Examination of Bronze Implements.

By Prof. C. O. BANNISTER and J. A. NEWCOMBE.

THE results of modern methods of research on the constitution of metallic alloys and on the effects of varying mechanical and thermal treatment on their structure and mechanical properties have increased our knowledge of these subjects enormously. Of these methods, the use of the microscope for the examination of the micro-constitution and crystalline condition of suitably polished and etched specimens is one of the most important. This method of examination is capable of indicating not only how the component metals exist in the alloy, but also what mechanical or heat treatment the alloy has undergone. As regards constitution, the microscopical examination is used in order to ascertain whether the component metals are present in the free state, in chemical combination, or mutually dissolved and retained in solution in the solid state. As regards treatment, the structure observed is used to decide whether the metal object was obtained by a casting process or was shaped by mechanical work, and is also capable of indicating whether any work has been applied to the object and also whether this work has been followed by an annealing process. Below are given some results of an examination of a chisel and a palstave of the Bronze Age found about 1898 in a brick-field near the Hanwood-Shrewsbury road and supplied by Mr. F. Drinkwater of West Kirby through Miss L. F. Chitty of Yockleton, near Shrewsbury.

With regard to the constitution of bronzes, these consist of alloys of copper and tin in varying proportions, and if the molten metals be allowed to solidify and cool very slowly, or if cooled normally and then reheated for the necessary length of time, the tin is soluble in the copper in the solid state up to 13 per cent. of tin. After such treatment, the bronze would show one constituent only under the microscope.

On cooling a liquid alloy containing 8-13 per cent. tin, the first portions to solidify are richer in copper than the portions solidifying last. On polishing and etching such an alloy, these copper-rich portions are found to have a fern-like structure, and the presence of these dendrites, as they are called, is indicative of cast metal. The alloy not being homogeneous throughout its mass has areas with a greater tin percentage than 13, and in these areas a pale blue constituent, which is a very intimate mixture of two solid solutions, makes its appearance. The more of this second constituent that is present the harder and more brittle does the metal become, and with any definite percentage of tin the more quickly the metal is cooled, within limits, the more of this constituent is present in the casting. If the cast bronze be now heated for some hours at a temperature below its melting point, diffusion takes place, the metal becomes more or less homogeneous in composition, and the dendrites and the second constituent more or less disappear, the metal becoming more homogeneous the longer the annealing or the higher the temperature. With cast bronze of less than 8 per cent. tin, the dendrites would appear as above, but little or no blue constituent would be present because the tin rich areas would contain less than 13 per cent. of tin.

If the cast metal were cooled in the mould very slowly, this would have, as regards the homogeneity of the metal, a similar effect to annealing. The rate of cooling of a casting will depend on three factors: first, the temperature of the metal when it is cast, it being obvious that the higher this temperature the longer will the solidifying and cooling take. Secondly, the material of which the mould is made. If the material conducts heat rapidly from the metal, the rate of cooling will be greater than in the case of a mould from which the heat was less rapidly removed. The stone mould commonly used for casting antique bronzes would be a bad conductor of heat, and the cooling would take place very slowly. A bronze mould would chill the casting, and cooling would be very rapid. A sand mould would have an effect intermediate between these two. The third factor would be the size of the casting, one of large bulk cooling more slowly than a smaller casting, as there would be more heat to disperse.

Another important characteristic in the structure of bronze is the outline of the crystals revealed by the etching. In the cast metal the crystals are very irregular, some crystals being of large size compared with others, and having interlocked boundaries. If the metal be now worked in some way by hammering or rolling, an examination will show the results of this work in the distortion of the original crystals, which are often elongated to a considerable extent at right angles to the direction of the work when this has been excessive. The effects of less drastic amounts of work are seen in the appearance of parallel lines on the crystals, these lines being known as slip bands. If the metal be annealed after working, new crystals will make their appearance, appearing quite different from the casting crystals and characteristic of the annealed metal. These crystals are much more uniform in size, and have sharp lines as their boundaries. They invariably show a great deal of twinning, which is recognised by the crystals having two or more parallel lines traversing them. As a result of this working the dendritic structure will be somewhat destroyed. Instead of being fern-like, it generally appears as thick, dark, irregular parallel bands over the specimen in a direction at right angles to the force applied. A long annealing entirely eliminates this structure, but the new crystals grow before this is effected, so that in annealed metal, traces of the dendrites may still be seen.

It will be gathered from these notes that much can be deduced from the micro-examination of antique bronzes. From the fern-like, dendritic, or core structure, as it is variously called, and the type of crystal boundaries, the cast structure is at once recognised, and with an 8-13 per cent. bronze some sort of deduction can be made as to the mould used, because with very little of the blue constituent present the metal would have cooled slowly, and it is probable that a stone mould would have been used. The twinned equi-axed crystals and the partial or total absence of dendrites indicate that the metal had been hammered and annealed.

Examination of Chisel.

The chisel was 15·5 cm. in length and, as is shown in Fig. 1, was fractured when received. The fracture showed a considerable amount of porosity. An analysis shows copper 85·5 per cent., tin 14·2 per cent. A section taken of a part near the fracture was polished and etched in a solution of ammonia containing a few drops of hydrogen peroxide. Fig. 2 shows the dendritic structure at a magnification of 15 diameters. The section was again polished and photographed unetched. Fig. 3, at a magnification of 25 diameters, shows how very porous the metal is; the holes were formed at the time of casting, and were due to the fact that the metal was cast at too high a temperature and insufficient provision was made for the escape of gases from the metal. Fig. 4 was taken to show the dendritic structure at the higher magnification of 60 diameters and is typical of cast bronze. Fig. 5, taken at a still higher magnification of 270 diameters, shows the blue constituent situated along the boundaries of the crystals. The percentage of tin present in the alloy would account for this apart from the heterogeneity of the metal.

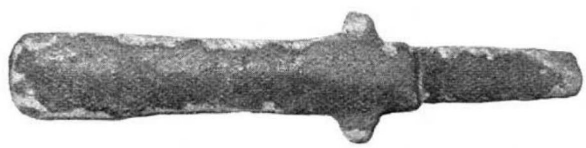

FIG. 1.

FIG. 2. ×15.

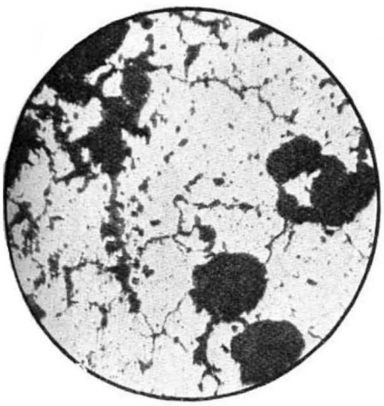

FIG. 3. × 25.

FIG. 4. ×60.

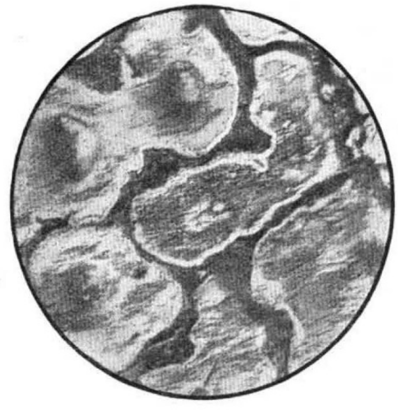

FIG. 5. ×270.

From the well-defined dendritic structure and the large proportion of blue constituent, it may be assumed that the metal cooled quickly in the mould, the small bulk of metal being sufficient to account for this, apart from the nature of the material of the mould. The amount of blue constituent and the number of blowholes would indicate the metal to be very brittle, and on examination the metal was found to be so brittle that it could be crushed by gentle tapping with a small agate pestle.

A very important matter brought out by the examination of this ancient chisel is the persistence of the dendritic or core structure, because it has been suggested that, during the course of a long time, even at ordinary atmospheric temperatures, diffusion would proceed in solid alloys, with the result that equilibrium would eventually be obtained exactly as it may be obtained at higher temperatures in a few hours. The dendritic structure of this chisel, however, is so typical of a recently cast bronze that it appears safe to say that no diffusion has taken place during the ages.

Examination of Palstave.

The palstave examined is shown in Fig. 6, and is 15 cm. long. An analysis shows copper 86·9 per cent., tin 12·7 per cent. A portion of the socket was polished and a photomicrograph was made of a portion adjacent to the corrosion product at a magnification of 75 diameters; this is shown in Fig. 7. The corroding agent operates in the first place along the crystal boundaries, this being the portion of the metal in which any traces of impurities present become concentrated, corrosion taking place more readily with impure than with pure material. The presence of corrosion of this type in bronze is a sure proof of its antiquity, and a check against the fraudulent "antiques" which are made with so much perfection at the present day. With recently cast bronze, although it is easy to imitate the effect of age on the outside by chemical means, age alone will allow the slow penetration of the corrosion around the crystal boundaries without too rapid attack on the crystals themselves.

Fig. 8 was very deeply etched by means of a solution of ammonia containing hydrogen peroxide to show the type of crystals present. The very irregular crystals can be seen, and it will be noticed that the corrosion follows the crystal boundaries. Some of the crystals show striations across their surfaces and these are slip bands. These slip bands are formed when a metal is subjected to an amount of work just sufficient to cause a permanent deformation in them. This would naturally be towards the end of the socket where the metal is thinnest, and would be caused by the force exerted on this part by the wooden handle fitted on to the socket when the palstave was in use. The smaller dark patches in Fig. 9 consist of the blue constituent, but the larger are the result of corrosion.

Fig. 9 shows more clearly the shape of the casting crystals and illustrates variation of size and interpenetration.

A section of the cutting edge was polished and etched, and the photomicrograph is shown in Fig. 10, at a magnification of 75 diameters. The crystals shown here are much smaller in size and of a totally different shape from those of Fig. 9. They are more uniform in size, they are sharp, and a large number of them are twinned. It will be observed that indications of dendrites are almost entirely absent. This structure shows that this end of the palstave has been hammered and afterwards heated. There is little doubt that the hammering was performed with the object of sharpening or resharpening the palstave, and the reheating operation

FIG. 6.

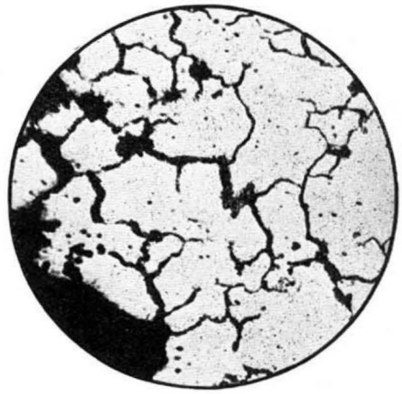

FIG. 7. ×75.

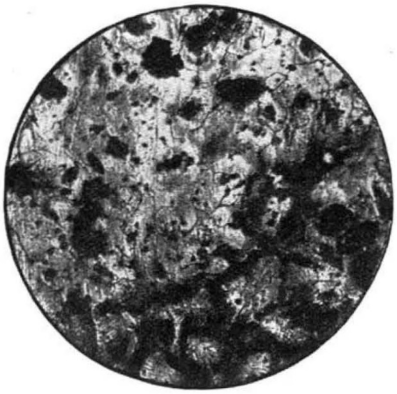

FIG. 8. ×70.

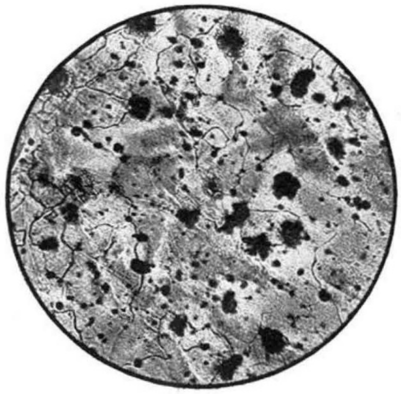

FIG. 9. ×75

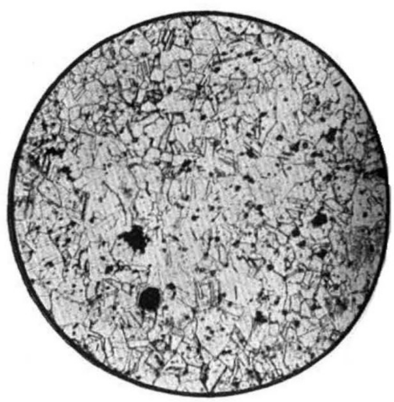

FIG. 10. ×75.

was used to remove the brittleness induced by the work, as it would soon become apparent to the ancient metallurgist that these operations would give a stronger and tougher metal. The metal could not have been hammered hot, because bronze of this composition is not malleable when hot. The palstave was finally annealed, as otherwise the effect of the work would have been apparent on the crystals in the photograph.

From Figs. 8 and 9 it is evident that the dendrites are not well defined, and very little blue constituent is present although the composition is near the maximum at which tin is soluble in copper. This is due to the comparatively long time the metal took to solidify and cool, thus allowing some diffusion to take place in the solid metal, and the composition to become approximately uniform.

It has been suggested that if an antique metal had been worked or strained, crystals may form at ordinary

FIG. 11. ×300.

temperatures during the ages similar to those that would be formed in a short time if the metal were heated. The evidence obtained from the examination of this palstave appears to prove that this is not so in the case of bronze. Fig. 11 is a photomicrograph of a portion near the cutting edge of the palstave and is similar in appearance to the structure shown in Fig. 10, but at a higher magnification of 300 diameters. This photograph was taken in order to illustrate the fact that corrosion on this part of the palstave follows the crystal boundaries, which are not of the casting crystal type but have been formed subsequent to mechanical work. The presence of the corrosion product in these boundaries indicates that these crystals must have been in existence before corrosion commenced and therefore had not been slowly formed during the ages. This photograph also shows that the crystals are still of the same size as they were when corrosion commenced and that no growth has taken place. This suggestion of the germination of crystals during the enormous time that has elapsed since the castings were made is further disproved by Fig. 8, as the slip bands shown in this photograph indicate strained metal and no new crystals are seen to have formed.

The Darling and Lothian Foundations for Research in Malaria.

SOME months ago we had to record (NATURE, May 30, p. 845), with much regret, the deaths in a motor-car accident, near Beirut in Syria, of Dr. S. T. Darling (United States of America), Dr. N. V. C. Lothian (England), and Mlle. Besson (France), members of the Malaria Commission of the League of Nations who, with Prof. Nocht (Hamburg), Swellengrebel (Amsterdam), Ottolenghi (Italy), Anigstein (Poland), and Colonel James (England), were undertaking a tour of investigation in Palestine, Syria, and part of Turkish Asia Minor. In the recently published report on the work of the fifth session of the League's Health Committee, held at Geneva on October 8-14, it is announced that the Committee, wishing to honour and perpetuate the memory of Dr. Darling and Dr. Lothian, has decided:

(1) To collect by private subscription a capital fund, the interest on which will be expended on a prize to be awarded periodically. This will be known as "The Darling Prize."

The prize (a medal or other reward) will be awarded by the Malaria Commission of the League of Nations to a scientific worker who, in its opinion, has carried out recent distinguished research on a subject connected with malaria which comes within the general scope of the Commission's investigations.

(2) To devote a portion of the credits provided for in the budget of the Health Organisation for the encouragement of malariological study to the establishment of a periodical scholarship to be known as "The Lothian Scholarship." This scholarship will be awarded by the Malaria Commission to a selected candidate whose course of study should be in conformity with the general programme of the Malaria Commission.

In our issue of August 8, p. 216, we printed the substance of an appreciation, from the pen of Prof. R. W. Hegner, of the life and work of Dr. Darling. In the Malaria Commission's report of the Palestine tour, which preceded the journey to Syria on which the tragic accident occurred, it is said that the Commission had frequent occasion for congratulation that Dr. Darling had found it possible to be one of the party. "His previous experience of malarial epidemiology and antimalarial operations in many countries was unrivalled. He appreciated very clearly the particular aspect of the subject with which the Commission's mandate is chiefly concerned, and his observations during the tour constantly proved that he was at the zenith of his powers as an expert adviser on antimalarial work."

Dr. Lothian joined the Secretariat of the Health Section of the League in May 1923, after a career of considerable achievement in the Royal Army Medical Corps. He had specialised in hygiene, and some of the scientific papers which he published during his army service were of outstanding merit and practical usefulness, notably his "historical inquiry into the load carried by the soldier of various periods," in which he showed that a soldier should not be required to carry more than 33 per cent. of his own weight; the load of a mule is 32 per cent. and of a horse 28 per cent., and to require a soldier to carry more than 33 per cent is to destroy his marching power and capacity for battle.

Dr. Lothian, during his two years' service with the League, travelled in many countries and came into close contact with administrators and public health officers of many nationalities. He accompanied and guided the "interchange courses" of foreign public health and medical officers which, in collaboration with the Rockefeller Foundation, now form a regular item in the programme of the Health Organisation at Geneva. He was secretary to the League's Malaria Commission, and in the report of the Commission's tour of investigation through eastern Europe and Russia, which was published last year, the chapter entitled "Summarised Impressions of the Tour" was wholly drafted by him. It is a sufficient illustration of his expert knowledge of the subject and of the industry which characterised all his work. His high sense of duty and his attractive personality gained him the highest regard and respect wherever he went, and the shock of his death was the greater because he was in the exuberant vigour of youthful manhood, looking forward with enthusiasm to the highest and best that life holds in store.