# The influence of aluminium and iron additions on copper-manganese-zinc alloys

H . K . L L O Y D and C . H . O X L E E

MANY alloys in the ternary system Cu-Mn-Zn form the single phase α brass type structure and in particular, the alloys approximating to the composition 70 Cu-20 Mn-10 Zn are sensibly white in colour. These latter alloys also possess mechanical properties and a corrosion resistance comparable with the brasses and nickel silvers. The potential of these alloys as substitutes for the white range of Cu-Ni alloys (nickel silvers) was originally investigated by R. S. Dean et al[1] in 1945 but was not pursued commercially due, it is throught, to the limited output and excessive cost of high purity manganese at the time. Today, it is possible to purchase high purity electrolytic manganese at a price similar to copper. The potential of these alloys as substitutes nickel silver has thus become a more attractive proposition.

The main aim of the present investigation was to evaluate some of the salient properties of the 70 Cu-20 Mn-10 Zn alloys and also to study the effects of separate additions of aluminium and iron as replacement elements for zinc.

## Experimental procedure

The experimental alloys used for the investigation were induction melted from the virgin materials e.g. tough pitch copper, distilled zinc, electrolytic flake manganese, super purity aluminium and Swedish iron (B.I.S.R.A. Ref. : A.P.M.). The alloys were divided into two series depending on whether aluminium or iron was used as the replacement element for zinc. The chemical analyses of the alloys are given in Table I (a)—Aluminium series, and Table I (b)—Iron series.

Some difficulty was experienced initially when casting the alloys due to the tenacious oxides of both manganese and aluminium, but this problem was overcome by using a preheated tundish to reduce turbulence during pouring.[2]

Each melt was cast into a preheated cast iron mould to produce a 4½ lb ingot which was then homogenised for 15 hrs. at 700°C to remove the cored as-cast structure. Following this treatment, the ingots were machined to remove the oxide skin and minor surface defects and then hot-rolled at 700°C to produce individual slabs of various thicknesses suitable for final cold-rolling. In this way, all the alloys were prepared to a standard finished strip thickness of 0·050 in. in either the 20%, 50% or 80% cold-rolled condition. Flat tensile specimens of 0·5 in. gauge width and 2·0 in. gauge length were then prepared from the rolled strip and tested on a Hounsfield Tensometer. Corrosion specimens and other samples for micro-examination and hardness tests were also prepared. The whiteness of each alloy in both series was also established by observation of polished specimens.

In addition, a standard annealing treatment of 1 hr. at 680°C was carried out on cold-rolled specimens of each alloy to establish :

(a) the properties of the alloys in the fully stress-relieved and recrystallised condition,
(b) the effects of aluminium and iron additions on the response of the alloys to heat treatment.

## Constitution of alloys containing aluminium

All the alloys containing up to 4·18% Al consisted of a twinned, single phase α solid solution in the cold-rolled and annealed condition. The 4·28% Al alloy showed the onset of the β (B.C.C.) phase at the α grain boundaries. The 7·38% Al alloy was wholly β, but some α could be retained by quenching from elevated temperatures to appear as a feathery constituent at the β grain boundaries. Confirmation of the above observations was obtained by X-ray studies.

## Constitution of alloys containing iron

While all the alloys containing up to 0·36% Fe again consisted of a single phase α solid solution, it was estimated that the maximum solubility for iron probably occurred around 0·7%. For higher additions (e.g.
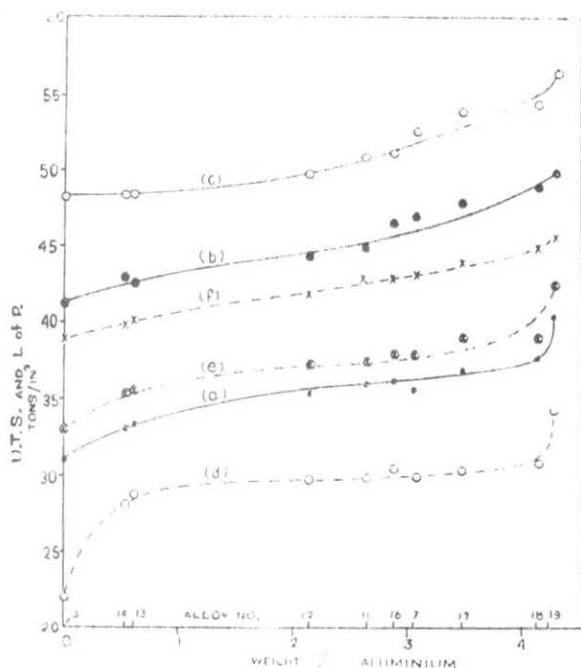
1   *Aluminium Series : U. T. S. values after (a) 20% (b) 50% (c) 80% cold reduction*

  *L. of P. values after (d) 20% (e) 50% (f) 80% cold reduction*
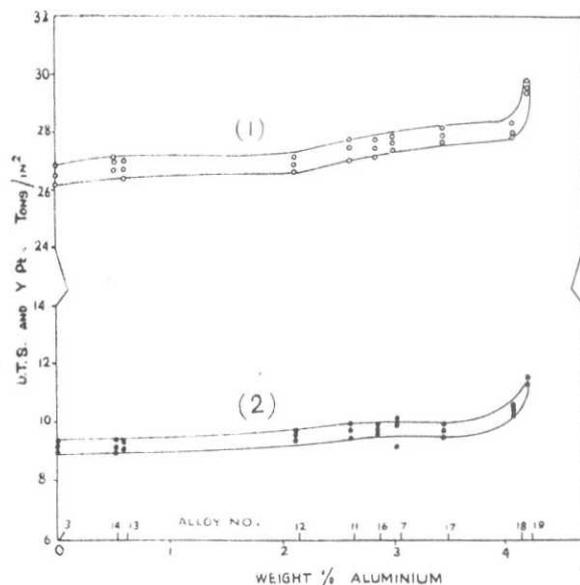


2   *Aluminium Series :*

*Area 1 U. T. S. values for alloys annealed for 1 hr. at 680°C after 20%, 50% or 80% cold reduction*

*Area 2 Y. Pt. values for alloys annealed for 1 hr. at 680°C after 20%, 60% or 80% cold reduction*

0·77% and 1·10% Fe) an iron-rich phase appeared in the form of a random spherical precipitate. This latter phase was similar to that found in other copper alloys with iron additions approximating to 0·75 per cent.[3]

## Mechanical properties

In reporting the following results, it should be borne in mind that the basic composition of the alloys (Table I) necessarily differed for each addition of aluminium or iron. Although the mechanical test results obtained are therefore also subject to the effects of minor variations in Cu, Mn and Zn contents, it was nevertheless possible to observe the following trends in the properties of the alloys as a consequence of the deliberate additions of aluminium or iron.

### 1. Aluminium additions

The effects of aluminium additions on the tensile properties of the cold-worked and annealed alloys are shown graphically in Figs. 1 and 2 respectively.

For the cold-rolled alloys, the addition of increasing quantities of aluminium caused a steady increase in tensile properties up to the onset of the β phase (alloy 19). The wholly β alloy (alloy 8) is not shown here

**TABLE I**   Chemical analysis of experimental alloys

*(a) Aluminium Series*

| Alloy No. | % Cu | % Mn | % Zn | % Fe | % Al |
|---|---|---|---|---|---|
| 3 | 67·1 | 21·7 | 11·20 | Nil | < ·01 |
| 14 | 67·9 | 24·0 | 7·57 | ,, | 0·53 |
| 13 | 67·7 | 22·8 | 8·94 | ,, | 0·56 |
| 12 | 67·7 | 23·5 | 6·66 | ,, | 2·17 |
| 11 | 67·3 | 24·2 | 5·90 | ,, | 2·60 |
| 16 | 69·6 | 21·0 | 6·56 | ,, | 2·84 |
| 7 | 65·8 | 23·6 | 7·65 | ,, | 3·06 |
| 17 | 71·1 | 20·1 | 5·17 | ,, | 3·63 |
| 18 | 72·3 | 19·8 | 3·72 | ,, | 4·18 |
| 19 | 67·8 | 21·5 | 6·42 | ,, | 4·28 |
| 1 | 65·6 | 23·5 | 3·62 | ,, | 7·38 |

*(b) Iron Series*

| Alloy No. | % Cu | % Mn | % Zn | % Fe | % Al |
|---|---|---|---|---|---|
| 3 | 67·1 | 21·7 | 11·20 | Nil | < ·01 |
| 10 | 69·8 | 21·6 | 8·48 | 0·12 | ,, |
| 4 | 67·1 | 22·9 | 9·81 | 0·19 | ,, |
| 6 | 67·2 | 25·3 | 7·24 | 0·26 | ,, |
| 5 | 67·3 | 23·1 | 9·34 | 0·36 | ,, |
| 15 | 71·3 | 20·8 | 7·13 | 0·77 | ,, |
| 2 | 67·7 | 21·9 | 9·30 | 1·10 | ,, |

3  *Aluminium Series : % Elongation values on 2 in. gauge length*

*(a) 20% (b) 50% (c) 80% cold reduction*
*(d) annealed for 1 hr. at 680°C after 20%, 50% or 80% cold reduction*

**TABLE II**  Vickers pyramidal hardness values for alloys containing aluminium

| Heat treatment | Alloy | %Cold work 20 | %Cold work 50 | %Cold work 80 |
|---|---|---|---|---|
| Annealed 1 hr. at 680°C | 3 | 90·2 | 90·2 | 94·0 |
| | 14 | 90·7 | 91·0 | 94·5 |
| | 13 | 91·0 | 91·2 | 94·5 |
| | 12 | 91·7 | 91·8 | 94·8 |
| | 11 | 94·8 | 95·2 | 96·5 |
| | 16 | 94·6 | 96·2 | 96·6 |
| | 7 | 95·4 | 96·5 | 97·0 |
| | 17 | 97·1 | 97·0 | 98·2 |
| | 18 | 98·4 | 98·0 | 99·8 |
| | 19 | 103·0 | 102·0 | 102·0 |
| Annealed 1 hr. at 720°C | 3 | 82·4 | 82·8 | 88·2 |
| | 14 | 85·3 | 85·6 | 89·2 |
| | 13 | 87·5 | 88·0 | 89·5 |
| | 12 | 88·3 | 87·9 | 89·6 |
| | 11 | 88·7 | 88·6 | 92·2 |
| | 16 | 89·4 | 89·0 | 91·8 |
| | 7 | 90·7 | 90·0 | 92·6 |
| | 17 | 92·4 | 92·5 | 94·6 |
| | 18 | 93·5 | 93·8 | 95·0 |
| | 19 | 98·3 | 98·2 | 100·0 |
| Annealed 1 hr. at 760°C | 3 | 78·6 | 78·8 | 80·2 |
| | 14 | 80·4 | 81·0 | 84·3 |
| | 13 | 81·9 | 81·5 | 84·5 |
| | 12 | 84·4 | 84·0 | 86·9 |
| | 11 | 85·0 | 85·3 | 87·8 |
| | 16 | 84·7 | 85·6 | 88·1 |
| | 7 | 86·8 | 86·0 | 89·6 |
| | 17 | 86·7 | 86·8 | 89·8 |
| | 18 | 90·0 | 90·3 | 94·1 |
| | 19 | 97·3 | 97·6 | 100·0 |

since only a limited amount of cold reduction (25%) was possible before serious cracking occurred. In general, however, it can be reported that within the fully α range (alloys 3–18) the presence of aluminium increased the U.T.S. by up to approximately 23% (30·6–37·5 tons/in²) after 20% cold reduction, 19% (41·0–48·8 tons/in²) after 50% cold reduction and 13% (48·0–54·3 tons/in²) after 80% cold reduction. Similar improvements were also obtained for the limit of proportionality values.

The effect of aluminium as a solid solution hardening element in the annealed range of α alloys was not marked. Thus, as will be seen in Fig. 2, the presence of aluminium up to 4·18% only increased the U.T.S. on average from 26·2 to 28·1 tons/in² and the Y.Pt. from 9·2 to 10·4 tons/in². The occurrence of the β phase (alloy 19) caused a marked increase in both of these properties. Although not shown in Fig. 2, it is pertinent to record that the wholly β alloy (alloy 8) had a U.T.S. of 47·4 tons/in² and a Y.Pt. of 7·3 tons/in².

The loss in ductility due to the aluminium additions in both the cold-reduced and annealed alloys is shown in Fig. 3.

Since one of the commercial interests in this series of copper-base alloys could be for stamping or coining operations, it was considered desirable to determine the hardness values of the annealed alloys—Table II. In this connection, it is pertinent to report that the acceptable hardness for alloys undergoing such opera-

tions is between 80 and 90 HV if excessive die wear is to be avoided.[4] Although the hardness of the alloys following the standard annealing treatment at 680°C was higher than this specified range, suitably low values were readily obtained by raising the annealing temperatures to 720°C or 760°C. This reduction in hardness was necessarily associated with a slight increase in grain size. It will also be apparent from Table II that the presence of aluminium did not significantly affect the softening characteristics of the cold-reduced alloys.

## 2. Iron additions

The effects of increasing iron additions on the tensile properties of both the cold-reduced and annealed alloys are shown in Figs. 4 and 5 respectively. The increases in U.T.S., L. of P. and Y.Pt. were steady and no marked change occurred at the onset of the iron-rich phase. Considering the α phase alloys in particular i.e. containing up to approximately 0·7% Fe, the U.T.S. values increased by up to 44% (30·6–44·0 tons/in²) for 20% cold reduction, 17% (41·0–48·0 tons/in²) for 50% cold reduction and 6% (48·0–51·0 tons/in²) for 80% cold reduction. In the annealed condition, the average increase in U.T.S. was from 26·2 to 30·0 tons/in² and for the Y.Pt. 9·2 to 16·0 tons/in².
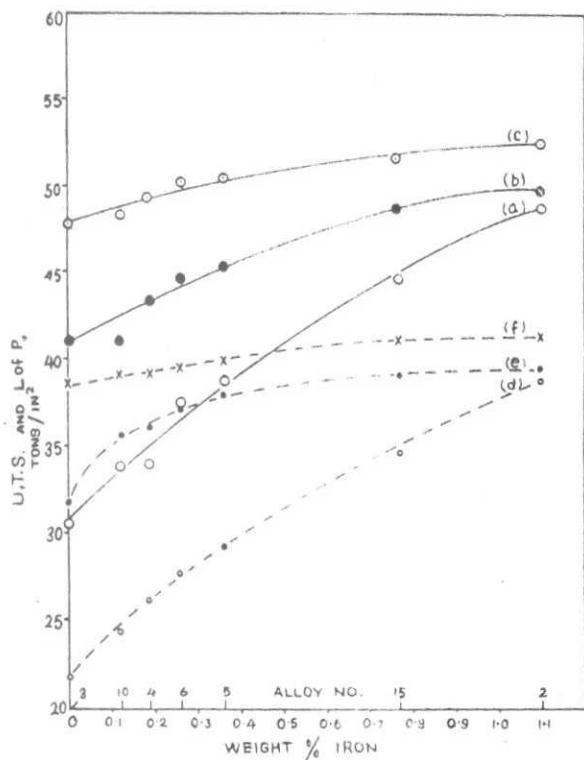
4  *Iron Series : U. T. S. values after (a) 20% (b) 50% (c) 80% cold reduction*

   *L. of P. values after (d) 20% (e) 50% (f) 80% cold reduction*



5  *Iron Series : U. T. S. values for alloys annealed for 1 hr. at 680°C after (a) 20% (b) 50% (c) 80% cold reduction. Y. Pt. values for alloys annealed for 1 hr. at 680°C after (d) 20% (e) 50% (f) 80% cold reduction*

The loss in ductility due to the iron additions in both the cold-reduced and annealed alloys is shown in Fig. 6. When compared with aluminium (Fig. 3), it will be seen that the presence of iron caused a far greater reduction in the ductility of the annealed alloys.

The hardness values of the annealed alloys are given in Table III. Though the hardness values following the

standard annealing treatment (680°C) were again above the optimum range for stamping or coining operations, suitably low values could be obtained for alloys 3, 10 and 4 by raising the annealing temperature to 720°C or 760°C. In this respect however, it was most noticeable that iron additions in excess of 0.2% significantly retarded the softening characteristics of the alloys.

### Corrosion resistance

All the alloys were sensibly white in colour and did not readily tarnish on prolonged exposure to either laboratory or outside atmospheres. It appeared that additions of aluminium enhanced the resistance to tarnishing but, as this behaviour could not be properly assessed, recourse was made to the following accelerated corrosion tests to compare the likely corrosion resistance of both series of prepared alloys.

(a) Static immersion in a 3% saline solution for 84 days.

(b) Salt spray test for 49 days in the following standard solution.

| | |
|---|---|
| NaCl | 26.50 gm. |
| $MgCl_2$ | 2.40 gm. |
| $MgSO_4$ | 3.30 gm. |
| $CaCl_2$ | 1.10 gm. |
| KCl | 0.73 gm. |
| $NaHCO_3$ | 0.20 gm. |
| NaBr | 0.28 gm. |

Water (distilled) to 1 litre.

TABLE III  Vickers Pyramidal Hardness Values for alloys containing iron

| Heat treatment | Alloy | %Cold work 20 | %Cold work 50 | %Cold work 80 |
|---|---|---|---|---|
| Annealed 1 hr. at 680°C | 3 | 90.2 | 90.2 | 94.0 |
| | 10 | 95.6 | 96.5 | 97.4 |
| | 4 | 95.8 | 100.4 | 103.0 |
| | 6 | 99.5 | 104.0 | 105.0 |
| | 5 | 102.5 | 106.0 | 110.0 |
| | 15 | 117.0 | 125.0 | 130.0 |
| Annealed 1 hr. at 720°C | 3 | 82.4 | 82.8 | 88.2 |
| | 10 | 83.6 | 84.2 | 88.4 |
| | 4 | 90.7 | 91.0 | 93.4 |
| | 6 | 101.0 | 102.0 | 104.0 |
| | 5 | 102.0 | 105.0 | 112.0 |
| | 15 | 113.0 | 122.6 | 124.0 |
| Annealed 1 hr. at 760°C | 3 | 78.6 | 78.8 | 80.2 |
| | 10 | 80.3 | 80.2 | 82.7 |
| | 4 | 88.4 | 88.7 | 91.7 |
| | 6 | 99.6 | 99.7 | 102.0 |
| | 5 | 101.8 | 104.3 | 110.0 |
| | 15 | 113.0 | 120.4 | 123.6 |

6 *Iron Series*, %*Elongation values on 2 in. gauge length.*
*(a-c) after (a) 20% (b) 50% (c) 80% cold reduction,*
*(d-f) annealed for 1 hr. at 680°C after (d) 20% (e) 50%*
*(f) 80% cold reduction*
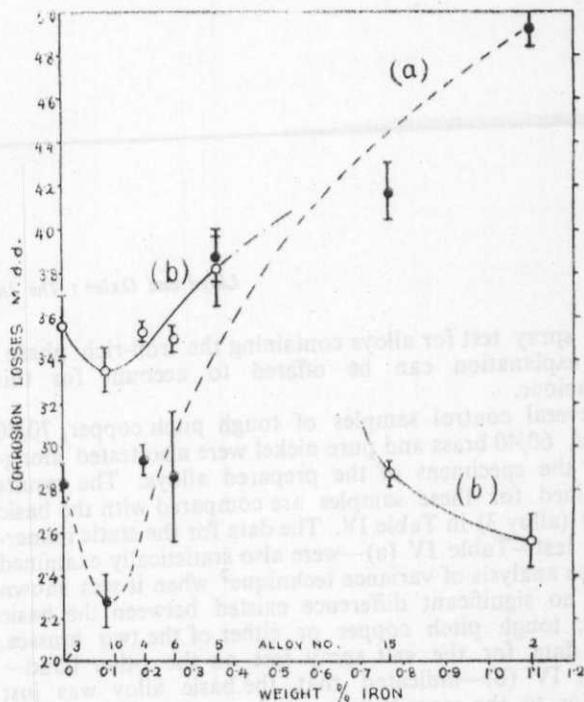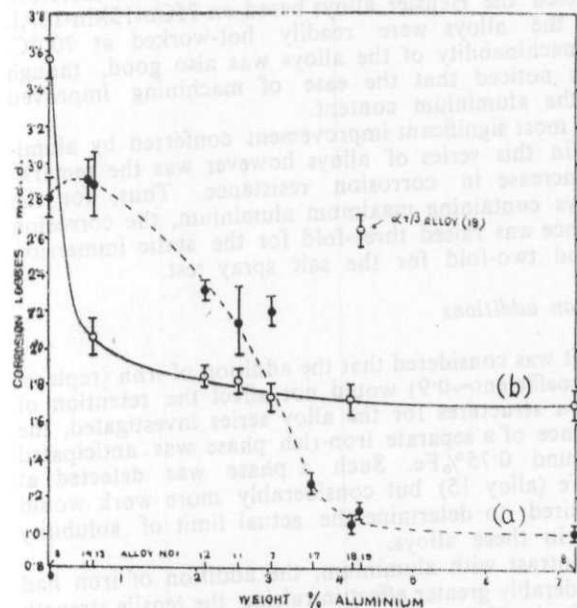


7 *Aluminium Series: Corrosion losses during*
*(a) Static Immersion Test—84 days*
*(b) Salt Spray Test—49 days*

8 *Iron Series: Corrosion losses during*
*(a) Static Immersion Test—84 days*
*(b) Salt Spray Test—49 days*

Several samples of each alloy were prepared from annealed sheets, 0·050 in. thick, and tested under both corrosive environments. On completion of the trials, the specimens were carefully cleaned[2] of all corrosion products and losses in weight determined. The final comparative losses were recorded as milligrams per square decimeter per day (m.d.d.). The mean value obtained together with the positive and negative standard deviations are shown graphically in Figs. 7 and 8.

In the case of aluminium (Fig. 7), it will be seen that the corrosion resistance of the basic alloy (alloy 3) was steadily improved by additions of this element; the improvement being particularly marked in the static immersion test— graph (a). The reduced corrosion resistance of the duplex $\alpha + \beta$ alloy (alloy 19), compared with its near neighbours, was most noticeable following the salt spray test—graph (b). This behaviour was not so prominent in the static immersion test. The difference, it was considered, was probably due to the removal of the corrosion products during the salt spray test by the condensed vapours washing the surface of the specimen and thereby continually exposing the two phase structure to corrosive attack.

With the exception of a slight improvement following a small addition of iron (0·12% Fe in alloy 10), the general effect of this element was detrimental to the corrosion resistance of the basic alloy (Fig. 8). A surprising reversal of this effect was however obtained in the

salt spray test for alloys containing the iron-rich phase ; no explanation can be offered to account for this behaviour.

Several control samples of tough pitch copper, 70/30 brass, 60/40 brass and pure nickel were also tested alongside the specimens of the prepared alloys. The results obtained for these samples are compared with the basic alloy (alloy 3) in Table IV. The data for the static immersion test—Table IV (a)—were also statistically examined by the analysis of variance technique[5] when it was shown that no significant difference existed between the basic alloy, tough pitch copper or either of the two brasses. The data for the salt spray test on the other hand—Table IV (b)—indicated that the basic alloy was just inferior to the same three control samples. As expected, the nickel samples were superior to the four other materials under both conditions of corrosion testing.

**TABLE IV** Comparison of corrosion test results between basic alloy (3) and other control samples

*(a) Static immersion test in a 3% saline solution for 84 days*

| Material | Corrosion losses (Mean) m.d.d. | Standard deviations |
|---|---|---|
| Basic Alloy (3) | 2·82 | ±0·09 |
| T. P. Copper 70/30 | 2·74 | ±0·04 |
| Brass 60/40 | 2·74 | ±0·05 |
| Brass | 2·85 | ±0·02 |
| Pure nickel | 0·42 | ±0·01 |

*(b) Salt-spray test for 49 days*

| Material | Corrosion losses (Mean) m.d.d. | Standard deviations |
|---|---|---|
| Basic Alloy (3) | 3·58 | ±1·2 |
| T. P. Copper 70/30 | 3·43 | ±0·03 |
| Brass 60/40 | 3·08 | ±0·05 |
| Brass | 3·16 | ±0·03 |
| Pure Nickel | 0 81 | ±0·01 |

It was unfortunate that no control samples of a nickel silver alloy could be included in this analysis, but it is well known that the corrosion resistance properties of these alloys are very similar to the α brasses.[6]

## Discussion

### (a) Aluminium additions

The most attractive alloys of the 70Cu-20Mn-10Zn type with aluminium as a replacement element for zinc are the α phase alloys. The maximum replacement appeared to be about 4·2%Al. Bearing in mind the high replacement coefficient of aluminium for zinc (~6%), this result would appear to be in good agreement with the known data for the ternary Cu-Mn-Zn system.

It has been shown that aluminium is a mild solid solution strengthening element and does not greatly alter the response of alloys either to work hardening or thermal softening. This behaviour was considered fortunate since it means that the alloys are particularly suited for heavy reductions by any cold forming technique. The occurrence of the β phase (alloys 19 and 8) caused a marked increase in tensile strength, but the wholly β alloy was not suitable for cold forming. This latter alloy was also ferro-magnetic and therefore resembled the Heusler alloys based on 75Cu-15Mn-10Al.

All the alloys were readily hot-worked at 700°C. The machinability of the alloys was also good, though it was noticed that the ease of machining improved with the aluminium content.

The most significant improvement conferred by aluminium in this series of alloys however was the remarkable increase in corrosion resistance. Thus, for the α alloys containing maximum aluminium, the corrosion resistance was raised three-fold for the static immersion test and two-fold for the salt spray test.

### (b) Iron additions

While it was considered that the addition of iron (replacement coefficient~0·9) would not affect the retention of wholly α structures for the alloy series investigated, the occurrence of a separate iron-rich phase was anticipated at around 0·75%Fe. Such a phase was detected at 0·77%Fe (alloy 15) but considerably more work would be required to determine the actual limit of solubility of iron in these alloys.

In contrast with aluminium, the addition of iron had a considerably greater effect in raising the tensile strength of the basic 70Cu-20Mn-10Zn alloy. Iron also reduced the grain size of the alloys to a far greater extent than aluminium, while a drastic reduction in grain size occurred with the separation of the iron-rich constituent. As a consequence of these latter effects, the presence of iron materially reduced the response of the alloys to thermal softening by restricting the rate of grain growth. Nevertheless, the hardness of the low iron content alloys could be reduced to 90 HV or less by raising the annealing temperature from 680°C to 760°C. For iron contents greater than 0·2% however, the response to heat treatment was insufficient to reach this optimum level.

Once again, all the alloys were readily hot-worked at 700°C. The machinability of the alloys, on the other hand, was inferior to the aluminium series and became noticeably worse when the iron-rich phase was present.

The addition of iron was not attractive from the

viewpoint of corrosion resistance. Thus, with the exception of the unexplained results obtained with the salt spray test, the corrosion resistance of the basic alloy was generally adversely affected.

## Conclusions

1. Alloys of the basic composition 70Cu-20Mn-10Zn, and containing zinc replacement by up to 7·38%Al or 1·1%Fe, are sensibly white in colour.
2. Both aluminium and iron improve the strength of the basic alloy, but iron is far more effective in this capacity.
3. Aluminium additions confer a marked improvement on the corrosion resistance of the basic alloy. Iron · additions on the other hand are generally detrimental.
4. The most attractive alloys for commercial use as substitutes for nickel-silver are the α alloys containing up to 4·18%Al. These alloys possess good resistance to corrosion and tarnishing, are readily machineable and can be softened to a sufficiently low hardness for cold fabrication by stamping or coining.
5. It is anticipated that some difficulty might be experienced when casting these alloys due to the tenacious oxide films of aluminium and manganese.

This problem is not unique however, and has been successfully overcome in the aluminium industry by suitable modifications to the casting procedure, e.g. Durville process.

## References

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