JOURNAL OF MATERIALS SCIENCE 5 (1970) 478-486

The Sintering Process of a High Permeability Ni-Fe-Cu-Mo Alloy Made by Powder Metallurgy

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The magnetic permeability of a 77 Ni-14 Fe-5 Cu-4 Mo wt % alloy made by powder metallurgy is known to be improved by extending the sintering time considerably beyond that normally used. The room temperature measurement of resistivity during the sintering cycle of such an alloy clearly shows the overlapping stages of change that occur during the sintering process. The variation in resistivity and its relationship with the changes in density, in weight and in bend strength of compacts shows that de-oxidation of the constituent element powders occurs initially. De-oxidation is followed by sintering and alloying of the nickel and iron which is followed in turn by alloying of the molybdenum. The final stage involves the alloying of the copper and the elimination of pores.

Electron microprobe analysis has shown that the copper does not alloy substantially until the copper particles melt, and that alloying is hindered if copper powder of large particle size is used. Sintering occurs more rapidly than alloying, but the rate of alloying is the most important factor in determining the electrical and magnetic properties of the alloy.

1. Introduction

A magnetic alloy with a composition close to 77 Ni-14 Fe-5 Cu-4 Mo wt % is manufactured under a variety of trade names and is widely used as a high-permeability material. In practice, three conditions must be satisfied to achieve optimum permeability. First, the material must be substantially strain-free; second, the composition of the alloy must be held within limits of about ±0.2% [1]; and third, the degree of short-range lattice order must be optimum [2].

Alloy sheet with very high initial permeability can be made from either powder metallurgy compacts, or from vacuum-melted and cast ingots. The composition of conventionally made powder metallurgy alloy sheet is very accurate [1] but generally the sheet has only moderate values of initial permeability* (~30 000 to 50 000). On the other hand, vacuum-melted alloy sheet can have very high values of initial permeability (~80 000 to 100 000) if the alloy has the optimum composition.

In previous work [3] it was suggested that the moderate initial permeability of conventionally made powder metallurgy alloy sheet is due to inhomogeneous alloying, which leads to a higher level of internal stress than exists in vacuum-melted alloy sheet. However, it was found that high initial permeability can be achieved in powder metallurgy alloy sheet if the conventional sintering time (~5 h) is prolonged; the variation of the initial permeability of alloy sheet with the sintering time of the compacts at 1300° C is shown in fig. 1 [3].†

The purpose of the present work is to describe and to explain the stages of sintering and of alloying, that occur during the sintering cycle of pressed compacts of composition 77 Ni-14 Fe-5 Cu-4 Mo wt %.

2. Preparation of the Alloys

The constituent element powders were weighed out in 50 g batches containing 77 Ni-14 Fe-5 Cu-4 Mo wt %, and were mixed for 4 h in a

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*Defined in this paper as the initial permeability measured in a field of 50 μOe rms at a frequency of 300 Hz.
†We hope to report on the effect of longer sintering times than 156 h in a future paper.

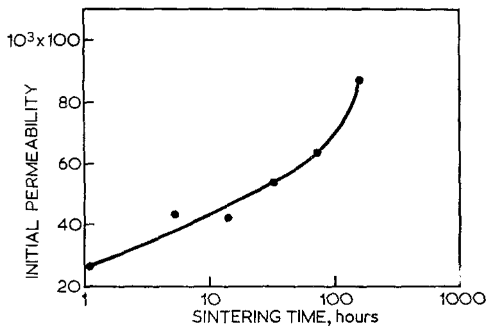

Figure 1 The variation of initial permeability with sintering time for 50 μm alloy sheet cold-rolled from sintered compacts and annealed at 1050° C for 6 h.

Turbula mixing pulsator (type 2). The mixed powders were pressed uniaxially with a pressure of 25 tons in.$^{-2}$* to form compacts measuring $3 \times 1 \times \frac{1}{8}$ in. Further compacts, which were used as control specimens, were pressed from powder batches containing 95 Ni-5 Cu wt %. The powders used in the investigation are described in table I. Scanning electron microscope photographs of the constituent powders are shown in fig. 2.

TABLE I Sources and particle sizes of the metal powders

Metal powder	Source	Grade	Particle size (μm)*
Nickel	International Nickel Ltd	carbonyl grade 123	4-7
Iron	International Nickel Ltd	carbonyl grade M C H P	7-14
Copper	Powder Metallurgy Ltd	high purity spherical copper	15-200†
Molybdenum	Murex Ltd	high purity	1-5

*The particle sizes represent the major fractions of each powder as stated by the manufacturers.

†Commercially available copper powder was used in this investigation. We have been unable to obtain copper powder with a substantially smaller particle size.

3. Experimental Procedure

3.1. Measurements

Changes in some of the room temperature properties of the compacts were observed during the two principal stages of the sintering cycle, namely, the continuous heating stage to 1300° C and the isothermal heat-treatment stage at 1300° C.

The following properties were measured:

(i) The resistivity of the compacts was measured using a four-probe method. Since the resistivities of the constituent powders and of the final alloy sheet are markedly different (about 10 μohm-cm and 60 μohm-cm, respectively), this measurement enabled the stages both of alloying and of sintering to be followed during the sintering cycle.

(ii) The loss in weight of the compacts was measured to provide information on the rate of de-oxidation of the constituent powders in the alloy compact during the sintering cycle. De-oxidation of the constituent powders was also measured separately.

(iii) The density of the compacts was measured to give an indication of their rate of sintering (i.e. the reduction in porosity).

(iv) The breaking load of compacts containing 77 Ni-14 Fe-5 Cu-4 Mo wt % was measured in a bend test using a Hounsfield tensometer. The breaking load test gives an indication of the particle-to-particle contact strength of the compacts.

3.2. Physical Methods of Examination

Compacts of composition 77 Ni-14 Fe-5 Cu-4 Mo wt % were examined by two methods:

(i) Representative surface areas were examined in a scanning electron microscope (Stereoscan) to show:

(a) the behaviour of a 35 μm diameter copper particle on heating to, and gas-quenching† from, 250, 700, 1100 and 1300° C successively;

(b) the changes in porosity after sintering at 1300° C for 5, 30 and 100 h.

(ii) Metallographically prepared samples were examined by electron microprobe line-scan analysis to show:

(a) the behaviour of a large copper particle on heating to 1100° C and gas-quenching;

(b) the degree of inhomogeneity with respect to copper after sintering at 1300° C for 12 h.

3.3. The Continuous Heating Stage

The compacts were heated to progressively higher temperatures at a rate of ~400° C h^{-1} up to 1300° C in an atmosphere of pure dry hydrogen (dew point −40° C) and the changes

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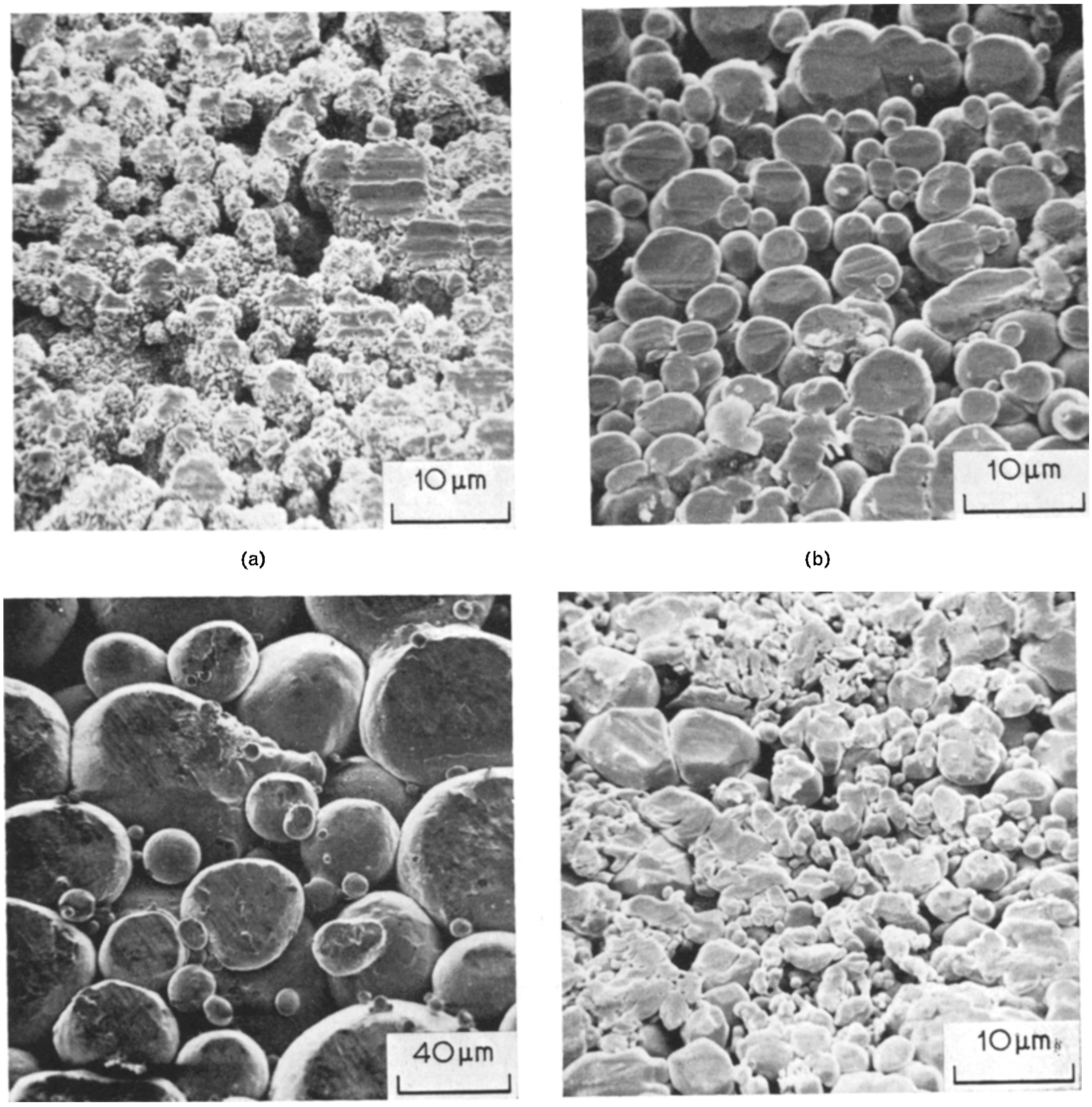
*1 ton in.$^{-2}$ = 15.44×10^6 Nm^{-2}.

†Gas-quenching entailed pushing the specimens rapidly from the hot zone of the furnace tube to its cold end where the hydrogen was introduced.



(a) (b)

(c) (d)

Figure 2 Scanning electron micrographs of the surfaces of compacts showing the shape and size distribution of particles in (a) the nickel, (b) the iron, (c) the copper and (d) the molybdenum powder.

in their resistivity, weight, density, and bend strength (quaternary alloy only) were measured after gas-quenching from each successive temperature.

3.4. The Isothermal Heating Stage

Once the compacts had been heated to 1300° C they were held at this temperature for increasing periods of time up to 100 h and then cooled at the natural rate of the furnace. Changes in resistivity and in density were measured after each increment in time.

4. Results

4.1. The Continuous Heating Stage

4.1.1. Resistivity

The variation of resistivity with quenching temperature for compacts containing 77 Ni-14 Fe-5 Cu-4 Mo wt % and 95 Ni-5 Cu wt % is shown in fig. 3.

The variation in resistivity for the 77 Ni-14 Fe-5 Cu-4 Mo wt % compact seems to consist of (i) An initial stage from about 100 to 500° C, in which the resistivity falls precipitously, indicating a considerable improvement in particle-to-

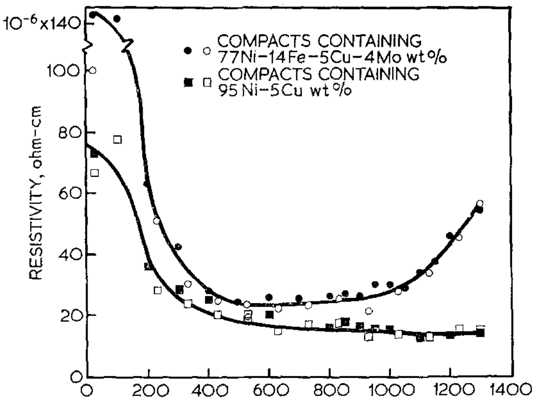


Figure 3 The variation of the compact resistivity with quenching temperature. The compacts were heated to the temperatures shown and then gas-quenched.

rapid loss in weight between 100 and 500° C indicating extensive de-oxidation of the metal particles. The loss in weight becomes less on heating to higher temperatures where the curve levels off, indicating that de-oxidation of the compacts is nearly complete.

The loss in weight that occurs on heating the constituent powders to 800° C is given in table II.

TABLE II The change in weight of metal powders on heating to 800° C

Metal powder	Loss in weight (%)
Nickel	0.21
Iron	0.15
Copper	0.18
Molybdenum	0.27

particle contact.

(ii) A second stage, from about 500 to 1000°C, in which the resistivity increases gradually, indicating that some initial alloying is taking place.

(iii) A third stage, from about 1000 to 1300° C, in which the resistivity increases rapidly, indicating that more extensive alloying is taking place.

The initial stage also occurs in the 95 Ni-5 Cu wt % compact, but after heating to temperatures of about 500° C the resistivity decreases gradually and continuously and the second and third stages are absent.

4.1.2. Weight Loss

The percentage loss in weight with quenching temperature is shown in fig. 4. There is a very

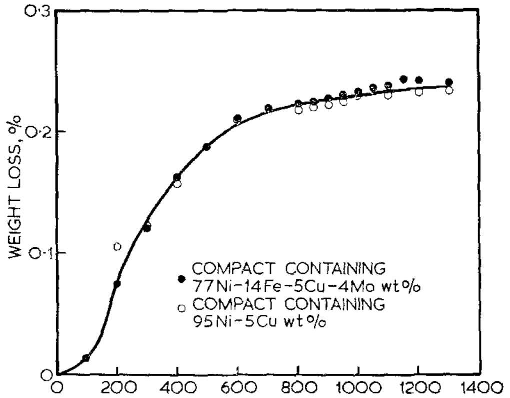


Figure 4 The percentage weight loss of compacts with quenching temperature. The compacts were heated to the temperatures shown and then gas-quenched.

The nickel powder and the iron powder samples sintered but the copper powder and the molybdenum powder samples did not. Fig. 4 shows that the loss in weight of both the quaternary and binary alloy compacts is similar.

4.1.3. Density

Fig. 5 shows the relationship between the density of the compacts and the quenching temperature. There is no detectable change in density on heating to 400° C, but the increase in density between 500 and 1000° C shows that there has been a reduction in porosity. The density continues to increase on heating to temperatures above 1000° C at a rate which suggests extensive pore reduction. The rate of densification decreases between 1000 and 1300° C; on reaching 1300° C the compacts have about 90% theoretical density.

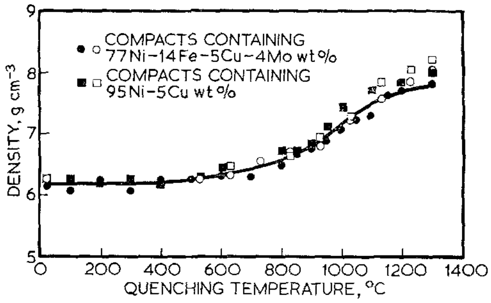


Figure 5 The variation of compact density with quenching temperature. The compacts were heated to the temperatures shown and then gas-quenched.

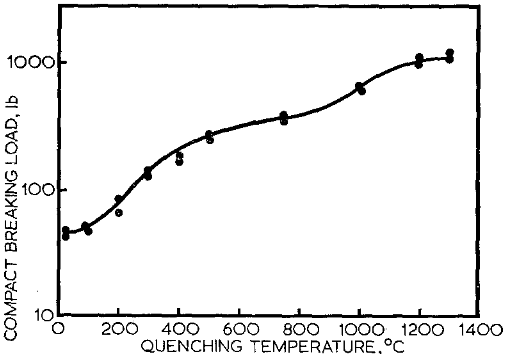


Figure 6 The variation of compact breaking load with quenching temperature for a compact containing 77 Ni-14 Fe-5 Cu-4 Mo wt %. The compacts were heated to the temperatures shown and then gas-quenched.

4.1.4. Bend Strength

Fig. 6 shows that an increase in strength accompanies the changes in resistivity, weight and density. There is a marked increase in strength between 100 and 500° C, which suggests an improvement in particle-to-particle contact. The strength continues to increase between 500 and 1000° C, indicating a considerable reduction in porosity and, possibly, some alloying. The increase in strength continues on heating above 1000° C but on approaching 1300° C the rate slows, indicating that the material is denser and that the elimination of pores is proceeding at a slower rate.

4.1.5. Scanning Electron Microscopy

Fig. 7 shows the changes that a small region of a compact surface undergoes on continuous heating. The poor contact between the large copper particle and the small nickel, iron and molybdenum particles that surround it, is noticeable in figs. 7a, b and c. The apparent lack of sintering of the nickel particles and the iron particles in fig. 7c is consistent with the fact that there is only a slight increase in compact density following heating to, and quenching from, 700° C (fig. 5).

Two kinds of porosity are apparent:

(i) Micro-porosity associated with sintering of the nickel, iron and molybdenum particles.

(ii) Macro-porosity associated with the melting of copper particles.

4.1.6. Electron Microprobe Analysis

Fig. 8 shows an electron microprobe line-scan for copper taken across a copper particle in a compact containing 77 Ni-14 Fe-5 Cu-4 Mo wt %, after it had been heated to 1100° C; the presence of the particle at this temperature demonstrates the sluggish rate of diffusion of copper in this alloy.

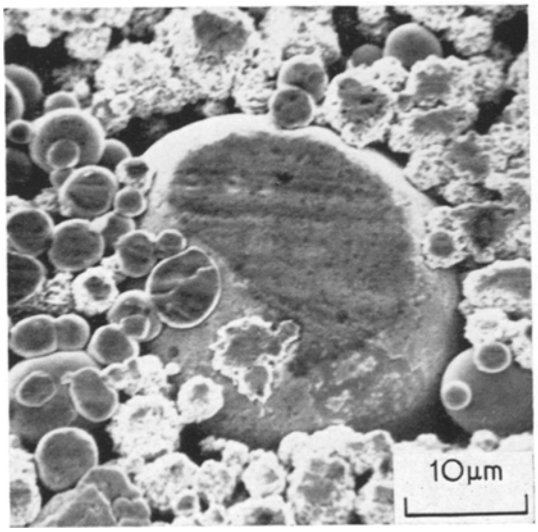
4.2. The Isothermal Heating Stage

The property changes in this stage are of lesser magnitude than those that occur in the continuous heating stage.

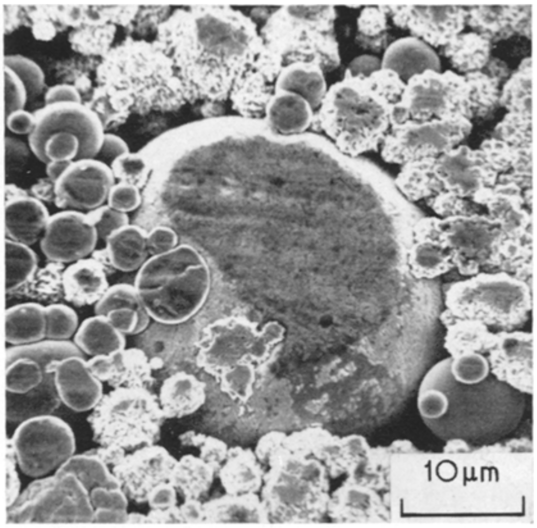
4.2.1. Resistivity

The results are shown in table III.

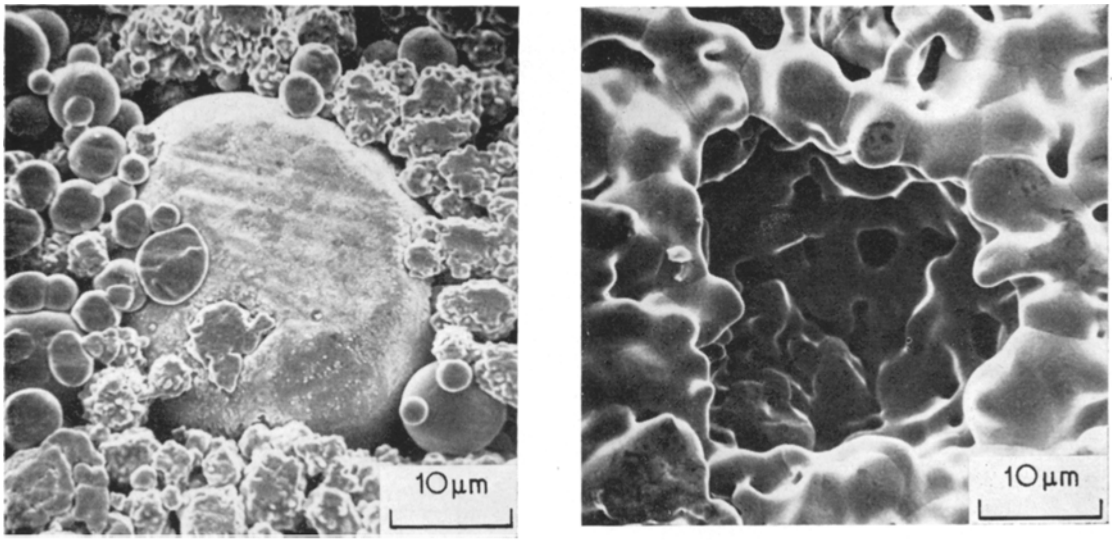
The results given in table III show that the resistivity of a compact containing 77 Ni-14 Fe-



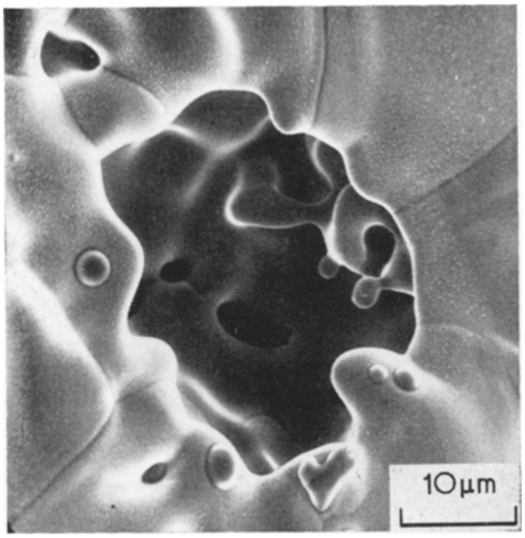
(7a)



(7b)



(7c) (7d)



(7e)

Figure 7 Scanning electron micrographs showing how the surface of a pressed compact (a) containing 77 Ni-14 Fe-5 Cu-4 Mo wt % changes on heating to, and quenching from, (b) 250° C, (c) 700° C, (d) 1100° C and (e) 1300° C.

TABLE III The change in resistivity of compacts following isothermal heating at 1300° C

Time at temperature (h)	Compact composition (wt %) 77 Ni-14 Fe-5 Cu-4 Mo	 95 Ni-5 Cu
	Resistivity (µohm-cm)	
0.1	56	15
0.3	59	14
1.0	60	14
3.5	60	—
10.5	62	12
31.0	59	12
100.0	57	11

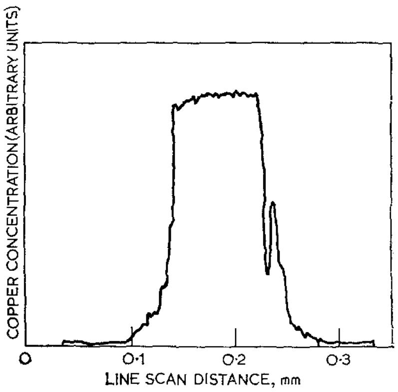


Figure 8 Electron microprobe line-scan analysis showing the variation in copper concentration across a region containing a copper particle in a compact containing 77 Ni-14 Fe-5 Cu-4 Mo wt % heated to, and quenched from, 1100° C.

5 Cu-4 Mo wt % continues to rise on holding at 1300° C, reaching a maximum value after about 10 h; thus up to about 10 h alloying is still proceeding. Between 10 and 100 h the resistivity falls, indicating further elimination of pores.

The resistivity of the 95 Ni-5 Cu wt % compact continues to fall during sintering. This fall in resistivity is continuous and gradual, and indicates the slowness with which the process of pore elimination takes place.

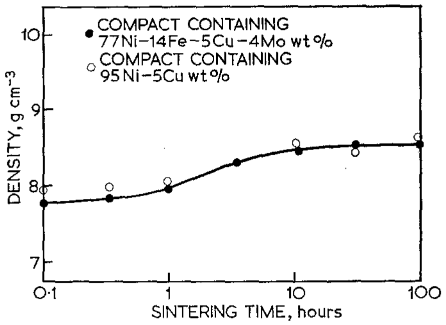
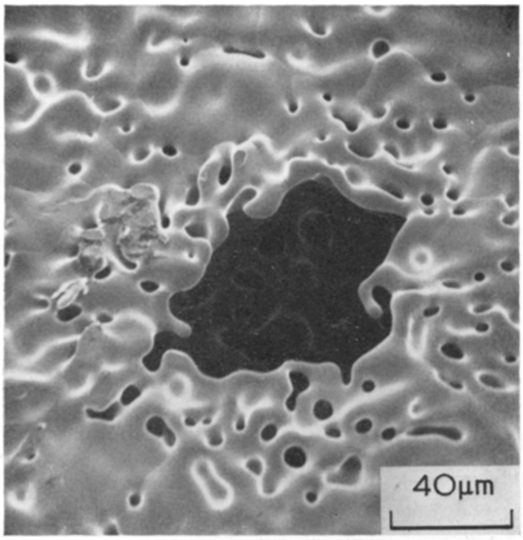


Figure 9 The variation of compact density with sintering time.



(a)

4.2.2. *Density*

The compacts of both compositions undergo similar changes in density, during sintering, as shown in fig. 9. The density of the compacts continues to increase following heat-treatment at 1300° C. There is an increase in density of approximately 8 % between 1 and 10 h, whilst between 10 and 100 h the change is only about 1 %. These changes again indicate the slow rate at which pores are eliminated.

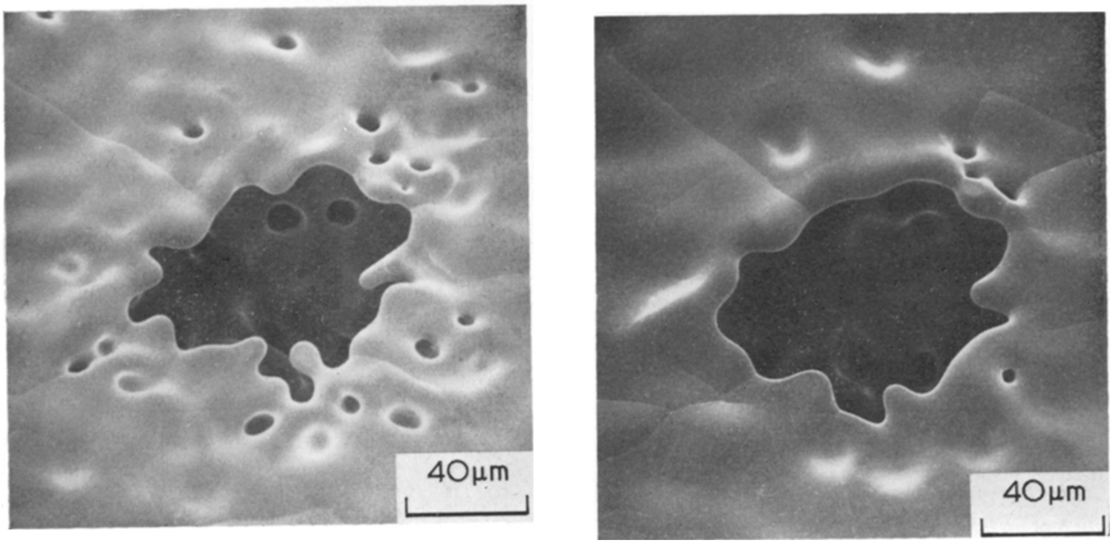
4.2.3. *Scanning Electron Microscopy*

Fig. 10 shows the changes in shape of a pore ~ 100 µm in diameter (formed by the melting of a copper particle of similar size) after sintering at 1300° C for 5, 30 and 100 h. Fig. 10 shows another type of micro-porosity, due to the Kirkendall effect, which occurs during the diffusion of copper into the matrix. This micro-porosity is almost eliminated after 30 h, but the large pores seem to be stable.

4.2.4. *Electron Microprobe Analysis*

Fig. 11 shows an electron microprobe line-scan across a porous region in a compact containing 77 Ni-14 Fe-5 Cu-4 Mo wt % that has been sintered at 1300° C for 12 h. It is evident that the copper is not uniformly alloyed.

Figure 10 Scanning electron micrographs showing the changes that occur on the surface of a compact containing 77 Ni-14 Fe-5 Cu-4 Mo wt % in the vicinity of a macropore, on sintering at 1300° C for (a) 5 h, (b) 30 h and (c) 100 h.



(b) (c)

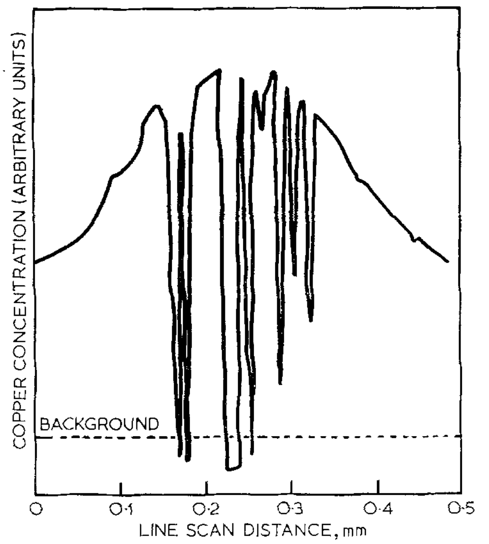


Figure 11 Electron microprobe line-scan analysis showing the variation in copper concentration across a porous region in a compact containing 77 Ni-14 Fe-5 Cu-4 Mo wt % sintered at 1300° C for 12 h.

5. Discussion of Results

5.1. De-oxidation of Compacts

The high resistivity of the as-pressed compacts is presumably due to surface oxide layers on the metal particles. The standard free-energy diagram for oxide formation [4] shows that the oxides of nickel, iron, copper and molybdenum are all unstable above room temperature in a hydrogen atmosphere with a dew-point of −40° C and the results given in table II show that the metal powders are de-oxidised on heating in hydrogen. The molybdenum powder shows the greatest individual loss in weight but as there is only 4 wt % molybdenum present in the quaternary alloy compacts, the bulk of the loss in weight is due to the de-oxidation of nickel; also the total loss in weight of both the quaternary and the binary alloy compacts, which are both nickel-rich, is similar.

5.2. Property Changes during the Continuous Heating Stage

During the initial stage of heating the precipitous fall in resistivity occurs through de-oxidation of the metal particle surfaces, which allows better particle-to-particle contact. Figs. 3, 4 and 6 show that the changes in resistivity, in weight and in the strength of the compacts are closely related. There is no detectable change in density after heating to 400° C, suggesting that very little neck-growth [6] occurs during this stage. On the other hand, the increase in compact strength shows that even in this low-temperature range, at least some localised diffusion must be taking place.

Metallography and electron microprobe analysis (see fig. 8) have shown that there is very little alloying of copper or molybdenum during the secondary stage between 500 and 1000° C. Thus the gradual rise in resistivity (fig. 3) is presumably the resultant effect of (a) the limited alloying of the nickel and the iron, which leads to an increase of the resistivity, and (b) the reduction in micro-porosity (fig. 7), which leads to a decrease of the resistivity. This conclusion is supported by the fact that, between 500 and 1000° C, the resistivity of the 95 Ni-5 Cu wt % compacts gradually decreases, due, presumably, to the simultaneous sintering of the nickel particles and the reduction in porosity.

Consideration of the constitution of all the possible binary combinations between nickel, iron, copper and molybdenum suggests that copper and molybdenum should alloy readily with nickel and with iron in the range 500 to 1000° C. Also, a consideration of the partial diffusion coefficients of the elements in the binary alloy combinations indicates that copper and molybdenum should alloy with nickel and with iron in preference to the alloying of nickel with iron. Thus the observed alloying behaviour in the range from 500 to 1000° C is contrary to predictions based on alloy constitution and on diffusion coefficients. Consequently, the particle size of the powders seems to be the controlling factor (see table I), for the nickel and iron powders have relatively small particle diameters and should sinter more readily at a lower temperature than powders with large particle diameters [5] (see also 4.1.2.). The molybdenum powder also consists of particles of small diameter, but this powder has been observed to agglomerate and large, unalloyed agglomerates (~40 μm in diameter) have been detected in compacts heated to above 1000° C. Both the sintering and alloying of the copper particles are hindered by the poor contact between the copper particles and those particles that surround them (fig. 7).

The principal effect in the continuous heating stage between 1000 and 1300° C is the marked increase in the resistivity of the quaternary alloy. Now during this stage there will be a continuation of the alloying of the nickel with the iron, leading to nickel and iron concentration gradients and hence to resistivities in the range 15 to 80 μohm-cm [7]. The increase in compact resistivity between 1000 and 1300° C is most likely to be due to extensive alloying of molybdenum with the Ni-Fe matrix. The addition of molybdenum to Ni-Fe alloys in the region of 80 Ni-20 Fe leads to a marked increase in resistivity [7]; for example the addition of 4 wt % Mo changes the resistivity of an alloy with 78.5 wt % Ni from about 20 μohm-cm to 60 μohm-cm.

It is noteworthy that the resistivity of the 95 Ni-5 Cu wt % alloy continues to decrease in this range, indicating the effects of the reduction in micro-porosity.

5.3. Property Changes during the Isothermal Heating Stage

In the present work, metallography has shown that continued heating of the quaternary alloy above 1100° C causes the copper particles to melt and that these particles are subsequently replaced by large pores. Fig. 11 shows that the peripheral material around such pores is rich in copper even after sintering for 12 h. The rise in resistivity (see table III) between 1 and 10 h, therefore, is due mainly to further alloying of the molybdenum, which seems to be virtually complete after about 10 h at 1300° C. The alloying of molybdenum is accompanied by an increase in density (fig. 9) so that the effect of alloying on the resistivity predominates over the effect of pore reduction.

The fall in resistivity between 10 and 100 h is presumably associated both with the gradual elimination of the remaining micro-pores, and with a reduction in copper concentration gradients in the compact. Since (a) almost 97% of theoretical density is reached after 30 h, and (b) the macro-porosity appears to be stable, the observed decrease in resistivity between 30 and 100 h must be due principally to a reduction in inhomogeneity; fig. 1 shows that the initial permeability increases rapidly with sintering time in this region. Thus sintering nears completion before alloying.

The resistivity of the 95 Ni-5 Cu wt % alloy decreases monotonically with sintering time, which is consistent with pore reduction and alloying occurring together.

6. Conclusions

If a high permeability alloy with a composition of 77 Ni-14 Fe-5 Cu-4 Mo wt % is made from powder metallurgy compacts sintered at 1300° C, then:

(i) The alloying of the minor additions, copper and molybdenum, occurs very slowly; the alloying of the copper is particularly slow.

(ii) The inhomogeneity of the alloy can be reduced by extending the sintering time.

(iii) The elimination of porosity is a slow process but sintering is completed before alloying.

(iv) The rate of alloying du.ing sintering is more important than the rate of sintering in determining the magnetic and electrical properties of the alloy.

(v) Metal powder with a large particle size inhibits both sintering and alloying, and leads to large stable pores.

Acknowledgement

The authors wish to thank Mr A. C. Lynch for helpful discussions and comments, and Dr E. W. Ward for the Stereoscan photography. The electron microprobe analyses were carried out by Mr D. Green of the University of Aston in Birmingham and by Mr M. J. Reynolds of Metals Research Ltd. The information in this paper is used by permission of the Senior Director of Development of the Post Office.

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Received 3 February and accepted 3 March 1970.