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NEW DATA OBTAINED BY THERMOMAGNETOMETRY, ON THE PHASE TRANSITIONS IN Ni, Co, Pt, Cu AND Fe–C ALLOYS

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On the basis of thermomagnetic and DTA measurements, together with data from the literature, it may be concluded that in some f.c.c. metals a phase transformation occurs just before melting.

Investigation of the phase transitions in some f.c.c. metals has been carried out by means of thermomagnetometry (TM) (measurement of the temperature-dependence of the magnetic susceptibility $\chi(T)$ during continuous heating and cooling). It has been established that the magnetic susceptibility (MS) changes non-monotonously near the melting and crystallization points: regular jumps, peaks and breaks are observed [1–4].

It has been assumed that the transition from a solid state with f.c.c. structure into the melt, and the reverse transformation, proceed through an intermediate b.c.c. or amorphous phase. Investigations on purest monocrystals by the TM and DTA techniques are presented here.

The MS is a structure-sensitive property characterizing the paramagnetic and diamagnetic states of a substance. The TM technique has some advantages for high-temperature investigations: 1. Accurate measurements are possible without direct contact. 2. Results are independent of the sample shape. 3. Any variations in the phase and structural state of a material are detected with high sensitivity.

Experimental and specimens

The measurements were made by Faraday's method, using the set described in [5]. Technical data of installation: the high-temperature limit was 2800°. The MS measurement error did not exceed 1% at temperatures up to 2000°; the sensitivity

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was up to 0.01%. A Sartorius electronic microbalance with a sensitivity up to 1×10^{-9} newton was employed. The masses of the specimens were 5–200 mg. The temperature was varied linearly with the help of a program regulator; it was measured with a photoelectronic pyrometer or a thermocouple. The method of HF heating with an intermediate heater was employed. The equipment was calibrated via standard samples. Special attention was paid to the equilibrium condition at any moment of measuring, and in particular to the necessary requirement of isothermality (no temperature gradients at any point of a sample). A tantalum or tungsten heater was used with a closed cavity, that represents an absolutely black body [1]. Thus, the need for spectral correction of the temperature measurement was eliminated. The measurement procedure and the data processing were performed fully automatically with a Hewlett–Packard computer. The samples are listed in Table 1.

Table 1 Parameters of samples

Material	Purity	Monocrystal	Polycrystal	Number of investigated specimens
Nickel	99.996	+	+	40
Cobalt	99.98	–	+	6
Copper	99.995	+	+	11
Platinum	99.9	–	+	6

Results

The variation in MS of a Ni monocrystal during continuous temperature change at 5 deg min^{-1} near the melting and crystallization points is depicted in Fig. 1. The MS decreases as the temperature increases. Twenty deg below the melting point, a sharp break (br.) is observed at Tbr. Upon further heating, the MS increases and attains the peak χ_p and the jump-down then occurs, caused by the melting. After the liquid state has been attained, the MS decreases monotonously with a slope smaller than that for the solid phase with f.c.c. structure, $\chi_{f.c.c.}$. The peak value is 1.5%.

On cooling, the melt supercooled. Crystallization is accompanied by a jump-down. This does not stop in the $\chi_{f.c.c.}$ heating curve, but the MS continues to decrease with decreasing temperature, having an opposite slope to that of the MS in the heating curve. A sudden increase in MS takes place exactly up to $\chi_{f.c.c.}$, and only then do the two polytherms merge. There is no doubt that the first jump indicates crystallization, while the second one is caused by the transition into the initial f.c.c.

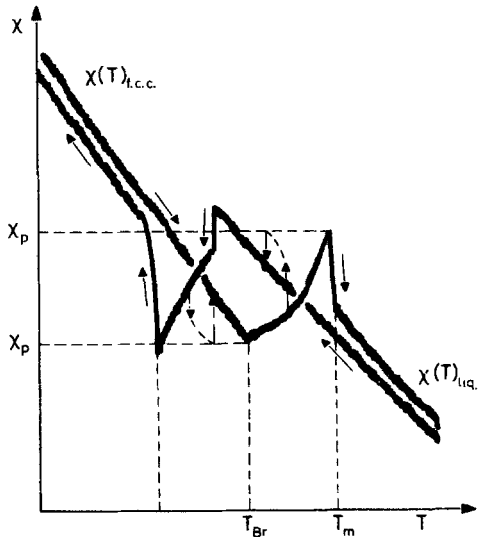

Fig. 1 Change of magnetic susceptibility of pure Ni monocrystal near points of melting and crystallization. →heating, ←cooling

structure. It is necessary to know the state that this transition took place from. These phenomena are not connected with the liberation or absorption of latent heat, because this state can be fixed by stopping the temperature variation. Furthermore, the temperature range of its existence is wide (up to 50 deg). This is not conditioned by the influence of admixtures and grain boundary melting, because the above-mentioned pecularities were displayed more clearly for the purest monocrystal specimens (though we observed grain and surface melting on polycrystals [3]). We have suggested that perhaps the transition from the dense f.c.c. structure into the liquid state, and the reverse transformation, take place through an intermediate phase with a more friable lattice (e.g. b.c.c. or amorphous), which exists in a narrow temperature range near the melting and crystallization points.

A sample heated up to $T_{br} < T < T_m$ and then cooled to room temperature changed its initial cubic shape: the apex of the cube remained sharp, but its edges and faces swelled so that its shape became like a pillow. The surface of the sample gave the appearance of melting. This can be caused by a transition into a more friable phase. The sample attained the shape of a sphere, however, only after heating to $> T_m$. If the increase of temperature is stopped in the interval $T_{br} < T < T_m$, the transition from the f.c.c. structure into the assumed intermediate phase and subsequent melting also occur, but very slowly (within tens of minutes): the MS slowly increases up to the value χ_p. Melting occurs only when χ_p is attained.

The MS jumpdown in the χ_{liq} curve is observed on melting (Fig. 1). Moreover, the transformation goes to the end, even if the temperature is decreased in these limits. While the specimen was not melted at higher temperature (dashed line), melting in this case is observed at a lower temperature. Therefore, the transition into the melt occurs only after the transformation into the intermediate phase has been completed. An analogous process occurs on cooling from the melt. The MS continues to decrease slowly to χ_{br} if the temperature is fixed (or increased up to the interval $T_{br} < T < T_m$) after the MS jump corresponding to crystallization. Only then is the jump in the f.c.c. curve observed. Hence, the transition into the initial f.c.c. phase occurs on cooling when the reverse transformation of the intermediate phase is completed. The transformation rate depends on the temperature difference $\Delta T = T - T_m$. All indicated peculiarities were registered if the sample was heated at a high rate. It is not yet clear whether the nuclei of the intermediate phase appear first and increase slowly until they totally occupy all the specimen volume, or the transformation slowly develops in the total volume simultaneously. Therefore, the intermediate phase has initial and final states. For some reason, transition between these states is slow. The effects of transformation and melting probably interfere, because T_{br} and T_m are very near.

The DTA investigations were performed with the Setaram equipment. In a number of cases, two peaks were recorded within the region of melting and crystallization. In other cases, a single peak was found, but this may be due to insufficient resolution.

The same pecularities in the changes in the MS and the DTA curves of Co, Cu and Pt were striking. The Fe–C alloys with a carbon content up to 1.5 weight % crystallized in a metastable b.c.c. phase, though the f.c.c. phase is stable in this temperature range [1, 6]. Analogous results have been found for Fe–Ni alloys [7]. It may be supposed that the transition from the f.c.c. structure into the liquid state is energetically advantageous if it takes place through an intermediate phase with a more friable structure (e.g. b.c.c. or amorphous). The following experimental data may be viewed as confirming our supposition: 1. Density measurements by the γ-method with simultaneous thermal analysis revealed the fact that the transition from the liquid state into the f.c.c. structure takes place in two stages, with two exothermic peaks [8]. The author of [8] agreed with our supposition. 2. Direct X-ray measurements suggest that the structures of liquid Ni and Pd at the melting points correspond to a b.c.c. lattice and not to a f.c.c. one [9]. Our measurements give evidence of the fact that these structural changes proceed even before melting. 3. Measurements of the electroconductivity of copper give grounds for the believe that its monotonous decrease is changed at $T \approx (T_m - 20)$K. There is information that heating of a Cu monocrystal to ≈ 20 deg below the melting point is accompanied by transformation into a polycrystal. 4. In a study of the grain

boundary melting in an aluminium bicrystal, it was found that the grain boundary split near 0.94 T_m (while no melting occurred along the boundary). This may be connected with the phase transformation in the solid state (formation of some nuclei of the new phase and their reverse transformation into the primary phase during cooling).

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Zusammenfassung — Auf Grund thermomagnetischer und differentialthermoanalytischer Messungen sowie Literaturangaben wird geschlossen, dass in manchen kubisch-flächenzentrierten Metallen wenig unterhalb der Schmelztemperatur eine reversible Phasenumwandlung, wahrscheinlich in eine kubisch-raumzentrierte oder amorphe Phase, stattfindet.

Резюме — На основании термомагнетых и ДТА измерений, а также соответствующих литературных данных, сделано заключение, что некоторые металлы с гранецентрированной кубической решеткой перед началом плавления претерпевают фазовое превращение.