



# Copper Phosphorus Based (Self-fluxing) Brazing Alloys used for Joining Copper and its Alloys

## Introduction

One of the most widely used methods of joining copper and its alloys is brazing. Many different types of brazing filler metals are employed, the most commonly used being those based on copper and phosphorus, these providing relatively low cost alloys with low melting points. Such alloys also have a unique property, the ability to join copper in air, without using a flux, the phosphorus within the alloys acting as a fluxing agent. These filler metals can also be used for joining copper alloys, but a flux must be employed to ensure good wetting and bonding of the filler metal to the parent materials. With certain copper alloys, where the addition of alloying elements is low, fluxless brazing can also be achieved. The use of these phosphorus bearing alloys is of course restricted to those copper alloys where no detrimental metallurgical effects arise. This excludes their use on materials like copper nickel alloys, where the brazing alloy/parent metal interface consists of a nickel phosphide layer, thus making the joint extremely brittle.

## Three Groups

The copper phosphorus based brazing filler metals fall into three distinct groups. Straight copper phosphorus alloys; silver copper phosphorus alloys; and alloys which are modifications of the two standard groups, where a further alloying addition has been made. Alloys of this latter type are recent developments, only becoming available in the last few years, whereas the copper phosphorus and silver copper phosphorus alloys have been known and employed for a considerable period.

For many years the alloy compositions of the first two groups remained constant, but of late a wide variety of different alloys has also been commonly available. In fact there has been an explosion in the number of alloys available. Some of the alloys developed do have certain technical and economic advantages, whereas others have been produced, particularly some of the silver containing alloys, for purely commercial reasons.

To determine whether one of these copper phosphorus based

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## Brazing alloys

alloys might have some technical and economic advantages in a particular application is not difficult. The two major alloying elements, ie, phosphorus; and silver; have defined effects on brazing characteristics, melting point, flow and mechanical properties of the alloys. To help initially in understanding the effect of these alloying elements, it would be useful to study the binary copper phosphorus alloy system.

### Straight Copper Phosphorus Brazing Alloys

The alloys used as brazing filler metals have phosphorus contents ranging from about 5%, to about 8,3%. As can be seen by making a reference to Fig 1, which is the copper rich end of the copper phosphorus thermal equilibrium phase diagram, the system contains a eutectic at 8,25% phosphorus. Thus, all the alloys used for brazing will have a solidus temperature of 714°C. As you can also see from the phase diagram, small changes in phosphorus content result in large changes in the liquidus of the alloys, there being approximately a 230°C difference between the eutectic and the liquidus of the 5% phosphorus containing alloy. This effect becomes more pronounced as the compositions approach the eutectic point, due to the steep angle of descent of the liquidus curve from the 7% point onwards. This effect is of great concern to both manufacturers and end users, since it dramatically affects both the mechanical properties

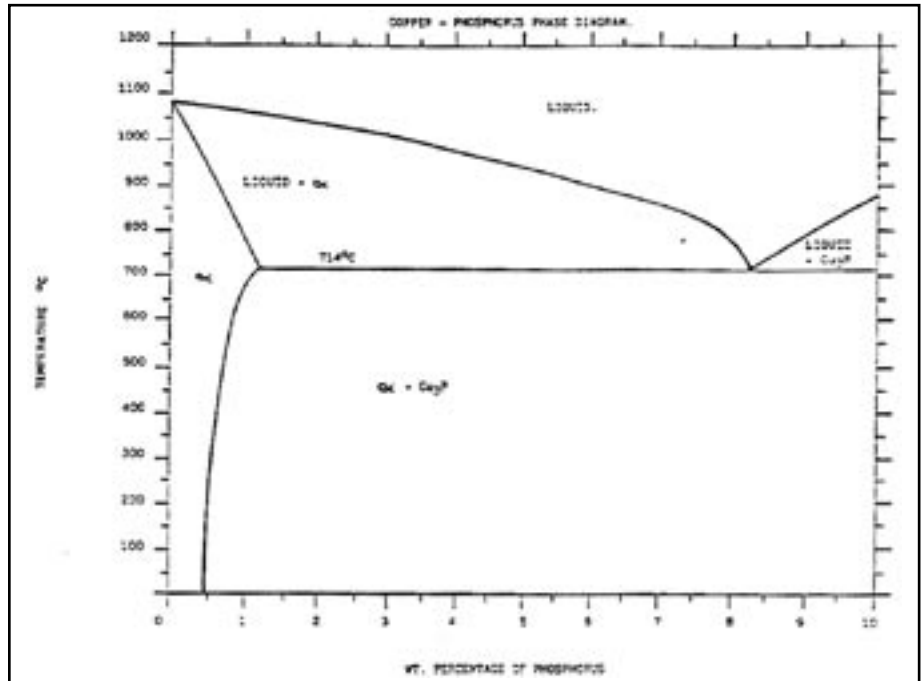


Fig 1 Copper Phosphorus Phase Diagram.

and the brazing characteristics of the alloys.

### Flow Properties

When referring to the brazing characteristics of an alloy, it is really the alloy's flow properties that are of interest, since these influence the capillary joint gap that the brazing alloy is capable of filling. The more free flowing the alloy, the finer the joint gap it can penetrate. However if the joint gap is too large, a free flowing alloy will run through it, producing a joint containing a large number of voids. An indication of an alloy's flow characteristics in

simple terms can be gained from its melting range. A narrow melting range means a free flowing alloy, a wide melting range, a sluggish alloy. Technically it is more complicated, the flow properties of an alloy being a function of the amount of solid and liquid phase present within the alloy at a given temperature. However the melting range of a brazing filler metal is a good practical indication of how the alloy is likely to flow.

Table I lists those copper phosphorus brazing filler metals which are manufactured to International Standards. As with the make up of all alloys, there is not a

Table I  
Range of copper phosphorus brazing alloys made to International Standards

International Standards	Designation	Composition		Quoted Melting Range °C
		% Phosphorus	% Copper	
Afnor	07B1	6,5-7,5	92,5-93,5	715-770
NF A 81 362	08B1	7,5-8,5	91,5-92,5	715-750
AWS-A5 8-81	8 CuP-1	4,8-5,2	94,8-95,2	710-924
	B CuP-2	7,0-7,5	92,5-93,0	710-793
BS1845:1984	CP3	7,0-7,8	92,2-93,0	710-810
	CP6	5,9-6,5	93,5-94,1	710-890
DIN 8513: 1979	L-CuP 7	5,9-6,5	93,5-94,1	710-880
	L-CuP 7	6,7-7,5	92,5-93,3	710-820
	L-CuP 8	7,6-8,4	91,6-92,4	710-710
				750

set composition, but a composition range over which the alloys can be manufactured. Typically a tolerance of plus or minus 1% on the nominal composition is the variation allowed on most brazing filler metals, however as will be realised from information previously stated in the text, such a tolerance would result in alloys based on the copper phosphorus system having extremely variable flow properties from one cast batch to another. If we consider an alloy containing nominally 7% phosphorus and apply to that the normal 1% tolerance, it can be seen from Fig 1 that an alloy containing the minimum 6% phosphorus would have an approximate melting range of 714 to 900°C, while one containing the maximum 8% phosphorus would have an approximate melting range of 714 to 760°C, the latter being an extremely free flowing alloy, the former having very sluggish flow characteristics. Because the phosphorus content of an alloy has such a dramatic effect on the alloy's flow characteristics, much tighter compositional tolerances are applied to the manufacture of these phosphorus bearing brazing filler metals than would normally be necessary, as can be seen from Table I. Even so it is still possible for operators to detect difference in the flow characteristics between different batches of alloy, particularly in cases where the alloy composition is at extreme limits of the compositional range. Most manufacturers are aware of this and therefore control the phosphorus contents of their alloys, even though this is difficult, to a much tighter degree than is required by the standards, on those alloys where this is necessary. This action can in itself cause some problems, as one manufacturer's tolerance within the limits of the specification may be different from another's, thus the same alloy could display somewhat different flow characteristics.

### Phosphorus Content

On an international scale the question of nominal phosphorus contents and compositional tolerances and therefore phosphorus alloy flow characteristics becomes even more

complex. As can be seen in Table I, alloys with similar phosphorus contents exist within all the standard specifications, but none is exactly the same. Industrially it is quite common for a customer to ask for an alloy with a nominal phosphorus content, typically 7%. What you get in these circumstances depends on who the manufacturer is and from which country they come. These differences in the international standards can and do cause problems for end users, who do not understand what a dramatic effect the phosphorus content of the alloy has on its properties.

It is possible to summarise the effect that phosphorus has on the brazing characteristics of a copper phosphorus based brazing alloy by a simple statement: "The higher the phosphorus content of the brazing alloy the better its flow characteristics." It should not be forgotten, however, that it only takes a small change in phosphorus content to produce a large change in the flow characteristics of the alloy.

### Effects of Phosphorus Content on Mechanical Properties

To discuss the mechanical properties of a brazing alloy is generally irrelevant, since the physical properties of a brazing alloy bear very little relationship to the physical properties of the joint made with that alloy. It is enough to say that a properly designed joint, brazed with a copper phosphorus alloy, when tested either in shear or tensile fashion will predominantly fail in the parent materials. It must also be said, that the copper phosphorus alloys are inherently brittle, being both notch sensitive and sensitive to the rate of loading. Very little, if any, quantitative data exists on the ductility of these alloys, due to the difficulty in obtaining consistent results, because of the notch and load sensitive nature of the materials. As-cast ductilities range from about 0% for the eutectic composition, around 2% for the 7% alloy, around 6% for the 6% containing alloy and about 10% for the 5% content alloy.

Available figures for impact resistance are virtually non-existent, but

some private work by our company has shown that the impact resistance of a copper joint brazed with a 7,25% phosphorus content alloy is low, being around 0,4 Joules, the fractures taking place in the brazing alloys themselves.

Although very little quantitative data exists, those who have had practical experience using or manufacturing alloys, would I am sure agree with this general statement. "The higher the phosphorus content, the less ductile, the more notch sensitive and the more load sensitive the alloys become".

### Practical Implications

In selecting a copper phosphorus brazing alloy for a particular application, there is normally a conflict between an alloy that possesses good brazing characteristics (a free flowing alloy) and one which will have sufficient ductility to resist any cracking if subject to any undue mechanical loads in service. In practice, the alloy which has been found to offer a good compromise between brazing characteristics and ductility is one that contains between about 7-7,8% phosphorus. At the recommended brazing temperature for this alloy, which is about 730°C, it is extremely free flowing. The alloy contains at this temperature only a relatively small amount of solid phase, and is therefore capable of penetrating joint gaps of between 0,02-0,08 mm. The ductility of this alloy in the as-cast condition will, as already indicated, be around 2%. However in a joint situation where the alloy takes into solution a certain amount of the parent materials, this will be increased. How much of an improvement takes place will depend on a number of factors, but an increase might be expected in a good capillary joint. In a joint where no true capillary exists and the alloy is being used to build up a fillet or fill a large joint gap, very little improvement above the as-cast ductility could be expected.

### Cracking

Using alloys with higher phosphorus contents gives a marginal improvement in brazing characteristics, but means that the alloy will be less ductile and more

liable to crack in service. Such cracking does not normally result in total joint failure, but seriously affects the leak tightness of the joints and could initiate a fatigue failure. Cracking of the joint normally results as a consequence of the joint being subject to undue movement or an impact. This can of course happen in service or during the installation or handling of a fabricated item.

Alloys with lower phosphorus contents have greater ductility but do not flow as readily, unless the brazing temperature is increased. These poor flow characteristics can be of advantage where poor joint fit ups exist, the alloys being far more capable of forming fillets.

Selecting one particular brazing filler metal is therefore a question of balancing the brazing characteristics of an alloy with the ductility required by the joint.

### Silver Containing Alloys

It is generally thought that the addition of silver to a copper phosphorus alloy will improve both its flow characteristics and ductility.

However this is not the entire story, because it is the combination of the phosphorus and silver content that

determines the flow characteristics and ductility of the alloys.

The silver copper phosphorus alloys used as brazing filler metals, range in silver contents from 17,75% to 0,4% and phosphorus contents from 7,25% to 4,65%. Table II in the appendix gives the compositions of silver copper phosphorus brazing filler metals that are made to International Standards, while Table III gives details of some of the proprietary silver copper phosphorus brazing alloys which are also available.

Alloys containing silver are of course more expensive than the straight copper phosphorus filler metals and by virtue of containing silver are believed to be superior. This is generally the case, but do alloys containing less than 1% silver possess properties sufficiently superior to some of the other alloys available, to warrant the extra expense involved with their use? The silver containing materials are also open to commercial abuse, as it is possible to produce a less expensive alloy, by putting in less silver. Likewise the flow property of an alloy can be improved by increasing its phosphorus content. In either case does the end user really gain? An understanding of the effect of the silver addition of these alloys

will help to answer these questions.

### Effects of Silver Addition

As can be seen in Fig 2 a ternary eutectic exists in the silver copper phosphorus system. This has a composition of approximately 186% silver, 7,1 % phosphorus, balance copper (to convert percentage of  $Cu_3P$  to P divide by 7,1 and the melting point of 646°C. Therefore as with straight copper phosphorus brazing alloys, the majority of the silver copper phosphorus brazing filler metals have solidus temperatures of around 646°C. Unfortunately very little work has been done on the solidus temperatures of the alloys, but it appears that the commonly used 2% silver containing filler metals have the eutectic solidus, as may also alloys containing 1%.

In common with the straight copper phosphorus alloys, it is the phosphorus content of silver copper phosphorus alloys which determines both their flow characteristics and ductility. A low phosphorus content produces an alloy with sluggish flow characteristics and good ductility, a high phosphorus content produces an alloy with better flow properties, but it is less ductile.

Table II  
Range or silver copper phosphorus brazing alloys made to International Standards

International Standards	Designation	Composition			Quoted Melting Range °C
		% Phosphorus	% Silver	% Copper	
Afnor NF A 81362	07B2	6,0-7,0	0,8-1,2	Balance	645-810
	06B1	5,5-6,5	1,5- 2,5	Balance	645-800
	06B2	5,5-6,5	4,5- 5,5	Balance	645-780
	05B1	4,5-5,5	14,5-15,5	Balance	645-770
AWS-A5 5-81	B CuP-6	6,8-7,2	1,8-2,2	Balance	643-788
	B CuP-3	5,8-6,2	4,8-5,2	Balance	643-813
	B CuP-7	6,5-7,0	4,8-5,2	Balance	643-771
	B CuP-4	7,0-7,5	5,8-6,2	Balance	643-718
	B CuP-5	4,8-5,2	14,5-15,5	Balance	643-802
BS 1845: 1984	CP2	6,1-6,9	1,8-2,2	Balance	645-825*
	CP4	5,7-6,3	4,5-5,5	Balance	645-815*
	CP1	4,3-5,0	14,0-15,0	Balance	645-800*
DIN 8513: 1979	L-Ag 2P	5,9-6,5	1,5-2,5	Balance	650-810
	L-Ag 5P	5,7-6,3	4,0-6,0	Balance	650-810
	L-Ag 15P	4,7-5,3	14,0-16,0	Balance	650-800

**AWS Alloys**

To demonstrate this point, let us assess the properties of two American Welding Society alloys (see Table II). B CuP-3 and CuP-4. Because the B-CuP-4 alloy contains 6% silver, it is thought to be by many end users a superior alloy in both its brazing characteristics and ductility to the B CuP-3 alloy, which contains only 5% silver.

The former is certainly true. The B CuP-4 alloy does have much better flow characteristics as is borne out by the two melting ranges of the alloys, B CuP-4 being quoted as 643-718°C and B CuP-3 as 643-813°C. Practically this is also true, the B CuP-4 alloy is more free flowing. However by looking at the phosphorus content, it can be seen why this is so. B CuP-4 contains 7,25% phosphorus whereas B CuP-3 only 6%. Knowing the phosphorus contents of the alloys, their ductility can be determined by reference to Fig 3. This clearly shows that the B CuP-4 alloy is in the brittle to 1% ductility zone, whilst B CuP-3 lies in the 1%-5% zone. Therefore although B CuP-4 does have a higher silver content and better flow characteristics, when

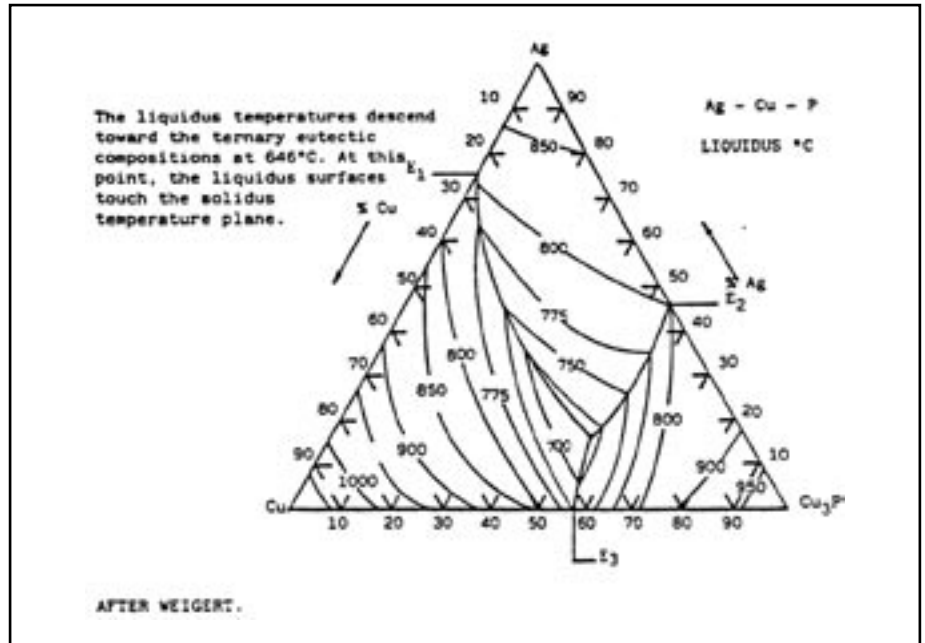


Fig 2

compared with the B CuP-3 alloy, this has been achieved by increasing the phosphorus content and thus reducing considerably its ductility.

So, phosphorus has the same effect on the silver copper phosphorus alloys as it does on the straight copper phosphorus materials. Increasing it

improves the alloy's flow characteristics while reducing its ductility and making the alloys more notch and load sensitive. Why then are silver containing alloys used in certain applications in preference to the straight copper phosphorus alloys? The reasons for this are twofold.

Table III  
Some proprietary copper/phosphorus based brazing alloys internationally available

Alloy No	Composition				Quoted Melting Range °C*
	% Phosphorus	% Silver	% Copper	% Others	
1	6,0-6,7	--	Balance	--	714-850
2	6,8-7,2	--	Balance	--	--
3	6,0	--	Balance	2 Sb	690-800
4	6,75	--	Balance	7 Sn	650-680
5	6,0	--	Balance	6 Sn	645-818
6	7,1	--	Balance	5,6 Sn	638-663
7	6,5	0,4	Balance	--	650-810
8	7,1	0,5	Balance	--	680-750
9	6,4	0,6	Balance	--	--
10	6,1	1	Balance	--	--
11	6,4	1	Balance	--	--
12	7,0	1	Balance	--	640-788
13	6,5	1,5	Balance	--	--
14	6,4	2,6	Balance	--	--
15	6,0	2,0	Balance	6 Sn	695-810
16	5,75-6,25	5,75-6,25	Balance	--	644-794
17	7,2	5,6	Balance	5,6 Sn	640-665
18	7,0-7,5	9,5-10,5	Balance	--	644-690
19	7,25	17,75	Balance	--	644

\* Melting range if given are those quoted by manufacturer or supplier

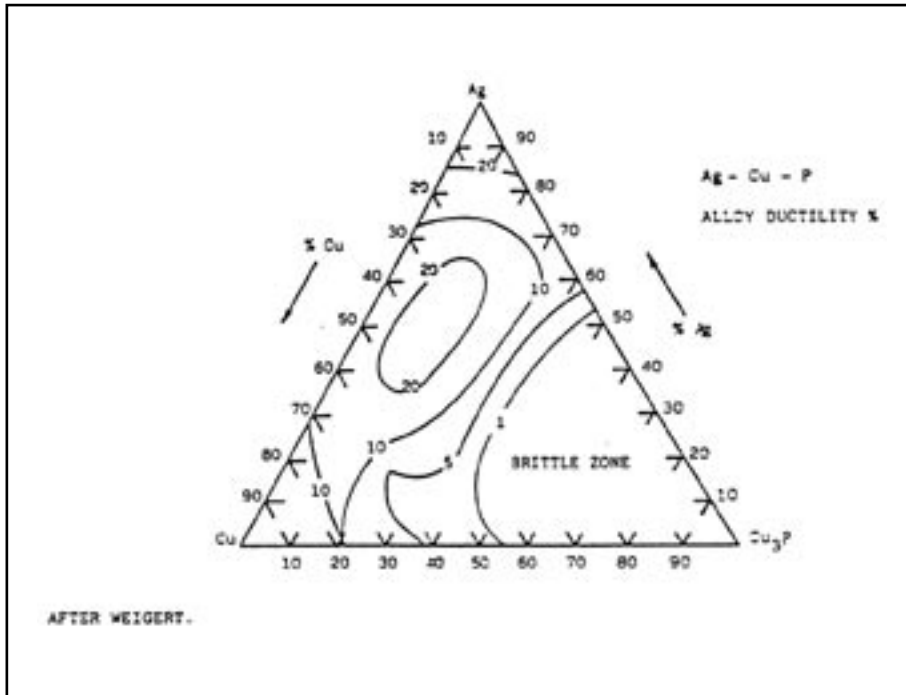


Fig 3

Firstly the silver containing alloys have lower brazing temperatures and hence at the same temperature exhibit better flow properties. Secondly it is possible by using a silver containing alloy, to have an alloy with similar brazing characteristics to a straight copper phosphorus alloy that exhibits much better ductility.

### Practical Implications

Clearly the same principles of selecting a silver copper phosphorus alloy for a particular application are used as those when selecting a straight copper phosphorus alloy. However an extra consideration must be taken into account. This is the cost of the alloy itself, since the silver content of the alloy dramatically affects its cost.

The question that needs to be asked is, does a silver containing alloy have sufficient advantage over a silver-free one to warrant its use, and if so what is the minimum silver content that can be employed to give the right brazing characteristics and ductility needed for any application?

A partial solution to this question can be gained by using Figs 2 and 3 which provide a means of establishing the technical properties of the alloy, the cost being determined by the manufacturer or supplier and the

world price of silver.

### The New Alloys

Due to the comparatively high cost of the silver containing alloys much time and effort has been devoted to the development of less expensive, low silver and silver-free alloys which exhibit improved properties, over the materials currently available.

One of the first materials to become available was a copper phosphorus antimony alloy, alloy 3 in Table III. This alloy was developed by our company and is the subject of a British patent. The addition of antimony lowers the alloy's solidus to 690°C from the 714°C of the straight copper phosphorus alloy, while also improving its ductility. This alloy exhibits brazing characteristics and mechanical properties similar to the BS 1845 CP2 alloy and has in the UK been used to replace this alloy, particularly when used for the fabrication of domestic hot water cylinders.

The latest alloys to be developed, these becoming commercially available in the late 70s early 80s are the tin bearing materials, tin additions being made not only to the copper phosphorus alloys but also to the silver copper phosphorus alloys, where it is used to replace a certain

proportion of the silver. Tin is added to these alloys as it has a similar effect to that of silver on their solidus temperatures, depressing them to around the same level. In addition it also seems to impart to the alloys a greater degree of fluidity, making them appear to flow more freely. However, the tin addition seems to do little to improve the alloy's ductility, one of the major reasons for adding silver, in fact it could be considered detrimental in this effect, brazed joints having similar mechanical properties to joints made with the high phosphorus content alloys.

The amount of tin which can be added is critical since it affects the self-fluxing characteristics of the alloys: alloy No. 4 in Table III which contains 7% tin requires the use of a flux even when brazing copper to copper joints. One unusual advantage of the tin brazing alloys, is that their surface finish after brazing is much superior to that of the conventional phosphorus based alloys, being smoother and more aesthetically pleasing. Commercially the use of tin partly or entirely means that the alloys are lower in cost.

The tin bearing alloys currently available on a commercial basis are detailed in Table III. Originally the alloys were only available as powder or brazepaste, but are now becoming increasingly available in extruded rod form, or in some cases as drawn wire. Although the alloys have some commercial advantages to their use, the technical disadvantages, both to the end user and to the manufacturer, because the alloys are difficult to fabricate seem to have restricted their use at present. The alloy which has found most favour so far is alloy No. 4 in Table III, this being typically used in brazepaste form for making joints between copper and copper alloys.

### Conclusions

The selection of a copper phosphorus based brazing filler metal for a particular application is primarily a function of assessing the ductility required from the finished joint and choosing an alloy that will meet this requirement. The ductility of these alloys is essentially determined by their phosphorus content, the higher

the phosphorus content the lower their ductility. Additions of other alloying elements such as silver to the copper phosphorus alloys reduces the alloys' solidus temperature and improves their ductility, however they do not improve the alloys' flow characteristics since this is essentially controlled by the phosphorus content.

Having decided what degree of ductility is required from the alloy,

the practical and economic aspects of using certain alloys require some consideration. The lower the melting temperature and the more free flowing the alloy, the easier it is to apply. Where alloys containing silver must be employed to meet the requirements of an application, the economics of using these alloys must be considered. However, because the silver containing alloys have low

melting temperatures they are easier and faster to braze with and also require less heat energy to be applied, making them less expensive to use. With them also possessing good ductility, the silver containing alloys can prove, in many applications, far more economic to use even though they are expensive alloys.