Copper Development Association

Equilibrium Diagrams

Selected copper alloy diagrams illustrating the major types of phase transformation

CDA Publication No 94, 1992

Equilibrium Diagrams

CDA Publication No 94

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Copper Development Association

Copper Development Association is a non-trading organisation sponsored by the copper producers and fabricators to encourage the use of copper and copper alloys and to promote their correct and efficient application. Its services, which include the provision of technical advice and information, are available to those interested in the utilisation of copper in all its aspects. The Association also provides a link between research and user industries and maintains close contact with other copper development associations throughout the world.

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Contents

Types of Phase Transformation Covered

Phase Transformation	**Copper Alloy system**
Complete miscibility in the solid state	Cu-Ni
Eutectic solidification	Cu-O
	Cu-Cr
	Cu-Al
	Cu-P
Peritectic solidification	Cu-Zn
	Cu-Sn
	Cu-Be
Monotectic solidification	Cu-Pb
Eutectoid transformation	Cu-Al
	Cu-Sn
Martensitic transformation	Cu-Al
Age hardening	Cu-Al
	Cu-Be
	Cu-Cr
Spinodal decomposition	Cu-Ni-Sn

Greek symbols for phases	
α	alpha
β	beta
γ	gamma
δ	delta
ε	epsilon
κ	kappa

Note Regarding Equilibrium Diagrams

Equilibrium diagrams as their name implies, show the phases present in each system at the composition and temperature ranges included. They are determined by such techniques as thermal analysis and microscopy after prolonged soaking at temperature in order to establish stability. The relationships do not necessarily represent those found in alloys that are conventionally cast metals since the cooling rates are far too fast for equilibrium conditions to be established.

The descriptions given in the text therefore describe the way in which alloys solidify during conventional slow cooling during casting, solidification and subsequent cooling to room temperature. Relatively fast cooling, especially in the solid state, can give significantly different effects. Advantage can be taken of this during heat treatment processes aimed at improving properties.

Note Regarding Structures

Copper itself has a face-centred cubic structure that is usefully ductile at room temperatures and can be deformed easily whether hot or cold. It work-hardens relatively slowly. Additions of other metals are frequently made to improve properties such as strength, hardness, machinability, corrosion resistance or for other special reasons. Most are soluble to some extent in the copper, retaining the alpha face-centred cubic structure up to the limit of solubility but with progressive effects on strength, hardness and rate of work hardening.

Increasing alloying contents above the solubility limits give second phases with differing structures, each of which has a significant effect on properties. A brief description of the main effects is included here, further detailed information is included in other relevant CDA publications.

The structures described apply to cast materials. Many metals are preferably used in the wrought condition after hot or cold working to modify the cast structures. These effects are also considered in other CDA publications (see Appendix II).

Introduction

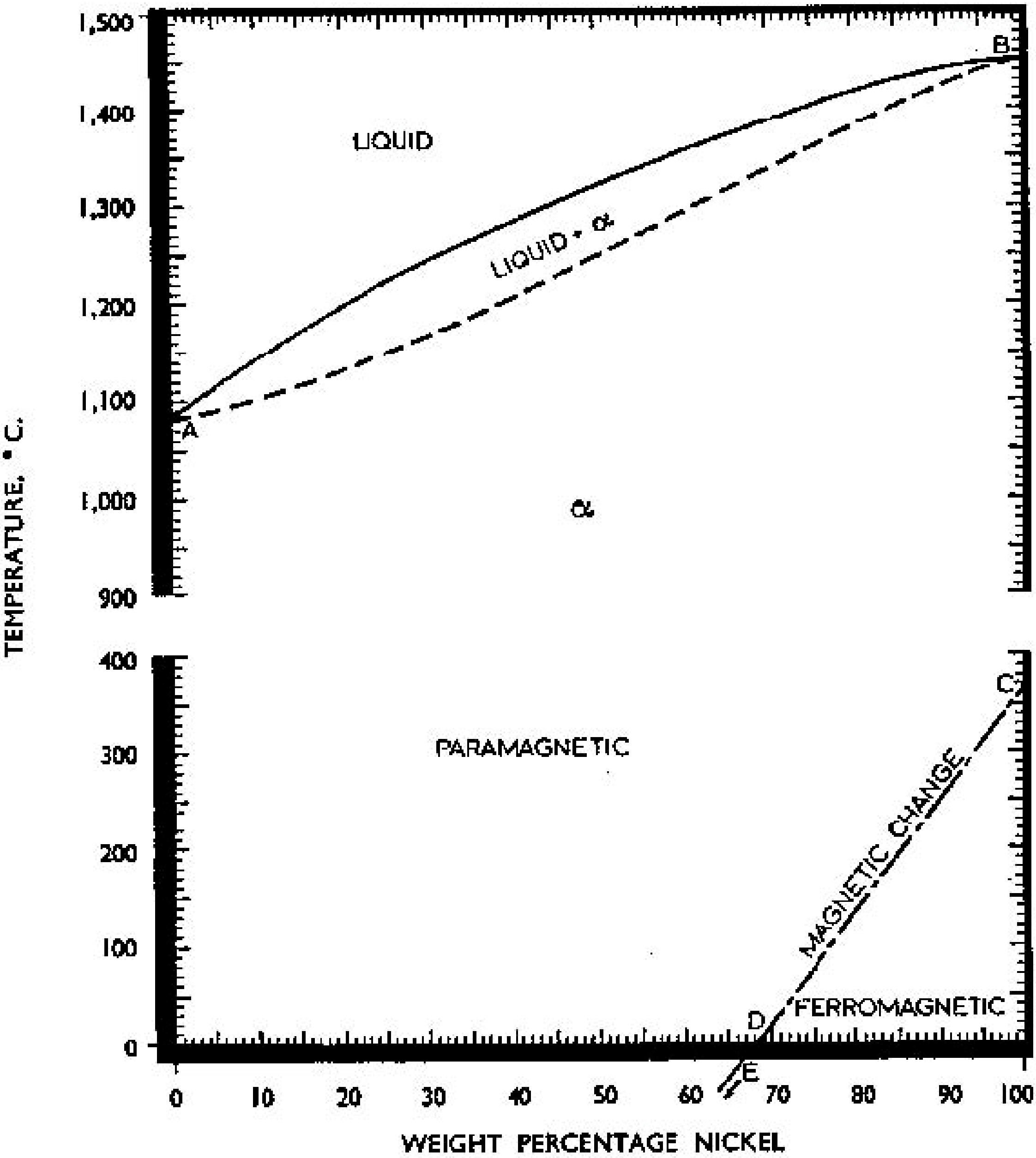
The study of phase transformations and microstructures is of great importance to students of metallurgy and materials science and it is essential that the equilibrium diagrams of alloy systems are understood and related to the observed microstructures. Structures have a significant effect on the mechanical and physical properties of materials and therefore their suitability for end-use applications.

There are many types of phase transformation. Good examples of most of them can be found in the binary equilibrium diagrams of the conventional copper alloys in industrial use. The following pages describe some of these systems, highlighting the relationship between microstructure and properties.

The theory of solidification in metals and alloys is well beyond the scope of these notes and can be found in detail in metallurgical text books. For these notes it will be assumed that the student is fully conversant with the growth of crystals from the melt under non-equilibrium conditions, and with the effect of the width of the temperature range of solidification on the occurrence of coring in the dendrites. It is also assumed that the reader is familiar with the basic principles of phase diagrams and the different types of transformation which occur.

The purpose of these notes is to provide good examples of industrially useful alloys which illustrate each of the most common phase transformations.

Copper-Nickel



Point	A	B	C	D	E
°C	1083	1453	368	20	-273
Ni, %	0	100	100	68.5	41.5

This is an example of complete miscibility in the solid and liquid states.

All copper-nickel alloys have identical single-phase structures. In the cast condition, the wide freezing range gives rise to heavily cored dendrites and, as the two elements interdiffuse slowly even at high temperatures, segregation usually persists in spite of repeated mechanical and thermal treatment, and this is seen as banding in the microstructure of a wrought sample.

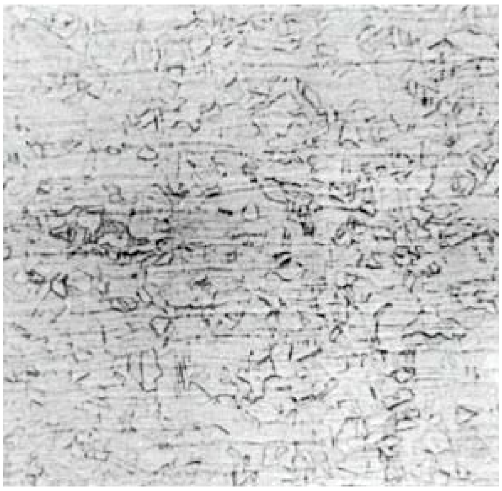
There are two commercially important groups of copper-nickel alloys in the 90/10 and 70/30 ranges. Both are renowned for outstanding corrosion resistance in sea water and for their resistance to marine biofouling. They can be hot or cold worked to plate and tube and are readily welded.

With either 1 or 2% each of iron and manganese added for a further improvement in corrosion resistance, they are particularly useful for sea water condenser systems and for cladding on off-shore structures.

A further group of copper-nickel alloys in commercial use is based on Cu-3%Ni. These alloys are used for electrical connectors and springs.

At room temperatures, alloys with up to 70% of nickel are paramagnetic, above that composition they adopt the ferromagnetism of nickel.

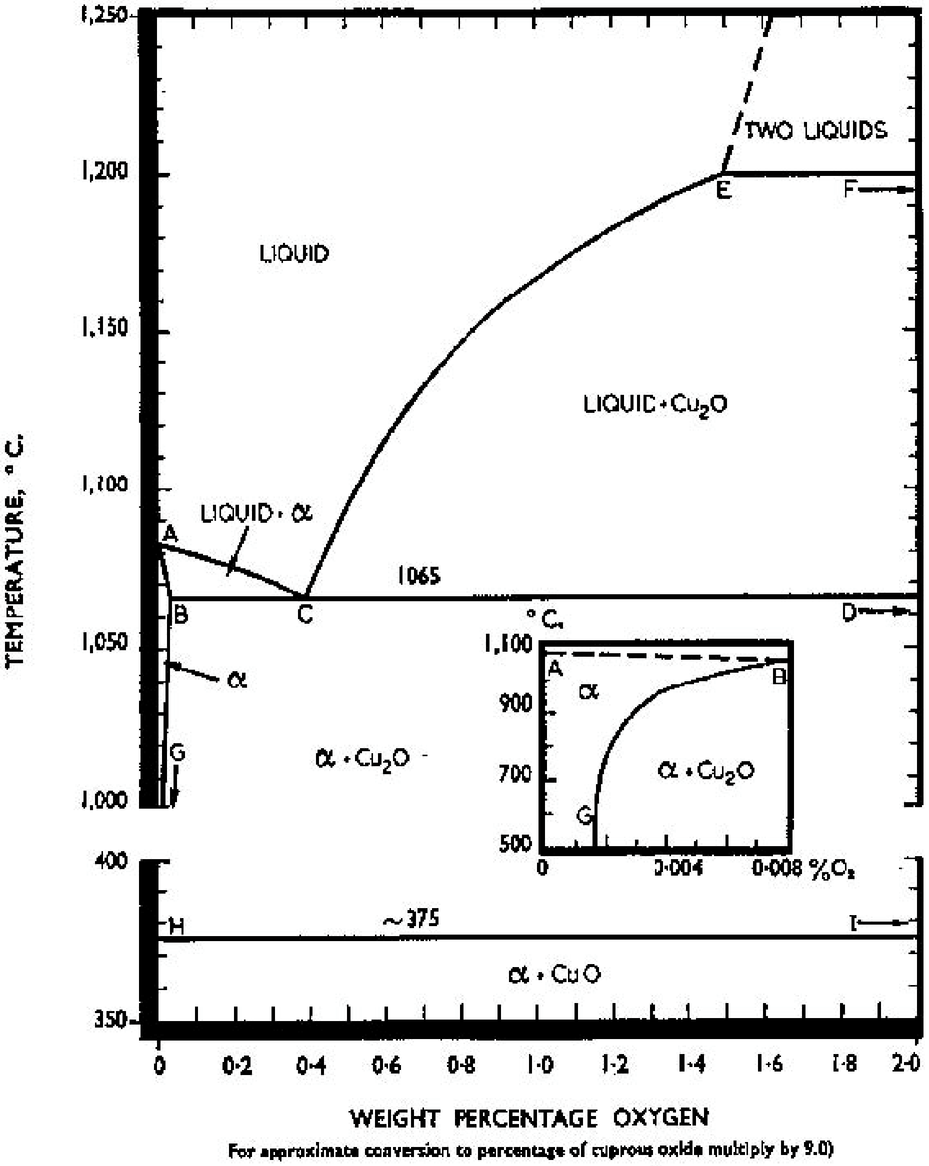
70/30 Copper-Nickel - Hot Worked



Alexander's reagent x 200

This alloy has a single-phase structure. Hot working has broken down the cast structure to give twinned equiaxed grains. Some banding is apparent which is the remains of the dendritic coring from the cast structure. The etchant used to prepare this specimen produces a minimum of structural relief and is recommended for the examination of all copper nickel alloys.

Copper-Oxygen



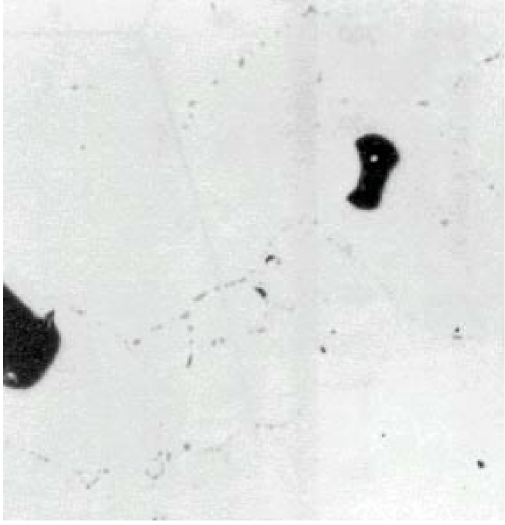
Point	A	B	C	D	E	F	G	H	I
°C	1083	1065	1065	1065	1200	1200	600	~375	~375
O_2%	0	~0.008	0.39	11.2	1.5	10.2	~0.0017	100	11.2

The copper-oxygen system is an example of a simple eutectic system. The high-conductivity copper used for the vast majority of electrical applications generally contains from 0.01 to 0.05% oxygen but may contain up to 0.1%.

Solidification commences with the formation of nuclei on cooling below the liquidus temperature (on line AC). As the temperature falls, these nuclei, which are essentially pure copper, proceed to grow in size, causing the liquid to become richer in oxygen. The composition of the liquid follows the liquidus AC until, at the eutectic point C, the liquid remaining between the primary grains solidifies at constant temperature to form the eutectic composed of α and Cu_2O. It will be seen from the diagram that the oxygen content of the melt controls the amount of residual liquid solidifying with eutectic composition; the relative proportions of primary and eutectic constituents therefore gives a good indication of the alloy's composition.

Until the advent of modern continuous casting plant for high-conductivity copper, porosity was always visible in the microstructure, being an important feature of what was known as tough-pitch copper. During fire-refining, air is injected into the molten copper to oxidise impurities. As a result, oxygen is absorbed by the copper. Hydrogen is also picked up in the furnace, particularly during the subsequent reducing or 'poling' operation, and co-exists in equilibrium with the oxygen. On solidification, this equilibrium is disturbed, the oxygen and hydrogen reacting together to form steam which becomes entrapped in the casting. By carefully reducing the oxygen content to a controlled level, the volume of the steam cavities may be made to counteract the natural solidification contraction of the metal and so produce wirebars or cakes with a level top surface ideal for subsequent fabrication.

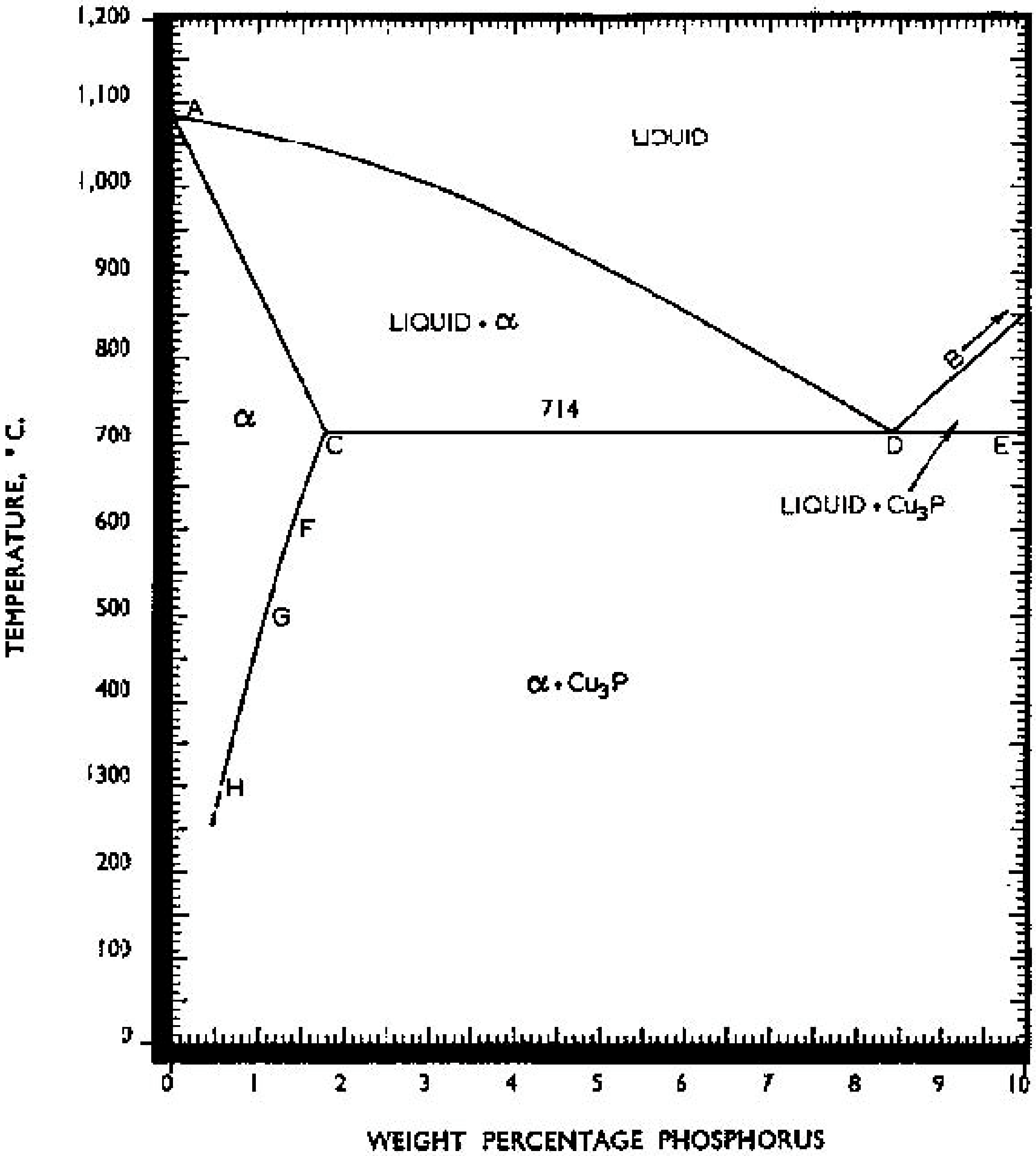
Tough Pitch Copper - Chill Cast



Unetched x 100

This microstructure consists of irregularly-shaped primary grains of outlined by a network of and Cu_20 eutectic. The constituent of the eutectic has become absorbed by the primary grains and is not visible as separate particles. The large black areas associated with the eutectic are gas cavities. Although under normal vertical illumination Cu_20 is blue-grey in colour with a purple sheen, it appears bright red in polarised or oblique lighting. This can be used to distinguish Cu_20 from other constituents of similar colour found in copper. Oxide is usually removed during etching so can only be identified on an unetched sample.

Copper-Phosphorus



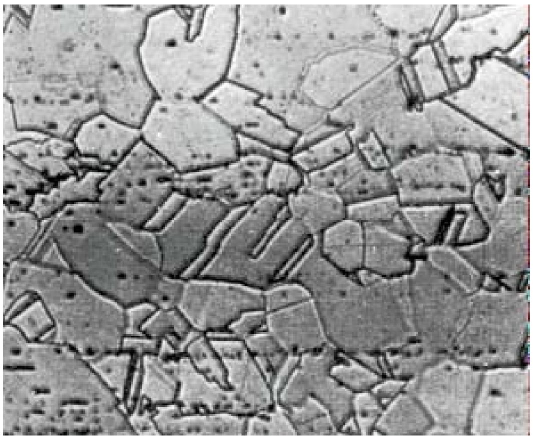
Point	A	B	C	D	E	F	G	H
°C	1083	~1020	714	714	714	600	500	300
P, %	0	14	1.75	8.4	14	1.4	1.1	0.6

The oxygen in tough-pitch copper can be converted to steam when the metal is heated in a reducing atmosphere such as may be encountered in welding or annealing operations. This is known as 'gassing' because hydrogen diffuses into the metal and reacts with the cuprous oxide to form insoluble water vapour. The expansion associated with this reaction forces the grains apart, embrittling the metal. For applications where copper must be resistant to gassing, oxygen is eliminated by the addition of a deoxidiser such as phosphorous to the molten metal before casting. Such copper is then specified as 'de-oxidised' (Cu-DHP).

The copper-phosphorus system also shows a simple eutectic. The residual phosphorus may be sufficient to be present as copper phosphide which appears blue in microstructures. It may easily be distinguished from cuprous oxide by the fact that the latter is translucent with a copper reflection in the centre. Cuprous oxide also reacts to polarised light.

Where casting is carried out in a closely controlled vacuum with very low concentrations of residual deoxidants and volatiles, it is designated 'oxygen-free' (Cu-OF).

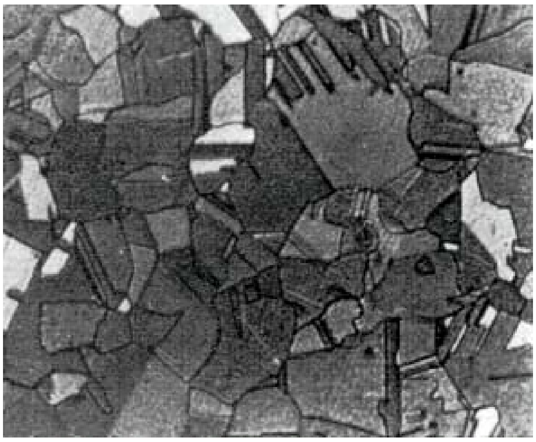
Tough Pitch Copper - Hot Worked



Hot working has broken down the cast structure to give twinned equiaxed grains. The Cu_20 eutectic particles have been aligned in the direction of working and their distribution is no longer confined to grain boundaries. All traces of porosity have been removed. The grain structure is lightly delineated by the use of ammoniacal hydrogen peroxide etchant.

Ammoniacal hydrogen peroxide x 200

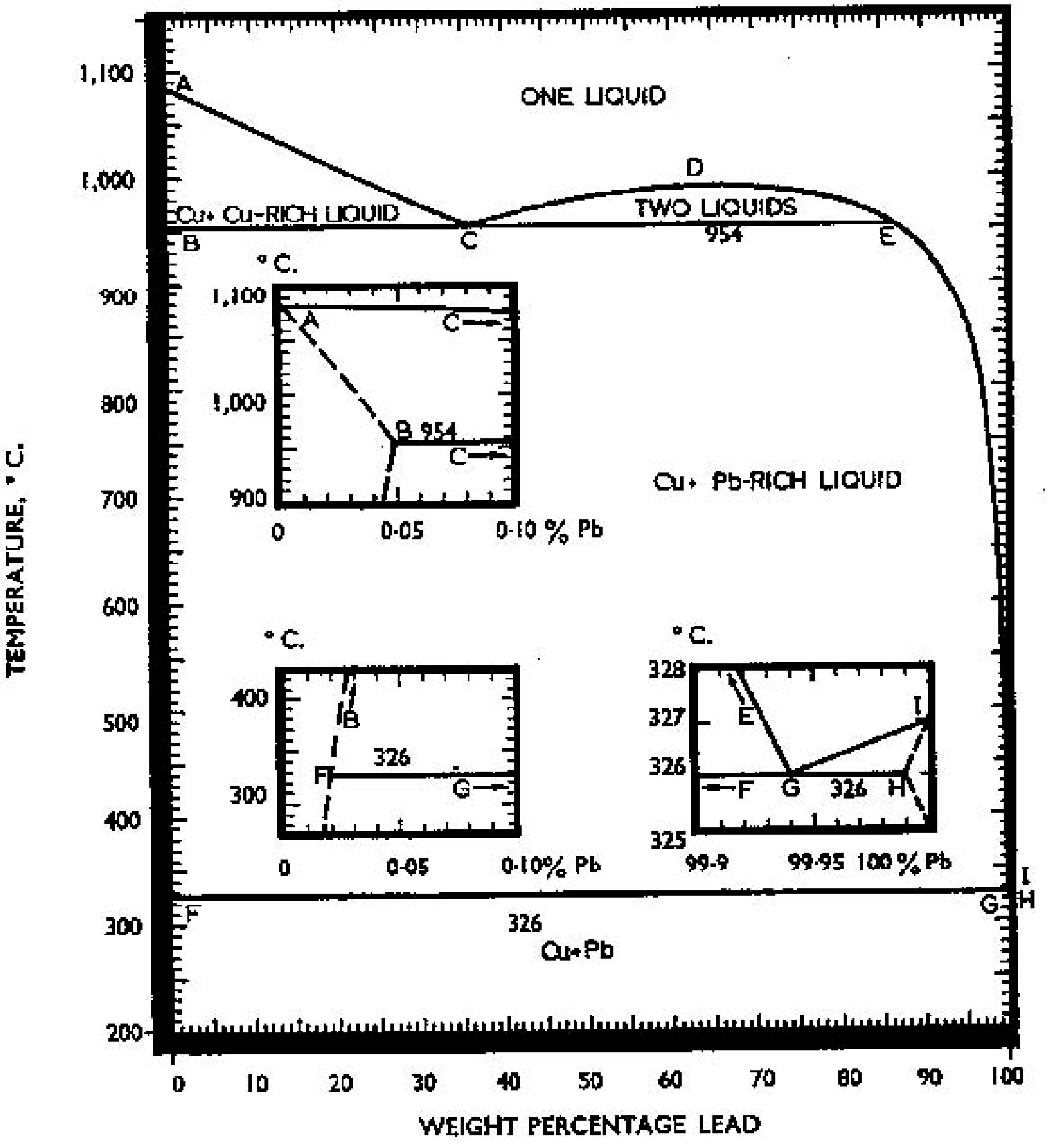
Deoxidised Copper - Hot Worked



This microstructure shows twinned equiaxed grains and a complete absence of the Cu_20 eutectic characteristic of tough pitch copper. Strong contrast between the grains is visible because of the use of alcoholic ferric chloride solution as etchant. This reagent is suitable for the metallographic preparation of most copper alloys, but attack is rapid and care is necessary to avoid over-etching and staining.

Alcoholic ferric chloride x 200

Copper-Lead



Point	A	B	C	D	E	F	G	H	I
°C	1083	954	954	~990	954	326	326	326	327
Pb, %	0	~0.05	36.0	~63	~87	~0.02	~99.94	~99.99	100

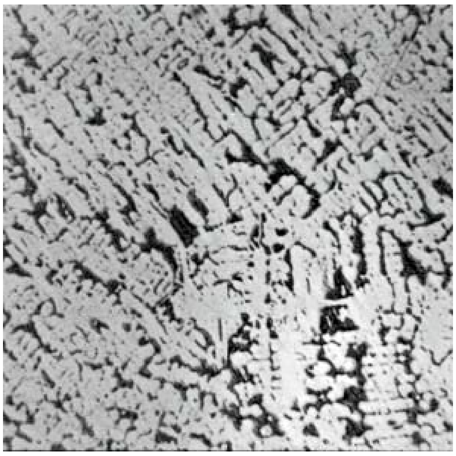
This is an example of a monotectic system. The monotectic is very similar to a eutectic except that at the monotectic point one of the two phases which form from the liquid is solid and the other is another liquid.

The diagram shows that the two metals are practically insoluble in one another in the solid state and are not completely miscible when liquid. Solidification commences by the formation of dendrites which, as the maximum solubility of lead in copper is only 0.05% (point B), consist of almost pure copper. The composition of the liquid follows the liquidus AC and at 954°C the remaining liquid decomposes by the monotectic reaction into solid copper and lead-rich liquid (composition E). The copper is deposited on the primary dendrites and more copper is added as the temperature falls by steady ejection from the lead-rich liquid along the line EG. At the horizontal FG, final freezing takes place with the solidification of almost pure lead.

A small amount of lead is added to pure copper and to many of the other copper alloys such as brasses and bronzes to produce special, free-machining materials. The fact that it is practically insoluble in copper means that it does not affect the structure and properties of the copper, but is precipitated in globular form at the grain boundaries. These globules of lead assist in chip break-up during machining and also provide 'in situ' lubrication.

Larger amounts of lead are added to copper to make a bearing material. The copper gives a rigid load-bearing support to the lead which acts as a solid lubricant. These bearing materials are unworkable and are produced by casting or by powder metallurgy methods.

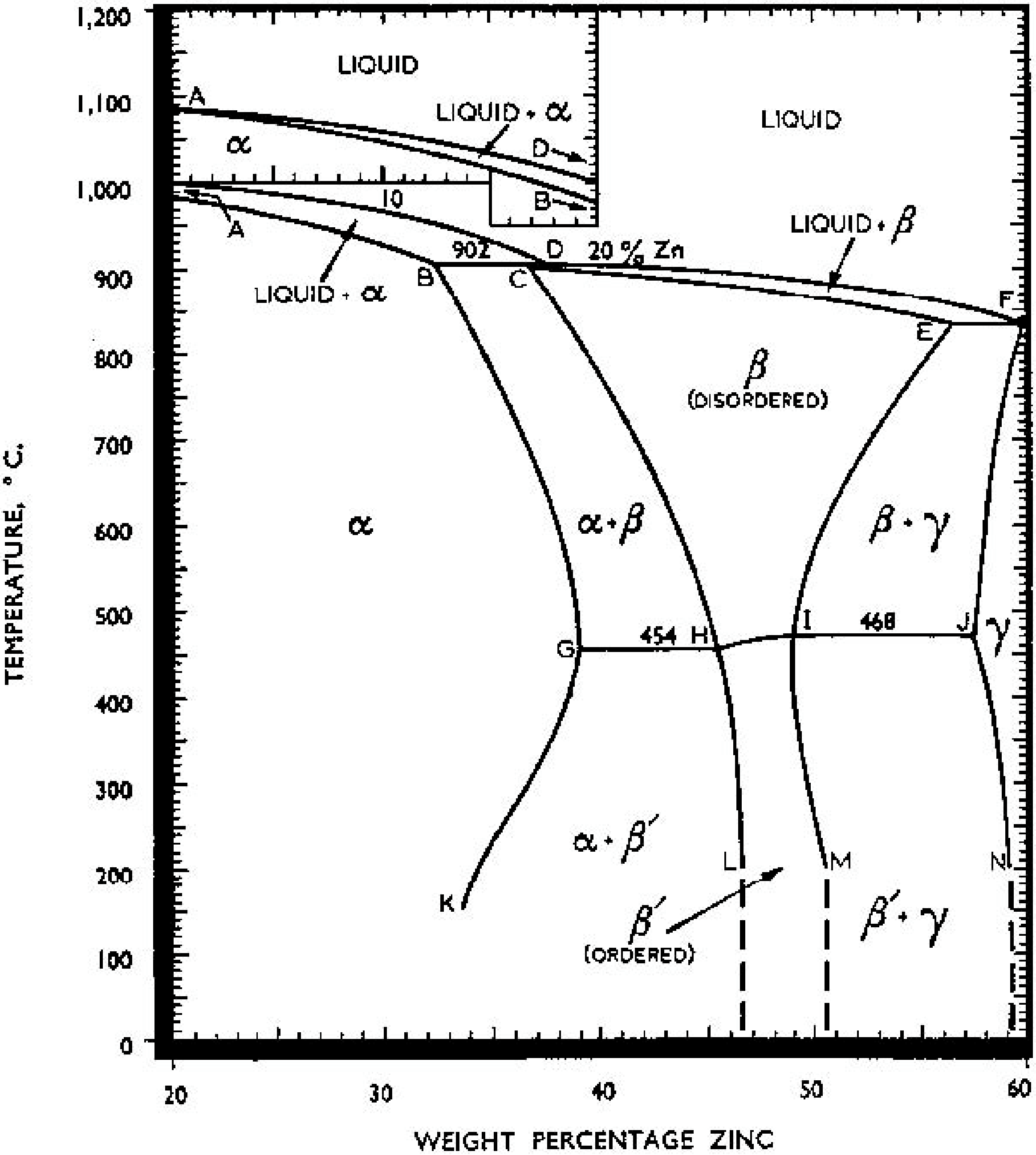
70/30 Copper Lead - Chill-Cast



Unetched x 100

The microstructure shows copper dendrites interspersed with globules of lead which are darker in colour.

Copper-Zinc



Point	A	B	C	D	E	F	G
°C	1083	902	902	902	834	834	454
Zn, %	0	32.5	36.8	37.6	56.5	60.0	39.0
Point	H	I	J	K	L	M	N
°C	454	468	468	150	200	200	200
Zn, %	45.5	48.9	57.5	33.6	46.6	50.6	59.1

Alloys of copper and zinc are called brasses. They form an important series of alloys with good strength and corrosion resistance. They exhibit a wide range of useful properties which are largely dependent on the zinc content. The equilibrium diagram is an example of a peritectic system.

Alloys containing up to about 35% zinc are single-phase and are renowned for their ductility and the ease with which they can be cold worked. Above 35% zinc, the body-centred cubic β phase appears and the hardness increases. Alloys in this region have limited cold ductility but excellent hot workability due to the plasticity of the β phase at high temperature. The practical limit for zinc is about 42%. Alloys containing more zinc than this are too brittle to have commercial use.

For all single-phase α alloys solidification begins with the formation of α dendrites on cooling below the liquidus temperature (on line AD). Some coring occurs which allows the dendritic structure to be visible in the microstructure after etching. The dendritic, as cast, structure is broken down by working and annealing to give twinned, equiaxed grains.

For the two-phase, or duplex α/β alloys the behaviour on solidification depends on whether the zinc content lies above or below the peritectic. Up to 37.6% (point D), α continues to be the primary phase, the β being formed by the peritectic reaction which occurs in the last liquid to solidify.

Above 37.6%Zn freezing occurs with the formation of β dendrites and, when solidification is just complete, the structure consists entirely of this phase. The freezing range is limited and so the β dendrites are almost homogeneous. On cooling, β retains less copper, as indicated by the slope of the (α +β)/ β phase boundary (line CH). At about 770°C, α begins to separate from the β and increases in quantity as the temperature falls. This reaction is diffusion controlled and may be suppressed by rapid cooling.

The α is precipitated at the crystal boundaries and on certain preferred crystallographic planes (octahedral planes) of the parent phase. This form of separation within the crystal is termed a 'Widmanstätten' structure.

70/30 Brass - Sand-Cast

The microstructure shows coarse grains with a dendritic structure made visible by etching deeply with alcoholic ferric chloride. This reagent reveals the changes in composition due to coring.

Alcoholic ferric chloride x 100

At approximately 450° - 470°C (line GHI), the β phase undergoes a transformation into a low-temperature modification known as β'. This transformation is due to the zinc atoms changing from a random to an ordered arrangement in the lattice. The appearance of the microstructure is unaffected and the influence on mechanical properties is negligible.

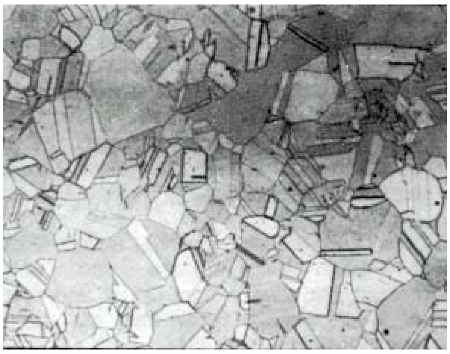
The most commonly used α-brass is 'Common Brass', the 64/36 alloy, because it is the least expensive (zinc being generally cheaper than copper). However, 'Cartridge Brass' with 30% Zn has better ductility and superior corrosion resistance. Commercially useful alloys exist with zinc contents as low as 5%. These high copper alloys have a beautiful golden colour and are known as gilding metals. Alloys may be cast or produced in wrought forms such as sheet, tube and wire.

The most commonly used two-phase alloy is 60/40 brass. It is frequently used for castings and is particularly suitable for die casting. Duplex brasses have excellent ductility at hot working temperatures and are therefore also produced in wrought form by extrusion, forging or hot rolling.

Other alloying elements are frequently added to brasses to vary properties such as strength, corrosion resistance and machinability for specific end uses. These additions each have an effect on the solubility of zinc in copper.

While most brasses are not normally ranked as 'heat treatable', some brasses of very closely controlled composition are cast or hot worked in the duplex α/β state and then annealed at about 450°C to convert the microstructure to an single phase of better resistance to corrosion by dezincification in aggressive supply waters.

70/30 Brass - Cold-Worked and Annealed



The microstructure shows twinned equiaxed α grains. Uniform attack of the specimen during etching indicates that the structure is homogeneous. Coring in brass is much less persistent than in copper-tin and copper-nickel alloys.

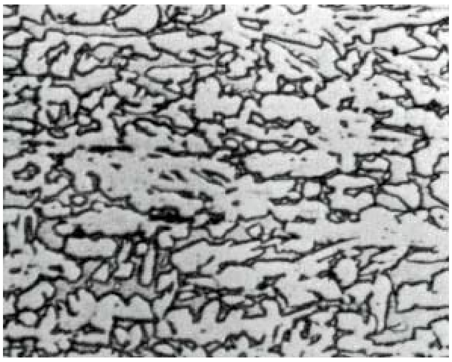
Alcoholic ferric chloride x 200

60/40 Brass - Sand-Cast

This specimen shows large β grains containing a Widmanstätten precipitate of α which is etched slightly lighter in colour.

Ammoniacal ammonium persulphate x 100

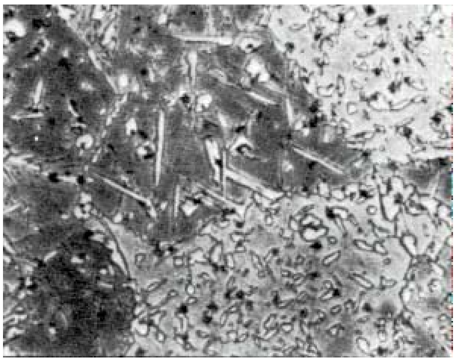
Leaded 60/40 Brass - Hot Worked



Ammoniacal ammonium persulphate x 200

This specimen shows areas of β slightly elongated in the direction of working, in a matrix of β. The body-centred cubic β phase does not develop annealing twins. Twins are, however, present in the α and would be revealed by deep etching. The lead (which has been added to improve machinability) appears as dark elongated particles.

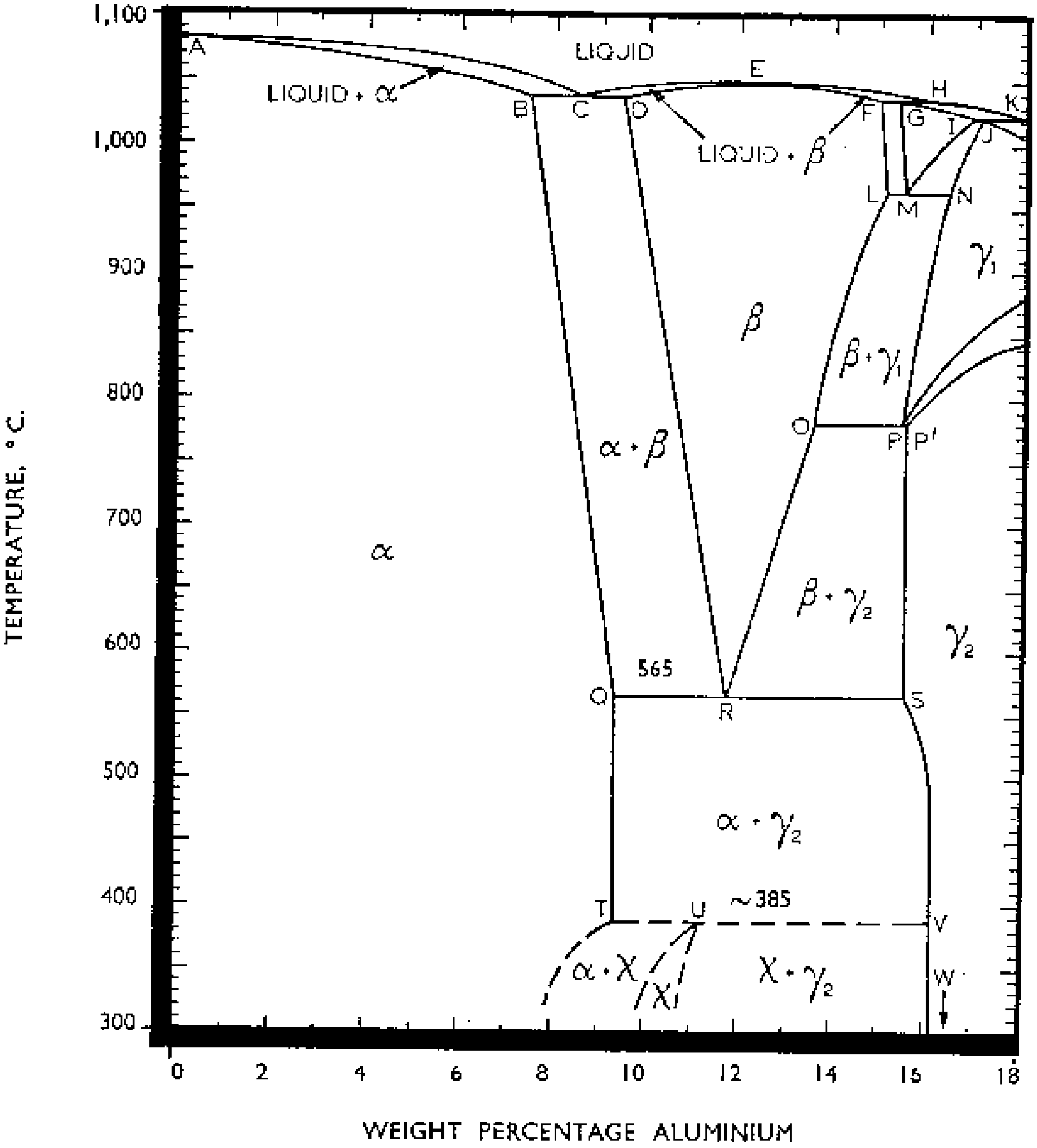
High Tensile Brass - Sand-Cast



Alcholic ferric chloride x 250

This microstructure is very similar to that of the sand cast 60/40 brass. The Widmanstätten structure and the β matrix are, however, considerably finer than those of the binary alloy. An iron-rich phase which has been blackened by the etchant is also visible as small, uniformly distributed particles, many having a rosette shape. In the unetched condition this constituent is grey, making it readily distinguishable from the lead often present in high tensile brasses which is much darker in colour.

Copper-Aluminium



Point	A	B	C	D	E	F	G	H
°C	1083	1037	1037	1037	1048	1036	1036	1036
Al, %	0	7.5	8.5	9.5	12.4	14.95	15.25	16
Point	**I**	**J**	**K**	**L**	**M**	**N**	**O**	**P,P^1**
°C	1022	1022	1022	963	963	963	780	780
Al, %	16.9	17.1	18	15.1	15.45	16.40	13.6	~15.6
Point	**Q**	**R**	**S**	**T**	**U**	**V**	**W**	
°C	565	565	565	~385	~385	~385	0	
Al, %	9.4	11.8	15.6	9.4	<11.3	16.2	16.2	

Copper-aluminium alloys are known as aluminium bronzes and they form an important group of engineering materials which are renowned for their strength and corrosion resistance. The properties are closely dependent on microstructure so that an understanding of the phase transformations which occur is essential for optimum properties to be ensured.

The binary diagram is complex, but for the commercially important binary alloys the most important reaction is the eutectoid which occurs at 565°C. Of great commercial importance also are alloys which contain iron and nickel. Both these elements have a significant influence on the phase relationships and affect the properties of the alloys.

Binary Cu-Al alloys

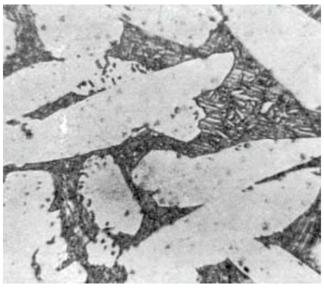
Alloys containing less than 8% aluminium are single phase α alloys. Solidification commences with the formation of α dendrites. The freezing range is short and so segregation is not pronounced and the alloy solidifies as a single phase.

An alloy containing 10% aluminium solidifies as β. When the temperature falls to about 930°C α begins to deposit from the β (at the line DR), the amount increasing with falling temperature. A Widmanstätten structure is produced directly comparable with that found in a 60/40 brass. At 565°C (line QRS) the remaining β begins to decompose into a lamellar eutectoid, $\alpha + \gamma_2$. The reaction is diffusion controlled and only goes to completion when the alloy is held for a considerable time at temperatures just below that of the eutectoid, such as can occur during slow cooling. Normal casting rates are too rapid to allow this reaction to occur and β is retained.

Retained β transforms into a hard acicular martensitic form by a process not requiring diffusion. Because it is a non-equilibrium phase, the martensitic change is not included in the equilibrium diagram. It does, however, have important implications for the mechanical properties of the alloy.

The eutectoid $\alpha + \gamma 2$ structure has certain undesirable features with respect to mechanical properties and corrosion resistance and is therefore avoided as far as possible for most commercial applications.

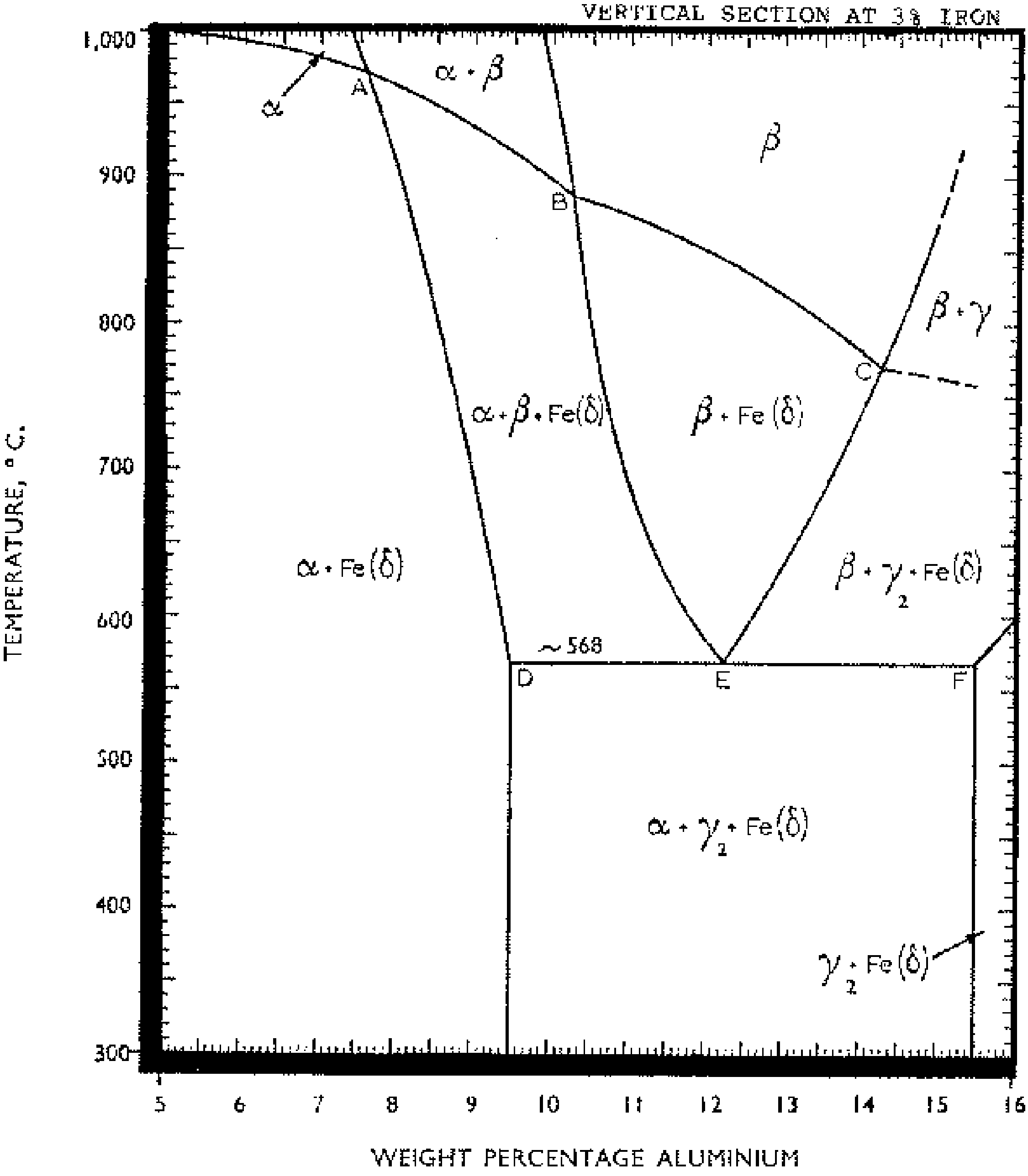
Aluminium Bronze. Cu – 9.5%Al – 2.5%Fe. Sand-cast



Alcoholic ferric chloride x 500

This microstructure is typical of the simpler aluminium bronzes. Light coloured areas of are visible in a matrix of darker-etching . An iron-rich constituent is apparent as uniformly distributed fine rosettes, pink in colour.

Copper-Aluminium-Iron

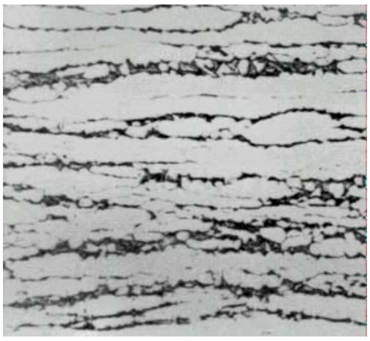


Point	A	B	C	D	E	F
°C	970	885	770	~568	~568	~568
Al, %	7.6	10.3	~14.3	9.5	12.3	15.5

Commercial alloys containing more than 8% of aluminium almost always have deliberate additions of iron. Iron acts a grain refiner both during solidification and during slow cooling, and improves the mechanical properties.

The influence of 3% iron on the copper-aluminium system is shown in the diagram. Iron additions of this order only slightly modify the binary diagram and particles of iron are precipitated throughout both the α and β phases. The solubility of the iron at high temperature varies according to the aluminium content; in all-α alloys, the iron begins to precipitate when the temperature drops below about 1000°C, whilst the alloys, with greater amounts of aluminium, do not precipitate the iron until the temperature has fallen, in some cases, as low as 850°C. The iron appears as a finely divided precipitate evenly distributed throughout the structure with no apparent tendency for concentration at grain boundaries.

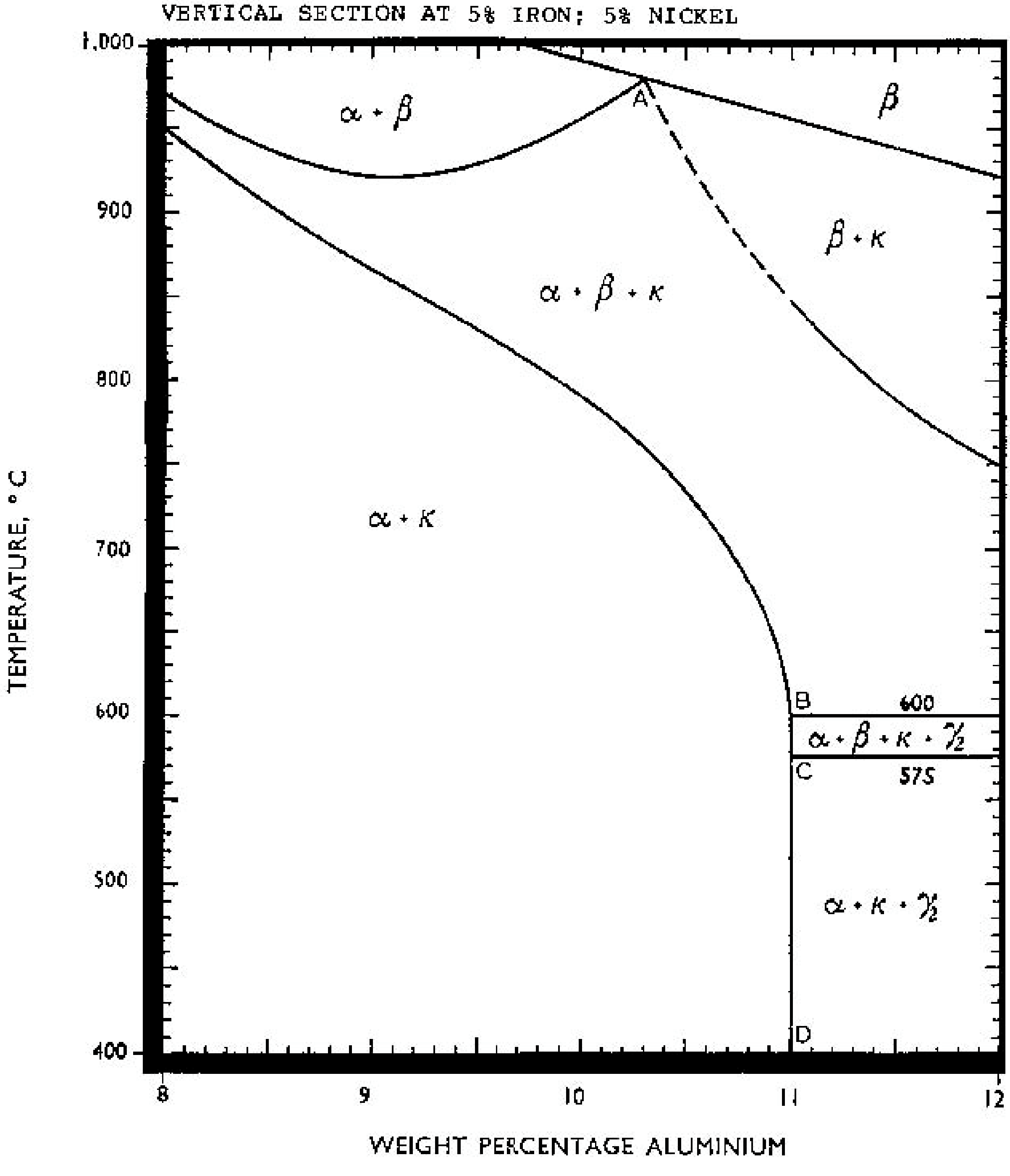
Aluminium Bronze. Cu – 9.5%Al – 3%Fe – 3%Ni, Hot-worked



Alcoholic ferric chloride x 100

This microstructure is typical of the general distribution of constituents produced by hot-working the duplex aluminium bronzes. The α is surrounded by a matrix of darker etching β, both constituents having been elongated in the direction of working. Twins are present in the and could be revealed by heavy etching. The iron-rich phase is present as tiny particles distributed throughout the microstructure, but not visible at the magnification of this micrograph.

Copper-Aluminium-Nickel-Iron



Point	A	B	C	D
°C	~980	600	575	400
Al, %	~10.3	11	11	11

Alloys containing 9-12% aluminium with additions of up to 6% each of iron and nickel represent a most important group of commercial aluminium bronzes. The common alloys, which normally contain 3-6% each of these two elements, have been fully investigated in view of their excellent combination of mechanical properties and corrosion resistance.

A vertical section through the Cu-Al-Ni-Fe quaternary diagram at 5%Fe and 5%Ni is shown. It can be seen that the system remains essentially the same as the binary system with the introduction of an additional phase, k. The k phase is related to the iron-rich phase in the Cu-Al-Fe system.

k absorbs aluminium from the matrix and hence extends the apparent range of the α field. Thus, under equilibrium conditions, β is not retained below 600°C unless the aluminium exceeds 11%, as compared with 9.4% in the binary system. The k precipitate in the α matrix has a pronounced effect on the properties and considerably increases the mechanical strength. At the same time the reduction in ductility is not as marked as would occur if β had been formed in a binary alloy to give an equivalent strength. This is the most outstanding advantage which alloys of this type have over other aluminium bronzes. The absence of β also avoids any danger from eutectoid formation, whatever the previous history of the material with respect to heat treatment or rate of cooling, unless the aluminium content is in excess of about 10.5%.

a) As cast structure

The 80/10/5/5 alloy solidifies with an all-β structure from which k and some α are precipitated on cooling to about 900°C. The k particles formed at this stage are coarse and rounded, and sometimes take the form of 'rosettes'. Below about 900°C the remaining β transforms to a finely divided mass of α + k with the k frequently being of a lamellar form. Further cooling to room temperature, if sufficiently slow, results in a further precipitation of finely divided k in all the α areas.

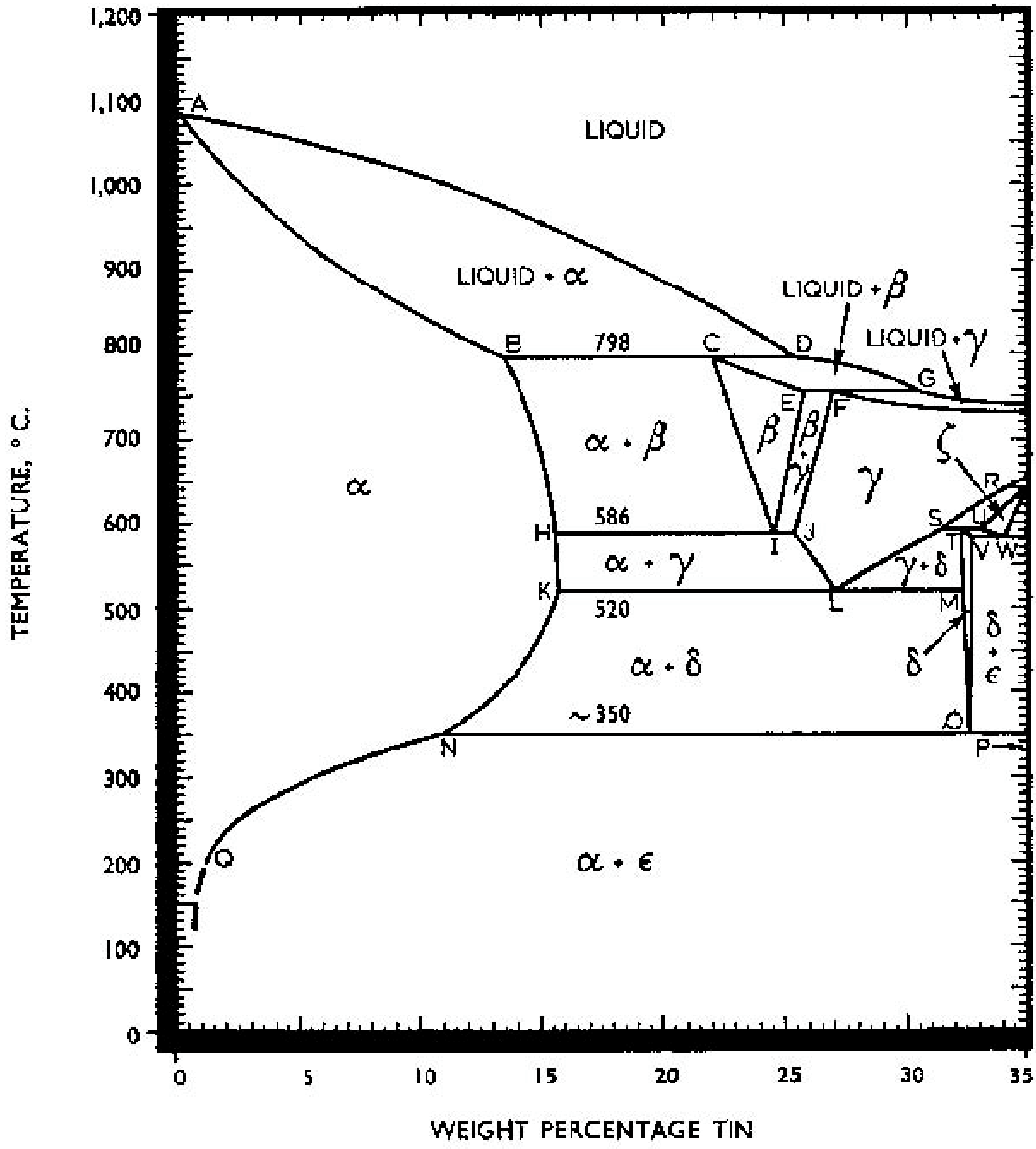
b) Hot working

Hot working is generally carried out at about 975°C. At this temperature the alloy has a β + k matrix containing areas of which become elongated in the direction of working. The structure of a hot rolled plate therefore consists of elongated α containing traces of k surrounded by dissociated β in the form of α + k.

c) Heat treatment

Quenching from 1000°C results in an all-β structure transformed to martensite exactly as in the binary alloy. Tempering results in dissociation of the β to form a fine mass of α and k which increases strength and hardness. The tempering temperature controls the coarseness of this precipitate and the mechanical properties.

Copper-Tin



Point	A	B	C	D	E	F	G	H
°C	1083	798	798	798	755	755	755	586
Sn, %	0	13.5	22.0	25.5	25.9	27	30.6	15.8
Point	**I**	**J**	**K**	**L**	**M**	**N**	**O**	**P**
°C	586	586	520	520	520	~350	~350	~350
Sn, %	24.6	25.4	15.8	27.0	32.4	11	32.55	37.8
Point	**Q**	**R**	**S**	**T**	**U**	**V**	**W**	
°C	200	640	590	590	590	582	582	
Sn, %	1.2	34.2	31.6	32.3	33.1	32.9	34.1	

The copper-tin binary equilibrium diagram is complex containing a peritectic reaction and a series of eutectoid reactions.

Copper-tin alloys are called bronzes. They have good corrosion resistance and strength and are used for applications such as gears and bearings. Commercially important alloys contain up to 11% Sn and frequently additions of lead.

In true equilibrium an 8% Sn alloy would solidify entirely as α, but in practice the wide freezing range causes extensive segregation to occur and the last liquid to solidify is generally so enriched in tin that it undergoes the peritectic reaction at 798°C to form β. On cooling the β transforms.

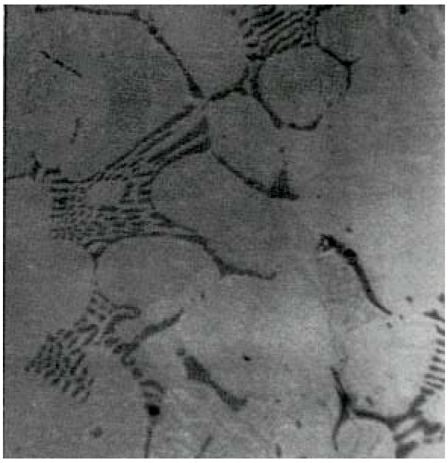
As can be seen from the diagram, in equilibrium there would be a series of eutectoid reactions where β would first give α and γ, then the γ would transform to α and δ and finally the δ would transform to $\alpha + \varepsilon$. In practice the phase generally seen in the microstructure is the $\alpha + \delta$ eutectoid because the $\delta \rightarrow \alpha + \varepsilon$ reaction occurs extremely slowly and would only take place with prolonged low-temperature heat treatment.

Many copper-tin alloys also contain phosphorus and these are known as phosphor bronzes. The phosphorus increases the wear resistance and stiffness of the alloy. A vertical section through the Cu-Sn-P ternary diagram at 5% Sn is shown, and it can be seen that the phosphorus is present as copper phosphide (Cu_3P) which forms by a eutectic reaction in the last liquid to solidify, and appears in the microstructure as a skeleton-like structure along with the eutectoid mixture of α and δ.

Phosphor bronzes containing around 5% Sn are commonly given extensive cold work to make spring materials.

Alloys with significantly higher tin contents cannot be cold worked but make excellent cast alloys for bearing purposes.

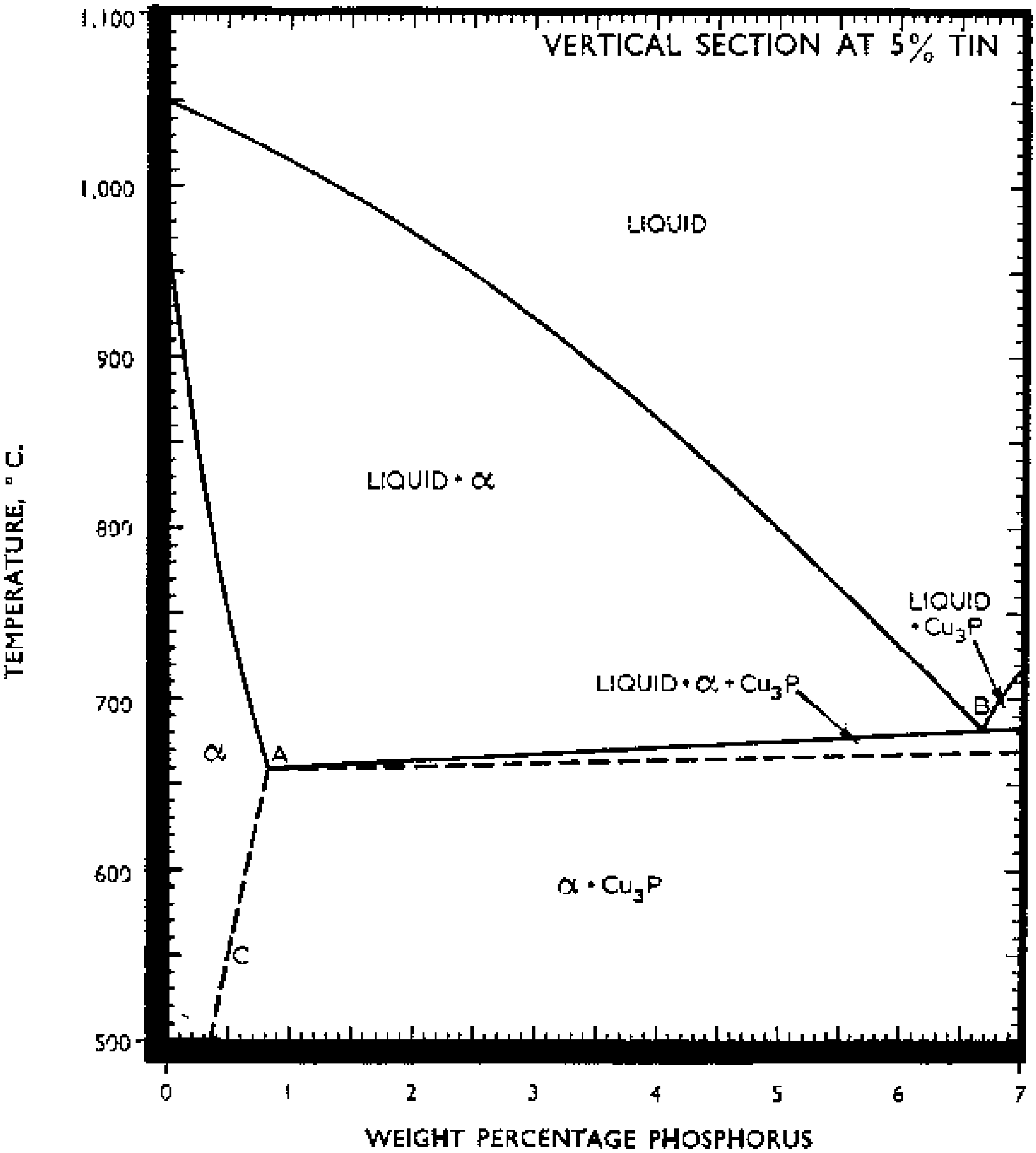
90/10 Phosphor Bronze - Sand-Cast



This specimen shows dark areas of the α and δ eutectoid between the arms of the α dendrites. The dendrites are heavily cored but this is not visible in the unetched specimen. The δ constituent of the eutectoid is pale blue. Phosphorus is frequently added to copper-tin alloys and copper phosphide, Cu_3P, can be seen as a darker blue constituent along with the eutectoid. In the etched condition both the δ and Cu_3P are white and cannot easily be distinguished.

Unetched x 500

Copper-Tin-Phosphorous



Point	A	B	C
°C	660	683	550
P1, %	0.8	6.7	~0.5

95/5 Phosphor Bronze - Cold-Worked and Annealed

Alcoholic ferric chloride x 200

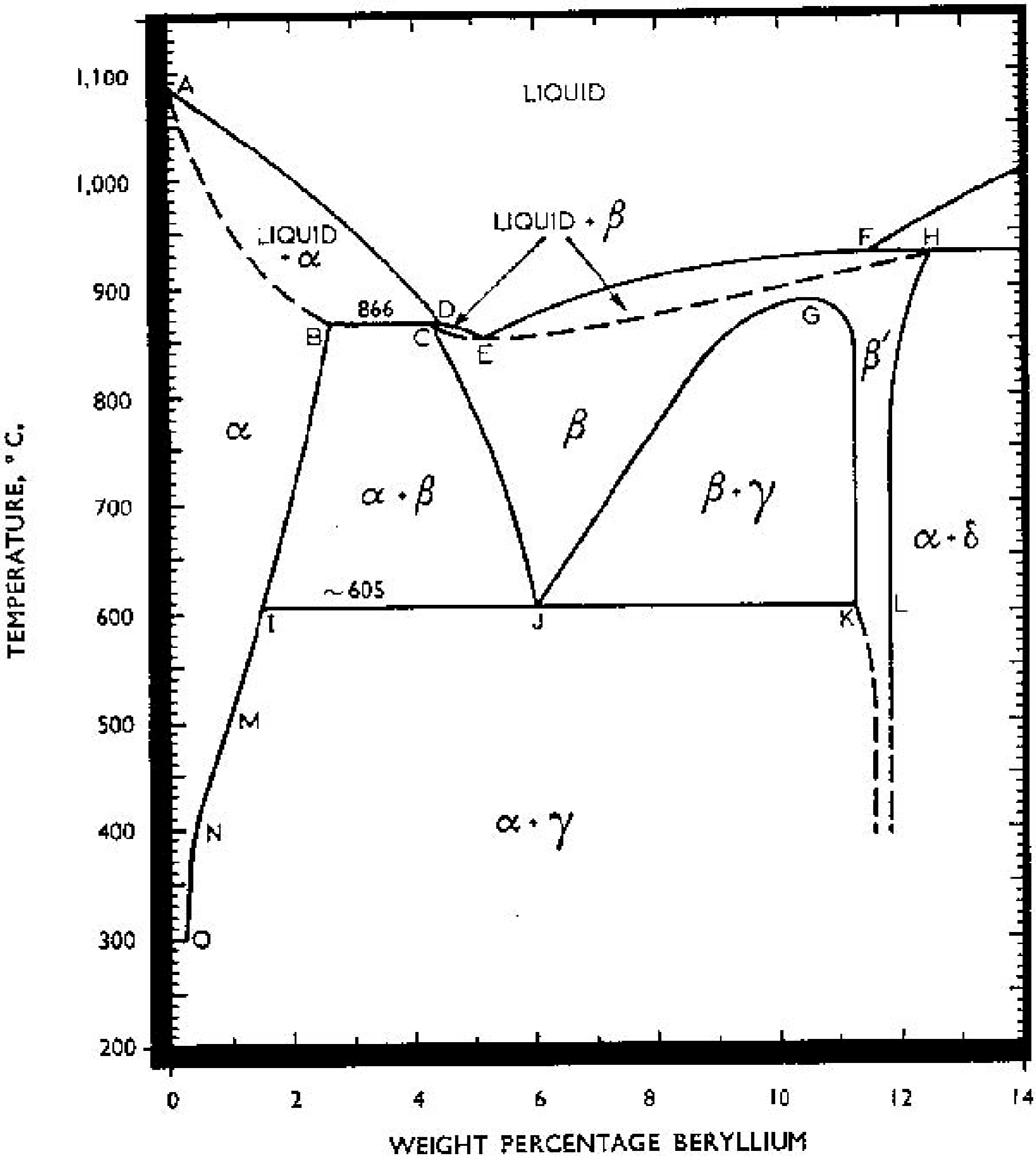
This specimen shows the typical recrystallised structure of twinned equiaxed grains.

95/5 Phosphor Bronze - Cold-Worked

Alcoholic ferric chloride x 200

This microstructure shows a specimen which has been cold worked after being wrought and annealed. The typical equiaxed, twinned crystals of the annealed structure have been elongated by the cold working and the twins have been bent. The grains are covered with a multitude of equidistant parallel lines called strain bands which change direction at grain boundaries. Some grains have suffered slip in two directions and show a pattern of crossed bands. Strain bands are not visible in the polished state and are only revealed by etching, phosphor bronzes showing them much more readily and clearly than most other copper alloys.

Copper-Beryllium



Point	A	B	C	D	E	F	G	H
°C	1083	866	866	866	~854	930	885	930
Be, %	0	2.7	4.2	4.3	~5.2	11.5	~10.6	12.5
Point	I	J	K	L	M	N	O	
°C	~605	~605	~605	605	200	400	300	
Be, %	1.6	6.0	11.3	11.8	1.0	0.4	0.2	

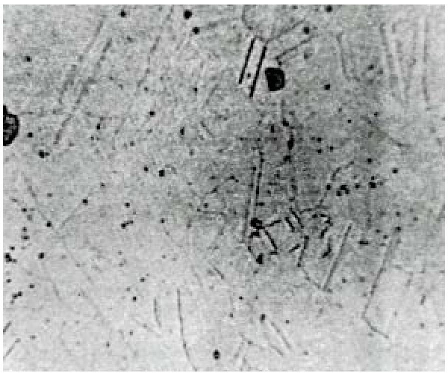
This is an example of a peritectic system but the most important aspect of the system is the marked temperature dependence of the solid solubility of beryllium in copper. This results in an age-hardenable alloy with excellent mechanical properties.

Commercially important copper beryllium alloys contain about 2% beryllium. In equilibrium this would solidify entirely as the α phase, but under some conditions a small amount of β is formed due to segregation.

The solubility of beryllium in copper at the solidification temperature is as high as 2.7% but at 300°C only 0.2% is soluble. When the alloy is cooled slowly the beryllium is precipitated out. Optimum mechanical properties are, however, obtained by water quenching from 800°C to retain the beryllium in supersaturated solution and then ageing to allow a very fine dispersion of the γ phase to be precipitated. Maximum hardening is obtained after an ageing treatment of about 2 hours at 335°C.

In the fully heat-treated condition beryllium copper is the strongest and hardest of the standard copper alloys and has a tensile strength of up to 1350 N/mm^2. Common applications include small springs, electrical contacts, flexible bellows and non-sparking tools. Normally, beryllium copper contains about 2% Be and an addition of cobalt, but other versions have about 2% Co and less Be often with an addition of nickel.

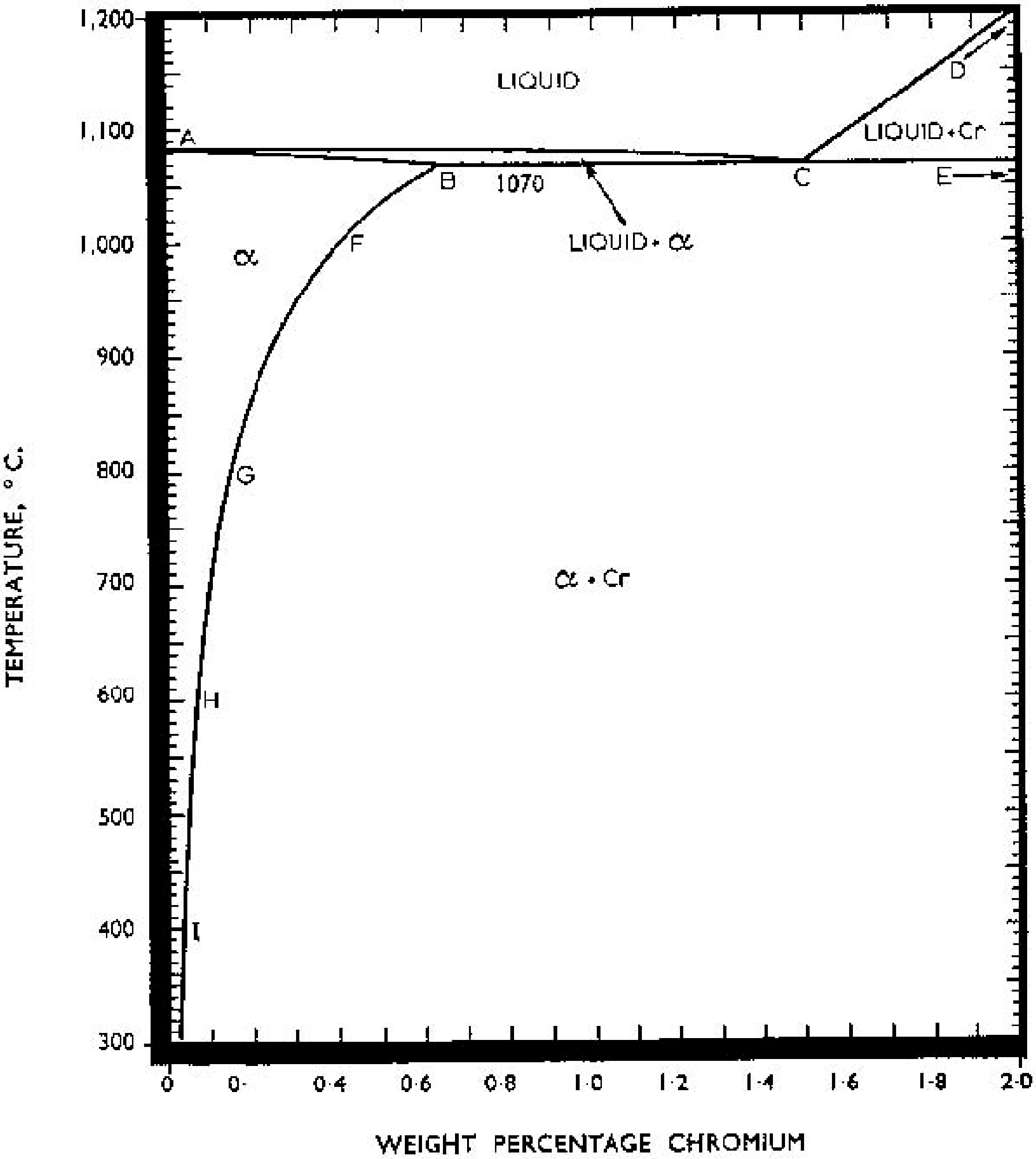
Copper Beryllium - Wrought. Solution-Treated and Precipitation-Hardened



Ammoniacal ammonium persulphate x 500

This specimen contains small spherical particles of β in the fine-grained α matrix. Not all commercial alloys contain the β phase. It generally only occurs where there has been incomplete supression of the transformation during cooling from elevated temperatures.

Copper-Chromium



Point	A	B	C	D	E	F	G	H	I
°C	1083	1070	1070	1470	1070	1000	800	600	400
Cr, %	0	0.65	~1.5	37	~100	0.4	0.15	0.07	< 0.03

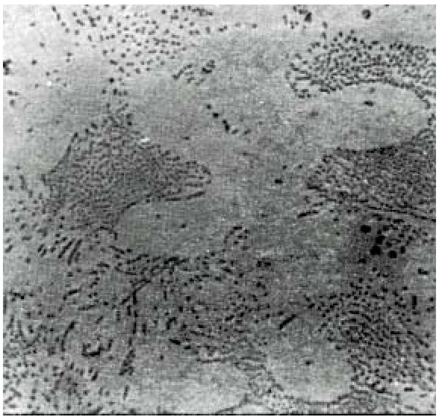
This is a simple eutectic system but the most significant aspect of the phase diagram from the point of view of commercially important alloys is the steep change in solid solubility of chromium in copper as the temperature falls. This gives rise to age-hardening characteristics.

Commercially important alloys contain about 1% Cr. Solidification starts with the formation of and the composition of the liquid moves down the liquidus AC to the eutectic. At 1070° the eutectic mixture of α and Cr is formed and this is seen in the microstructure as a typical lamellar structure. Slow cooling from this temperature will allow precipitation of chromium out of solution, but this is not done in practice because much superior mechanical properties can be obtained by quenching to retain the chromium in supersaturated solid solution and then ageing to allow a very fine dispersion of chromium particles to form throughout the matrix. A typical heat treatment would be a water quench from 1000°C followed by ageing at 450° for 4 hours.

The great advantages of this alloy in the fully heat-treated condition are high conductivity and retention of good mechanical strength continuously at temperatures up to approximately 400°C and, for short times, much higher. Because of these characteristics the alloy finds application as sand castings for items such as furnace parts, cylinder heads and electrical switchgear. In wrought forms it is used principally for resistance welding electrodes and holders, commutators and disc brakes.

Chromium has a high affinity for the oxygen and carbon frequently present during industrial melting and casting processes. Microstructures can therefore appear to be more complex than would be expected from the binary equilibrium diagram.

Copper Chromium - Sand-Cast. Solution-Treated and Precipitation-Hardened



Ammoniacal ammonium persulphate x 100

This microstructure shows areas of primary surrounded by the eutectic consisting of and blue chromium particles. The precipitate responsible for hardening is not visible at this magnification.

Copper-Nickel-Tin

Alloys in this ternary system which lie in the range Cu-4%Ni-4%Sn to Cu-15%Ni-8%Sn exhibit the phenomenon known as spinodal decomposition. A number of commercial alloys have been developed the most important of which are CuNi9Sn6 and CuNi15Sn8.

Spinodal decomposition is similar to an age hardening reaction and involves quenching and subsequent heat treatment, but instead of precipitates forming by a conventional nucleation and growth mechanism, regular variations in composition occur in the lattice with an extremely fine spacing between them. The two constituents have the same crystal structure but different lattice parameters. The strain hardening produced leads to particularly good mechanical properties, and no distortion occurs during the heat treatment.

Copper-nickel-tin alloys are used for electrical connectors and springs. They exhibit excellent corrosion resistance and are very resistant to stress relaxation.

References

Constitution of Binary Alloys. M Hansen and K Anderko, McGraw Hill Book Co, 1957.

Smithells Metals Reference Book. Sixth Edition. Editor, E A Brandes, Butterworth & Co Ltd, 1983.

Handbook of Binary Phase Diagrams. W Moffat, Genium Publishing Corp 1991.

Appendix I - Composition of Etchants

Ammoniacal hydrogen peroxide	0.880 Ammonia solution	25ml
	Water	75ml
	A few drops of hydrogen peroxide	
Alcoholic ferric chloride	Ferric chloride	5m
	Ethyl alcohol to	100ml
	Slightly acidified with hydrochloric acid	
Ammoniacal ammonium persulphate	0.880 Ammonia solution	10ml
	Ammonium persulphate	10g
	Water to	100 ml
Alexander's reagent	Acetic acid (75% aq solution)	30ml
	Concentrated nitric acid	20ml
	Acetone	30ml

Appendix II – CDA Publications for further details on properties of coppers and copper alloys

TN 26	The Brasses, Nickel Brass and Nickel Silver – Technical Data (1988)
TN 30	Copper-Nickel Alloys – Properties and Applications (1982)
TN31	Copper-Nickel 90/10 and 70/30 Alloys – Technical Data (1982)
Publication 71	The Nickel Silvers (1965)
Publication 80	Aluminium Bronze Corrosion Resistance Guide (1981)
Publication 82	Aluminium Bronze Alloys Technical Data (1981)
Publication 83	Aluminium Bronze Alloys for Industry (1986)
Publication 86	Aluminium Bronze – Essential for Industry (1987)
Publication 117	The Brasses – Properties and Applications (2005)
Publication 118	90/10 Copper-Nickel (1997)
Publication 120	Copper and Copper Alloys, Compositions, Applications and Properties (2004)
Publication 122	High Conductivity Copper Alloys for Electrical Engineering (1998)
Publication 139	Copper-Nickel Fabrication (1999)
CD4 or see link to online version	Copper Key – CD giving chemical composition of copper alloys worldwide, their material designation and national standard. It automatically gives equivalent materials from international, European and other national standards and enables chemical compositions to be compared. Online version at www.copper-key.org/index.php?lang=english

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