A FUNDAMENTAL APPROACH TO THE STUDY AND CONTROL OF FAILURES DUE TO A LIQUID OR A BRITTLE PHASE ENVELOPING GRAINS.

By

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ABSTRACT

The concept that the microstructure is the resultant spatial distribution between phases and grain interfaces is developed on the fundamental law of the triangle of forces. Microscopical evidence of this is presented by a study of the intergranular penetration of lead, bismuth, phosphorous and others in copper and brass showing also the effect of alloying additions on the angle of penetration or the 'dihedral angle'. This concept of the dihedral angle is adapted to formulate a theory of the mechanism of intergranular failures. It has also been shown how by a proper and judicious addition of an alloying element the interpenetration of a liquid or a brittle phase could be avoided thus preventing an intergranular failure. The importance of this approach in the study and control of such intergranular failures as that of boiler plates, brasses, stainless steels & such others is stressed.

INTRODUCTION

It is a well known rule that the property of a material is dependent on the shape, size and distribution of the constituents and by the distribution within them. There are a number of investigations which go to prove the importance of the exact manner of distribution of phases on the physical properties and usefulness of an alloy. It is surprising that despite this observation little attention has been paid to the study of certain failures from this new angle namely the spatial arrangement of grains and phases that are observed.

The basis of this new approach to the study of a certain type of failures is the simple concept* that "generally the microstructure is the resultant spatial distribution between phase and grain interfaces whose surface tensions balance at the points and along the lines where they meet." This concept brings forth a number of corrolories and it is the purpose of this paper to present their significance and the formulation of a theory of the mechanism of such failures and in the consequent better design of the alloys for the service in question.

THE CONCEPT AND PRINCIPLES

In the words of Adams[2] "two and three phase interfaces in fluids seek a condition of minimum energy and approach a geometerical configuration in which the various forces are in vectorial balance." A quantitative value for the relative value of the surface forces involved can be obtained by a measurement of the angles established between the interfaces when in equilibrium. When three phases which are immiscible in one another meet, the geometry of the boundaries would be such that the lowest total energy is involved for all the three interfaces. From elementary mechanics it is clear that when three forces are in equilibrium, any one of them has a value equal to and has a direction which is opposite to the resultant of the other two.

In Fig. 1, A, B and C represent the three interface tensions at the three phase junctions, and α, β and γ the angles between the phases. By the law of the triangle of forces we have:

$$\frac{A}{\operatorname{Sin} \alpha} = \frac{B}{\operatorname{Sin} \beta} = \frac{C}{\operatorname{Sin} \gamma}$$

This shows that the three interfacial tensions are in the same ratio as the sines of the angles subtended by the phases opposite each particular interface.

* References are given at the end of the paper.

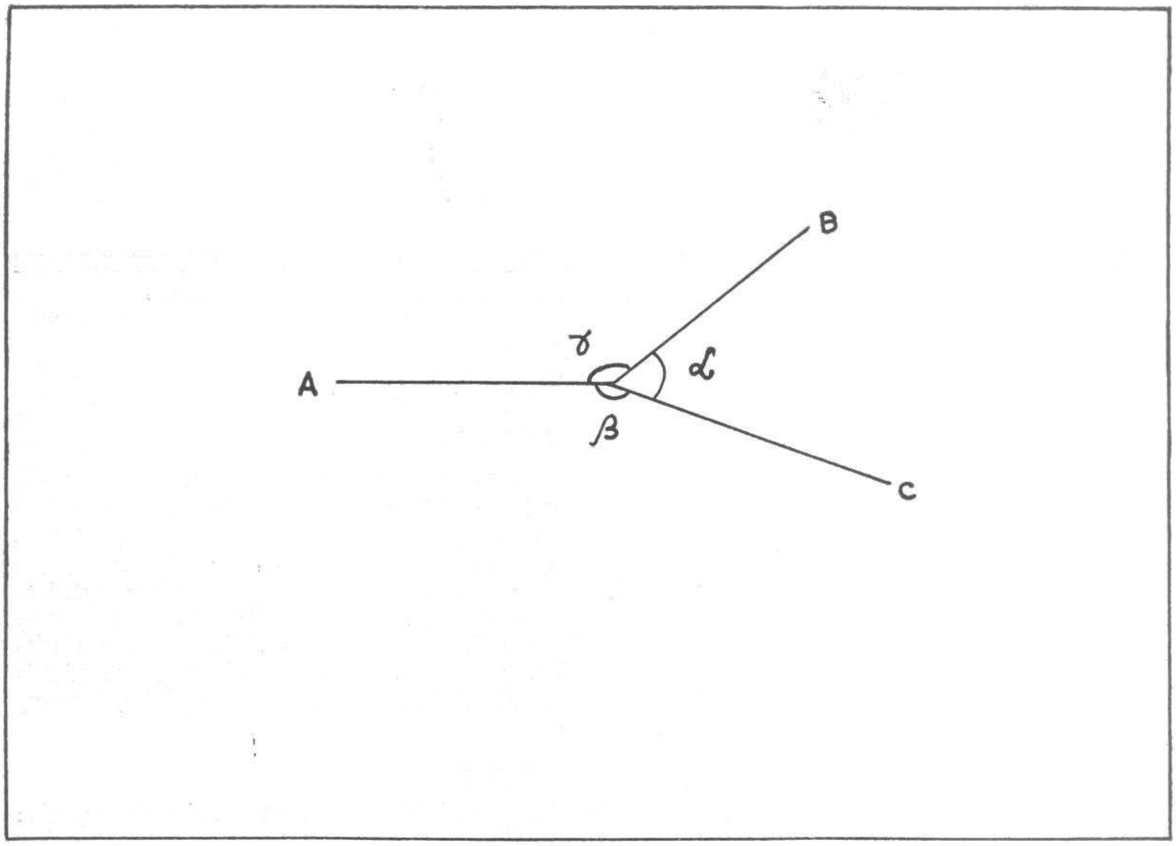

Fig. 1

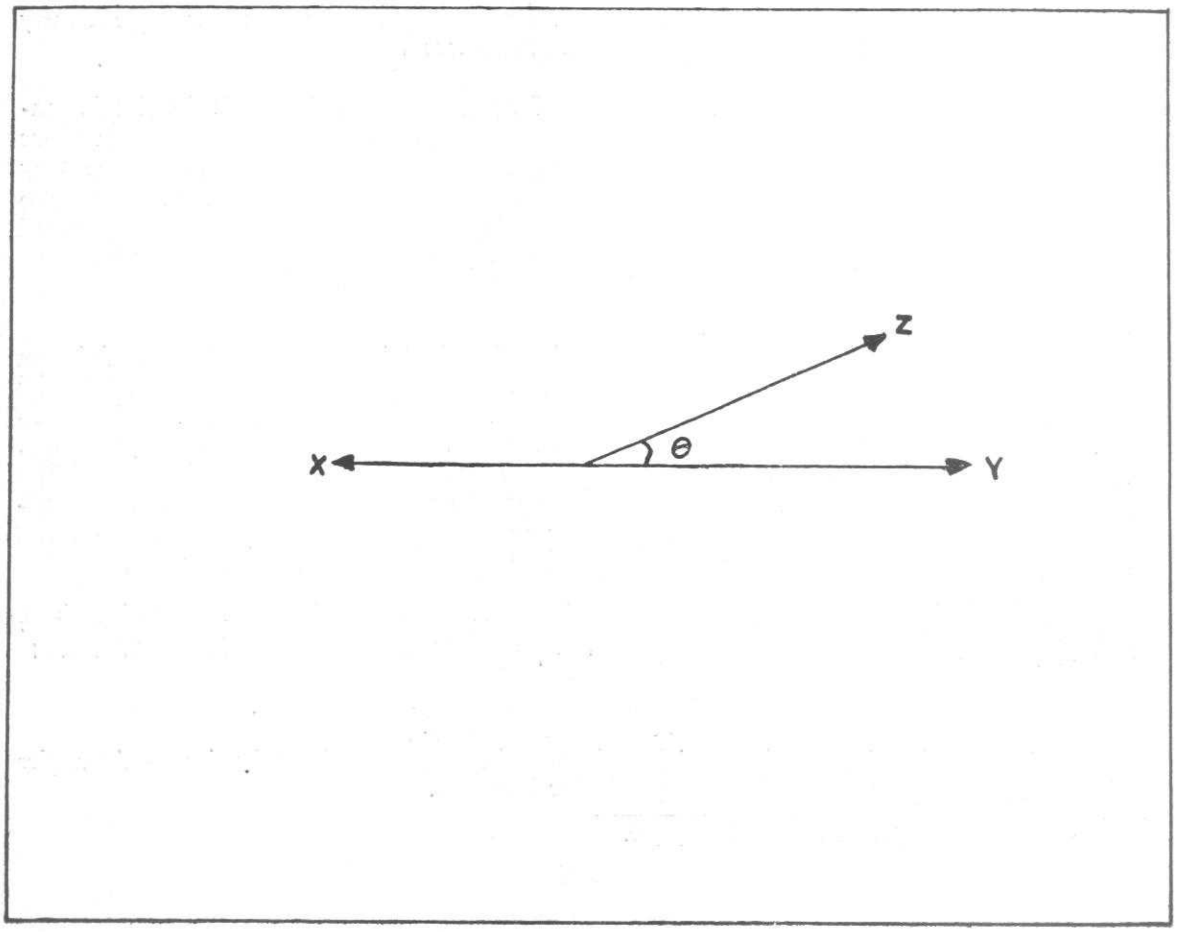

Fig. 2

In cases where one of the phases is rigid and plane, and the two others are fluids as in Fig. 2, the resultant of the tensions of the fluid-fluid interface acting in the plane surface must be equal to the difference between the interfacial tensions of the two liquids against the solid i.e.,

$$X - Y = Z \cos \theta$$

Obviously, this equation cannot be satisfied if Z is $<$ X$-$Y. Under this situation one fluid phase spreads indefinitely over the surface of the solid and entirely displaces the second fluid phase. This is a case of complete wetting and such a condition is of significance in the study of failures of stressed metals during soldering or brazing.

Phase boundaries are the only interfaces possible in the case of fluids, but in the case of solids it is possible to have grain boundary interfaces between phases or grains having different orientation. These grain boundary interfaces have characteristics which are similar to those of normal interfaces between two different phases.

In the case of interfaces between grains of different phases, the situation is different. In a system where three interphases or inter-crystal boundaries are involved, the equilibrium position is such as to give minimum surface energy for the condition. When two grains of one phase meet one grain of second phase the one grain boundary will geometrically establish itself in such a way as to be in equilibrium with the two interphase boundaries, and the angles measured in the plane normal to the line of intersection will be determined by the relative values of the interfacial tensions.

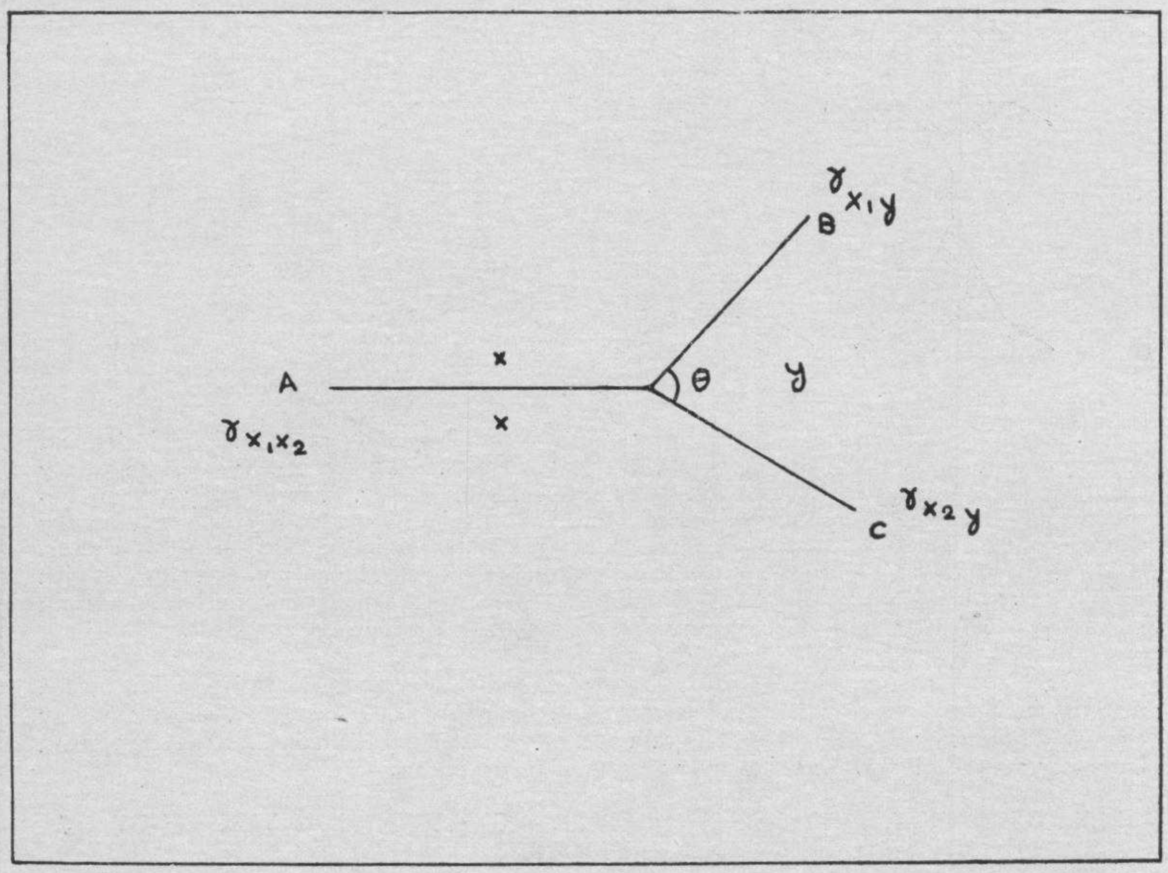

FIG. 3

In Fig. 3, let us assume that the interphase boundaries are not subject to crystallographic influences so that the interfacial tensions

$$\gamma x_1 y = \gamma x_2 y = \gamma xy$$

Then $$\gamma x_1 x_2 = 2\gamma xy \ \mathrm{Cos}\ \frac{\theta}{2}$$

Or $$\frac{\gamma x_1 x_2}{\gamma xy} = 2\ \mathrm{Cos}\ \frac{\theta}{2}$$

This shows that if the interphase boundary tension is more than that half of the grain boundary in one phase, θ will be positive, if the tensions are equal θ will be 120° and if the interphase boundary tension exceeds the grain boundary tension θ will be more than 120°. But, if the interphase tension energy is less than half that of the grain boundary, there is no value of θ that can satisfy the equation and the second phase will penetrate along the boundary indefinitely.

In Fig. 4 is shown an idealised form of shapes for various values of θ, which a small volume of a second phase must have if it appears at the corners of three grains. The angle θ may be called the 'dihedral angle' in Fig. 3, specifically it is "y vs x/x dihedral angle". The dihedral angle is constant and reproducible for a given pair of phases for it is determined only by the relative value of interphase and intergrain boundary tensions.

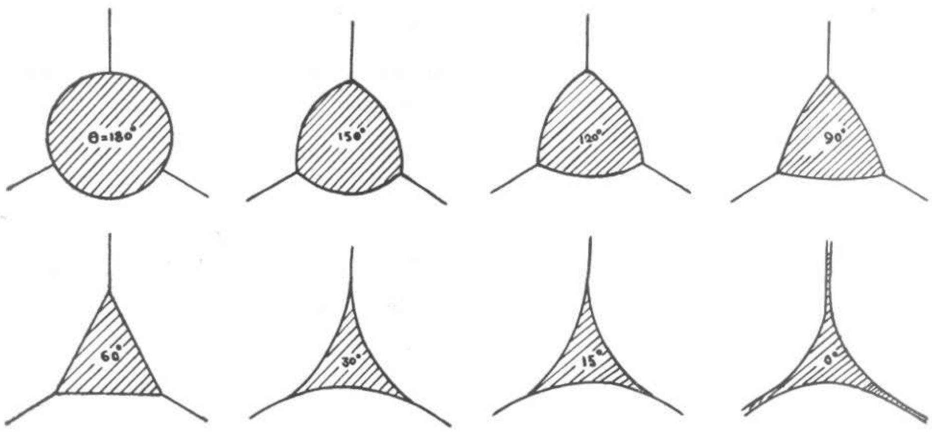

Fig. 4

Phases of low dihedral angles appear much more frequently at grain boundaries and corners than do phases of high angles and interface energies. A phase of low interface energy cannot spheroidise when it is at a grain boundary of higher energy. More nearly a phase becomes spherical, higher the dihedral angle, and less will be its change in shape and energy when it meets a grain boundary. In short whatever may be the initial distribution of a phase of low dihedral angle, it will tend to spread as it encounters a grain boundary, and this will pick up the phase as it migrates during grain growth. When such a phase is collected at a grain boundary, it will move with the boundary and the boundary will move only with it.

On the other hand, phases with high dihedral angles prevent co-operative action by the material in virtue of their small independent and near-spherical shape, and also the energy change produced by the coincidence of grain and phase boundary is small. As such the grain boundary passes easily one at a time over a series of small spheres.

MICROSCOPICAL EVIDENCE AND THEIR SIGNIFICANCE IN THE STUDY OF FAILURES

The metallographic micro sample is a plane section cut at random through a three-di-

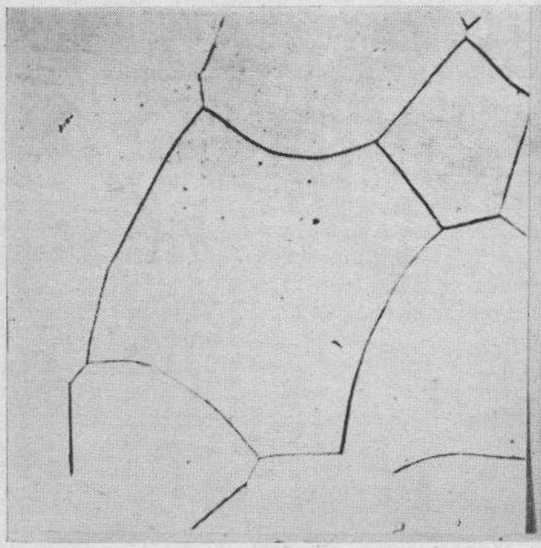

Fig. 5—Polygonal grains in annealed iron. ("Puron." annealed 1,000 Min., 850°C. Nital Etch. x 375.) [C. S. Smith]

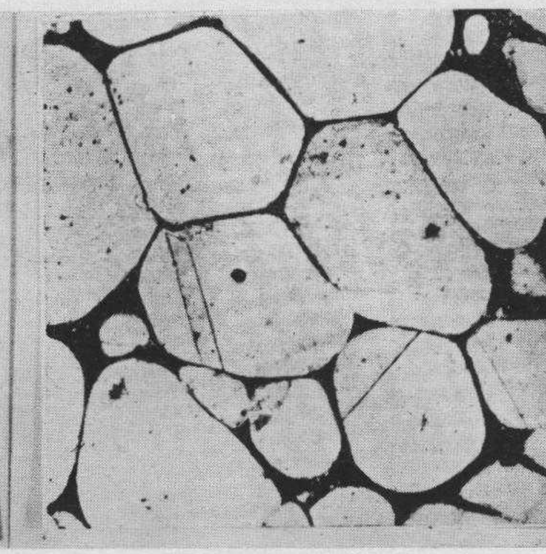

Fig. 6—Partly melted silver-copper alloy (15 pct Ag, quenched from 850°C. Dichromete Etch. x 375). [C. S. Smith]

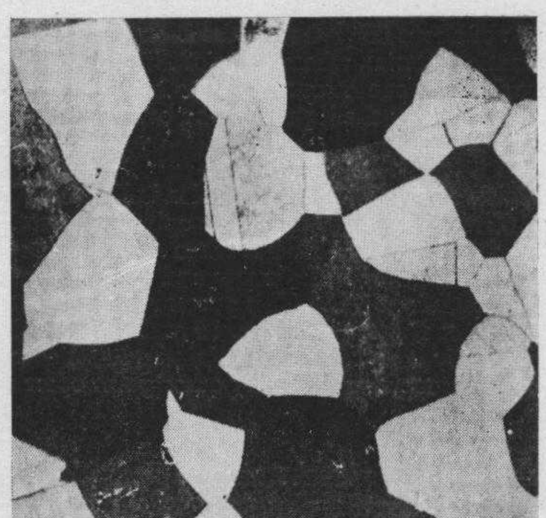

Fig. 7—Alpha-Beta brass (60-40 Cu-Zn annealed 4 days at 700°C, quenched. Dichromate and ferric chloride etches. x 150). [C .S. Smith]

mensional structure and an angle between two planes may appear on this section as any value between 0° to 180°, though with greatly differing probabilities. It has been shown by calculation and measurement that the most probable angle in every instance is the true dihedral angle.

Microstructure of annealed iron showing polygonal grains of a single metal phase is shown in Fig. 5. Structure of copper-silver solid solution annealed just above solidus and quenched is shown in Fig.6 This shows a case where the dihedral angle is zero, because the liquid phase has completely spread along the grain boundaries and almost completely isolates the grains. In Fig. 7 is seen the structure of α-β brass. Here the tension of the boundary between grains of different phases is less than that of the α grain boundary but more than half. This is shown by the second phase jutting sharply at places where the α grain boundary is encountered. The grains are rounded and are completely surrounded by films of liquid. Fig. 8 which shows a copper-lead alloy where the dihedral angle being above 60°, the lead has collected into little triangles at the corners of grains. Fig. 9 also shows that lead in copper does not form harmful continuous layers of liquid impairing the boundary cohesion. Though it is possible that they may act as stress raisers and affect hot rolling properties adversely they do not interfere with crystal to crystal cohesion.

Addition of zinc to copper brings about a change in the dihedral angle of liquid leavsd alpha grain boundary, the angle increasing with increasing zinc content. The sharp lead triangles in Fig.9, become more blunt. At about 10% zinc the dihedral angle approaches a value of about 80°, and lead prisms and triangles become disconnected spheroids placed away from corners and some appear away from the boundary as seen in Fig. 10. This clearly shows that the harmful effect of lead in pure copper has been mitigated by the addition of zinc to copper. With the appearance of beta the distribution of lead has a marked change. The dihedral angle of liquid lead vs a beta grain boundary is about 110°, which means that the lead takes a globular shape, and thus lead from being slightly harmful becomes completely harmless as seen in Fig. 11.

A good illustration of the significance of the dihedral angle of a liquid phase is witnessed in the study of the effect of bismuth in copper. In Fig. 12 and 13 are shown structures illustrating the striking difference in the attack on copper by lead and bismuth. Copper has yielded to the attack by lead upto an angle of about 65°, whereas the bismuth has completely penetrated between the grains leaving a brittle material, whose value of dihedral angle is obviously zero. Lead and bismuth to a first approximation can be considered to be insoluble in copper at temperatures below 900°C, and in a Cu-Pb-Bi alloy the liquid can be considered to consist of lead and bismuth in the proportion added.

With the gradual addition of bismuth to a copper-lead alloy the dihedral angle of the liquid phase goes on decreasing. There is no evidence of complete penetration and wetting of grain boundaries till a ratio of Pb :Bi is kept at 1 :1, but when bismuth exceeds the value of lead content the triangular prisms get sharper and sharper and a zero value for the dihedral angle is reached when bismuth to lead ratio is as 3 :2. This penetration completely destroys the material making it extremely brittle both cold and hot. Figs. 14 and 15 show clearly the effect and how the brittleness in copper caused by bismuth can be minimised and averted by adding an equal quantity of lead, though it is no sane step from any other point other than its effect on the dihedral angle of bismuth.

Small additions of zinc, oxygen, phosphorous and probably many other elements may change copper containing bismuth from being brittle to ductile, by changing the dihedral angle. Indeed a very small quantity of bismuth is all that is needed to render copper brittle and so identification of the bismuth by microscopic means is very difficult.

Schofield and Cuckow[3] report the existence of grain boundary films in brittle copper containing bismuth, and state that such copper when rendered ductile by large additions of phosphorous showed bismuth in the form of tiny triangles at the grain boundaries and not enveloping the grains as film. This is another instance of the validity of the theory of the dihedral

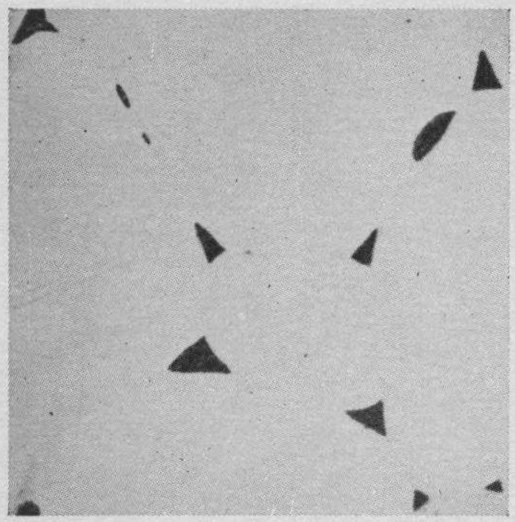

Fig. 8—Copper + liquid lead (97-3 Cu-Pb, annealed 1 hr. at 900°C. Dichromate etch. x 750). [C. S. Smith]

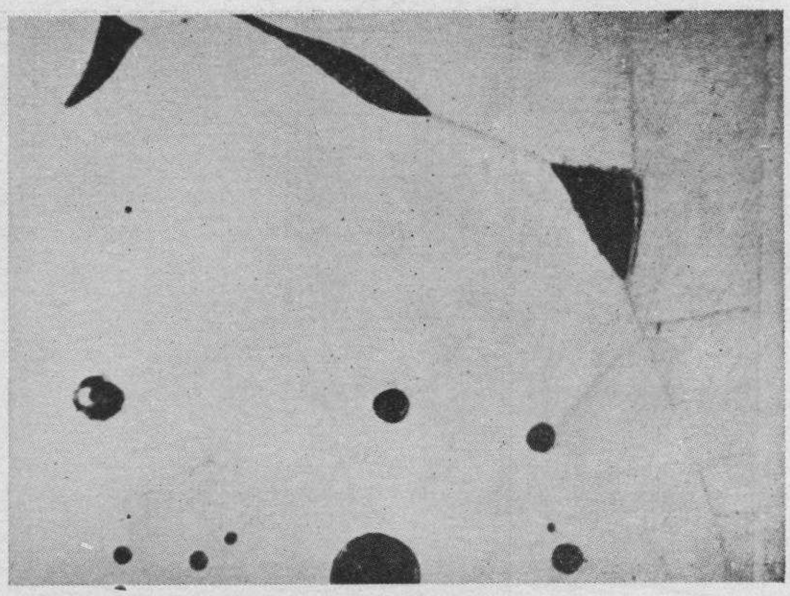

Fig. 9—Copper + liquid lead. Note Circular cross-section of liquid drops in center of grain and triangular shape at grain corner. (Same specimen as Fig. 8; different field. x 1500) [C. S. Smith]

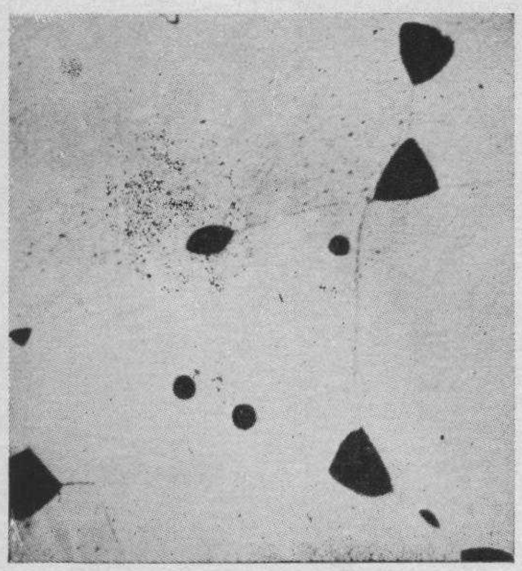

Fig. 10.—Alpha + liquid in leaded brass (67-30-3 Cu-Zn-Pb. Annealed 16 Hr at 750°C, quenched. Dichromate etch. x 750). [C. S. Smith]

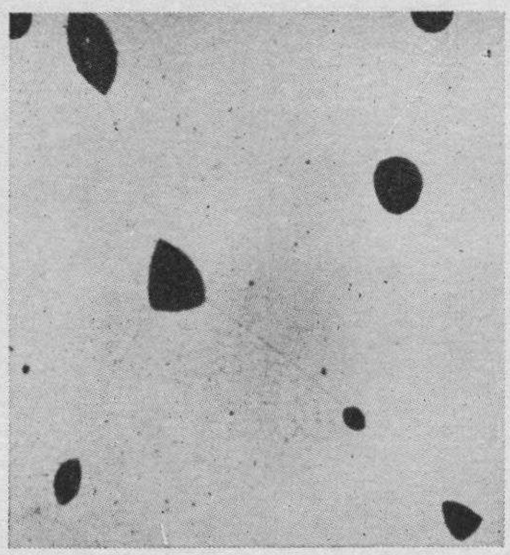

Fig. 11—Beta + liquid in leaded brass (51-46-3 Cu-Zn-Pb. Annealed 16 hr. at 700°C, quenched. Dichromate Etch. x 375). [C. S. Smith]

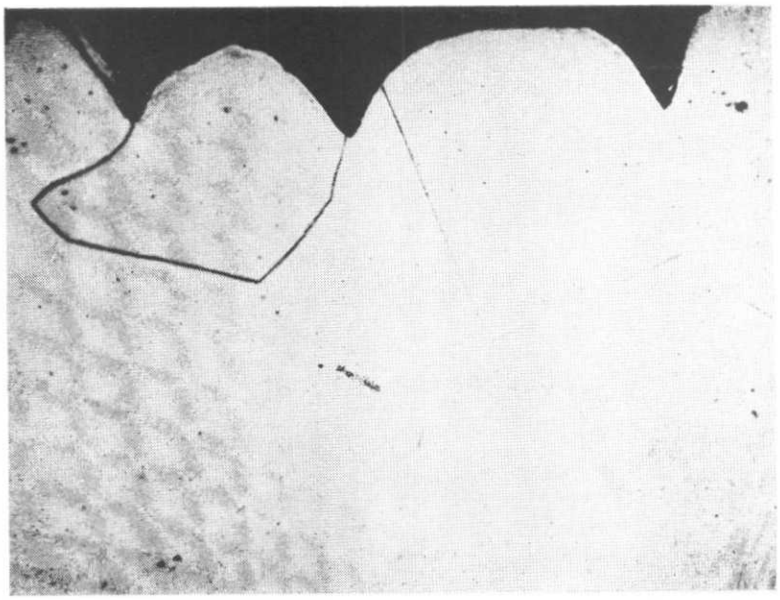

Fig. 12—Section through surface of copper heated in contact with liquid lead, 24 at 700°C. (Dichromate Etch. x 750). [C. S. Smith]

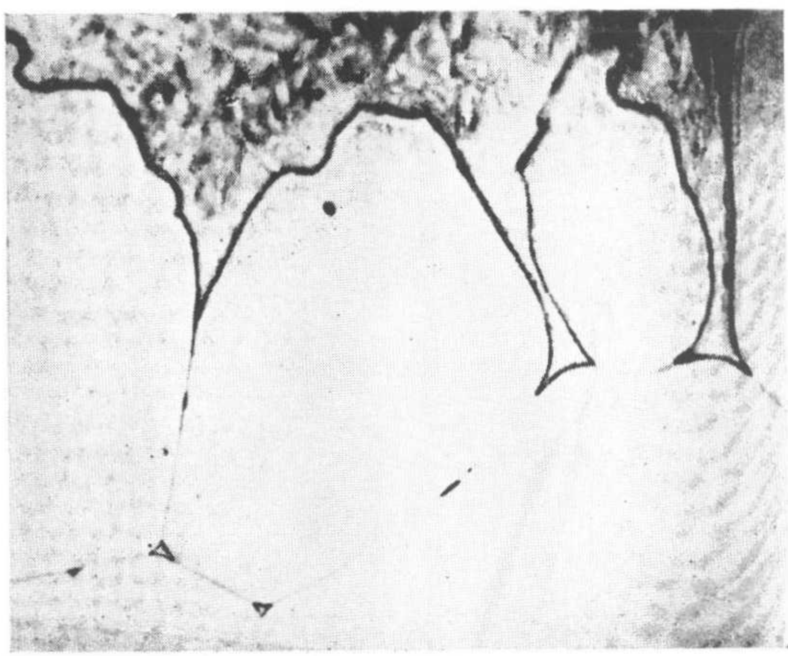

Fig. 13—Section through surface of copper heated in contact with liquid bismuth 24 hr at 700°C. (Dichromate Etch. x 750). [C. S. Smith]

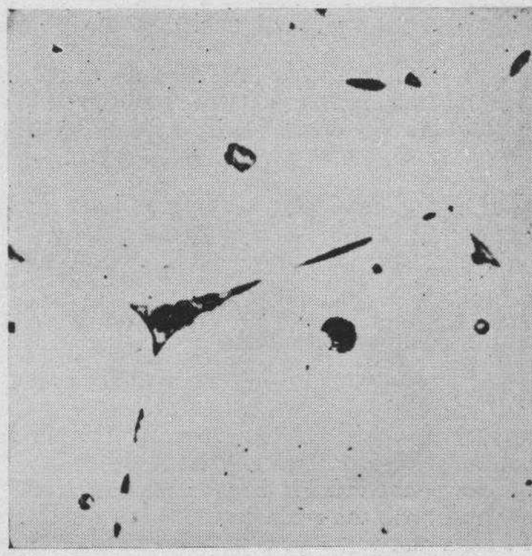

Fig. 14—Liquid in copper-bismuth-lead alloy ($99\text{-}\frac{3}{4}\text{-}\frac{1}{4}$ Cu-Bi-Pb. Annealed 16 hr. at 750°C, quenched. Dichromate Etch. x 750). [C. S. Smith]

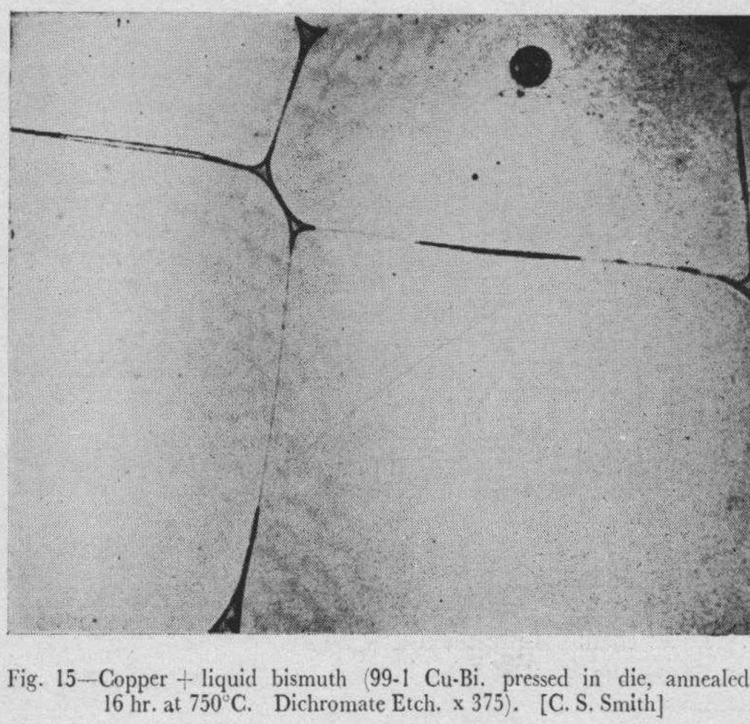

Fig. 15—Copper + liquid bismuth (99-1 Cu-Bi. pressed in die, annealed 16 hr. at 750°C. Dichromate Etch. x 375). [C. S. Smith]

angle. The role of phosphorous here is not that of a deoxidiser but a surface energy modifier showing that it is no chemical effect but a physical one.

Just as in the case of lead, the harmful effect of bismuth in copper is ameliorated by the addition of zinc. In alpha-beta brass bismuth is much more tolerable and if additions of phosphorous are also made the alloys become commercially acceptable. The explanation looks indeed surprising but not so when surface energies and dihedral angles are considered.

It has been shown by Parker and Smoluchowski [4] that on a plane iron surface silver will not spread due to a small positive contact angle, but it is seen to spread on a groved surface. Copper with zero contact angle will spread indefinitely on a steel surface.

THE MECHANISM OF INTERGRANULAR FAILURES DUE TO A LIQUID OR A BRITTLE PHASE

Based on the fundamental law of triangle of forces, the concept of the 'dihedral angle' and the microscopical evidence of the distribution of liquid or brittle phases in certain metals and alloys, a mechanism of such types of failures can be proposed. It can be stated that the difference between a harmful and harmless impurity which is present either in a molten condition or as a brittle solid phase is entirely one of the relation between the interfacial tensions concerned and the resulting angles of equilibrium with the grain boundary at the lowest temperature at which adjustment could occur. Failures due to a liquid or brittle interphase occurs when their dihedral angle is zero, because then they penetrate continuously along the grain boundaries thus separating the grains, and destroying the intergranular cohesion.

This action can of course be accelerated by stress. The penetration will occur lineally along grain edges as long as θ is below 60° and will spread progressively over the grain phases as θ approaches zero.

Small alloy additions bring about a change in the value of the interphasial energies and consequently the dihedral angle. By an addition of a suitable alloying element in proper proportions, the value of the dihedral angle can be altered and kept well above 60° thus preventing a lineal penetration along the grain boundaries and consequent intergranular failure.

CONCLUSION

Intergranular failures of materials caused by a liquid or a brittle phase, enveloping the grains, which may be present as impurities in the material, or may be an environmental one though not quite too many are indeed significant.

It is a common knowledge that overheating an alloy produces liquid especially at the grain boundaries and results in the ruin of the material. The hot shortness of steels and many non-ferrous alloys with common impurities can be attributed directly to the presence of a liquid phase wetting the grain boundaries. The easy penetration of mercury into brass under low stresses and the cracking of steel by molten brazing solder are all related to this. Many cases are known where the liquids are not harmful for example lead in brass and fusible selicates (but not always sulphides) in steel. Addition of lead in reasonable amounts to copper and brass makes them hot short for rolling, but will not interfere in extrusion, also their effects on ductility and strength at room temperature are not much.

The ameliorating influence of additions of zinc in hotshort leaded copper, and that of lead and phosphorous in improving the ductility of bismuth-embrittled-copper have been explained with this theory of the dihedral angle supported with microscopical evidence. The change in the interphase and intergrain boundary tensions, so as to keep a large dihedral angle has been brought about by an alloy addition in both the cases. In the case of the former the alloy has joined hands with the bulk grain material, and in the latter case the alloy has been seen to join the brittle interphase. These examples present a new approach to the study and control of intergranular failures and show the effect of suitable alloy additions to mitigate brittleness and consequently brittle failures.

Stainless steel of the 18 :8 variety fail under certain conditions by intergranular corrosion. Accelerated laboratory tests of such a corrosion reveal that when the 18 :8 is given a sensitising treatment that is heating for a definite time between 500° and 750°C, carbides precipitate in the grain boundaries of the bulk material. Under such a condition the steel becomes susceptible to attack which means that the corrosive liquid penetrates the grain boundaries destroying the cohesion and causing the failure. The answer to this again may be the dihedral angle. With the change in the composition of the bulk grain, a decrease in value of the dihedral angle may have been brought about which has resulted in the intergranular penetration. It is also seen that a small addition of titanium to 18 :8 brings about a stabilising influence against such intergranular attack. The role of titanium here may find a parallel to the role of zinc in bismuth embrittled copper !

In the case of failures by corrosion fatigue it is seen that the endurance of a metal is considerably reduced when chemical attack is taking place during alternating cycles of stress. Failure will occur in time at stresses below the fatigue limit of the material under normal (non-corroding) test conditions. It is possible that a change in the interphasial energies has been brought about due to alternating cyclic stress, and the dihedral angle has been considerably lowered as to bring about the easy penetration of the corrosive agent and consequent failure of the material.

The problems of the intercrystalline cracking of boiler plates, the season cracking of brass, the intergranular corrosion of stanless steel, tin plate failures by liquid tin penetration, failures of galvanised material, certain intergranular corrosion failures, certain high temperature failures due to liquid or brittle interphase, and many similar failures may find an answer, partly atleast, though not in its entirety, in this theory of the dihedral angle and a remedy may be sought in a suitable alloy addition. At first thought it may be argued that the attacks may be of a chemical nature and the physical aspect may not have anything to do, but one can soon see the fallacy as no chemical attack can take place where the physical contact is barred proving that the physical aspect is the more important criterion. Very little work along this direction has been done though this new field of enquiry is pregnant with possibilities. Though of course it must be evident that it is not merely the surface tension effects that determines the microstructure because of various factors like non-equilibrium conditions for lack of time, concentration gradients, local distortions due to inclusions, residual strains and such others, nevertheless, the importance of the study based merely on the theory of the dihedral angle, is of no mean significance both in the study and control of such failures and in the consequent design of better material for the service in question.

ACKNOWLEDGMENT

The microscopic data in this article is from the paper "Grains, phases and interfaces; an interpretation of microstructure" by Cyril Stanley Smith, but an adaptation has been made of the same as a suitable material for the study and control of some type of failures of metals and alloys.

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