and nickel—vanadium were not found in the literature. For the heat of formation of the metallic compound Ni_3Ti, which forms from the melt during crystallization, the value proposed by Kubashevsky in work (^{7}) may be used.

In the present work, determination of the heats of phase transformations in the systems nickel—iron, nickel—manganese, nickel—chromium, and nickel—vanadium was carried out by the thermographic method developed by L. G. Berg and V. Ya. Anosov (^{8}). The method consists in comparing the areas of the peaks on the differential heating curve that correspond to thermal effects in the standard and in the sample. In our work the method of a separate standard was used (^{9}). Iron was chosen as the comparison standard; the thermal effects of the magnetic $\alpha \to \beta$ and polymorphic $\beta \to \gamma$ transformations of iron have been measured calorimetrically and tabulated [10]. Knowing the thermal effects of these two transformations, one can determine the relative error of the chosen method by calculating the magnitude of one thermal effect from the known magnitude of the other and comparing it with the tabulated value. As the calculations show, the discrepancy between the experimental value of the heat of the $\alpha \to \beta$ Fe transformation and the tabulated value lies within 2-5%, i.e., within the accuracy limits of the method used.

In determining the thermal effects of transformations in alloys of nickel with manganese, nickel with iron, and nickel with chromium, nickel was used as a standard along with iron. The areas of the thermal effects were measured by a convenient and simple method of geometrical integration using a linear planimeter [22].

Fig. 1. Heating curves of the alloy Ni_3Fe:
a—nickel standard; *b*, *v*—iron standard

Fig. 2. Heating curve of the alloy Ni_3Mn:
a—after annealing for 700 h; *b*—the same after 1400 h.

It should be noted that the thermographic method for determining thermal effects has undergone extensive experimental verification on salt systems and natural compounds, but has scarcely been used for the study of metals and alloys. At the same time, such systems, owing to the high thermal conductivity

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* The heat of dissociation is the heat of transition of the compound into a solid solution at the critical transition temperature.

Fig. 3. Heating curve of the alloy Ni_3V after annealing of the alloy for 1400 h at 950°.

Figure 3: Fig. 3. Heating curve of the alloy Ni_3V after annealing of the alloy for 1400 h at 950°.

and compactness of the material, are very convenient objects for applying this method to the investigation of heats of reaction in the solid state.

Alloys of composition Ni_3Me were prepared in an electric-arc furnace in an argon atmosphere from electrolytic nickel, iron, manganese, chromium, and carbothermic vanadium containing 99.8% vanadium. The alloys for study were selected by chemical analysis and corresponded almost exactly to the stoichiometric composition Ni_3Me. The thermal treatment of the alloys consisted of high-temperature homogenizing annealing and prolonged annealing below the critical transformation temperature: for Ni_3Fe, Ni_3Mn, and Ni_3Cr at 450°; for Ni_3V at 950°. The thermal effects were determined after 700, 1000, and 1400 h of annealing, i.e., as a function of the time required to bring the alloys into the equilibrium state. The conditions for recording the heating curves of all the investigated alloys of composition Ni_3Me were strictly standardized, which contributed to good reproducibility of the experimental results.

Figure 1 presents the heating curves of the alloy Ni_3Fe paired with nickel

and in combination with iron after 700 h of annealing. They have appreciable endothermic effects of dissociation of the metallic compound Ni_3Fe formed as a result of prolonged annealing. The magnitude of this thermal effect, ΔH, corresponding to the equilibrium state, was determined both by comparison with nickel and by comparison with iron and is 1.97 kcal/g-at. It is greater than the value proposed in work ([6]) and may be attributed to a more nearly equilibrium state of the alloy, attained as a result of the heat treatment carried out in our work. Reproduction of the record on several specimens gave deviations in the values of no more than 5%. The dissociation temperature of the compound is 570°.

Figure 2 shows the heating curves of the alloy Ni_3Mn, annealed for 700 and 1400 h. As is seen from the thermogram, increasing the duration of annealing to 1400 h gives a considerable increase in the magnitude of the thermal effect, by about an order of magnitude. A further increase in the annealing time does not change the magnitude of the thermal effect (the area of the peak on the differential curve). For the equilibrium state it is equal to 2.40 kcal/g-at. The dissociation temperature of the compound Ni_3Mn corresponds to 540°. The heating curves of an alloy of composition Ni_3Cr also have distinct endothermic effects of phase transformation. Increasing the annealing time from 700 to 1400 h gives an increase in the magnitude of the thermal effect by only a factor of two, and further extension of annealing at the same temperature does not change the value.

Fig. 3. Heating curve of the alloy Ni_3V after annealing of the alloy for 1400 h at 950°

Annealing for 2000 h at 400° and at 500° does not give an increase in the thermal effect; on the contrary, the thermal effect decreases.

The largest value of ΔH, attained after 1400 h of annealing at 450°, is 0.41 kcal/g-at, i.e., it is appreciably lower than the values of ΔH for Ni_3Fe, Ni_3Mn, and Ni_3V. It may be assumed that the process of compound formation proceeds extremely slowly and that the equilibrium state of the alloy was practically not reached. The question of the compound Ni_3Cr, in view of the low value of its heat of formation (dissociation), requires further investigation, all the more since some authors ([12]) assume the presence of a K-state in the annealed alloy, while others assume the composition of the compound to be Ni_2Cr instead of Ni_3Cr ([3]).

The magnitude of the thermal effect of dissociation of the compound Ni_3V, corresponding to the equilibrium state, which is reached after 1400 h of annealing of the alloy—

Table 1

Compound	Chemical composition, wt.% theor.	Chemical composition, wt.% found	Critical temp., °C (Kurnakov point)	Heat of dissociation of the compound ΔH, kcal/g-at	Heat of dissociation of the compound ΔH, cal/g	Relative measurement error, %
Ni_3Fe	24.08	24.20	570	1.9 ± 0.1	34 ± 2	5
Ni_3Mn	23.77	23.40	540	2.40 ± 0.09	41.5 ± 1.6	3
Ni_3Cr	22.80	22.75	585	0.41 ± 0.005	7.2 ± 0.1	1.5
Ni_3V	22.44	22.60	1070	3.60 ± 0.2	63.5 ± 3.4	5
Ni_3Ti	–	–	1380	8.4	–	–

at 950°, is 3.60 kcal/g-atom (Fig. 3). The dissociation temperature is 1070°.

Table 1 summarizes the data on the chemical composition of the compounds studied, their formation temperatures, and heats of dissociation.

Attention should be drawn to the considerable magnitude of the heats of dissociation, amounting to an integer number of large calories per 1 g-atom. The only exception in this respect is the compound Ni_3Cr. Evidently, the strength of the chemical bond in long-annealed alloys is of a different nature than in solid solutions, and the ordering processes in the alloys studied are associated

Fig. 4. Dependence of the heats (ΔH) and dissociation temperatures of Ni_3Me compounds on the position of Me in the periodic system: *a*—heats of dissociation, *b*—dissociation temperatures.

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with the formation of strong and stable metallic compounds. They must have, on the phase diagram of the system, independent regions of existence and, as first-order phase transformations, two-phase regions. A classic example of such a transformation has been found in the copper-gold system for the composition Cu_3Au ([1,3]).

Figure 4 presents the dependence of the heats and temperatures of dissociation of the compounds Ni_3Fe, Ni_3Mn, Ni_3Cr, Ni_3V, and Ni_3Ti on the position of the metals in the periodic system of the elements. From comparison of the data it may be concluded that the heats of dissociation for all the compounds are commensurate; they increase, with the exception of ΔH for Ni_3Cr, as the metal participating in the compound becomes more remote from nickel in the periodic system. Thus, for the series of compounds studied, the known dependence of the properties of chemical compounds on the position of the components in the periodic system is observed. The strength of the chemical bond in the compounds Ni_3Fe, Ni_3Mn, Ni_3V, and Ni_3Ti also, apparently, is determined by the heats of formation (dissociation); it increases with increasing difference in the chemical properties of the interacting metals, i.e., is related to the position of the reacting elements in the periodic system.

Fig. 4. Dependence of the heats (ΔH) and dissociation temperatures of Ni_3Me compounds on the position of Me in the periodic system: *a*—heats of dissociation, *b*—dissociation temperatures.

The increase in the strength of the chemical bond in the series of compounds Ni_3Fe, Ni_3Mn, Ni_3Cr (?), Ni_3V, Ni_3Ti should be reflected in the mechanical strength of these compounds, which requires additional investigation.

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