Embrittling Effects of Trace Quantities of Aluminium and Phosphorus on Joints Brazed in Steel

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Johnson Matthey & Co Limited, London

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When two similar or dissimilar metals are joined by brazing, the part of the bonding medium is played by another metal or alloy whose melting point must be lower than that of either of the parent metals (i.e., materials brazed). The only other basic requirement that a brazing alloy must meet is that it must be capable of wetting the parent metals. If the latter condition is satisfied, a drop of molten brazing alloy applied to a parent metal will spontaneously spread over its surface; it will also fill by the mechanism of capillary flow a narrow gap between two closely fitting metal parts, thereby making a brazed joint.

When a joint is made by this mechanism between chemically unreactive materials, the bond formation (which is implicit in wetting, spreading and capillary flow) is a surface phenomenon. It is not dependent on the formation of a new compound or alloy at the bonding medium, parent material interface, nor does it entail any changes in the composition of these materials. In these circumstances no volume interaction of any kind occurs; the adhesion between the bonding medium and the parent material is an outcome of the action of surface forces only.

In brazing practice, however, there is always some chemical affinity between the parent metal and the brazing alloy. As a result, the act of adhesive bond formation by the mechanism described above is immediately followed by volume interaction; in other words, interalloying takes place. Its extent and character depend mainly on the composition of the interacting materials, on the brazing temperature, and on the time during which the brazing alloy remains molten.

Depending on these factors, interalloying will involve diffusion of brazing alloy constituents into the parent metal, dissolution of the parent metal by molten brazing alloy, or both. The resulting changes are often limited to small variations in the composition of alloy or metal phases already present in the joint region. Sometimes, however, interalloying may lead to the appearance of new phases including solid solutions, intermediate phases and intermetallic compounds, which may be formed in the parent metal surface layers, in the brazing alloy, or at the parent metal brazing alloy interface. Depending on their character and location, these products of interalloying may have a marked effect on mechanical properties of brazed joints.

The composition of brazing alloys intended for joining a given parent metal must therefore be such as to ensure that the joint strength is not adversely affected by products of interalloying. The problem of ensuring this metallurgical compatibility of brazing alloys and parent metals is complicated by the fact that not only their major constituents but also their numerous impurities interact during brazing.

This fact is borne in mind when impurity limits are laid down for various brazing alloys. The impurity levels in parent metals are also controlled but on the basis of different considerations which (take no account of the possible effects of interalloying in brazing applications. In many cases this does not matter. Sometimes, however, the presence of certain impurities in parent metals may affect the mechanical properties of brazed joints in an unexpected and unforeseeable way.

Complications on this account are most likely to arise in the joining of dissimilar metals. A striking example of undesirable effects that interalloying may produce in these circumstances was provided by a series of isolated instances (spread over a period of several years) of apparently anomalous variation in the strength and ductility of brazed joints between steel and certain copper-based alloys.

The applications in question involved the use of a low melting-point alloy of the silver-copper-zinc-cadmium type for brazing mild steel to leaded brass. Normally the joint strength and ductility were commensurable with the corresponding properties of the brazing alloy which has a tensile strength of about 30 ton/in.^{2} and elongation of 35 per cent. Occasionally, however, joints produced under identical conditions were so weak and brittle that a brazed part would fall apart when dropped on the floor. This catastrophic loss of joint strength could not be attributed to any faults in the brazing alloy because it produced perfectly satisfactory joints when used to braze steel to steel or brass to brass; this, incidentally, indicated that there was nothing basically wrong with the parent metals, either.

In fact, no differences which at that time could be regarded as significant by normal standards were found between the composition of materials that produced ductile and brittle joints. This provided one clue to the possible explanation of this anomalous variation in joint strength. The other clue was provided by the character of fracture of faulty joints which, unlike satisfactory joints, always broke at or near the steel brazing alloy interface and produced smooth fracture surfaces whose colour was distinctly different from the colour of the brazing alloy.

It was postulated on the basis of this evidence that the undesirable effects observed were produced by certain impurities in brass which, when present in sufficiently large quantities, were picked up by molten brazing alloy, diffused to the steel surface and interacted with steel (or its constituents) to form a continuous layer of a brittle alloy which reduced the joint strength and ductility.

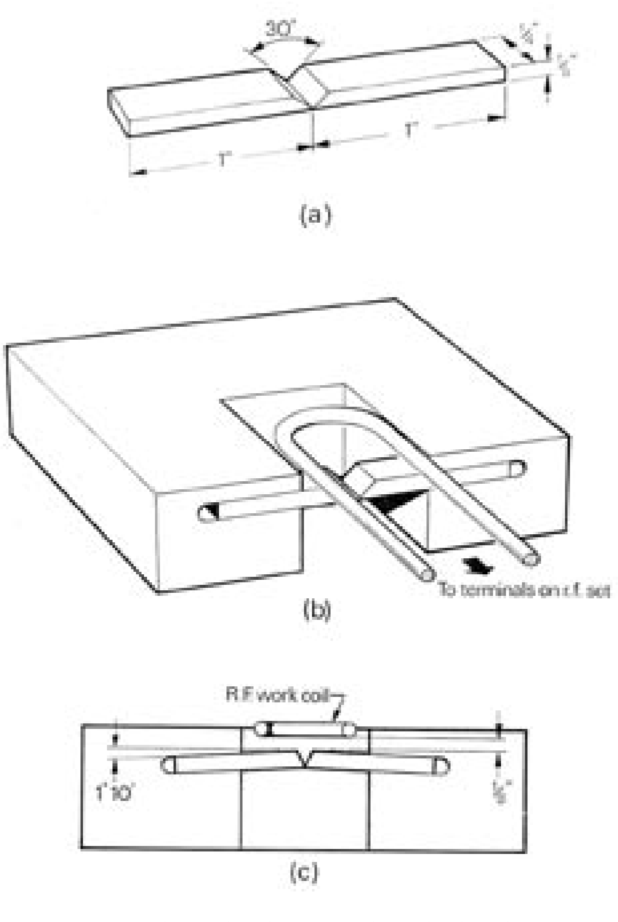


Fig. 1 Details of the design and method of brazing of impact bending test-piece used in the investigation of brazed joint embrittlement by trace impurities; (a) shape and dimensions of the test-piece; (b, c) brazing jig and positioning of the HF. induction heating coil relative to the work-piece

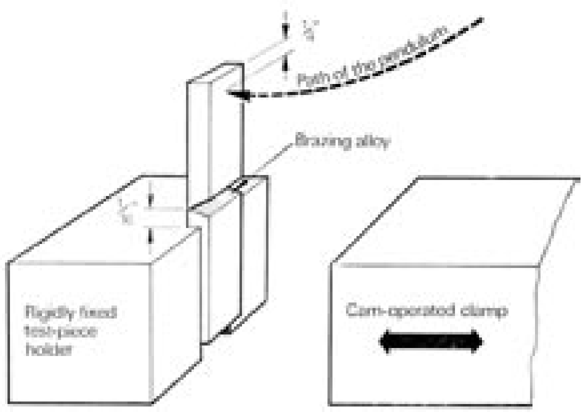


Fig. 2 Schematic representation of the impact testing procedure

This hypothesis was verified by a series of laboratory investigations which proved conclusively that the loss of joint strength and ductility in the case under consideration was closely related to occasional increases in the concentration of aluminium or phosphorus in brass, in which they are sometimes present as impurities. The most recent of these investigations[1] were concerned with determining the threshold concentrations of these impurities in the low melting-point brazing alloys of the quaternary silver-copper-zinc-cadmium type; their results arc summarized in this article.

Preparation of Experimental Alloys

Systematic experimental work was confined to the most widely used alloy of this kind (BS. 1845 Type AG1) whose nominal composition is 50% Ag—15% Cu—16% Zn—19% Cd.

A standard production melt of this alloy was used to prepare two batches of experimental alloys; one containing phosphorus in concentrations ranging from 0—500 parts per million (p.p.m.) (0—005 wt. %) and the other with aluminium additions covering the same concentration range.

The actual composition of the starting material is given below:

Silver	50.3 wt.%
Zinc	15.8 wt %
Cadmium	18.7 wt %
Copper	Remainder.

The only impurities detected by spectrographic analysis included nickel (50 p.p.m.), lead (30 p.p.m.), silicon (3 p.p.m.), tin (30 p.p.m.), bismuth (8 p.p.m.), iron (5 p.p.m.) and traces of aluminium, magnesium, sodium and potassium (less than 1 p.p.m.).

A part of this melt was used to make two master alloys; one containing about 025 wt % aluminium and the other the same quantity of phosphorus. The experimental alloys with various aluminium or phosphorus contents were prepared by diluting the master alloys; after casting, these were cold rolled to 0040 in. thickness (with intermediate anneals at 500ºC and cut in to 0.125 in. wide strip.) The concentration of added impurities was determined at this stage by chemical and spectrographic analyses.

Preparation of Brazed Joint Specimens

Impact bending tests were chosen as the best method of studying the effect of impurities on the mechanical properties of brazed joints because previous experience had shown that tensile or shear tests under static loads often give high values for joints whose capacity to carry static or impact bending loads is practically nil.

A series of preliminary experiments was carried out to determine the most suitable shape and size of the impact test-piece. The test-piece shown in Fig. 1a was eventually chosen because it can be tested on inexpensive equipment (a miniature Avery impact testing machine of 10 ft lb capacity), is relatively cheap to make (requiring little machining before and after brazing) and presents no difficulties in producing a joint free from faults (flux inclusions, voids, unwetted areas) that could affect the reliability and accuracy of the test. The actual test-pieces were made by brazing two 10 in. lengths of a (in. by (in. mild steel bar, each with a 15 bevel milled at the joint end.

Table I

Results of Impact Bending Tests on Mild Steel Test-Pieces Brazed with a Silver Solder (50% Ag—15% Cu—16% Zn—19% Cd alloy) Containing Trace Quantities of Phosphorus. (Each Value is an Average of 12 Test Results)

Alloy No.	Phosphorus content, ppm	Energy Absorbed by the test-piece ft lb	Remarks
1	0	3.94	Test-pieces brazed with alloys Nos. 1—8 deformed plastically without fracturing; test pieces Nos. 9 and 10 failed by brittle fracture without any plastic deformation (see Fig. 4)
2	3	4.21	
3	4	3.91	
4	10	4.05	
5	40	3.8	
6	60	3.88	
7	80	4.32	
8	115	5.06	
9	140	0.28	
10	500	0.15	

Table II

Results of Impact Bending Tests on Mild Steel Test-Pieces Brazed with a Silver Solder (50% Ag—15% Cn—16% Zn—19% Cd alloy) Containing Trace Quantities of Aluminium. (Each Value is an Average of 12 Test Results)

Alloy No.	Aluminium content, ppm	Energy Absorbed by the test-piece ft lb	Remarks
1	0	4.15	Test-pieces brazed with alloys Nos 1-5 deformed plastically without fracturing; test-pieces Nos 6—10 failed by brittle fracture without any plastic deformation (see Fig. 4)
2	5	4.32	
3	6	3.95	
4	8	3.96	
5	10	4.3	
6	16	0.1	
7	28	0.16	
8	90	0.12	
9	400	0.1	
10	500	0.12	

To maintain the brazing conditions as near constant as possible throughout the experiments, H.F. induction heating was used for brazing. The method of jigging the work-piece, the type of working coil and the positioning of the coil relative to the work-piece are shown in Figs 1b and c; the slight inclination (1 10') of each half of the jig to the horizontal was found necessary to ensure that the test-pieces were flat after brazing.

The brazing was done in air under a cover of a standard brazing flux. After assembling the work-piece it was heated under such conditions of coupling and H.F. current that the brazing temperature (about 650 C) was reached in approximately 15 s. At the end of this period the brazing alloy in the form of a strip ((in. by 0040 in.) was applied by hand in a quantity sufficient completely to fill the joint gap.

The time during which the molten brazing alloy remained in contact with the work-piece was limited to 15 5; the maximum temperature of the joint during this period ranged from 680—700^{0}C. After brazing, each test-piece was allowed to cool in air, and was then cleaned and surface-ground to flatness on all its four faces. The final cross-section of the test-piece ranged from 0224 in. by 0115 in. to 0234 in. by 0119 in.

Impact Bending Tests and Metallographic Examination

A series of 12 tests was carried out for each experimental alloy. The method of clamping the test-piece in the holder of the testing machine is shown schematically in Fig. 2. The results are given in Tables

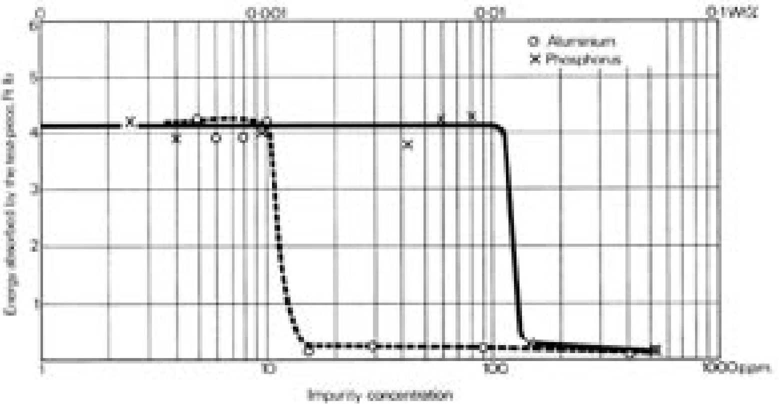
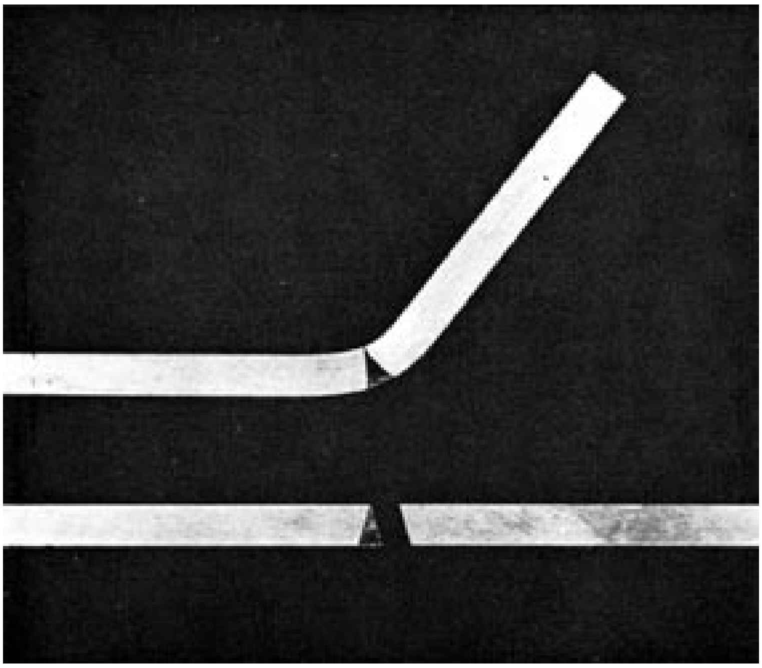


Fig. 3 Variation in the impact strength of joints made in mild steel with a 50? Ag—15 %, Cu—16 % Zn— 1920 Cd alloy in relation to the concentration of trace quantities of aluminium or phosphorus in the brazing alloy. (Each experimental point is the average of 12 test results)

1 and 2 and reproduced graphically in Fig. 3. (It should be pointed out that the values cited can be compared with the results of other tests only if they are conducted under the same conditions on rest-pieces of the same shape and size.)

Test-pieces brazed with alloys in which the aluminium or phosphorus concentration was below a certain critical level deformed plastically (without rupturing) under impact loads, bending through an angle sufficiently large (about 45) to allow the pendulum of the testing machine to clear. Occasionally small cracks were observed in brazed joints of this kind; these were usually associated with stress raisers in the form of pinholes present in the brazing alloy. The average energy expended in plasticity deforming test-pieces of this type was 40 ft lb.

Fig. 4 Brazed mild steel specimens after impact tests. Top: unbroken test-piece illustrating high strength and ductility of joints brazed with alloys containing less than 140 p.p.m. of phosphorus or 10 p.p.m. of aluminium. Bottom: specimen that failed by brittle fracture typical of joints made with alloys with aluminium or phosphorus concentration above the critical level



Test-pieces brazed with alloys containing excessive quantities of phosphorus or aluminium failed by brittle fracture with practically no plastic deformation; the energy expended in fracturing these test-pieces was of the order of 0~2 ft lb. Figure 4 shows a ductile and a brittle specimen after test.

It is interesting to note that there was no gradual decrease in the strength and ductility of the joints with increasing concentration of the impurities in question; the transition from the ductile to the brittle state occurred over a very narrow impurity concentration range. In the case of phosphorus-contaminated alloys this transition occurred between 115 and 140 p.p.m.: An alloy with 115 p.p.m. of phosphorus produced joints as strong and ductile as those made with phosphorus-free material, whereas a phosphorus content of 140 p.p.m. in the brazing alloy was sufficient to reduce the joint impact strength and ductility to zero.

The ductile to brittle transition in joints contaminated with phosphorus was reflected in the microstructure of brazed joints. Evidence of the formation of a brittle iron phosphide layer, not observed in ductile specimens, was found in every brittle joint examined. The results of electron microprobe analysis showed that the composition of the phosphide corresponded to Fe_0P. Typical appearance of the phosphide layer in joints made with alloys containing 500 and 140 p.p.m. of phosphorus is illustrated in Fig. 5. The plane of fracture in brittle joints ran through the phosphide layer which accounted for the characteristic, relatively smooth, silvery-grey appearance of the fracture surfaces.

An interesting feature of phosphorus embrittlement of joints of the kind under consideration is that the iron phosphide layer, initially formed at the brazing alloy steel interface, becomes detached from the steel surface (most probably as a result of internal stresses due to different specific volumes of steel and Fe_2P) if the brazing alloy remains molten for more than a few seconds. In joints of the "open" design, such as those used in this investigation, the phosphide layer could —on prolonged heating — float to the surface of the molten brazing alloy pool and be either machined off, or left in the joint but so oriented relative to the direction of applied load that its effect on the joint strength and ductility is greatly minimized. This effect should be borne in mind in experimental studies of joint embrittlement caused by interalloying between molten brazing alloys and parent metals.

Another point worth mentioning is that when the phosphorus content in an experimental brazing alloy was below the critical level, the formation of a brittle phosphide layer could not be induced by prolonged heating. Joints made with the alloy containing 115 p.p.m. of phosphorus remained strong and ductile, even when the time of contact between the molten and brazing alloy and steel was increased to 120 s.

Superficially the effects of phosphorus and aluminium on the mechanical properties of joints made with quarternary silver brazing alloys in plain carbon steel are similar: both impurities may reduce the joint impact strength and ductility to zero and the embrittlement in both cases is due to these impurities interacting with iron. There are some differences, however.

For instance, the critical concentration of aluminium in Ag-Cu-Zn-Cd alloys is much lower: 10 p.p.m. as compared with 140 p.p.m. in the case of phosphorus. Furthermore, the plane of weakness in phosphorus-contaminated joints follows the location of the iron phosphide layer which, as pointed out above, may be displaced from the site of its formation. In contrast, the products of interaction between iron and aluminium always remain at the steel, brazing alloys interface along which the fracture of aluminium embrittled joints always takes place; the strength of joints made with aluminium contaminated alloys is not affected by prolonged heating.

Finally, the presence of iron phosphide layers in embrittled joints can be revealed by metallographic examination using the optical microscope; in contrast, no differences between ductile and aluminium embrittled joints can be detected by this method (see Fig. 5a and c).

A direct proof that the embrittlement of joints made with alloys containing excessive quantities of aluminium is due to this impurity diffusing towards the steel surface and interalloying with iron was obtained by electron microprobe analysis. The results, some of which are reproduced in Fig. 6, showed clearly the presence of a narrow (about 2 microns wide) aluminium-enriched zone at the steel / brazing alloy interface; no increase in the concentration of other impurities or the major constituents of the brazing alloy was detected in this zone. An additional proof that this zone is responsible for the loss of strength and ductility of aluminium-contaminated joints was obtained by electron microprobe analysis of the fracture surfaces of broken impact test-pieces brazed with an alloy containing 500 p.p.m. of aluminium: both surfaces (i.e., surfaces on each side of the plane of fracture) had regions at which the aluminium concentration exceeded many times the nominal content of this impurity in the brazing alloy.

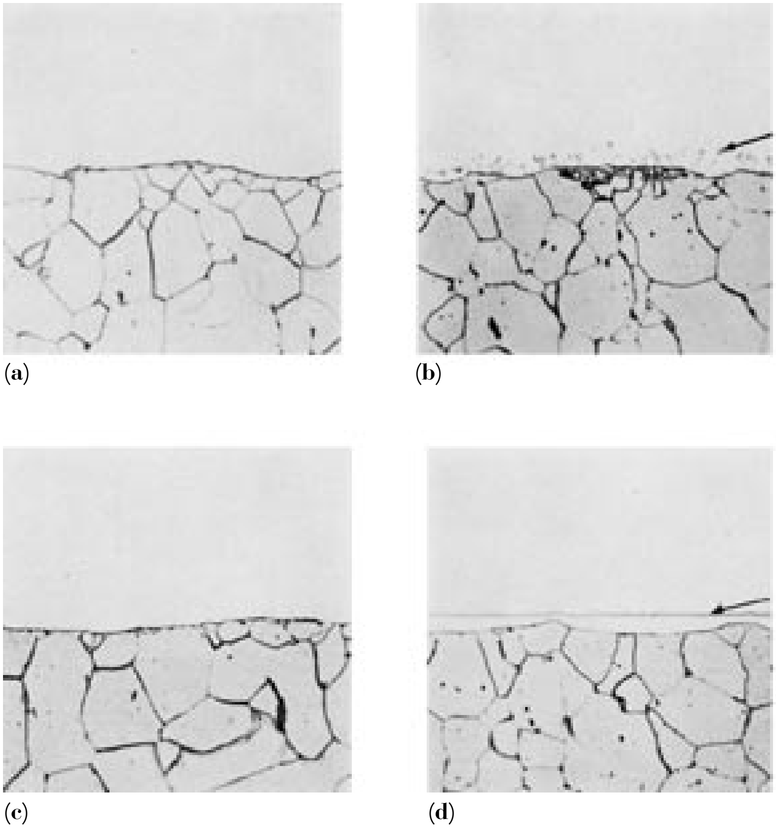


Fig. 5 Microsections of mild steel test-pieces brazed with 5000 Ag 150 ~ Cu 160 Zn 19? Cd alloys containing (a) no aluminium or phosphorus, (b) 140 p.p.m. of phosphorus, (c) 500 p.p.m. of aluminium, and (d) 500 p.p.m. of phosphorus (Note: the microphotographs below are reproduced to show the effect of phosphorus on the micro-structure of brazed joints and the absence of a corresponding effect in joints brazed with aluminium contaminated alloys). X750

Because of the relatively small size of the aluminium-enriched zone it has not yet been possible to determine the composition and constitution of the products of interalloying between steel and trace quantities of aluminium in the brazing alloy.

It is worth mentioning in this connection that, according to the results of a series of tentative experiments, excessive quantities of phosphorus in a brazing alloy will produce embrittlement of joints brazed in steel regardless of the composition of the steel or the brazing alloy. On the other hand, the effect of aluminium does vary depending on this factor: a Ag-Cu-Zn-Cd alloy which contains 10 p.p.m. of aluminium (and which from the point of view of impact strength and ductility is useless for joining plain carbon steel) produces strong and ductile joints

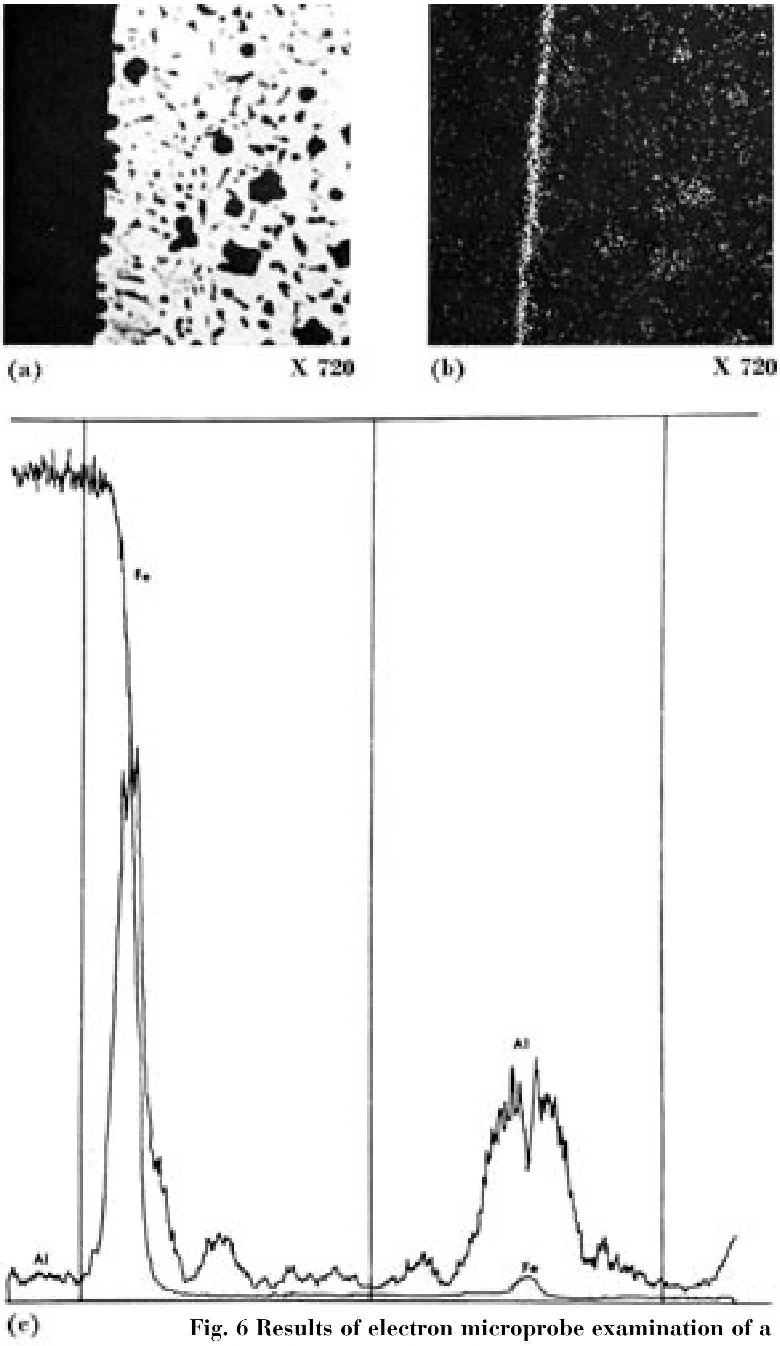


Fig. 6 Results of electron microprobe examination of a mild steel test-piece brazed with a 5020 Ag—15?,, Cu 16% Zn 1920 Cd alloy containing 500 p.p.m. of aluminium: (a) cross-section showing the brazing alloy/steel interface; (b) aluminium Ka image of the joint region shown in (a); (c) a line traverse showing the variation in the concentration of iron and aluminium in the same joint region

in austenitic stainless steel of the 18 8 type; at the same time no evidence of any loss of impact strength or ductility is observed in joints brazed in plain carbon steel with a gold-nickel alloy (820 , Au— 18% Ni) containing 020,, aluminium which is 200 times more than the permissible concentration of this impurity in Ag-Cu-Zn-Cd alloys.

All these facts seem to indicate that there is a basic difference in the character of phases produced by Interalloying between steel and these two impurities and in the mechanism of the formation of these products. Further extensive studies would be necessary to elucidate this problem.

Conclusions

A. 720 1. The impact strength and ductility of joints made in steel with low melting-point brazing alloys of the Ag-Cu-Zn-Cd type may be reduced practically to zero by trace quantities of aluminium or phosphorus initially present in the brazing alloys or picked up from parent metals during brazing.

2. The maximum permissible concentration of these impurities in joints of the type studied were determined at 140 p.p.m. (0~0l4 wt.”$_0$) for phosphorus and 10 p.p.m. (0001 wt.”,) for aluminium.

3. When these critical concentration levels are exceeded, interaction takes place between steel and aluminium or phosphorus leading to the formation of new brittle phases at the steel ‘brazing alloy interface and to a reduction in joint strength and ductility. The new phase formed by the phosphorus has been identified as Fe_2P; the precise character of the brittle phase formed by aluminium is not yet known.

4. The presence of brittle alloy layers formed in brazed joints by the mechanism described above may be not revealed by static tensile or shear tests. A bending or, preferably, impact bending test of the type used in this investigation provides a reliable means of quantitatively estimating the undesirable variation in the mechanical properties of brazed joints due to anomalous interalloying phenomena.

5. Stringent precautions must be taken in the fabrication of brazing alloys to exclude from them potentially harmful impurities. However, the number and concentration of impurities of this kind in parent metals cannot be controlled. The risk of the deterioration of the joint quality or even a catastrophic loss of strength and ductility is therefore always present. One way of eliminating it is to use a bending impact test for frequent spot checks on specimen joints made in samples of each new batch of the parent metal or metals used.

References

1 J. D. Boughton, C. R. N. Clark and G. R. Willoughby, The Effect of Trace Impurities in Silver Brazing Alloys Upon the Strength and Ductility of Brazed Joints. Unpublished research reports. Johnson, Matthey & Co Ltd. Research Laboratories, London.

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