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Ferromagnetic Impurities in Metals

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I. INTRODUCTION

IT is well known that magnetic studies contribute to our knowledge of the solid state. This is because magnetic properties, especially ferromagnetic ones, are very sensitive to changes in the solid state. The discussion in this paper will be limited to the particular case of impurities of ferromagnetic materials in metals. This case is important because it is practically impossible to prepare such common metals as copper, brass, etc., without introducing at least some iron impurity. But, because of the much greater order of magnitude of ferromagnetism compared with that of paramagnetism or diamagnetism, such an impurity, if ferromagnetic, may make an important contribution to the magnetic properties of the metal even though the amount of impurity may be very small. It has been found possible experimentally to detect an iron impurity of one millionth of one percent provided such an impurity retains the magnetic properties of ordinary iron.[1] In the case of non-metals, on the other hand, ferromagnetic impurities are not as likely to be present. This has been verified experimentally in the case of amber, paraffin, and samples of various kinds of glass.[1]

Consider, then, a complex consisting of a non-ferromagnetic metal, such as copper, containing iron as an impurity. The state of such a complex may be altered in several ways, such as by:

(1) Varying the composition (or amount of impurity);
(2) Mechanical treatment;
(3) Heat treatment.

In each case the state of the impurity, as well as that of the parent metal, will be altered. Such changes may be followed through their resulting effect on the magnetic properties of the impurity. In this way our knowledge of the solid state may be increased. On the other hand, if known changes in the state of the complex can be produced and the resulting variations in magnetic properties noted, certain questions concerning the nature of ferromagnetism may be answered. In this connection the three methods of altering the state of the complex listed above will be considered in more detail.

II. MAGNETIC PROPERTIES AND COMPOSITION

The first factor to be considered is whether or not the impurity may be completely dissolved in the parent metal in the form of a solid solution. There are three possibilities: (1) no amount of the impurity will dissolve in the parent metal, e.g., iron in silver, (2) a limited amount of the impurity may be dissolved in the parent metal, e.g., iron in copper, (3) the two metals form a complete series of solid solutions, e.g., nickel and copper.

In the first case, where the impurity cannot possibly dissolve into the parent metal, one would expect the impurity to exist in the form of grains or inclusions between the crystals of the parent metal. Such grains of, say, relatively pure iron would most probably be ferromagnetic.

In the second case, if the solubility limit is exceeded, the situation will be similar, and grains of impurity will exist. But if the solubility limit is not exceeded for that temperature at which equilibrium is established, then in the second as well as the third case the impurity may be in the form of a solid solution. However, even here a solid solution is by no means certain but will depend on giving to the impurity adequate opportunity to diffuse into the parent metal. This, in turn, will depend on the previous heat treatment, as discussed below. Even though the impurity has dissolved into the parent metal, there is still the question whether the diffusion has been complete, or whether there are significant fluctuations in the concentration of the impurity. Local fluctuations might result to some extent in the formation of ferromagnetic domains, whereas uniform diffusion would prohibit domains and mean that each iron atom did not have other iron atoms for nearest neighbors, and so ferromagnetism would not occur. The question of fluctua-

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[1] F. W. Constant and J. M. Formwalt, Phys. Rev. 56, 373 (1939).

tions has been discussed by Bitter,[2] and he points out that it is quite possible that the fluctuations may be large enough to produce local concentrations of iron atoms which are ferromagnetic. This would account for the ferromagnetism observed by the author in the case of annealed alloys of platinum or palladium containing only a few percent of cobalt or nickel.[3] In the case of these alloys and generally in the case of dilute iron alloys, it has been found that when they are ferromagnetic the coercive force is large (several hundred oersteds) and the saturation magnetization high.[1, 3–10]

Careful series of experiments on several alloy series such as Cu-Fe, Au-Fe, Cu-Ni, and Au-Ni have been carried out by Bitter, Kaufmann, and their co-workers.[8, 11–14] In this work series of samples containing small known amounts of iron or nickel were prepared, and their magnetic properties studied over a wide range of applied field and temperature. As the percentage of iron in the Cu-Fe series was increased from 0 to 2.7 percent, the tendency toward ferromagnetism increased, and the 2.7 percent alloy was ferromagnetic even though the solubility limit for iron in copper at the temperature from which the specimens were quenched was near 3 percent. Further evidence that the iron atoms were not distributed at random was found.

It appears, then, that the solubility limit at the temperature of heat treatment is not the only criterion for determining whether an iron impurity in a given alloy is ferromagnetic. One must also consider whether ample opportunity was given for complete diffusion and whether, even if this has been done, the iron atoms will actually be distributed at random with a uniform density of distribution.

III. MAGNETIC PROPERTIES AND MECHANICAL TREATMENT

There is a close correlation between mechanical and magnetic properties, notably in the case of iron and steel where magnetic hardness is associated with mechanical hardness. It is to be expected that mechanical treatment, or cold work, will alter the magnetic properties of a metal.

It was shown by Bitter,[15] and also by Lowance and Constant[16] that cold work decreased the diamagnetic susceptibility of metals such as copper, silver, and bismuth, and increased the paramagnetic susceptibility of platinum. This effect may be attributed to a change in the electron orbits resulting from the cold work, or as suggested by Kussmann and Seemann,[17] to a precipitation of a ferromagnetic impurity by the cold work.

Coming back to such a case as that of an iron impurity in copper, it is possible that cold work may alter the magnetic properties by (1) causing a change in the parent metal itself, (2) inducing precipitation of a ferromagnetic impurity, (3) increasing the fluctuations in density of the impurity, or (4) inducing a phase change or other alteration in an impurity which is already present in the form of inclusions. The second possibility will arise primarily in the case of a specimen quenched from a high temperature, the impurity forming a supersaturated solid solution at room temperature. The third possibility might occur if there are short range forces present tending to form local concentrations of the ferromagnetic atoms, in which case the cold work would supply the energy and mobility needed for the growth of such possible domains. Evidence regarding the fourth possibility has been given by Smith,[18] who showed by x-ray analysis that cold-rolling certain specimens of brass that had been rendered nonmagnetic by heat treatment resulted simultane-

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[2] F. Bitter, Phys. Rev. **37**, 1527 (1931).

[3] F. W. Constant, Phys. Rev. **34**, 1217 (1929); **36**, 1654 (1930).

[4] L. Graf and A. Kussmann, Physik. Zeits. **36**, 544 (1935).

[5] U. Dehlinger, Zeits. f. Metall. **29**, 388 (1937).

[6] J. C. Slater, J. App. Phys. **8**, 385 (1937).

[7] M. Fallot, Ann. de physique **10**, 291 (1938).

[8] F. Bitter and A. R. Kaufmann, Phys. Rev. **56**, 1044 (1939).

[9] H. Schröder, Ann. d. Physik **36**, 71 (1939).

[10] G. T. Rado and A. R. Kaufmann, Phys. Rev. **60**, 336 (1941).

[11] F. Bitter, A. R. Kaufmann, C. Starr, and S. T. Pan, Phys. Rev. **60**, 134 (1941).

[12] S. T. Pan, A. R. Kaufmann, and F. Bitter, J. Chem. Phys. **10**, 318 (1942).

[13] A. R. Kaufmann and C. Starr, Phys. Rev. **63**, 445 (1943).

[14] A. R. Kaufmann, S. T. Pan, and J. R. Clark, Rev. Mod. Phys. **17**, 87 (1945).

[15] F. Bitter, Phys. Rev. **36**, 978 (1930).

[16] F. E. Lowance and F. W. Constant, Phys. Rev. **38**, 1547 (1931).

[17] A. Kussmann and H. J. Seemann, Naturwiss. **19**, 309 (1931); Zeits. f. Physik **77**, 567 (1932).

[18] C. S. Smith, Phys. Rev. **57**, 337 (1940); Am. Inst. Min. Metal. Eng., Tech. Pub. No. 1934 (1942).

ously in a return of ferromagnetism and the appearance of body-centered cubic lines in the x-ray pattern which had not been present before the rolling. In this case the impurity was believed to be present first as a non-magnetic precipitate whose crystal structure was more or less continuous with the face-centered cubic lattice of the copper. The effect of the cold work was then to transform the non-magnetic precipitate into a ferromagnetic one with a body-centered lattice, the normal magnetic form of iron at room temperature.

IV. MAGNETIC PROPERTIES AND HEAT TREATMENT

Closely related to mechanical treatment is heat treatment, which also affects both the mechanical and magnetic properties of metals. But the effects are even more varied and complicated. The important factors to be considered and controlled are: (1) the temperature at which the heat treatment is performed, (2) the length of time of the treatment, (3) the method of cooling the specimen, and (4) the atmosphere in which the treatment is carried out. The possible ways in which each of these factors may affect the state of an impurity of a ferromagnetic material in a metal will be discussed.

1. Temperature

Heat treatment at high temperatures (just under the melting point) will tend to send an undissolved impurity into solution in the parent metal in those cases where solid solutions are possible. If there is a solubility limit, this limit will be greater at the high temperature than at room temperature, permitting more impurity to go into solution during the heat treatment. This will be accompanied by a decrease in and possible disappearance of the ferromagnetism due to the impurity. If the impurity is already in solution, the heat treatment may be expected to make the diffusion of the impurity more complete. In those cases where the impurity cannot dissolve in the parent metal, the heat treatment may produce a phase transformation in the impurity, such as that from body-centered iron to face-centered iron, which, of course, is non-magnetic.

Heat treatment at intermediate temperatures, such as 450°C, may be expected to produce aging effects. In the case where such treatment follows that at high temperatures, it is possible that the aging process will induce precipitation of at least part of the impurity. If the precipitate is, say, body-centered iron in the form of grains, it will probably be ferromagnetic. However, as mentioned above, Smith[18] has shown that in the case of iron in brass (or copper), the iron inclusions are first in the face-centered phase which corresponds to that of the copper in which they are imbedded, and that it is only after subsequent cold work that the iron inclusions become body-centered and ferromagnetic. If precipitation does occur at intermediate temperatures, it is not easy to picture how the precipitated atoms of impurity migrate sufficiently to form grains or inclusions which could later be made ferromagnetic. It may be, as will be pointed out below, that chemical oxidation-reduction effects are also involved.

2. Time of Treatment

The heat treatment should be maintained for a time sufficient to enable the complex to reach equilibrium at a given temperature. At high temperatures this will naturally be much shorter than at intermediate temperatures.

3. Method of Cooling

Two methods of cooling are usually involved, quenching and annealing. Quenched specimens are cooled as rapidly as possible so as to "freeze" the complex in the state it attained at the high temperature. Thus in the case of iron in copper the solubility limit for iron in copper is near 3 percent at 1000°C but drops to practically nil at room temperature,[19] hence it is quite possible to quench a saturated solid solution and obtain one which is supersaturated at lower temperatures. It is also possible by quenching to retain a crystal structure or phase which is the stable one at high temperatures but not at room temperature, such as face-centered gamma-iron, for example.

Slow cooling, on the other hand, furnishes opportunity for the complex to adjust itself to equilibrium conditions all the way down. Precipitation of the impurity will occur when the solubility limit has been reached.

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[19] M. Hansen, *Der Aufbau der Zweistofflegierungen* (Verlagsbuchhandlung Julius Springer, Berlin, 1936).

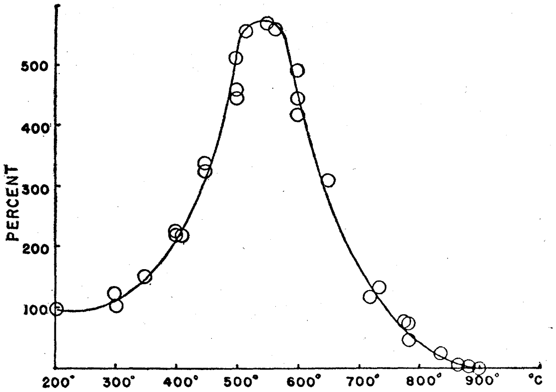

FIG. 1. Copper heat treated in hydrogen: ratio of final to original remanence *vs.* temperature of heat treatment.

4. Atmosphere Used for the Heat Treatment

Experimental work by the author and his co-workers,[20] which is described below, has shown that the atmosphere in which a specimen is heat treated may have a very important bearing on the resulting magnetic properties of the impurity. This applies not only to the atmosphere in which the specimen is heated but to that through which it may pass if quenched.

In most cases of heat treatment, a reducing atmosphere is used in order to prevent oxidation of the specimen, but, during quenching, the specimen is frequently exposed to air. In this connection it is necessary to bear in mind that, since volume effects are more important than surface ones, the important factor is one of diffusion. Now at a given temperature, hydrogen diffuses much more rapidly than oxygen. At 500°C the diffusion of hydrogen into a metal is considerable, being sufficient to reduce any oxides which the metal may contain as impurities. The diffusion of oxygen into a metal such as copper does not become important until temperatures above 800°C are reached. But at 900°C, or higher, if a specimen is exposed to oxygen, its impurities may rapidly become oxidized.

The atmosphere used may have other effects in addition to oxidation-reduction ones. Fitzwilliam, Kaufmann, and Squire[21] observed some interesting results in the case of Ti and Zr specimens which were allowed to soak up hydrogen. The solution of hydrogen in these metals altered their crystal structures, and, in the case of the Zr, an iron impurity was precipitated out in a ferromagnetic state.

V. EXPERIMENTAL

To illustrate the above discussion, some experiments by the author and his co-workers[1,20] on iron impurities in various metals will be summarized. The samples used were taken from stock in the storeroom of the shop. The copper came from cotton-covered magnet wire, the brass from brass rods, and the aluminum from commercial castings. The presence of iron as an impurity was verified chemically. The ferromagnetic properties of the impurity were observed by magnetizing in a strong field a specimen whose surface had been carefully cleaned and then afterwards (1) measuring the residual magnetic moment, (2) measuring the coercive force, (3) measuring hysteresis loops, and (4) finding the Curie point of any ferromagnetism present. Such measurements were carried out in conjunction with various kinds of heat treatment and cold work.

In the first place, it was found that when ferromagnetic impurities were present, the residual magnetic moment was large for the amount of impurity present and the coercive force high, (100–500 oersteds). Saturation was hard to attain and was several times the residual magnetic moment or remanence. Curie points were generally in the neighborhood of 500°C.

In Table I are listed the values of I_R, the intensity of magnetization, or magnet moment/cc, of the residual magnetism due to ferromagnetic impurities in various metals.

TABLE I. Volume impurities for various materials.

Material	$I_R \times 10^4$
Brass	820.0
Silver—sterling	19.0
—C.P.	3.3
Copper—magnet wire	3.8
—C.P., (0.000% Fe)	0.5
—National Bureau of Standards, (O_2-free)	0.06
Bismuth—extruded rod	1.4
—crystallized, C.P., (0.00% Fe)	0.1
Cadmium—C.P., (0.003% Fe)	0.14
Tin—C.P., (0.003% Fe)	0.02
Aluminum—drawn rod	0.03
—cast	0.01
Molybdenum	None
Platinum	None
Tungsten	None

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[20] F. W. Constant, R. E. Faires, and H. E. Lenander, Phys. Rev. **63**, 441 (1943).

[21] J. Fitzwilliam, A. Kaufmann, and C. Squire, J. Chem. Phys. **9**, 678 (1941).

From the above list the following were chosen for more complete study: copper, brass, silver, and aluminum.

1. Copper

Samples of No. 12 D.C.C. magnet wire, which had previously been checked for uniformity of volume impurity, were used. After a sample had been magnetized in a strong field and its remanence measured, it was subjected to heat treatment. After cooling, it was again placed in the strong field, and the remanence remeasured. The ratio of the final to the original remanence was expressed as a percentage and plotted against the temperature at which the heat treatment was carried out. Figure 1 shows the results of 8-hour heat treatments in a hydrogen atmosphere, while Fig. 2 gives the results of 8-hour runs in an atmosphere of tank nitrogen. The importance of the atmosphere is evident. Tank helium and air gave results similar to those for the nitrogen. Purification of the nitrogen by passing it over red-hot granulated copper indicated that it contained oxygen as an impurity, and that it was the oxygen which gave the unusual results above 800°C. Further experiments showed that if a sample had been rendered non-magnetic by heating in hydrogen, it could be made more magnetic than originally by reheating in an oxygen-contaminated atmosphere at 900°. This was not a surface effect. This cycle could be repeated indefinitely unless temperatures above 1020°C were used in which case the magnetism returned with more difficulty. Reheating a non-magnetic sample in air or hydrogen at 500°C did not cause the magnetism to return, although subsequent cold-rolling did.

These results may be explained as follows: at least a part of the iron impurity exists originally as a magnetic oxide imbedded in the copper; at around 500°C hydrogen can diffuse through the specimen and reduce the oxide to iron giving an increase in magnetism; at higher temperatures the iron is transformed into the non-magnetic face-centered phase and may at the highest temperatures actually dissolve into the copper lattice; introduction of oxygen is only effective above 800°C when the oxygen may diffuse into the specimen and either oxidize the impurity or cause dissolved iron to be precipitated out as an oxide; cold work following aging produces a phase transformation from face-centered back to body-centered iron in the grains of impurity. The fact that the problem is so complicated and so many factors are involved explains why experimental results of different observers have not always been in agreement.

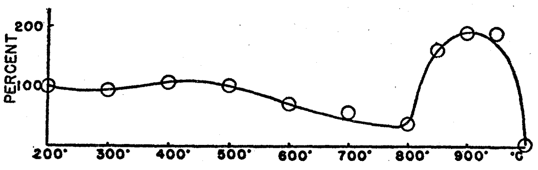

FIG. 2. Copper heat treated in tank nitrogen: ratio of final to original remanence *vs.* temperature of heat treatment.

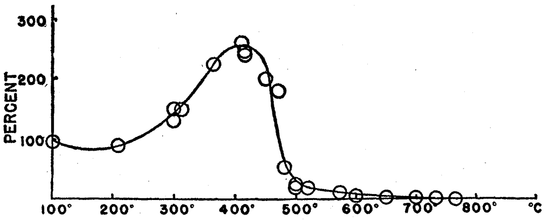

FIG. 3. Brass heat treated in hydrogen: ratio of final to original remanence *vs.* temperature of heat treatment.

2. Brass

The results for brass were similar to those for copper except that larger amounts of impurity were involved. However, as shown in Fig. 3, which is for heat treatment of brass in hydrogen, the magnetism could easily be eliminated by heating at high temperatures. On the other hand, it was easier to cause the magnetism to return, either through the combination of reheating to 500°C followed by cold work, or by exposure to oxygen (or air), at around 900°C.

3. Silver

The results of heat treating silver in a hydrogen atmosphere are shown in Fig. 4. Heating up to the melting point failed to eliminate the ferromagnetism of the impurity. This is to be expected since iron and silver are completely insoluble in one another both in the liquid and solid phases. Whereas the lattice constants of copper, brass and face-centered iron are all close to 3.6A, that of silver is 4.1A.[22]

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[22] R. W. G. Wyckoff, *The Structure of Crystals* (The Chemical Catalog Company, New York, 1931).

4. Aluminum

The experiments on aluminum are mentioned because they illustrate a different phenomenon. As indicated in Table I, whatever impurity is present in cast aluminum is practically non-ferromagnetic. However, iron was present as an impurity but, as microscopic analysis showed, in the form of Al_3Fe which is non-magnetic and will not precipitate out. When such a specimen of aluminum was partly dissolved in HCl (but *not* in more strongly oxidizing acids such as H_2SO_4 or HNO_3), then as the specimen went into solution the iron plated back out on the remaining aluminum surface and formed a strongly ferromagnetic film. This effect has also been investigated by Mason.[23] The magnetic moment/cc of aluminum dissolved was 850×10^{-4}, indicating a large amount of impurity was actually present in the cast aluminum used. This plating-out effect occurred only with aluminum because this was the only metal tested which is above iron in the electromotive series.

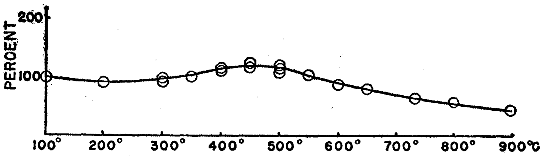

FIG. 4. Silver heat treated in hydrogen: ratio of final to original remanence *vs.* temperature of heat treatment.

In conclusion it may be said that the problem of ferromagnetic impurities in metals is a most complicated one, but it is also one with many interesting details, the study of which is helpful in giving us a better understanding of both the solid state and ferromagnetism.

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[23] R. B. Mason, Trans. A. Elec.-chem. Soc. 56, 45 (1929).