Structure of Alloys*

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WHEN one metal is alloyed with another, in a series of varying relative proportions, generally several new alloy structures (phases) appear which are different from each other and from the structures of either pure metal. In the usual type of diagram, the composition of the alloy is represented along a horizontal scale starting with the pure metal *A* on the left side and ending with the pure metal *B* on the right side: temperatures are plotted vertically. In a typical case, the addition of small quantities of the metal *B* to the metal *A* does not alter its characteristic structure, the atoms remaining in the same relative arrangement. Atoms of *B* replace a corresponding number of atoms of *A* in an apparently random manner, and the only observable change is a uniform contraction or expansion of the *A* lattice. There is thus a more or less extended single phase region on the left of the diagram. As the proportion of *B* is increased, a limit is reached at which the *A* structure can no longer absorb *B* atoms in this way, and beyond this point a new phase appears. The new phase, which is richer in the *B* constituent, has a different atomic arrangement, as has been confirmed by X-ray analysis. Throughout a certain range of composition the two phases co-exist and each is constant in composition, the amount of the first phase decreasing and of the second phase increasing in passing through the two-phase region from left to right. The first phase finally disappears, and a new region of single phase is entered, to be succeeded by two-phase regions and single phase regions alternately. The last single phase region on the right hand side includes as a limiting case the pure metal *B*.

Such phase diagrams have been worked out for many alloys by metallurgical methods. The boundaries between single phase and two-phase regions are determined by examining polished and etched surfaces under the microscope, and thermal and electrical measurements aid in outlining the diagram. The single phase regions are bounded on each side by lines of which the departure from the vertical shows that the extent of the phase is, to some extent, dependent upon temperature. The liquidus and solidus boundaries above each phase region show at what temperatures solidification from the melt begins and ends.

In recent years, X-ray methods have played an important part in the construction of phase diagrams, the 'powder method' being particularly suitable for this purpose. Westgren's name will always be associated with this field of inquiry, in which he was a pioneer. Several methods differing in their experimental detail have been used. In one method the alloy in the form of a fine powder

is placed in a Debye-Scherrer camera, and irradiated with monochromatic X-rays of suitable wave-length. The diffracted beams form a pattern of lines upon a strip of photographic film, which is in the form of a cylinder with the powder at its axis. The pattern is characteristic of the alloy structure, and if not too complex, the structure can be completely analysed by studying the pattern it produces. In a single phase region the character of this pattern remains the same throughout the range of composition, the only change being a shift in the positions of the lines due to the expansion or contraction of the lattice. When the boundary of the single phase region is passed and the two-phase region is entered, the photographs show the pattern of both constituent phases superimposed. The lines of one become fainter, and of the other stronger, as the region is traversed. Since in this region each phase is constant in composition, the lines, though altering in intensity, do not shift their positions. If the lattice dimensions of a phase as determined by the powder photograph are plotted against composition, a sloping line is obtained in the single phase region and a horizontal line in the two-phase region. The composition at which the two lines intersect is a highly accurate index of the position of the phase boundary.

X-RAY TECHNIQUE

The wave-length of the radiation used in making the photographs must be adapted to the alloy which is being examined. It must not be absorbed too heavily by the alloy powder, both because the diffracted lines are then weak, and because the absorption implies a re-scattering of radiation in all directions with consequent darkening of the background. For example, cobalt, iron and chromium $K\alpha$ radiations are excellent for examining iron alloys, since they are of lower frequency than the iron 'absorption edge' and hence are little absorbed. A cobalt radiation gives a large absorption of cobalt $K\beta$ rays in the specimen if these waves have not previously been filtered out. Copper radiation is extremely inefficient owing to the very large absorption, which produces a blackened film on which scarcely any lines are discernible.

It is possible to obtain powder photographs which at the same time give the pattern of lines throughout the complete circle, and enable the lattice dimensions to be worked out with high accuracy. The latter are most useful indices in elaborating the phase diagram. A recent design of camera by Bradley, combined with an ingenious method of evaluating the results, enables spacings to be compared with an accuracy approaching 1/50,000 when the crystalline material is suitable,

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while at the same time the camera is of the ordinary circular type utilising short exposures and including the complete pattern. All 'precision methods' of measuring spacing depend upon the useful feature that rays diffracted backwards through nearly 180° enable a very accurate comparison of spacing with wave-length to be made. The particular feature of the method referred to above is the way in which errors due to incorrect placing of the specimen, absorption in the specimen, film shrinkage, and uncertainty as to camera-radius, are automatically eliminated.

Powder cameras must be calibrated by taking in each camera a photograph of a crystal with known spacings. Quartz is very suitable for this purpose. It is constant in composition, has a small temperature coefficient, and gives a large number of very clear lines. The quartz photograph may become as important in X-ray work as the comparison iron spectrum in spectroscopy.

NATURE OF A 'PHASE'

The determination of phase boundaries by X-rays is merely the application of a new method to a problem already dealt with by well-established metallurgical technique. The particular contribution of X-ray analysis is its determination of the atomic arrangement in the alloy. It is found that each phase has a characteristic geometrical pattern of atomic positions. This is in accord with the findings of analysis in other crystalline bodies such as inorganic and organic compounds, but there is a new feature in alloy structures which is peculiar to them. The phase is an absolutely definite arrangement of 'sites' for atoms, if one may put it in that way, but in many cases the way in which the atoms are distributed amongst these sites turns out to be of secondary importance, and may vary widely. Such a feature is foreign to the typical inorganic or organic compound, where the atoms of various kinds have each their appointed positions.

An example of this peculiar feature is given by the structures of two closely related alloys the compositions of which approach the ideal formulæ Cu_5Zn_8 and Cu_5Cd_8 . These alloys, which appear as phases in the copper-zinc and copper-cadmium systems, are obviously similar in nature. They are hard and brittle with a characteristic fracture and sheen. X-ray analysis by Bradley has determined their complex structure, in which there are 52 atoms in the unit cube, the ' γ structure'. From the similarity in atomic ratio and the correspondence in chemical properties of zinc and cadmium, it would be expected that the arrangement of zinc atoms in one and of cadmium atoms in the other would precisely correspond. The sites for atoms in the two alloys are indeed almost identical, but Bradley has been able to show that the distribution of zinc atoms amongst these sites in the one alloy is entirely different from the arrangement of cadmium atoms in the other. Clearly the peculiar complex γ structure is determined by

something apart from the distribution of the atoms; the latter is a secondary feature influenced by the relative sizes of zinc and cadmium atoms.

We find similar phases, or arrangements of atomic sites, in different alloys. For example, the alloys of copper, silver, gold with metals of the B sub-groups such as zinc, cadmium, aluminium, gallium, tin form an α face-centred cubic phase like that of copper, silver, gold themselves, a body-centred β phase, and a complex γ phase with 52 atoms in the unit cell. All γ phases have similar physical characteristics such as their extreme hardness. Since the geometrical arrangement of atomic sites in each phase appears to be quite definite, while at the same time independent of the atomic distribution, by what is it determined?

HUME-ROTHERY'S LAW

The answer to this question is provided by a brilliant hypothesis which we owe to Hume Rothery, the truth of which has now been verified by a large number of examples. Hume-Rothery's law states that each phase appears when the ratio of valency electrons to atoms has a value characteristic of that phase. For example, the β phase, which is body-centred cubic, is found when there are three valency electrons to every two atoms, examples being the alloys CuZn , Cu_3Al , Cu_3Sn . Assigning one valency electron to copper, two valency electrons to zinc, three to aluminium, and four to tin, it will be seen that in the first of these compounds there are three electrons to two atoms, in the second six electrons to four atoms, and in the third nine electrons to six atoms. An even more striking example is found amongst the γ structures to which reference has already been made. Here the electron-atom ratio is $21:13$, examples being Cu_5Zn_8 , Cu_5Al_8 , $\text{Cu}_{31}\text{Sn}_8$. A hexagonal, close-packed ϵ structure which appears in many of the alloy systems has a ratio $7:4$, as evidenced by CuZn_3 , Cu_3Sn , AgZn_3 , Ag_3Al , AuCd_3 . A very large number of alloys obeying this law is now known, and it will no doubt be added to as other systems are examined.

There are exceptions to the rule. It must further be borne in mind that an alloy phase is not definite in composition but extends over a range in the phase diagram which may be broad or narrow. The composition which gives one of the above ideal electron-atom ratios may be towards one side of the single phase region, or even just outside it. It is justifiable to say, however, that the electron-atom ratio is a main factor in determining the arrangement of atomic sites in the phase. The range of the phase is modified by other factors, which make it broad or narrow and displace it one way or the other, but they are of secondary importance. Starting with copper, silver, or gold and alloying them with other metals, we run through a similar series of phases. The higher the valency of the second metal, the smaller is the amount of it which has to be added in order to produce each new phase. Quantitatively this may

be expressed by saying that its contribution is to be reckoned in terms of added valency electrons, according to Hume-Rothery's law.

It is an interesting feature that the metals of the triads iron, cobalt, nickel; ruthenium, rhodium, palladium; osmium, iridium, platinum; form similar phases of the β and γ types. In these alloys the valency *zero* must be assigned to the transition metals; for example,

To sum up, the arrangement of atomic sites in an alloy phase appears to be due not to the interaction between the metals of one kind and those of another kind, but to the interaction between all the metal atoms on one hand, and the common electronic structure, to which they join in contributing their valency electrons, on the other hand. The metal atoms can be shuffled about between the phase-sites without a profound alteration of the nature of the phase, as if the structure were almost indifferent to the nature of the atoms in the various sites so long as they provided the quota of valency electrons. It has been shown by Bradley, for example, that ternary alloys and presumably alloys of any complexity assume the γ phase if the total electron-atom ratio is 21 : 13.

SEGREGATION OF ATOMS INTO PHASE-SITES

Two aspects of the problem of alloy structure may thus be distinguished. The first concerns the geometrical arrangement of the sites for atoms, characteristic of each type of phase. Its elucidation must be sought for in the electron-atom interaction as part of the problem of metallic structure in general. The second concerns the way in which the atoms distribute themselves amongst these sites. It has been known for some time that this distribution may vary in a given phase. On one hand, atoms of each kind may segregate into certain positions in a symmetrical way, so as to build a crystal structure of definite pattern like those found in inorganic and organic compounds. In some of the γ alloys, for example, similar atoms occupy certain sets of the sites which are related by the crystal symmetry, and the other atoms occupy the remainder.

Alternatively, we may find the formation of a *super-lattice*. In a simple β structure of the body-centred cubic type, for example, there are two atomic positions in each unit cubic cell, at corners and centres, which are crystallographically identical. In such structures as CuZn, or FeAl, one atom occupies the corners and the other the centres. In β alloys of more complex composition, however, the unit of pattern repeats in a larger distance, so that it is necessary to stack several cubes together and select symmetrically certain positions from the large unit for one of the atoms, in order to represent the unit of pattern. An X-ray photograph of such an alloy shows as a

primary feature the lines due to the body-centred cubic arrangement characteristic of all β phases. In addition, subsidiary lines due to the super-lattice appear, which indicate that the unit of pattern is upon a larger scale. The segregation of the atoms into preferred positions may be followed by studying these lines.

As opposed to the formation of a super-lattice or of a regular crystalline segregation, we find in other cases that the X-ray diagram indicates merely the arrangement of the atomic sites, as if the atoms were arranged in an absolutely random manner amongst these sites. Such a random arrangement would affect the X-ray diffraction pattern as if each site were occupied by an identical unit of mean composition. Many examples might be quoted, a very striking one being given by Westgren. The alloy Cu₅Si has a complex structure in which there are twenty atoms in the unit cube. This β' structure is assumed instead of the simple β structure by certain alloys with a 3 : 2 electron ratio, and is similar to one form of the element manganese, the β -manganese structure. An X-ray photograph of Cu₅Si gives lines identical in arrangement and relation in intensity with those of β -manganese, in which, of course, all atoms have the same scattering power, so that the scattering by each atomic site must be that of a mean effective atom. Further, it may be noted that the six atoms of Cu₅Si cannot be distributed in any regular way between twenty atomic positions, since 6 is not a factor of 20. Structures which give such an effect are said to be structures of *random replacement*.

The transition between the two extremes of regular and random replacement may be observed in one and the same alloy. Alloys at high temperatures or which have been rapidly quenched from high temperatures show random arrangement, whereas alloys subjected to prolonged annealing have a regular or super-lattice structure. The potential energy of the symmetrical structure must be less than that of the disordered structure, and hence it is the stable structure at low temperatures. At high temperatures, however, the thermal movements are causing the atoms constantly to change places, a disordered arrangement having a higher entropy than an ordered arrangement.

The study of these changes in arrangement is of great interest and importance, because they affect the physical properties of the alloy. It is to be emphasised that we are not concerned here with a phase change, since the phase remains the same throughout. We are dealing with continuous changes from order to disorder within the same phase structure.

The segregation of atoms into regular positions was surmised by Tammann in 1919 as an explanation of the changes in resistance of annealed alloys. One of the most fully examined cases is that of the gold copper alloy AuCu studied by Johannson and Linde. In this case we are dealing not only with regular and irregular distribution of atoms,

but also with an alteration of crystalline form. The alloy of perfect arrangement is tetragonal in symmetry, and the symmetry passes by change of axial ratio into the cubic type as the temperature is raised. A similar but simpler case will be discussed here, where the arrangement of the atomic sites remains the same throughout. This is the case in the iron aluminium alloys examined in detail by Bradley.

The alloy of composition FeAl is a structure of the β type, with iron atoms and aluminium atoms at corners and centres of the unit cube. Iron has itself a body-centred cubic structure, and it is found that, when aluminium is dissolved in iron, there is a very wide continuous range of this body-centred cubic phase extending from pure iron to FeAl. The added aluminium atoms simply replace iron atoms. Two types of super-lattice are built up. When the composition is FeAl, iron atoms at the centres of the cubes are entirely replaced by aluminium atoms, so that the structure is of the type known as a 'CsCl' structure. It may be noted that there is no crystallographic distinction between corners and centres, so that we might equally well describe the arrangement as one of aluminium atoms at corners and iron atoms at centres. When the composition is Fe_3Al , and the alloy is carefully annealed, one half of the cube centres chosen in a symmetrical way are occupied by aluminium and the other half remain iron atoms.

By observing the super-lattice lines in the photographs, Bradley has been able to follow out the process of replacement at all compositions between pure iron and FeAl. Taking first annealed alloys, the first aluminium atoms to enter the structure replace iron atoms at random. At a certain concentration, the aluminium atoms desert cube corners and one set of cube centres, and tend to concentrate in the remaining set of cube centres, finally at Fe_3Al occupying it entirely. Past this point, since one set of cube centres is now full, the further aluminium atoms start filling up the remaining set of cube centres. At a certain point, in order to equalise the distribution between the two sets of centres, these two share the available aluminium until finally at FeAl they are completely filled. The quenched alloys show a curious phenomenon. Up to 25 per cent atomic aluminium they have apparently random replacement. Past that point, within less than 1 per cent change in composition, they change over into a distribution in which all corners are occupied by iron, and centres by a random replacement of iron by aluminium.

RANDOM REPLACEMENT

When an X-ray photograph shows an apparently random replacement, are we to interpret this as meaning that the atomic sites are occupied by iron and aluminium as if they were the 'black and white balls' of a problem in probabilities? On physical grounds this is not to be expected. The Fe_3Al and FeAl structures show us that aluminium

atoms under conditions of ideal equilibrium tend in the first place to avoid being nearest neighbours by segregating into cube centres, leaving the corners for iron, and further to avoid being in cubes which are side by side (Fe_3Al structure). We must postulate a slight increase in potential energy when aluminium atoms are at centres of contiguous cubes, and a larger increase when two find themselves at a corner and centre of the same cube. I am indebted to Dr. Williams for calculations concerned with this effect. If we suppose a small increase V of potential energy to be produced by one of these undesirable contacts, it is then possible to calculate the proportion of atoms in 'disorder' as opposed to 'order' at a series of temperatures.

The calculation shows that it is impossible to account for the whole range between complete order (which we know to exist by the evidence of super-lattice lines) and complete disorder, in any range of temperature experimentally available. The difference between annealing and quenching could at the most produce a slight disorder. The conditions we have set are, however, not true to actualities. As the structure becomes more disordered, the contrast between the ordered position and disordered position for a given atom becomes less, and so V must be supposed to diminish, until finally one can picture a state where no criterion is possible—the atom is completely demoralised by the corrupt state of society in which it finds itself.

It is possible, however, that what appears to be random replacement is not really a purely fortuitous distribution. We may suppose that within each small crystallite of the metal there is for the most part an ordered distribution, but that this ordered distribution is frequently getting 'out of step'. To take a simple case of a linear row, we may suppose an alternation Al-Fe-Al-Fe to take place for a part of the row, and that then owing to an excess of iron, two iron atoms follow, so that when the alternation recommences, aluminium and iron atoms have changed places. This process may be frequently repeated. Since the effects of all atoms in crystal planes are summed when the X-rays are diffracted by the crystallite as a whole, the result as regards diffraction would be an apparently random replacement of iron by aluminium. A kind of structural twinning within the crystal, which does not alter the orientation of its axes but only the succession of its atomic planes, is possible.

The behaviour of the quenched iron aluminium alloys suggests some such explanation. So long as aluminium is present in quantities less than 25 per cent in atomic proportions, there is apparent random replacement. Beyond this point the segregation suddenly appears by which aluminium goes into cube centres alone. May not this be because below 25 per cent the excess of iron causes the structure to get 'out of step', two successive layers of iron atoms causing a part of the crystallite with aluminium at centres of cubes

to continue as a pattern in which the same atoms go to corners? Beyond 25 per cent aluminium, each cube must have contiguous cubes containing aluminium at centres, so that there is no question as to what is a centre and what is a corner. The plan of iron at corners and aluminium at centres is therefore carried out throughout the crystallite.

Though so many problems of alloy constitution

are still to be solved, an important step forward has been made by the recognition that the arrangement of atomic sites and the segregation of atoms into these sites are separate problems, and by the discovery of similar phase-structures in alloy series of different metals. There is promise of reducing to order the vast array of hitherto uncorrelated data.

Medical Research in Great Britain

THE annual report of the Medical Research Council* again indicates the great variety of the scientific investigations carried out under its auspices with the ultimate aim of improving the health and well-being of the community. The scope of the research work initiated and aided by the Council has, as in previous years, been widened by grants from a number of public bodies interested in research work within the medical field, by the availability of university laboratories for use by investigators receiving grants from the Council, and by co-operation with Government departments and the committees of Privy Council for Industrial and Agricultural Research. The Council has exercised the strictest economy in the use of its available funds: the salaries of all its officers, and of all members of the scientific staff and whole-time grant holders have been 'cut' on the Civil Service scale. The reduction of various subsidies received from other public bodies imperilled the progress of different schemes of research, the abandonment of which, at the stage reached, would have been a very wasteful procedure. Fortunately, voluntary benefactions from private sources and notably those received from the Rockefeller Foundation and the Leverhulme Trustees prevented the setback in the work of the Council from being, it is hoped, more than temporary.

Three changes occurred in the composition of the Council during the year, Mr. W. S. Morrison, Prof. E. D. Adrian and Prof. A. E. Boycott taking the places of Major A. G. Church, Prof. R. Muir and Sir J. Herbert Parsons respectively.

The Council points out that the promotion of clinical research has always been given a primary place in its policy from the beginning of its work. The problem has been to find means of promoting the conditions in which clinical research work can be brought to its fullest development. With the co-operation of University College Hospital, London, the Council has maintained a Clinical Research Department there, with Sir Thomas Lewis as director, with charge of beds and free from all preoccupations except those of gaining new knowledge by clinical research. During the past year, the Rockefeller Foundation has generously provided a sum of money to endow in perpetuity the directorship of this Research Department,

thereby releasing funds which the Council will apply to further clinical research elsewhere. The University of Aberdeen and the National Hospital for Nervous Diseases, Queen Square, London, have also shown their sympathy with clinical research: at the latter, a Research Department is in course of formation and Dr. E. A. Carmichael has been appointed by the Council as whole-time director.

The scope of the clinical work at University College has been widened. In earlier years the Department of Clinical Research dealt chiefly with cardiac problems and especially those of cardiac mechanism; more recently it has taken up problems of the peripheral blood circulation. At present, studies of hypertension and cardiac asthma are bringing problems of kidney function into view, and special attention is being paid to the symptom, pain. Interesting correlations between anginal pain and that derived from muscular ischaemia have been found.

The National Institute for Medical Research has continued the regular distribution of the standards held under the Therapeutic Substances Act, and of those held on behalf of the Health Organisation of the League of Nations. The international standards for vitamin A (carotene) and vitamin D (a solution of irradiated ergosterol in olive oil) were prepared in the Institute and together with the standard for vitamin B₁ (a dry adsorption product from an extract of rice bran prepared in Java) have now been issued for general use. Work has also been carried out on serum standards and a standard for Type I antipneumococcus serum has been prepared and issued. A review is at present in progress of different preparations coming under the general title of "Tubercle Vaccine", to ascertain the practical interpretation given by manufacturers to the regulations made under the Therapeutic Substances Act. The Institute also has obligations with regard to standards required by the new "British Pharmacopoeia", other than those already held under the Therapeutic Substances Act, namely, those for digitalis, strophanthin and strophanthus tincture: the latter two were prepared during the year. A conference was held in London in July under the auspices of the Health Organisation of the League of Nations to discuss the possibility of establishing a uniform notation in units for the oestrus-producing hormone and eventually for other hormones for the reproductive functions. The conference

* Report of the Medical Research Council for the year 1931-1932. Committee of the Privy Council for Medical Research. (London: H.M. Stationery Office, 1933.) 2s. net.