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METHODS OF PRODUCING HARD-SOLDERED OR WELDED JOINTS

Hans Edner, Dessau, Germany; vested in the Alien Property Custodian

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This invention relates to methods of producing hard soldered or welded joints.

The existing methods of hard-soldering or welding have in common the feature that the union takes place through the diffusion of molten metal in the material welded or soldered. This "fluid diffusion" is attended with the drawback that at low temperatures i. e. in the case of working temperatures near the melting point of the solder the rate of flow is comparatively low so that the soldering or welding operation takes a comparatively long time to perform, and in order to attain speedier diffusion of the metal comparatively high working temperatures are needed. In the case of the soldering agents hitherto in use, however, both the protracted working period and the higher working temperature have the defect of damaging the material because the melting points of said agents are already in the neighbourhood of temperatures at which the metallic material being soldered or welded is exposed to damage from so-called gasification (occluded hydrogen) or internal transformations in the material such as coarsening of the grain, structure. The resulting difficulties can best be explained with reference to the conditions occurring in brazing, hard-soldering or welding copper.

Hitherto the hard-soldering of copper has been effected with the aid of:

(1) Brazing solder; (2) Phosphorus-copper solder or phosphorus-copper-silver solder; (3) Technical silver solder (copper-silver-zinc).

When brazing solders are employed their high melting point (820–900° C) has the drawback that very high working temperatures (980°–1050° C.) must be employed in order to reduce the working time to economic limits. In the case of fine-gauge material in particular these high working temperatures cause a considerable coarsening of the grain, and when a reducing atmosphere is present, moreover, so-called "hydrogen sickness" results; both of these greatly impair the mechanical strength of the copper. Moreover, brazing solders have always been used in association with a flux, which forms another source of the risk of hydrogen sickness since these fluxes invariably contain water in some form or other. Furthermore, when solid or liquid fluxes are used, residues and compounds with the oxides of copper are always formed and have to be removed subsequently by pickling, thus causing a considerable loss of material and entailing prolonged working periods. Brazing solders have the further defect that in soldering thin sheet metal it is impossible to gauge the requisite amount of solder with precision since the thickness of commercial brass sheets or foils imposes a limit which is soon reached. As the result of the consequently unavoidable excess of brazing solder used, thin sheet copper is very liable to become alloyed right through in places, the brass completely penetrating the copper and weakening its structure as by causing perforation.

The existing commercial grades of phosphorus-copper solders—containing 7–9% of phosphorus at the most—allow the working temperature to be lowered to about 785° C., their melting point being in the most favourable circumstances 707° C. However, both this working temperature and the time required for soldering permit the occurrence of the aforesaid metal sicknesses in a pronounced degree. The phosphorus-copper solders have the further defect that owing to the difficult process of preparation their phosphorus content can never be maintained at a precisely uniform level and consequently the phosphorus content and therefore the soldering qualities (especially that of ready fusibility) vary in a very considerable degree in one and the same stick of solder. It is also very difficult to apportion the phosphorus-copper solder with accuracy because owing to its brittleness it cannot be worked up into foil or thin wire but is obtainable only in the form of cast sticks about 3 mm. in diameter or in granular form, the grain size of which is too coarse to enable uniform distribution to be obtained on level surfaces. On steeply tilted or vertical surfaces it is impossible to use this granular solder. Since the phosphorus contained in the solder remains substantially intact in the solder present in the welded seams, the latter are apt to be brittle.

Technical silver solders (copper-silver-zinc, or copper-silver-cadmium) have the advantage that on account of the still lower melting point (630° C. in the most favourable circumstances), the working temperature can be further reduced. On the other hand they have the inconvenience of being very expensive and in the case of low working temperatures near the melting point of the solder the rate of diffusion of the latter is so low that operating at these low temperatures would take up a disproportionate amount of time. Moreover, within the temperature range in question, the resulting hydrogen sickness favours the extensive breaking down of the copper. Another defect of the silver solders is that a flux, the particular kind being immaterial, has to be used which also increases the cost and in the case of the usual liquid or solid fluxes also leads to losses of material in the subsequent pickling.

As in the case of brazing or hard-soldering the welding of copper has hitherto encountered serious difficulties. In fusion welding the copper sustains such local overheating that this method can be applied only to articles of stout metal as thin sheets are easily damaged. Extraordinary difficulties are met with in the electrical-resistance welding of copper because the high electrical and heat conductivity of the metal necessitates a very high current density on the one hand and extremely accurate judging of the duration of the welding operation on the other which is attainable only by the aid of very expensive welding machines having inertialess grid control. Moreover, the process as applicable to only such parts as will not be distorted by the pressure essential for carrying out the welding operation.

As already mentioned it is a feature common to all these known methods of brazing or hard-soldering and welding that the union is effected solely by the diffusion of the metals in a state of fusion. Though a partial volatilisation of zinc occurs when brazing solder is employed, the extent of this is so slight that it cannot have any influence on the soldering operation. Moreover, the resulting zinc vapour is partially oxidised by the oxygen present so that there can be no question of any "gaseous diffusion" in fact in certain circumstances the effect is to impede the soldering. A partial volatilisation of phosphorus occurs in the case of the known eutectic copper-phosphorus alloy, but for the most part the vaporised phosphorus is consumed in deoxidising the surfaces under treatment and therefore in this case also no "vaporous diffusion" can occur. Up to the present this idea of predominantly "liquid diffusion" has been upheld with reference to all hard-soldering and welding methods, and the attempts to remedy the defects of these methods have always been confined to lowering the melting point of the solder with a view to arriving at more favourable working temperatures and time consumption.

However, not only temperature and time but also, as third variant, the state of aggregation of the solder or the article under treatment has a determinative influence on the kinetics of the soldering or welding operation. The invention is based on the perception that the diffusion in the "liquid" condition must always be attended with the drawback that the duration of the reaction is longer than diffusion in the "vaporous" condition.

According to the present invention hard-soldered or welded joints are produced by a method which includes the use of a soldering agent adapted to form an alloy with the material of the article under treatment and to exert a reducing action and which wholly or partially vaporizes at a temperature below that at which the quality of the material under treatment becomes impaired, said agent being used in such quantities that even after as much of it as is required for the reduction of the surface of the metal has been used up there is still available a sufficient quantity of vapour to initiate a spontaneous "vaporous" diffusion. By means of the method according to the invention a very speedy reaction and therefore short working periods are obtained even at low working temperatures. The advantageous effect of this is to protect the materials and the working appliances and also to reduce the consumption of energy for performing the operation. The soldering agent may consist of metals and metalloids or mixtures or combinations thereof.

The invention will now be described with reference to several typical methods of its application to material composed of copper.

For example a thin layer of phosphorus in any of its modifications can be applied by itself to the metallic parts to be soldered and the soldering effected by heating in known manner such as in a flame, furnace or welding machine. In so doing it has been found preferable to employ red phosphorus because it is harmless and non-poisonous at room temperature and is also cheap. At about 600° C. red phosphorus passes spontaneously into the condition of vapour which exerts a reducing action on the surrounding metallic surfaces and very quickly converts them, owing to its high rate of diffusion, into a readily fusible alloy, thereby establishing metallic union. By suitable apportionment of the amount of the the solder seams are obtained which are visible only under the microscope and are undistinguishable from a good electrical resistance weld. By comparison with the existing hard-soldering methods in which layers of solder are recognisable by the unassisted eye, the method according to the invention consumes an insignificant amount of the soldering agent. Owing to the absence of a thick layer of solder, the heat-conductivity of a soldered union obtained in accordance with the invention is naturally substantially better than in the case of the seams obtained by the existing methods of hard soldering. Moreover, owing to the reducing action of the phosphorus vapour the employment of a special flux becomes superfluous. On the other hand in the hitherto customary hard-soldering methods using fluxes, vitreous borax enamels are formed which are difficult to remove and in their removal lead to considerable losses of material.

The employment of phosphorus offers the further great advantage that the soldering agent can be applied in the finest state of division and therefore in accurately apportioned quantity to the seat of the join since the phosphorus can be used in the form of a suspension. Owing to the good properties of the soldering agent in respect of apportionment, uniform distribution and high reaction speed it is even possible to connect copper-plated light metals by means of a welding-roller machine at the rate customary in welding iron, whereas welding or hard-soldering of such copper-plated light metals has hitherto been impossible. The use of red phosphorus as a soldering agent also enables copper to be united with other metals such as with iron or nickel in a similar manner.

Instead of employing phosphorus by itself mixtures or compounds of phosphorus with copper or other metals of lower melting point than the material under treatment (copper in the present instance) may be used for performing the method according to the invention.

Examples

Example 1.—90% of powdered copper (grindings) are mixed with phosphorus. The soldering agent obtained has a lower reaction speed than that of phosphorus itself. It thus becomes possible to control the depth to which the diffusion extends a result which may be desirable in the case of thin or plated materials.

Example 2.—Copper phosphides are added to phosphorus (e. g. 50% of copper phosphides to 50% of red phosphorus). The soldering agent produced has speedier reaction qualities than that of phosphorus alone, thus enabling rolled welds to be produced at high speed.

Example 3.—Copper phosphides are intimately mixed with one or more metals or metallic phosphides of lower melting point than copper, for example, 15% of copper phosphide are mixed with 85% of tin. The soldering agents obtained melt between 300° and 600° C. and are preferably used in place of soft solder in cases where importance is attached to mechanical strength or resistance to corrosion in the weld.

Example 4.—Soldering agents are prepared by intimately mixing phosphorus with metals or metallic phosphides of lower melting point than copper, a typical mixture being 25% of red phosphorus and 75% of tin.

In examples 1 to 4 phosphorus may be replaced by other metalloids of Groups V and VI of the periodic system (e. g. arsenic, solenium and tellurium), either singly or in admixture or combination with phosphorus. The method according to the invention can be applied not only in the case of copper but also to other metals especially nickel and platinum.

HANS EDNER.