

PHOTOSTIMULATED EXOELECTRON EMISSION DURING PHASE TRANSFORMATIONS OF BINARY AND TERNARY NICKEL ALLOYS

BY T. GÓRECKI

Physics Group, Engineering College, Opole*

AND B. SUJAK

Department of Solid State Physics, Institute of Experimental Physics, B. Bierut University, Wrocław**

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The temperature-dependence of photostimulated exoelectron emission from electrolytically obtained thin films of Ni-Zn and Ni-Co alloys was studied by using an open air point counter with saturated ethanol quenching vapour. The $\frac{N}{t} = f(T)$ curves were found to exhibit maxima of exoelectron emission intensity at points corresponding to the Curie temperature of the examined substances.

Investigations also concerned the temperature-dependence of photostimulated exoelectron emission intensity for magnetically soft Fe-Ni and Fe-Ni-Mo (Permalloy) alloys. The $\frac{N}{t} = f(T)$ curves has emission intensity maxima at temperatures corresponding to first- and second-order phase transformations occurring in the examined alloys. The Curie points of the Fe-Ni alloys determined on the basis of the positions of exoelectron emission intensity maxima corroborate the magnetic transformation line in the system Fe-Ni made according to data tabulated by Kaczkowski, thereby being in disagreement with the diagram given by Sachs.

The same dependence was also studied for the three-component alloys of Cu, Ni and Zn. Maxima in the $\frac{N}{t} = f(T)$ curves appear in the vicinity of the Curie temperatures for the processes of ordering changes in the examined alloys. The Curie temperatures for the ordering processes were found to coincide with the line for the quasi-binary Cu-Ni (3:2) — Cu-Zn (2:1) section of the Cu-Ni-Zn system.

It is shown that the phenomenon of exoelectron emission may be applied as a quick method of determining complete phase diagrams of thin-film and bulk systems of many components, regardless of the shape of the samples.

* Address: Zespół Fizyki, Wyższa Szkoła Inżynierska, Opole, Ozimska 75, Poland.

** Address: Instytut Fizyki Doświadczalnej, Uniwersytet Wrocławski, Wrocław, Cybulskiego 36, Poland.

If the phase diagram of the binary or quasi-binary system is exactly known for the examined substance, the exoelectron emission technique can provide a very accurate determination of the sample's chemical composition.

1. Introduction

Kramer was the first researcher who reported the appearance of intense exoelectron emission during the freezing process of Wood's metal. This effect constituted the basis for the now obsolete theory linking the phenomenon of induced electron emission with exothermal phase transformations in the surface layer of a sample (Modifikationstheorie) [1]. Later, intensity maxima of exoelectron emission had been observed many times during phase transformations of metals and alloys. Futschik, Lintner and Schmid [2] used this phenomenon for determining the phase diagram of the system Pb–Sn. Sujak and coworkers [3] performed similar measurements for the system Cd–Bi and showed that for a maximum of emission intensity to appear at the phase transformation point it is necessary to illuminate the sample's surface with UV radiation during the measurement. These authors observed emission maxima when the sample was heated and cooled alike, thereby proving that the observed effects are not conditioned by the thermal effects of phase transformations.

Kortov and Mints [4] found the appearance of enhanced exoelectron emission from BaTiO₃ and (Ba, Pb)Nb₂O₅ at the ferroelectric Curie point of these substances. Soon after, Kedavichius and coworkers [5, 6] utilized the exoelectron emission phenomenon for determining¹ the ferroelectric Curie points of SbSI and Bi₂S₃.

All of the papers mentioned thus far concerned emissive effects accompanying first-order phase transformations.

Sujak, Biernacki and Górecki [11] revealed that there is also intense exoelectron emission from nickel at the temperature corresponding to the ferromagnetic Curie point of this metal (631°K). Subsequent studies by Sujak and coworkers [13, 14] have confirmed this fact. Notwithstanding, conclusive proof of the relationship between the maximum in the curve of exoelectron emission intensity against temperature and the magnetic phase transformation of nickel required further studies to be carried out.

Sujak and coworkers demonstrated in a series of studies [11, 12, 15] that intensity maxima of photostimulated exoelectron emission also appear during the magnetic phase transformations, *i.e.* second-order transformations, of a number of other substances (Cr, NiO, Cr₂O₃, Fe_{1-x}S). These results have been corroborated by Gaprindashvili and Egolaev [16], who observed this effect during the magnetic transformation of ferromanganese austenite in the deformed alloy T23.

The experimental facts referred to above point to the possibility of utilizing the phenomenon of exoelectron emission for finding complete phase diagrams (*i.e.* ones

¹ As is implied by the results of measurements by Sujak and Kusz [7–10], the measurements of Kedavichius and coworkers [5, 6], and presumably some others, involved "apparent emission", which occurs due to the phenomenon of electrical microdischarges in the gas surrounding the ferroelectric substance, discovered by Sujak and Kusz.

containing the lines of both first- and second-order transformations) of multi-component systems.²

The measurements of the temperature-dependence of the intensity of photostimulated exoelectron emission from thin films of Ni-Zn and Ni-Co presented in this paper constitute a successive link of systematic researches. As stems from the phase diagrams of Ref. [24], an addition of cobalt to nickel causes the system's Curie point to go up, whereas an addition of zinc causes it to go down, relative to that of nickel itself. Hence, if the maximum in the $\frac{N}{I} = f(T)$ curves observed in earlier studies really is associated with the magnetic phase transformation of nickel, then an addition of cobalt to nickel should bring about a simultaneous shift of the Curie temperature and the temperature at which the maximum in the $\frac{N}{I} = f(T)$ curves occurs towards the higher temperatures. On the other hand, an addition of zinc should cause a downwards shift of both the Curie point and the temperature of the emission intensity maximum.

In order to check and to recognize the advantages and disadvantages of the exoelectron emission method, the present study also included measurements of the temperature-dependence of the intensity of photostimulated exoelectron emission from magnetically soft Fe-Ni and Fe-Ni-Mo (Permalloy) alloys.

Investigation of the processes of ordering changes in alloys are of enormous practical significance. Traditional methods of observing these processes (roentgenography, electron radiography, thermal analysis) are very time-consuming and require the use of expensive and very special equipment. Moreover, they are often found to be insensitive to the effects under study [18]. This is why a search is going on for new simple methods of detecting "order-disorder" phase transformations in alloys. The positive result of the application of the phenomenon of photostimulated exoelectron emission for detecting structural changes in brasses [19] suggested the possibility of using the exoemission method more extensively in studies on order-disorder phase transformations. This hypothesis, however, demanded further confirmation in the form of a positive result when this new method is applied for detecting changes in ordering in more intricate multi-component alloys.

Therefore, in the present study we also discuss the results of measurements of the temperature-dependence of the intensity of photostimulated exoelectron emission from Cu-Ni-Zn alloys, since the kinetics of the processes of changes in the structural order of these alloys is now well known thanks to the work carried out by Köster and Schüle [20, 21]. These researchers determined the position of the Curie point of ordering processes along several quasi-binary sections of the system Cu-Ni-Zn. It must be emphasized, however, that the method of measuring the Hall constant and electric conductivity of the examined alloys used by the authors was very tedious and laborious. In particular, it was very difficult to prepare the samples for measurement. Under these circumstances acquire-

² A comprehensive study of the problem of the exoelectron emission accompanying the phase transformations of nickel, its alloys and oxides is the subject of the doctor's dissertation of T. Górecki, Faculty of Mathematics, Physics and Chemistry of the Wrocław University, 1971.

ment of compatible results by the exoemission method would be an enormous achievement, considering the rapidity of the measurement with this method and the ease with which samples are prepared for measurement.

2. Experimental conditions

Measurements of the intensity of photostimulated exoelectron emission as a function of temperature were carried out by means of the arrangement described in detail in Ref. [12]. Exoelectrons were detected by means of an open air point counter with saturated ethanol quenching vapour. Measurements were performed in atmospheric air. The sample temperature changed at a rate of 50°K/min, and its surface was irradiated throughout the measurement by UV radiation from a quartz lamp with a Q-400 burner. For each of the alloys under study a series of seven to ten measurements were made, and the reproducibility of the shape of the $\frac{N}{t} = f(T)$ curves was quite satisfactory. It must be stressed that these samples were not submitted to any exciting factors such as X-rays, electron bombardment or plastic deformation prior to measurement.

Three groups of samples were investigated:

- a) thin films of binary Ni-Zn and Ni-Co alloys deposited electrolytically onto copper sheet;
- b) Fe-Ni and Fe-Ni-Mo (Permalloy) alloys cut from Permalloy tape hardened by rolling;
- c) Cu-Ni-Zn alloys of compositions in the vicinity of the quasi-binary section Cu-Ni (3 : 2) — Ni-Zn (2 : 1).

3. Sample preparation

a) Thin Ni-Zn and Ni-Co films

The binary alloys Ni-Zn and Ni-Co were deposited electrolytically on copper cathodes. They were electrodeposited from the solution:

NiSO ₅ · 7H ₂ O	— 240 g/l
KCl	— 20 g/l
H ₃ BO ₃	— 30 g/l
CoSO ₄ or ZnSO ₄	— quantity depending on intended concentration of Co ⁺⁺ or Zn ⁺⁺ ions in solution.

The solvent was distilled water. All reagents (manuf. POCh Gliwice) were labelled as being analytically pure. When Ni-Zn alloys were deposited the anode was of nickel sheet (insoluble anode [17]). Electrolyte temperature was maintained at 323°K by placing the electrolysis tank in a water bath with an Electrovag Wien 434a thermostat. The parameters of the electrodeposition of Ni-Zn alloys are gathered in Table I.

Ni-Co alloys were deposited at room temperature with a combined nickel and cobalt anode [17]. The ratio of the metal Ni and Co sheet surfaces of the anode was approxi-

TABLE I

Series	Ratio of concentrations of nickel and zinc ions in solution*	Current density [A/dm ²]	Electrolysis duration [min]
Ia	96 : 1	2.5	30
Ib	96 : 1	5.0	15
Ic	96 : 1	7.5	10
Id	96 : 1	10.0	5
Ie	96 : 1	20.0	2.5
IIa	32 : 1	2.5	30
IIb	32 : 1	5.0	15
IIc	32 : 1	10.0	5
IId	32 : 1	20.0	2.5

mately equal to the ratio of Ni⁺⁺ and Co⁺⁺ ion concentration in the solution. The parameters of the Ni-Co alloy deposition processes are given in Table II.

TABLE II

Series	Ratio of concentrations of nickel and zinc ions in solution*	Current density [A/dm ²]	Electrolysis duration [min]
IIIa	9 : 1	2.5	40
IIIb	9 : 1	5.0	20
IIIc	9 : 1	10.0	10
IIId	9 : 1	20.0	5
IVa	19 : 1	2.5	40
IVb	19 : 1	5.0	20
IVc	19 : 1	10.0	10
IVd	19 : 1	20.0	5

* Assuming that the degree of dissociation of the nickel, cobalt and zinc salts is the same

The cathodes coated with the alloy were rinsed in running and distilled water, and then dried in a stream of warm air. Samples were cut from the alloy-covered copper sheet in the form of disks of 12 mm diameter for use in the exoelectron emission measurements. Some of the samples were saved for control measurements of the Curie temperature by the magnetic method.

Control measurements of the Curie temperature of the examined Ni-Zn and Ni-Co alloys were carried out by means of the magnetic balance of Obuszko [22].

b) Fe-Ni and Fe-Ni-Mo (Permalloy) alloys

Measurements were performed on a strain-hardened Permalloy strips of Fe-Ni and Fe-Ni-Mo alloys produced at the Experiments Department of the Institute of Non-Ferrous Metals in Gliwice during work associated with the preparation of the Polish Standard No. PN-67/H-87047. The compositions of the alloys and the results of Curie temperature measurements performed by their manufacturer are given in Table III.

TABLE III

Grade	Symbol	Alloy composition [% weight exoem.]				Curie point T_C [°K]	T_{max} [°K]
		Ni	Mo	Cu	Fe		
Nifeperm 794	P79	79	4	—	17	763	755
Nifemax 795	P79S	79	5	—	16	673	670
Nifeperm 763	P76	76	3	5	16	693	700
Nifeperm 50	P51	50	—	—	50	773	765
Nifeperm 49	P50	49	—	—	51	763	755
Feniperm 36	P36	36	—	—	64	523	540

TABLE IV

No	Name of alloy	Symbol	Composition [% weight]			Polish standard
			Cu	Ni	Zn	
I	cupro-nickel	MNM401	59	40	—	PN-69/H-87052
II	argentan	MZN18	55	18	27	PN-69/H-87027
III	argentan	MZN15	65	15	20	PN-69/H-87027
IV	argentan	MZN12	64	12	24	PN-69/H-87027
V	nickel brass	MN65	65	6	29	PN-69/H-87025

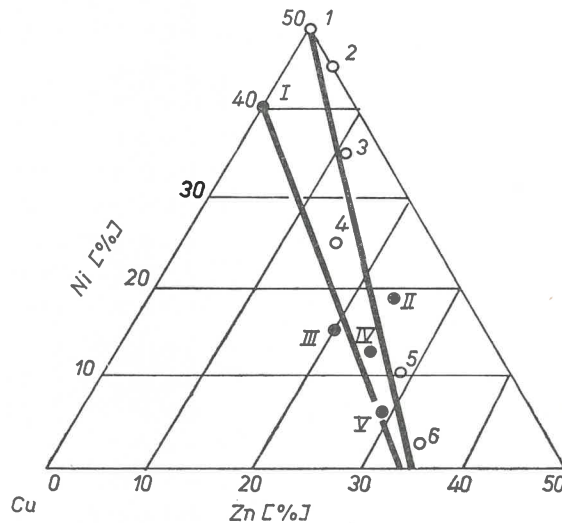


Fig. 1. Position of examined Cu-Ni-Zn alloys in the phase diagram: I-V alloys studied in this work, 1-6 alloys studied by Köster and Schüle [21] by the method incorporating Hall constant measurements

The strips obtained from the manufacturer were from 0.1 to 0.3 mm thick. Samples 16 mm in diameter were cut out with a die.

c) Cu-Ni-Zn alloys

Measurements concerned samples of Cu-Ni-Zn alloys lying near the quasi-binary section Cu-Ni (3:2) — Cu-Zn (2:1). The compositions of the tested alloys are presented in Table IV, whereas their position in the phase diagram is illustrated in Fig. 1. The argentan alloy samples came from the Non-Ferrous Metals Rolling Mill at Czechowice, whereas the cupro-nickel and nickel brass were obtained from the Institute of Non-Ferrous Metals in Gliwice. The sheet acquired from the producers were rolled to 0.2 mm thickness and by means of a special die samples in the form of disks 16 mm in diameter were cut.

Measurements of the temperature-dependence of the intensity of photostimulated exoelectron emission were carried out two weeks after the samples were prepared.

4. Results of measurements

a) Thin-films of binary Ni-Zn and Ni-Co alloys

The experimental curves of the temperature-dependence of the intensity of photostimulated emission of exoelectrons from Ni-Zn alloys of the Ia-e and II-a-d series are presented in Figs 2 and 3. In all of the $\frac{N}{t} = f(T)$ curves there are maxima appearing at temperatures lower than that at which the analogous exoemission intensity maximum

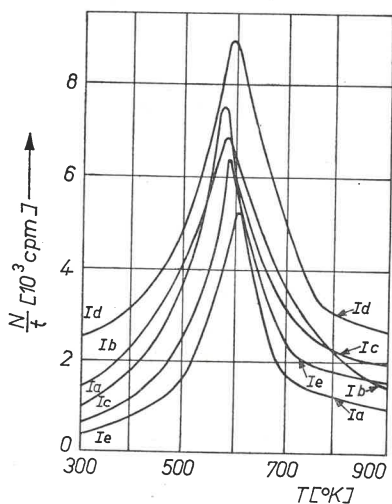


Fig. 2

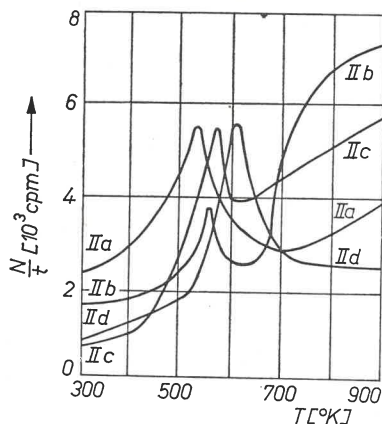


Fig. 3

Fig. 2. Temperature-dependence of intensity of photostimulated exoelectron emission from Ni-Zn alloys of series Ia-e

Fig. 3. Temperature-dependence of intensity of photostimulated exoelectron emission from Ni-Zn alloys of series IIa-d

appears for pure nickel [11, 12, 23]. As the current density applied during the electrode position of the alloys is increased, the maxima shift towards the higher temperatures. An increase in the zinc content in the alloy achieved by increasing the concentration of Zn^{++} ions in the solution brings about a drop in the temperature at which the maximum in the $\frac{N}{t} = f(T)$ curve appears (Fig. 6).

Figures 4 and 5 present the results of measurement of the intensity of photostimulated exoelectron emission against temperature for the Ni-Co alloys of the IIIa-d and IVa-d

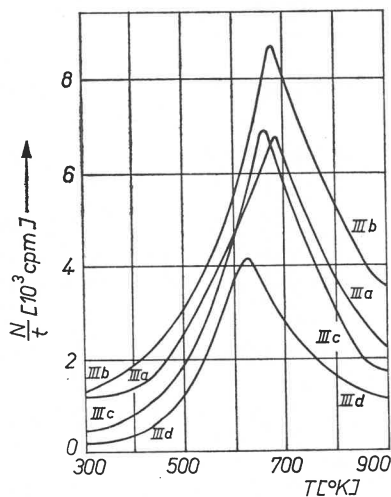


Fig. 4

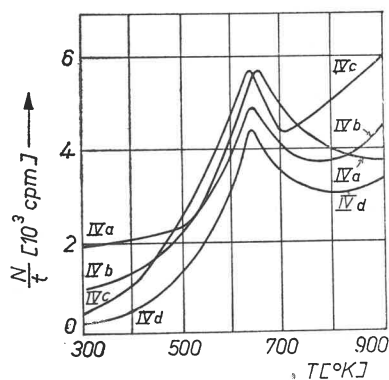


Fig. 5

Fig. 4. Temperature-dependence of intensity of photostimulated exoelectron emission from Ni-Co alloys of series III a-d

Fig. 5. Temperature-dependence of intensity of photostimulated exoelectron emission from Ni-Co alloys of series IV a-d

series. The maxima in these curves are at temperatures higher than the Curie temperature of pure nickel. With increasing current density applied during electrolysis the maxima shift towards lower values of temperatures. An increase in the cobalt content in the alloy, associated with an increase in the Co^{++} ion concentration in the solution, causes the maximum in the $\frac{N}{t} = f(T)$ curve to appear at a higher temperature (Fig. 6).

The Curie points determined by the thermomagnetic method for the powders of all of the examined alloys demonstrate excellent agreement with the temperatures of the photostimulated exoelectron emission maxima of these materials (Fig. 6).

b) Fe-Ni and Fe-Ni-Mo (Permalloy) alloys

All experimental curves of the temperature-dependence of the intensity of photostimulated emission of exoelectrons from Fe-Ni alloys (Figs 7 and 8) have two distinct maxima.

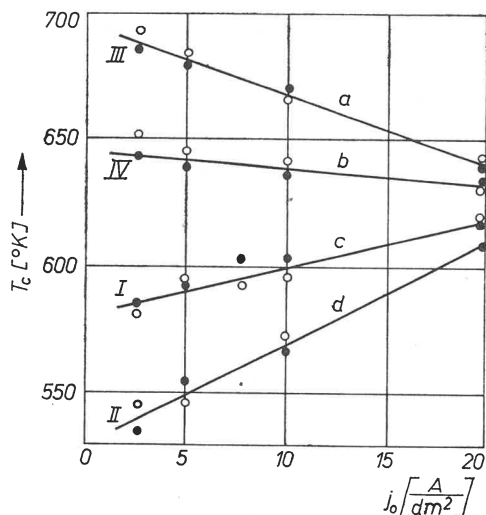


Fig. 6. Comparison of Curie temperatures of examined Ni-Zn and Ni-Co alloys determined on the basis of the position of maximum photostimulated exoelectron emission (open circles) and by the thermomagnetic method (dots)

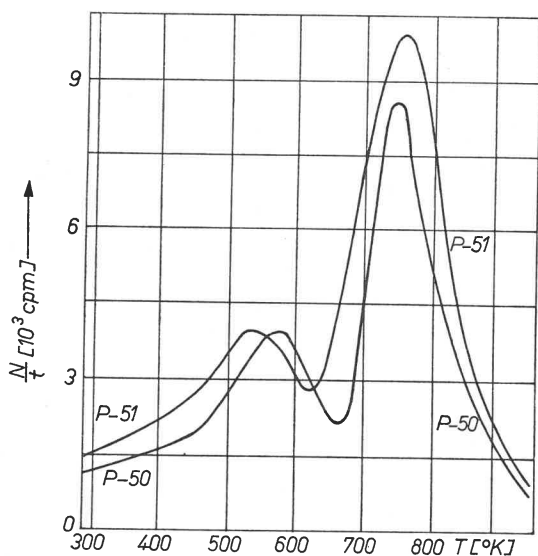


Fig. 7

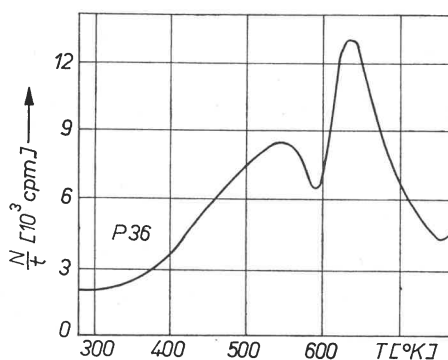


Fig. 8

Fig. 7. Intensity of photostimulated exoelectron emission *versus* temperature for alloys P50 and P51

Fig. 8. Intensity of photostimulated exoelectron emission *versus* temperature for alloy P36

The temperature at which one of them appears, coincides (within experimental error) with the Curie temperature determined in magnetic studies (Table III). The other maximum presumably should be related with the $\alpha \rightarrow \gamma$ polymorphic transformation taking place in the examined alloy. With an increase of the nickel content in the sample, the temper-

ature of this maximum drops, what is in conformity with literature data regarding the course of the $\alpha \rightleftharpoons \gamma$ transformation line in the phase diagram of the system Fe–Ni [24]. It should be emphasized that the $\alpha \rightleftharpoons \gamma$ transformation lines have been determined in many phase diagrams for samples submitted to special heat treatment stabilizing the α -phase. The samples used in this work were not treated thus, thereby the $\alpha \rightarrow \gamma$ transformation in them occurred at a temperature lower somewhat than would stem from these diagrams.

In the literature concerning the phase diagram of the system Fe–Ni there is a large discrepancy of views regarding the run of the magnetic transformation line in Fe–Ni alloys, especially in the range of nickel concentrations of 30 to 60% by weight. This is illustrated in Fig. 9, which also includes the Curie points of the investigated Fe–Ni alloys determined by the magnetic (x) and exoemission (o) methods. As follows from this figure, the magnetic Curie points and their corresponding temperatures of peaks in the

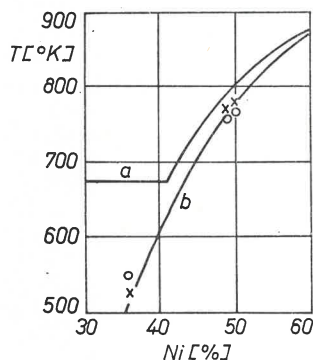


Fig. 9. Course of magnetic transformation line in the system Fe–Ni: *a* – according to phase diagram given by Sachs [29], *b* – according to tabulated data in paper by Kaczowski [25], \circ – Curie points determined in this work by the exoemission method, \times – Curie points determined by magnetic methods by the alloy manufacturer

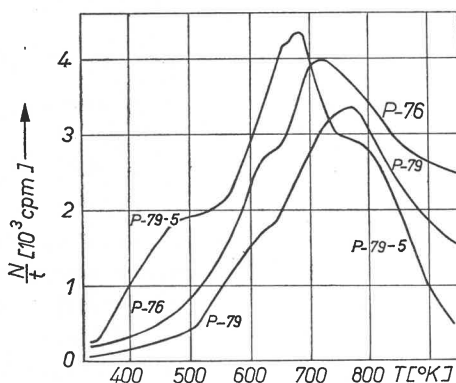


Fig. 10. Curve of the dependence of intensity of photostimulated exoelectron emission from alloys P76, P79 and P79S upon temperature

$\frac{N}{t} = f(T)$ curves are well aligned on the curve plotted according to the data of Kaczkowski [25] (curve *b*); this appears to definitely settle the matter to the disadvantage of the diagram given by Sachs [29].

The curves of the temperature-dependence of the intensity of photostimulated exoelectron emission from Fe–Ni–Mo alloys are also found to exhibit maxima at the Curie temperature (Fig. 10). These maxima, however, are very broad, and their slopes have inflexions which imply that the measurement gives curves which are the envelope of several exoemission maxima, presumably associated with additional phase transformations in the examined alloys. The inflexion at the low temperature side of the Curie point maximum should probably be ascribed to processes of changes in structural order in the examined substances (compare shape of ordering temperature curve in phase diagrams of Fe–Ni [24, 30]).

c) Cu–Ni–Zn alloys

The experimental curves of the temperature-dependence of the intensity of photostimulated exoelectron emission for these materials are shown in Figs 11 and 12. A distinct maximum is seen to appear in the $\frac{N}{t} = f(T)$ curves for all of the examined alloys.

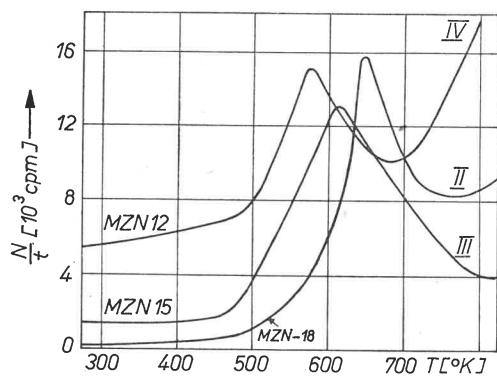


Fig. 11

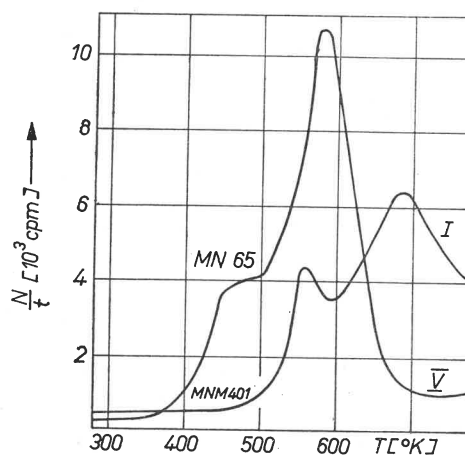


Fig. 12

Fig. 11. Curves of the temperature-dependence of intensity of photostimulated exoelectron emission from argentan alloys MZN 12, MZN 15 and MZN 18

Fig. 12. Curves of the temperature-dependence of intensity of photostimulated exoelectron emission from cupro-nickel MNM 401 and nickel brass MN 65

When proceeding along the quasibinary section under study the position of the maximum in the $\frac{N}{t} = f(T)$ curve systematically drops from 690°K for the composition Cu–Ni (3 : 2) to about 560°K for the composition Cu–Zn (2 : 1) (Fig. 13).

As stems from the data of Köster and Schüle [21] and Suchkov [26], the temperatures at which the α -phases of the Cu–Ni and Cu–Zn alloys become ordered are 700°K and 550°K, respectively. This lets the observed maxima to be connected with the changes in ordering in the examined alloys. Indeed, this is fully corroborated by comparing the course of the transformation temperature along the Cu–Ni (3:2) — Cu–Zn (2:1) section found according to the positions of the maxima in the $\frac{N}{t} = f(T)$ curves and the course of the ordering temperature for the Cu–Ni (1:1) — Cu–Zn (2:1) section studied by Köster and Schüle [21]. The latter was determined on the basis of the position of the minimum of the Hall constant in $A_H = f(T_{\text{hardening}})$ curves. As follows from Figs 13 and 14,

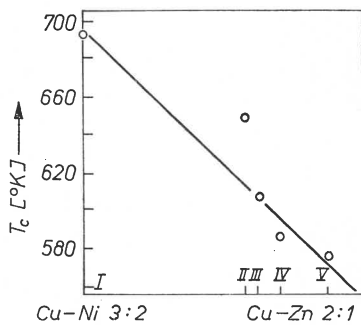


Fig. 13

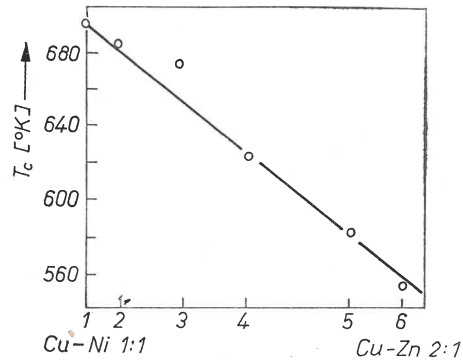


Fig. 14

Fig. 13. Temperature-dependence of order-disorder transformation of Cu–Ni–Zn alloys along Cu–Ni (3:2)—Cu–Zn(2:1) section. The curve is plotted on the basis of exoemission measurements
 Fig. 14. Dependence of ordering temperature of Cu–Ni–Zn alloys upon composition along quasibinary Cu–Ni(1:1)—Cu–Zn(2:1) section. The curve is plotted on the basis of the dependence of Hall constant upon temperature of alloy hardening [21]

there are linear changes of the order-disorder transformation temperature along the considered quasibinary section in both cases. Also, the numerical values of the temperature of transformation for alloys of similar compositions are comparable.

5. Discussion

The values of Curie temperatures for the examined alloys determined by the thermomagnetic and exoemissive methods compared in Fig. 6 are a confirmation of the anticipated and postulated relationship between the maxima in the temperature-dependence of the intensity of photostimulated exoelectron emission and the magnetic phase transformations in the examined samples. This appears to show that the method of exoelectron emission measurements may be used to detect magnetic phase transformations in all metals and alloys. The simplicity of measurements and the speed with which the temperatures of phase transformations may be found by the exoemission method must be

emphasized. Whereas the thermomagnetic method enables the Curie point to be determined by several hours of measurements, the same can be obtained by analogous measurements by the exoemission method within about 30 minutes.

A second, no less important, feature of the proposed method is its sensitivity. As shown by Lewowski [27] and Sokolov [28], exoelectrons are emitted from a thin surface layer of the sample of a thickness of the order of 100 nm, while the highest probability of emission is for the depth of the order of 10 nm. This means that the method of exoelectron emission makes possible a determination of the phase transformation temperature of thin films deposited by cathodic sputtering or sputtering in vacuum. If it is considered that the samples used in exoemission measurements have an area of approximately 1 cm², then at a definite depth of emergence of exoelectrons it is easily computed that this method may be used for detecting phase transformations in small quantities of substances of volumes of the order of 10⁻⁶ cm³, hence, a mass of the order of 10⁻⁶ to 10⁻⁵ g.

The method of exoelectron emission allows both first- and second-order transformations to be detected. Hence, it could be successfully applied for speedy determinations of complete phase diagrams of multi-component systems. Once such a diagram is plotted by the exoemission method, only the properties of the phase in the various diagram fields remain to be determined by traditional techniques. Thus, the measurement procedure would be considerably simplified and — what is just as important — considerably shortened in time.

The problem may also be reversed. If the phase diagram of a binary or quasibinary system, of which the examined substance is a part, is known, then the determination of the phase transformation point position by the exoelectron emission method can be the basis for finding the sample's composition. The accuracy with which the concentration of a constituent of a binary system may be measured is defined by the formula

$$\Delta c = \frac{\Delta T_m}{k}$$

where Δc is the error of measurement of the concentration of one of the constituents, ΔT_m is the accuracy of measurement of the temperature at which the exoemission intensity maximum associated with the given transformation appears, and k is the steepness (directional coefficient) of the phase transformation line in the phase diagram.

For example, at an easily attained accuracy of determination of the temperature of the exoemission intensity maximum of $\Delta T_m = 5^\circ\text{K}$ and a frequently encountered directional coefficient of the phase transformation line of $k = 20^\circ\text{K}/\%$, the accuracy of the concentration estimate would be 0.25%. It seems that a particularly favourable case is when in the range of temperatures accessible to exoemission measurements the sample goes through two or more phase transformations whose lines run in two opposite directions (*e. g.*, the $\alpha \rightleftharpoons \gamma$ transformation and Curie point in the system Fe–Ni). Under such circumstances the accuracy of the concentration measurement of one of the components may be even higher.

6. Conclusions

The results presented here and their conformity with data found by other authors with the use of acknowledged conventional measuring techniques prove that every phase transformation in metals and alloys can be accompanied by intense photostimulated exoelectron emission.

The method of determining the Curie temperature of processes of ordering changes in alloys on the basis of the positions of the maxima in the curves of photostimulated exoelectron emission intensity *versus* temperature may be advantageously employed also in the case of complicated multi-component alloys.

The phenomenon of exoelectron emission during phase transformations may even be utilized for determining complete phase diagrams of multi-component systems. It can be used also for determining the composition of binary or quasibinary alloys, provided the exact phase diagram of the system to which the examined sample belongs is known.

Merits of the exoemission method as compared with the now traditional methods are its simplicity, expedition of measurements and the ease of sample preparation. A certain drawback is the indistinction of the exoemission peaks corresponding to the various types of transformation and the fact that when the phase transformation points are near each other the emission effects accompanying the transformations become aggregated, thereby rendering determination of the transformation temperature more difficult. Subsequent studies should therefore go in the direction of searches for conditions under which the widths of the exoemission maxima corresponding to phase transformation would be the smallest.

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