Magnetic Characteristics of Ni-Pd-Mn Ternary Alloys for "Thermoseed"*

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This paper describes the development of the "Thermoseed," a thermally self-regulating implant for induction thermocoagulation of brain lesions. The thermoseed should have a low Curie temperature and a high saturation magnetization that will cease heating at a predetermined temperature, i.e., 343–373 K.

In contrast to many nickel base alloys, the saturation magnetization of nickel increases or remains constant with the addition of manganese and/or palladium, in spite of the decrease in the Curie temperature. The Ni-Pd-Mn ternary system introduced by Köster and Sallam has been re-examined, and the composition dependence of both the Curie temperature and the saturation magnetization has been determined in the ternary *fcc* solid solution range. The desired composition for a thermoseed is selected as the intersection of the saturation magnetization ridge and the desired Curie temperature contour.

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I. Introduction

This investigation has been made to develop new magnetic materials for the "thermoseed," a thermally self-regulating implant for induction thermocoagulation of brain lesions^{(1)~(3)}. For this application, if the thermoseed is over-heated to a temperature high enough to carbonize cell, normal living cells as well as abnormal cells may be destroyed.

For such a thermoseed, it is convenient to utilize the phenomenon of the inductive heating by hysteresis and eddy current losses in a magnetic material ceasing with its rapidly decreasing permeability and magnetization above the Curie temperature (T_c).

From the above, the requirement is that the thermoseed is a ferromagnetic alloy with a low Curie temperature and a high saturation magnetization that will thermally self-regulate at a predetermined temperature (i.e., 343–373 K), thus attacking the abnormal cells alone.

The process of inductive heating and thermal

self-regulating within the thermoseed works much effectively the more drastically the saturation magnetization disappears at the Curie temperature (T_c)⁽²⁾. From this reason, the thermoseed requires a large saturation magnetization (or magnetic moment) as well as a low T_c for the magnetic material. It would appear that some Ni alloys have a T_c below 373 K, and that, generally speaking, alloying makes the magnetic moment lower, together with the T_c ⁽⁴⁾⁽⁵⁾. However, Ni-Mn, Ni-Pd and Ni-Rh alloys are exceptions⁽⁴⁾⁽⁶⁾, and in Ni-Pd alloy, the addition of Pd leaves the value of the magnetic moment of Ni constant over a wide composition range, in spite of a monotonically decreasing T_c . Moreover, the addition of Mn appears to increase the magnetic moment of Ni, in spite of a monotonic decrease in T_c . The utility of Ni-Pd alloy for a thermoseed has already been investigated and reported on by Burton *et al.*⁽³⁾ The primary purpose of the present paper is the development of a new magnetic material for thermoseeds having both a low T_c , below 373 K, and a high magnetic moment. Such a magnetic material could possibly be made using the Ni-Pd-Mn ternary system, made from the two typical Ni-Mn and Ni-Pd alloy systems.

The equilibrium diagram of the Ni-Pd-Mn ternary system has been already reported by Köster and Sallam⁽⁷⁾, but not in sufficient detail for the present investigation. The second

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purpose of the present paper is to give more details of the ternary *fcc* solid solution range and to remedy the deficiencies in the diagram of Köster *et al.*⁽⁷⁾

II. Experimental Procedures

The raw materials were 99.99% electrolytic Mn, 99.98%Pd and 99.95%Ni, the Ni having been pre-melted three or four times in an electron beam furnace. The Ni-Pd-Mn alloys were made on a copper-hearth in an argon atmosphere by arc-melting, using a tungsten electrode. The alloy ingots were up to 0.005~0.008 kg in mass. Each ingot was repeatedly remelted after turning it over so as to homogenize it. During melting, it was found that a little Mn was lost by evaporation. The mass loss of the ingots during melting was assumed to be caused by the evaporation of Mn, and the composition of ingot was corrected by taking the mass loss to be almost equal to that of Mn. This assumption has been already experimentally ascertained by chemical analysis⁽⁸⁾.

The specimens, taken from the ingots after homogenization at 1173 K for 7.2 ks in vacuum, were heat-treated under the pre-determined conditions.

The Curie temperature was obtained from the temperature dependence of the magnetization of a 2 mm × 2 mm × 0.3 mm specimen, vacuum-encapsulated in a quartz tube, which was heated at the rate of 0.058 K/s in a magnetic

field of 8.4×10^5 A/m. The measuring apparatus used consisted of an automatic magnetic balance made from an electronic balance, the electric magnet and a pen recorder. The saturation magnetization was measured in disk-like specimens 5 mm in diameter and 0.2 mm in thickness at room temperature under a maximum field of 3.4×10^5 A/m, using the vibrating sample magnetometer (VSM-M155) made by the Princeton Applied Research Company.

X-ray diffraction patterns were observed on polished and etched specimens after heat-treatment. The determination for the alloy phase was performed by X-ray diffraction with a Mo target and Zr filter, and the lattice parameter was obtained from the (311) $K\alpha$ diffraction line using a Fe target with a Mn filter. The X-ray diffractometer used was made by Shimazu (VD-1A).

III. Experimental Results and Consideration

1. Ni-Pd-Mn ternary equilibrium diagram

Figure 1 shows the X-ray diffraction profile of a 35Ni-35Pd-30Mn[†] alloy, water-quenched after holding at 1223 K for 7.2 ks. In this, a line due to a second phase, other than the *fcc* phase (γ) was observed, and is considered to be due to the Pd₃Mn₂ phase, having a AuCu 1

† Composition is expressed in atomic percent throughout this paper.

Fig. 1 X-ray diffraction profile of a 35Ni-35Pd-30Mn alloy quenched from 1223 K, indicating the two phases $\gamma + \beta'$ (Pd₃Mn₂). Numerals shown are the index and relative intensity of the Pd₃Mn₂ phase, calculated from $a = 4.0495 \times 10^{-10}$ m and $c/a = 0.8826$.

structure, the so-called β' or β_1 phase, appearing at a relatively low temperature in the Pd-Mn binary system. In Fig. 1 both the diffraction angle (2θ) and the observed relative intensity, as well as the intensity ratio calculated with an assumed lattice constant $a=4.0495 \times 10^{-10}$ m and an axial ratio $c/a=0.8826$ for the β' phase are shown. These agree with the results obtained previously for Pd-Mn binary alloys^{(9)~(11)}. Moreover, it has already been found that the lattice constant and the axial ratio of the β' phase of Pd_3Mn_2 are not changed even if the Pd is partially substituted by Ni. From Fig. 1, the observed intensity is consistent with the calculated one. It cannot be said from the above whether crystalline anisotropy was apparent in any specimen. The volume fraction of β' in γ is estimated from these results to be about 50%. The solubility limit of β' in γ in Ni-Pd-Mn alloy was determined continuously from a phase examination by X-ray diffraction, metallographic observation and the measurement of the lattice constant, this being necessary for the determination of the magnetic properties of the single γ -phase alloy. From Fig. 2, which shows several examples, it can be seen that the lattice constant increases linearly at first with the solution of the precipitates into the alloy on increasing the

solution treatment temperature, and then becomes constant above a certain temperature as a result of the solution of all the precipitates. Figure 3 shows the Ni-Pd-Mn ternary system, summarizing these results. The diagram in the Mn-rich region is the same as that shown by Köster *et al.*⁽⁷⁾ The fine line indicated in Fig. 3 was also obtained by Köster *et al.* for the solubility limit of β' in γ at 1223 K. The two-phase coexistent region ($\gamma+\beta'$) investigated in the present paper appears to extend further towards the corner of the Ni side than Köster *et al.*'s results. Köster *et al.* did not investigate in detail the Ni-rich region, which is probably the cause of the differences between the present results and theirs.

The lattice constants of the γ single-phase Ni-Pd-Mn alloy obtained by quenching after solid solution treatment are shown in Fig. 4. It can be seen from Fig. 4 that the lattice constants of the Ni-Pd-Mn ternary *fcc* solid solution correspond to those of the binary system obtained so far⁽¹²⁾, monotonically increasing from the corner of Ni toward the Pd-Mn side.

2. Magnetic properties of the Ni-Pd-Mn *fcc* solid solution

As shown in Fig. 3, the γ single-phase region of the Ni-Pd-Mn ternary system is quite narrow in the low temperature region. Each sample used to determine T_c of the γ phase was thus used after solution treatment at different temperatures in the range of 1223~1423 K, depending on the composition. The results obtained are summarized in Fig. 5, where it can be seen that the Curie temperatures of alloys studied are lower than 573 K. Furthermore, from measurements during cyclic heating and cooling, it can be concluded that the $\gamma \rightarrow \beta'$ transformation does not arise, since the magnetization was constant. It can be seen from Fig. 5 that the decrease in T_c due to the addition of both Pd and Mn to Ni is more gentle than the decrease in T_c due to the single addition of either Pd or Mn.

The magnetic moment of an alloy is generally obtained from measurements of the saturation magnetization at low temperature, but because of the apparatus used here, the saturation

Fig. 2 Temperature variation of the lattice constant for several *fcc* Ni-Pd-Mn alloys.

magnetization (I_0 , in Wb/m^2) and the magnetic moment or Bohr magneton number (n_0) per atom at 0 K were calculated from data on

the saturation magnetization (I_s) at room temperature and the Curie temperature (T_c in K), using the theoretical molecular field

Fig. 3 Solubility limits of the β' (Pd_3Mn_2) phase in the fcc Ni-Pd-Mn solid solution.

Fig. 4 Lattice constants (in 10^{-10} m) for the fcc Ni-Pd-Mn system.

Fig. 5 Isotherms of the Curie temperature (in K) for the fcc Ni-Pd-Mn solid solution.

approximation[†],

$$I_s/I_0 = \tanh(I_s/I_0)/T/T_c, \quad (1)$$

$$n_0 = A \cdot I_0 / N_0 \cdot d \cdot \mu_B, \quad (2)$$

where A is the effective molar mass of the atom (kg/mol), d is the density (kg/m³), N_0 is Avogadro's number (mol⁻¹) and μ_B is the Bohr magneton (Wb·m). The density d is calculated from the lattice constant measured here. The relation between the saturation magnetization and the temperature is a theoretical one with the assumption that the total angular momentum $J=1/2$, since this theoretical value is in good agreement with experiment for many metals and alloys⁽¹³⁾. Some values of n_0 for Ni-Pd and Ni-Mn binary alloys have already been reported⁽⁴⁾⁽⁶⁾⁽¹⁴⁾⁽¹⁵⁾. It can be seen from Fig. 6 that, comparing n_0 as calculated by the above formula with these reported values, the agreement is good, within the experimental error. It is concluded that, in all the alloys, the variation of the magnetization obtained with the magnetic balance from room temperature to T_c satisfies Fig. 1 adequately. From the above, it is considered that the value of n_0 for the ternary alloy system obtained in this investigation is reasonable. Figure 6 shows values of T_c compared with previous results,

[†] Satisfactory thermal self-regulation for thermoseed material can be attained by a rapid variation of I_s around T_c . Here, it is assumed that the parameter $(I_s/I_0) - (T/T_c)$ is normalized, regardless of the alloy composition, and then that the rapid variation of I_s around T_c is expressed by the value of I_0 , and particularly by n_0 . For practical use, this must be expressed by I_0 , since the object is thermal self-regulation under constant volume conditions, but since A and d are practically constant in the range of compositions investigated, the results are not very different.

Fig. 6 Saturation magnetization and Curie temperature for Ni-Mn and Ni-Pd alloys.

also. The variation of n_0 with composition in the *fcc* solid solution Ni-Pd-Mn ternary system, obtained by the above method, is shown in Fig. 7. It can be seen that the peak in the saturation magnetization that occurs at 8–9 at%Mn in the Ni-Mn binary system forms a ridge towards the Pd corner in the Ni-Pd-Mn ternary system.

From Fig. 8, which shows the relation between n_0 and T_c for Ni-base binary alloys, many Ni alloys (with Cu, V, Cr, Ti or Zn) show a similar trend to a decreasing n_0 in proportion to the variation of T_c . However, Ni-Pd and Ni-Mn alloys show a different behavior. In Fig. 8, the relation between n_0 and T_c along the ridge of the maximum in the saturation magnetization, shown by the dotted line in Fig. 7, is also shown. From this, it is obvious

Fig. 7 Contours of the magnetic moment per atom for the *fcc* Ni-Pd-Mn solid solution. The magnetic moment is shown in Bohr magneton number per atom.

Fig. 8 Relation between the Curie point and the magnetic moment per atom in various nickel-base alloys. The magnetic moment is shown in Bohr magneton number per atom.

that Ni-Pd-Mn alloys have the largest n_0 amongst those Ni alloys having a T_c below 473 K. The alloy with a composition at the intersection between the ridge representing the maximum saturation magnetization in Fig. 7 and a T_c isotherm line, as shown in Fig. 5, is the best thermoseed alloy for maintaining a temperature T_c . For example, the composition of the Ni-Pd-Mn alloy recommended for a thermoseed alloy for a temperature of 373 K is 33Ni-65Pd-2Mn. Field tests of the thermosed material have been carried out, with good results, which will be reported elsewhere.

IV. Conclusion

In the *fcc* single-phase region of the Ni-Pd-Mn ternary solid solution, the solubility of the β' phase, and the composition dependence of the Curie temperature and the saturation magnetization were investigated. The results obtained are summarized as follows:

(1) The equilibrium diagram was drawn based upon results obtained by an examination of the phases in equilibrium at several temperatures in the Ni-Pd-Mn alloy system, and the deficiencies in the diagram reported by Köster *et al.* were remedied.

(2) It was found that the composition dependence of the Curie temperature in the Ni-Pd-Mn ternary solid solution is less

extreme if both Pd and Mn are added than if a single addition of Pd or Mn is made. This fact cannot be simply assumed from the separate Ni-Pd and Ni-Mn binary systems.

(3) The trend of increasing saturation magnetization in the Ni-Mn binary system with the addition of Mn was found also in the Ni-Pd-Mn ternary solid solution, and also in the high Pd composition range, where T_c is comparatively low.

(4) In the Ni-Pd-Mn ternary system, the alloy with the composition where the ridge of the saturation magnetization vs composition curve and the T_c isotherm curve intersect each other is the best thermoseed alloy for maintaining itself at temperature T_c .

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