

The Development of an Improved Non-magnetic Alloy Based on the Copper-Beryllium System

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The erratic magnetic properties exhibited by the copper-beryllium alloy system have limited its use for ultra-low permeability applications. This work examines the factors controlling the magnetic properties and isolates the beta phase which, in combination with small quantities of iron, present as an impurity, is the major cause of the erratic behaviour. Methods of eliminating the beta phase are recommended and an improved non-magnetic alloy, based on beryllium-copper, has been developed. This shows mechanical properties of 80 tsi with 10% elongation whilst maintaining a low magnetic permeability of 1.0000 to 1.0002.

1. Introduction

The use of copper-beryllium alloys, which show much improved mechanical properties over other currently used non-magnetic alloys, has been limited for ultra-low permeability applications by the erratic behaviour of its magnetic permeability. Rae [1] has shown that the permeability of a copper-2% beryllium alloy can vary from 1.0000 to 1.0100. Butts and Reiber [2] describe the magnetic properties as poor, probably due to the presence of impurity iron which is usually inherent in production methods for beryllium-copper. They further indicate that in many copper alloys the magnetic properties can be profoundly influenced by the appearance of a second phase.

Work has been undertaken at AWRE, Aldermaston to determine the factors controlling the magnetic permeability of copper-beryllium alloys to eliminate erratic magnetic behaviour and subsequently to use this alloy system as a base for the development of non-magnetic alloys with improved mechanical properties.

2. Experimental

Alloys were generally prepared from electrolytically pure materials but the copper-beryllium alloys containing iron were made from stock material containing 0.12% iron. The alloys were

melted in vacuum to eliminate any contamination from extraneous sources e.g. fluxes. Proprietary fluxes claimed to be free from magnetic material were found to contain particles which could be picked out by a magnet. Precautions were taken to minimise any inhomogeneity of the melt during casting, and high melting point additions were made as master alloys with copper. These were melted first and held at a temperature high enough to ensure good homogeneity; they were allowed to cool before other alloying additions were made. The alloys were cast into CO₂-sand or graphite moulds washed with alumina paint.

The beryllium-copper-nickel alloys were produced by the following method. The copper-nickel master alloy (50% nickel) was melted first and held at 1100° C to ensure that dissolution was complete. The copper-beryllium and the remainder of the copper were then added, the melt was cooled to 1000° C and was then cast by bottom pouring into an alumina-painted graphite mould. The mould coating was necessary since beryllium can form a series of carbides by reaction with graphite. The graphite mould gave a partial chill to the cast plates which showed fine grain (> 1 mm) equiaxed structures.

Similar results were obtained with CO₂-sand moulds. Plates were cast in a variety of sizes, e.g. 15 × 10 × 2.5 cm, 12.5 × 25.5 × 2.5 cm and

*1 tsi = 1.575 kg/m²

33 × 23 × 1 cm. The head was normally one quarter of the weight of the plate but for the 1 cm plates this was increased to one third to ensure adequate feeding. Good solid plates were obtained with little porosity.

The material was worked by either forging or rolling in a two-high mill. Subsequent to any working process the surfaces of the material were cleaned by abrasion to remove any ferromagnetic material picked up from the hammer or roll surface. The extent of contamination from this source can be considerable and in one case increased the permeability of a copper-2% beryllium alloy from 1.0000 to 1.0030.

Magnetic measurements were made using a Förster Permeameter [3] which measures the alloy permeability in a field strength of 1000 oersteds. Permeability changes during heat-treatment cycles were repeated on the same face of a single specimen to avoid errors due to inhomogeneity.

3. Results and Discussion

3.1. Magnetic Properties

The ferromagnetic elements iron, cobalt and nickel can all be present in copper-beryllium alloys. A content of up to 0.15% iron is inherent in the production methods, and cobalt is used for grain refinement. To determine the effects of these elements on magnetic properties, controlled additions were made to copper and copper-beryllium alloys.

Pure copper is diamagnetic but the presence of small quantities of ferromagnetic material can have a considerable effect on its magnetic characteristics. Alloys of copper with iron show a very low permeability, 1.0000 to 1.0003, in the solution-treated condition. Ageing such material at 400° C causes a considerable increase in permeability as shown in fig. 1. In unworked material iron precipitates in the paramagnetic face-centred-cubic form and the permeability increases as shown in fig. 1b. Working the material causes a transformation from the face-centred to body-centred form, which is ferromagnetic, and permeability varies as shown in fig. 1a. The shape of this curve can be explained theoretically. In very small particles a condition known as superparamagnetism exists [4]. In this condition the particles show very strong paramagnetic behaviour and the permeability increases rapidly as the particles grow. At a critical particle size ferromagnetic domains [5] begin to form. A single domain particle is extremely

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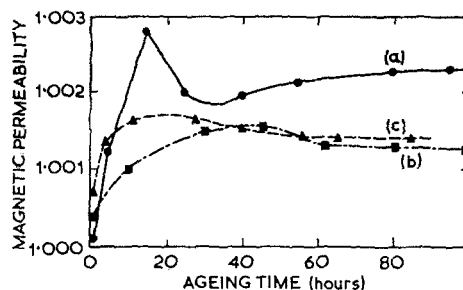


Figure 1 Ageing time/permeability curves for copper-iron alloys (a) 0.195% Fe, solution-treated, cold-worked and aged at 400° C. (b) 0.194% Fe, solution-treated and aged at 400° C. (c) 0.194% Fe, as-cast and aged at 400° C.

difficult to magnetise and the permeability falls sharply. As particle size increases further more domains can form and the permeability increases until a saturation level, dependent on iron content, is reached. The extent of the permeability variation on ageing with iron content is shown in fig. 2. Fig. 3 shows the maximum permeability obtained during the ageing cycle as a function of iron content. Maxima occur at approximately 0.225% iron in both the worked and unworked conditions. In specimens aged from the as-cast state the permeability for short ageing times showed a considerable increase over the solution-treated specimens (fig. 1c).

The effect of cold-work on the permeability of aged copper-iron alloys is shown in fig. 4. In alloys containing more than 0.04% iron cold-work results in a considerable increase in permeability.

The addition to copper of 0.3% cobalt, which

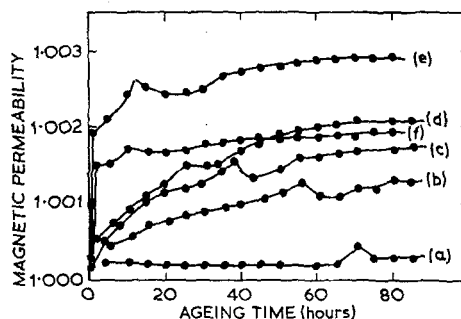


Figure 2 The effect of iron content on the permeability/ageing characteristics of solution treated and cold-worked copper-iron alloys aged at 500° C. (a) 0.01% Fe. (b) 0.04% Fe. (c) 0.08% Fe. (d) 0.13% Fe. (e) 0.22% Fe. (f) 0.23% Fe.

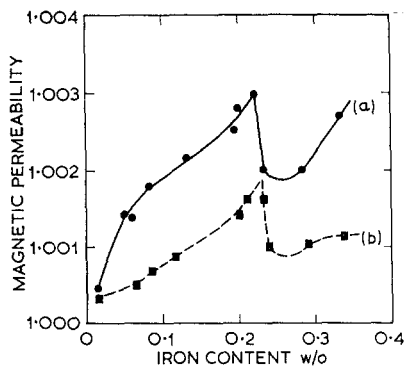


Figure 3 The effect of iron content on the maximum permeability of copper alloys solution-treated and aged in (a) worked and (b) unworked conditions.

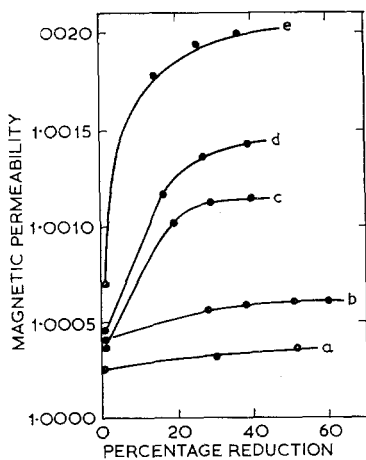


Figure 4 The effect of cold-work on the permeability of aged copper-iron alloys. (a) 0.01% Fe. (b) 0.04% Fe. (c) 0.05% Fe. (d) 0.08% Fe. (e) 0.13% Fe.

is ferromagnetic in both its crystalline forms, results in a permeability increase on ageing similar to that shown by ferromagnetic iron. A permeability maximum of 1.006 is obtained compared with 1.003 for 0.3% iron.

The addition of nickel to copper causes no such large increase in permeability. When nickel is added to copper the spare valency electrons from the copper are taken up by the nickel atoms. Since nickel has 0.6 vacancies in the 3d shell, which are responsible for its magnetic behaviour, it would be expected that up to 40% nickel could be added to copper at room temperature before ferromagnetism is exhibited. The main danger with nickel additions is that the nickel may not be taken fully into solution and localised regions

may exceed 40% nickel with resultant high permeabilities.

The addition of iron to copper-beryllium alloys showed permeability-ageing effects similar to those obtained on addition of cobalt or ferromagnetic iron to copper (fig. 1a). This is because beryllium stabilises the body centred form of iron.

The addition of cobalt and nickel to beryllium-copper causes no increase in permeability. This is because non-magnetic intermetallic compounds of beryllium with cobalt or nickel are formed. The quantity of the intermetallic compound present increases with the amount of cobalt or nickel added. Entwistle and Wynn [6] assumed the compound to be BeCo in the cobalt alloy but electron probe analysis has shown 44% cobalt, 16% copper and 40% beryllium which indicates the likely composition as $Co_{21}Be_5$. Small casts of the beryllium-cobalt intermetallic were made and shown to be paramagnetic with a permeability of 1.0013. However, when such a compound is present as a dilute dispersion in a non-magnetic matrix the overall permeability is very low (1.0002) and up to 2% cobalt has been added to beryllium-copper without increasing this value. (In copper 0.3% cobalt shows a permeability of 1.006.) The permeability of the beryllium-cobalt compound did not increase on cold-work. Additions of small amounts of iron, however, caused a very rapid increase in permeability and appear to cause a reversion to a ferromagnetic state. 0.2% iron, which in copper alone would result in a permeability of 1.0020 to 1.0030, caused the permeability of the compound to increase to 1.0900.

The alpha, beta and gamma phases of copper-beryllium alloys produced from electrolytically pure materials were found to be non-magnetic. Alloys produced from commercial copper-beryllium stock, which contains up to 0.15% iron, showed that although the alpha and gamma phases remained non-magnetic, the beta phase was magnetic with estimated mass susceptibility of 26.6×10^{-6} cgs units.

Specimens of as-cast 2.1 and 2.8% beryllium alloys containing impurity iron (0.07%) were heat-treated at successively decreasing temperatures over the range 800 to 300° C. The same specimen being reheated to a lower temperature after permeability measurements had been made. Figs. 5 and 6 show results for specimens furnace-cooled or quenched from the heat-treatment temperature. Both curves show a marked

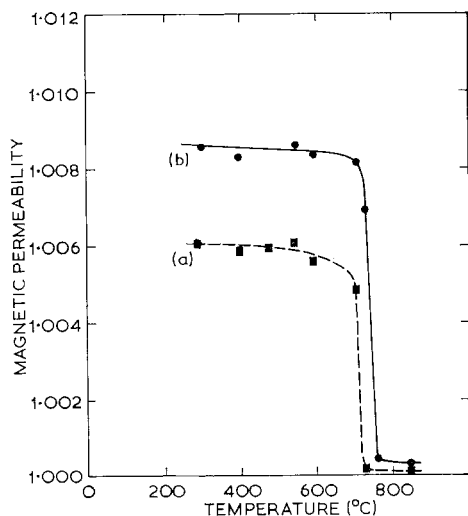


Figure 5 The effect of heat-treatment temperature on the permeability of copper-beryllium alloys which have been furnace-cooled from successively decreasing temperatures (a) Cu-2.1% Be-0.07% Fe. (b) Cu-2.8% Be-0.07% Fe.

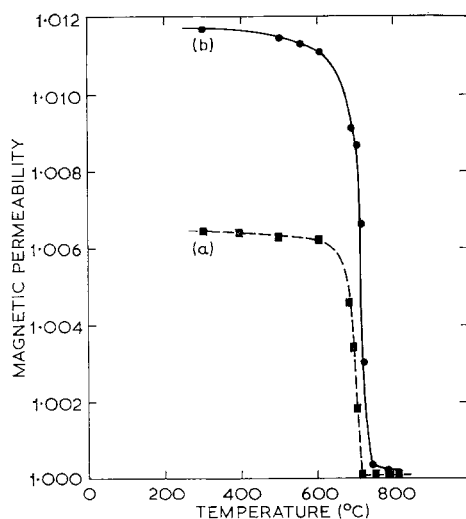


Figure 6 The effect of heat-treatment temperature on the permeability of copper-beryllium alloys quenched from successively decreasing temperatures. (a) Cu-2.1% Be-0.07% Fe. (b) Cu-2.8% Be-0.07% Fe.

increase in permeability as the heat-treatment temperature falls below about 720°C for the 2.1% beryllium and below 760°C for the 2.8% beryllium alloy. These values correspond closely to the reported positions of the alpha to alpha + beta phase boundary [7, 8]. The 2.1% alloy showed an increase in permeability from 1.0002 (when cooled from 750°C) to 1.0065 (when

cooled from 600°C), this corresponds to an increase in the amount of beta phase present of 0.3 to 13%. Reheating at temperatures below 700°C followed by quenching (fig. 6) showed, for the 2.8% beryllium alloy, a higher permeability than did furnace-cooling. Again this higher permeability corresponds to the presence of more beta phase. The reasons for this difference are not clear but may be associated with compositional differences between specimens.

Reheating the same alloys and quenching from progressively higher temperatures (fig. 7) produced a marked increase in permeability above

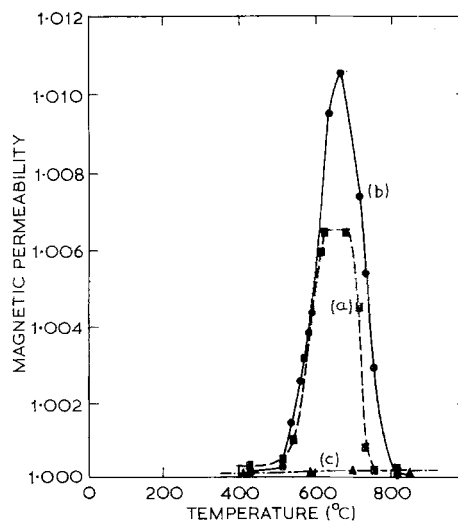


Figure 7 The effect of heat-treatment temperature on the permeability of copper-beryllium alloys which have been quenched from successively increasing temperatures. (a) Cu-2.1% Be-0.07% Fe. (b) Cu-2.8% Be-0.07% Fe. (c) Cu-2.8% Be-2.9% Ni-0.07% Fe.

about 525°C i.e. close to the eutectoid temperature at which the formation of the beta phase can be expected. Reheating to above 675°C lowered the permeability and corresponds to the approximate temperature above which beta would transform to alpha. Up to 600°C both alloys show almost identical changes in permeability. This can be predicted, as the eutectoid transformation temperature is independent of composition. Whereas the 2.1% beryllium alloy shows an increase in permeability at 720°C the corresponding increase in the 2.8% beryllium alloy occurs at 760°C . Again this can be predicted from the equilibrium diagram in which the alpha + beta to alpha transition is composition-dependent.

Specimens of a 2.1% beryllium alloy with < 0.01% iron were given similar treatments to those containing iron. The permeability showed no large increase in the region 720 to 500° C. Thus the data shown in figs. 5 to 7 indicates that the beta phase in the copper-beryllium system is magnetic in the presence of 0.07% iron. The phenomenon is not shown with 0.01% iron and the material remains non-magnetic. The alpha and gamma phases remain non-magnetic with both high and low iron contents.

When the 2.8% beryllium alloy with 0.07% iron was aged at 630° C, subsequent to quenching from 800° C, a high permeability resulted which generally increased with time (fig. 8). This

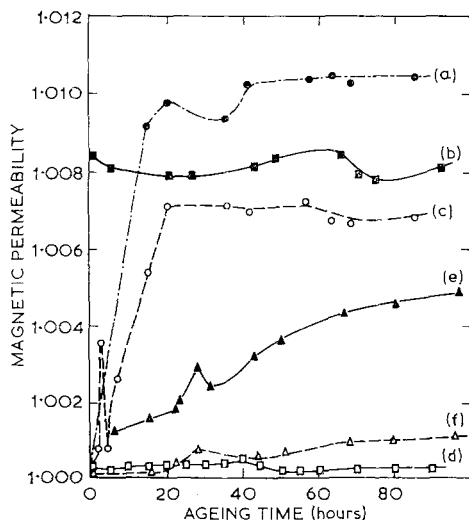


Figure 8 Permeability variations in copper-beryllium alloys aged under differing conditions. (a) Cu-2.8% Be-0.07% Fe aged at 630° C after 800° C quench. (b) Cu-2.8% Be-0.07% Fe aged at 500° C after 630° C quench. (c) Cu-2.1% Be-0.07% Fe aged at 630° C after 800° C quench. (d) Cu-2.1% Be-0.01% Fe aged at 500° C after 800° C quench. (e) Cu-2.1% Be-0.07% Fe, as-cast, aged at 500° C. (f) Cu-2.1% Be-0.07% Fe, solution-treated, aged at 500° C.

corresponds to the expected alpha to alpha + beta transformation at 630° C. Ageing at 500° C, i.e. in the alpha + gamma regions, after prior treatment at 630° C to give the alpha + beta phase resulted in little change with time in a relatively high permeability of 1.008. This suggests that the transformation from alpha + beta to alpha + gamma is very slow at 500° C or that the gamma phase, like beta, has a high magnetic permeability in the presence of iron. Ageing the 2.1% beryllium alloy (0.07% iron), quenched from the alpha condition, at 630° C i.e.

in the alpha + beta phase field, produced a maximum permeability of 1.007 after 20 h. Little further change was observed at up to 90 h. Forging at 500° C of a similar specimen caused a reduction in permeability and it appears that mechanical shock can initiate the beta to gamma transformation. A solution-treated 2.1% beryllium specimen (0.07% iron) aged at 500° C i.e. in the alpha + gamma phase field shows a permeability (curve (f), fig. 8) which is of the same magnitude as an alloy of 0.08% iron in copper. This indicates that the gamma phase is not magnetic in the presence of iron. With 0.01% iron, curve (d) is followed. If the iron containing specimens are aged from the as-cast condition much higher permeabilities of up to 1.004 are indicated. The superparamagnetic peak occurs after similar ageing times and it appears likely that any permeability difference is due to a change in precipitate shape and mode of distribution from the cast to the solution-treated condition. Similar high permeability effects have been noted in the copper-iron and copper-silicon-iron systems.

An incubation period, derived from permeability-ageing curves, of 2 h at 700° C and 3 h at 630° C is normally necessary for the formation of the beta phase. Cooling rates are not, therefore, particularly critical. In practice, material ostensibly rolled in the alpha phase region has given high permeability values. Subsequent annealing at 800° C reduced this permeability to 1.0001. It appears, therefore, that the temperature was allowed to fall into the beta region. The incubation period for the alpha to beta transition is obviously reduced by the introduction of mechanical work.

The addition of nickel or cobalt to copper-beryllium alloys stabilises the alpha phase by effectively reducing the beryllium content of the matrix. A permeability/solution-treatment temperature curve for a copper-3% beryllium-3% nickel alloy is shown in fig. 7. This indicates that no magnetic phase change occurs between 800 and 400° C. A further beneficial effect of the nickel addition has been found by ageing an alloy containing 0.07% iron in the alpha + gamma phase field at 500° C. In both the as-cast and solution-treated conditions the permeability remained low, generally below 1.0003. In the absence of nickel the cast condition may show 1.0040 and the solution-treated condition up to 1.0010 with the same iron content. This is probably due to the fact that nickel widens the

TABLE I

Alloy	Supplier	Composition	Condition	0.1% PS tsi	UTS tsi	EI %	Magnetic permeability
Hidurax Special	a	Cu-2.5% Al-15% Ni-1% Fe	wrought	40	39	14	1.0009
Hidurel 5	a	Cu-2.3% Ni-0.5% Si	wrought		26	30	1.0002
Hidurel 6	a	Cu-Cr	wrought		37	47	1.0002
Hidurel 6	a	Cu-Cr	cast		20	20	1.0002
Hidurax 7	a	Cu-7% Al-2% Si	wrought		40	38	1.0003
Ti 680	b		1 h 805 WQ aged 24 h, 500° C	80	88	18	1.0003
Ti 160	b		annealed 675° C	33	42	33	1.0003
Ti 230	b		hot-rolled and annealed 790° C	32	42	21	1.0003
Ti 230	b		sol'n-treated and aged	37	45	10	1.0003
Ti 318	b		annealed 730° C	58	65	19	1.0003
Ti Ex 700	b		sol'n-treated and aged	79	89	7	1.0003
Berylco 25		Cu-2% Be-0.25% Co	aged from annealed condition	45-50	62-75	5-10	1.0001
Berylco 25		Cu-2% Be-0.25% Cu	aged from hard condition	60-65	75-85	2-6	1.0100

Suppliers (a) Langley Alloys Ltd, Slough; (b) IMI (Kynoch) Ltd.

solid solution phase field of iron in copper, allowing iron to be retained in solution on ageing.

The magnetic permeability of copper-beryllium alloys can therefore be controlled by (a) complete elimination of iron from the alloys and if this is not possible (b) the addition of alpha phase stabilising elements such as nickel or cobalt, and (c) careful control of heat-treatment and working temperatures. All alloy surfaces should be cleaned subsequent to working or machining processes.

3.2. Mechanical Properties

The mechanical properties obtainable with some currently used low magnetic permeability alloys are shown in table I.

The ductility of copper-beryllium alloys in the aged condition is generally very low at 2 to 3% elongation with an 80 tsi tensile strength. Strengths of this level are well in excess of those of the more usual copper-base alloys. Titanium, while showing very good mechanical and corrosion properties, suffers the disadvantages of high cost.

Additions of nickel were first made to copper-beryllium alloys. This stabilises the alpha phase which should improve ductility and stabilise magnetic properties. Nominally 0, 1, 3 or 5% nickel was added to copper-2 or 3% beryllium. Mechanical properties were obtained in the as-cast, wrought and aged (with a standard treatment of 2 h at 300° C) conditions. The results are

TABLE II The mechanical properties of copper-beryllium-nickel alloys

Alloy composition	% Ni	As-cast			Cold-forged			Hot-forged (800° C)			Solution-treated and aged		
		UTS tsi	EI %	VPN	UTS tsi	EI %	VPN	UTS tsi	EI %	VPN	UTS tsi	EI %	VPN
Cu-2.1% Be	0	28	42	193	50	10	268	33	45	168	60	5	435
	1	32	30	199	54	5	300	39	30	218	70	15	341
	2.9	33	35	183	52	8	286	36	34	193	43	33	199
	3.4	30	28	186	50	8	268	32	32	168	33	30	143
Cu-2.8% Be	0	48	23	257	69	7	345	45	30	271	82	5	510
	1.0	39	30	208	58	6	303	47	28	262	81	10	386
	3.9	40	30	199	59	8	341	47	21	257	74	13	393
	3.4	39	28	199	60	6	412	48	22	254	73	13	391

shown in table II. The alloys showed good working properties on both hot- and cold-forging and rolling to in excess of 50% reduction, although the cold-worked alloys containing > 3% nickel showed very slight edge-cracking.

The 3% beryllium alloys were superior to the 2% alloys and showed very promising mechanical properties. Further work was undertaken to optimise the as-aged properties. Age hardening curves were obtained at 250, 300 and 350° C. These are shown in figs. 9 to 11. The curves are unusual in that they show two hardness maxima. This may be due to the superimposition of the age hardening curves for the copper-beryllium system and that for the precipitation of second-

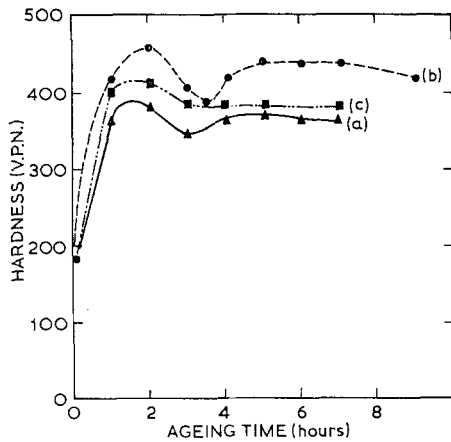


Figure 9 The age-hardening response of an alloy of Cu-2.8% Be-1.0% Ni. (a) Aged at 250° C. (b) Aged at 300° C. (c) Aged at 350° C.

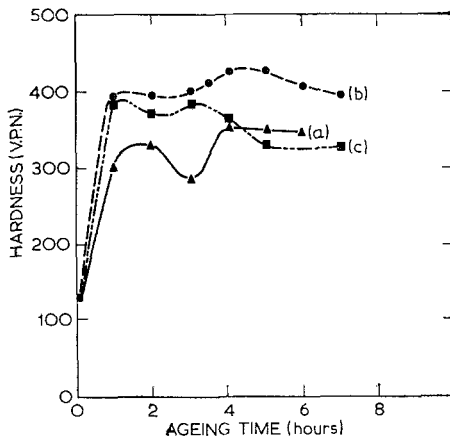


Figure 10 The age-hardening response of an alloy of Cu-2.8% Be-2.8% Ni. (a) Aged at 250° C. (b) Aged at 300° C. (c) Aged at 350° C.

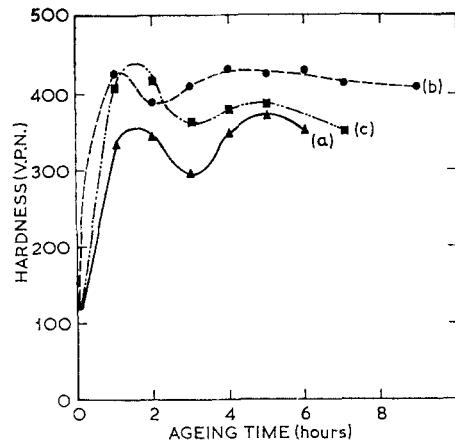


Figure 11 The age-hardening response of an alloy of Cu-2.8% Be-3.4% Ni (a) Aged at 250° C. (b) Aged at 300° C. (c) Aged at 350° C.

ary beryllium-nickel compound. Alloys aged at 300° C showed much better hardening characteristics than those treated at the other temperatures. The relationships between hardness, tensile strength and elongation for alloys aged at 300° C are shown in fig. 12. A strength of 80 tsi with 10% elongation is obtainable in all the alloys. A maximum of 89 tsi with 6% elongation was obtained with the copper-3% beryllium-1% nickel alloy.

In an attempt to improve corrosion resistance 3% aluminium was added to alloys of copper with 3% beryllium and 1 or 3% nickel. The alloy with 3% nickel was found to be superior in mechanical properties to the 1% nickel alloy under all conditions of heat-treatment. The optimum ageing temperature for the copper-3% beryllium-3% nickel-3% aluminium alloy was found to be 400° C and the variation of mechanical properties with hardness in specimens aged at this temperature is shown in fig. 13. The best mechanical properties obtainable with this alloy are shown in table III. The magnetic permeability remained below 1.0003.

4. Conclusions

- (i) Erratic magnetic properties are caused by:
 - (a) the presence of small amounts of iron, which in conjunction with the beta phase of the copper-beryllium system, form a magnetic compound, which exhibits much higher permeabilities than would normally be caused by a similar amount of iron alone, in a copper alloy. This phenomenon may be eliminated by ensuring that the iron

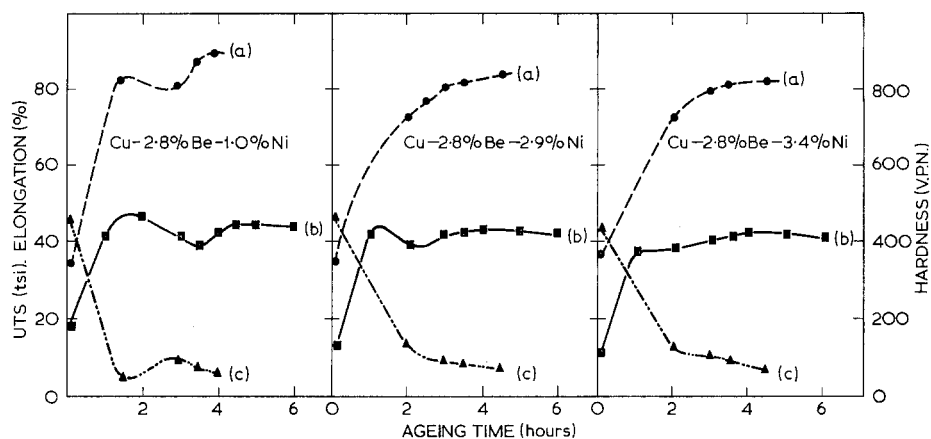


Figure 12 The effect of ageing at 300° C on the tensile strength, elongation and hardness of copper-beryllium-nickel alloys. (a) Tensile strength. (b) Hardness. (c) Elongation.

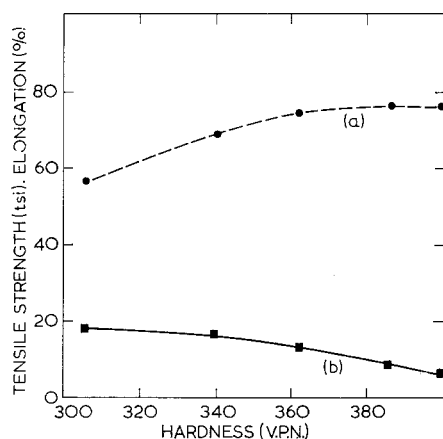


Figure 13 The relationship between hardness, tensile strength and elongation for an alloy of Cu-2.8% Be-2.9% Al-2.7% Ni aged at 400° C. (a) Tensile strength. (b) Elongation.

TABLE III

Alloy	Condition	UTS tsi	0.1% PS tsi	E1 %
Cu-2.8% Be -2.7% Ni 2.9%Al	as-cast	44.0	19.2	41
	hot-rolled 800° C	53.2	38.0	23
	cold-rolled	67.6	54.0	7
	aged to 365 V.P.N	75.0	50.0	13

content of the alloy is kept to below 0.01% by careful choice of raw materials. If this is not possible then the addition of nickel or cobalt to stabilise the alpha phase or careful control of heat-treatment or working temperatures will eliminate the formation of the beta phase.

(b) The presence of iron in the absence of the beta phase in copper-beryllium alloys has an effect on permeability. In the as-cast condition an alloy containing 0.07% iron may show a permeability of 1.0040 on ageing. In the solution-treated condition ageing produces a maximum permeability of 1.0010. A similar alloy with 0.01% iron shows a maximum of 1.0004. This phenomenon may be eliminated by ensuring the absence of iron by using stock of high purity.

(c) Ferromagnetic impurities may be picked up from the rolls or forging hammer during working processes. This effect can be completely eliminated by the removal of the affected surface by abrasion.

(ii) Alloys of copper-beryllium can show stable magnetic properties, even in the presence of impurity levels of iron of up to 0.1%, provided that the alpha phase is stabilised by nickel. Furthermore since fine particles of a nickel-beryllium intermetallic, which is insoluble in the matrix, are produced, the alloy is effectively dispersion-hardened with resultant improved mechanical properties. A normal age-hardening treatment causes further precipitation giving very good high strength properties.

(iii) The addition of aluminium to the copper-beryllium-nickel alloys also shows an improvement in mechanical properties although age-hardening is not as effective as in the alloys not containing aluminium. Ductility is, however, improved.

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