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# SUMMARY

A brief literature study has addressed the effects of impurities on OF copper to which 50 ppm of phosphorus has been added. This copper is the candidate material for the corrosion resistant coating to be applied to the container under development by SKB for the disposal of high level nuclear waste. The levels of impurities expected in this grade of copper and the final use have controlled the focus of the work.

It is concluded that the impurities of greatest importance in the context of the proposed application are sulphur, phosphorus, bismuth and lead.

The addition of 50ppm of phosphorus should ensure very low oxygen content in the copper such that, As, Ni, Mn, Cr, Fe, Sn, Zn, Si, Al, Sb and Cd present as impurities all remain in solution in the copper at all temperatures of interest. In this state they will exert no material effect on the fitness for purpose of the material.

Sulphur is expected to be present in amounts exceeding the solubility limit such that it will occur as grain boundary films or particles. Such segregation can cause embrittlement and it will be more serious as grain size increases. There is no evidence to support the assertion that the phosphorus addition modifies the segregation behaviour of sulphur.

There is evidence that sulphur will combine with V, Zr, or Ti, even when they are present at extremely low levels, but there is no indication of the likely effects of these combinations on the segregation behaviour or embrittling effects.

There is clear evidence that when creep failure occurs by intergranular cracking, sulphur causes the creep strain to fracture to be reduced to less than 1%. The amount of sulphur required for this is very low (i.e. less than the amount permitted in the specification) and dependant on grain size.

The transition from transgranular to intergranular failure in creep is influenced by temperature, stress, grain size, and composition. The addition of phosphorus increases the temperature at which the transition occurs for a given stress.

The available evidence indicates that neither sulphur nor phosphorus is concentrated by a zone refining mechanism during electron beam welding.

Bismuth and lead form low melting point grain boundary films that lead to both hot shortness and cold shortness.

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Table 1 Comparing ASTM and BS specifications on impurity levels with current industrial production

| | ELEMENT ppm | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ALLOY | P | Se | Te | Bi | Sb | As | Sn | Pb | S | Ag | O | Fe | Cd | Mn | Cr | Si | Zn | Co | Hg | Ni | Total impurity ppm |
| Cathode BS 6017 | - | 2 | 2 | 2 | 4 | 5 | - | 5 | 15 | 25 | - | 10 | - | - | - | - | - | - | - | - | 65 |
| Cathode ASTM B115-83a | - | 4 | 2 | 2 | 5 | 5 | 10 | 8 | 25 | 25 | 200 | - | - | - | - | - | - | - | - | - | 90 exc. O |
| Cathode 1 (IMI Walsall)[5] | - | <0.3 | <0.1 | <0.8 | <1.0 | 0.6 | <0.3 | <2.0 | 5 | 13 | - | 4 | 0.1 | 0.2 | <0.5 | 0.5 | <1.5 | <0.5 | - | 1 | 31.4 |
| Cathode 2 Outokumpu[6] | - | <0.2 | <0.1 | 0.5 | 1.4 | 1.2 | - | <1 | 5 | 12 | - | <1 | - | - | - | - | - | - | - | - | |
| OFE-ASTM | 3 | 3 | 2 | 1 | 4 | 5 | 2 | 5 | 15 | 25 | 5 | 10 | 1 | 0.5 | - | - | 1v | - | 1 | 10 | 100 |
| OF Ec (Draft EU Standard)[7] | 3 | 2 | 2 | 2 | 4 | 5 | 2 | 5 | 15 | 25 | a | 10 | 1 | 5 | - | - | 1 | - | - | 10 | 100 |
| PHCEc (Draft EU Standard) | 60 | 2 | 2 | 2 | 4 | 5 | 2 | 5 | 15 | 25 | - | 10 | 1 | 0.5 | - | - | 1 | - | - | 10 | 100 |
| Outokumpu OFE-OK | 1 | 1 | 1 | 0.5 | - | - | 0.5 | 1 | 0.6 | - | 1.5 | - | 0.5 | - | - | - | 0.5 | - | - | - | 30 |
| Outokumpu OF-OK | 10 | 2 | 2 | 2 | 4 | 5 | | 5 | 15 | 25 | 3 | 5 | 1 | | | | | | 1 | | 100 |
| OF (Draft EU Standard) | - | - | - | 5 | - | - | - | 50 | - | - | a | - | - | - | - | - | - | - | - | - | 500 |
| PHC (Draft EU Standard) | 60 | | | 5 | | | | 50 | | | | | | | | | | | - | | 500 |
| HCP (draft EU Standard) | 70 | | | 5 | | | | 50 | | | | | | | | | | | - | | 500 |
| PDO (IMI Walsall) | 213 | <1 | <1 | <1 | 1 | 2 | 2 | 2 | 6 | 11 | | 19 | <1 | <1 | <1 | 1 | <2 | <1 | - | 4 | 270 |

# 1. INTRODUCTION

The canister, which is under development by SKB for the disposal of high-level nuclear waste, has been the subject of detailed study over a number of years[33]. In the present concept it is a composite canister with a load bearing liner of cast iron and corrosion resistant "overpack" or outer vessel which is designed in Oxygen Free (OF) copper to which phosphorus has been added at the level of approximately 50 ppm. The choice of OF-copper is based on the fact that copper is a noble metal of moderate price and tonnage quantities of the OF grade which has a very low impurity content and consistent quality, is produced in normal industrial practice.

The purpose of the phosphorus addition is to increase the recrystallization temperature, to improve creep resistance and in particular to eliminate the effects of a low creep strain to fracture mechanism that was observed in early studies[12].

Table 1, opposite, is taken from reference 32, it gives the specifications for cathode, OF and OF (E) coppers together with the quality which are currently achieved by Outokompu. It is unlikely that Outokompu would be the exclusive supplier for canister production and it seems likely that a specification similar to the PHCEc will finally be adopted. Additional constraints will be applied and these will include Sulphur less than 8ppm, Selenium plus tellurium less than 3ppm and hydrogen less than 0.6ppm[33].

It is important for SKI as the regulator to consider the factors that might influence the lifetime of the canister in its service environment. As part of that process it is necessary to examine the effects of impurities which will be present in the selected material on its mechanical properties and manufacturing performance. This study is part of that process.

It has been necessary to consider literature that has been published over the last seventy years and to be selective in deciding which to use. The writer's judgement on the relevance of the work to the canister problem has guided the selection process. The key papers have been summarised in section 5 and where appropriate, the information provided has been interpreted and its relevance to the canister has been discussed.

In section three the effects of sulphur, phosphorus and oxygen and hydrogen are summarised individually because of their importance to the case in question. The remaining elements are discussed in three groups according to their solubilities in copper.

# 2. THE EFFECTS OF IMPURITIES ON THE PROPERTIES OF OF-COPPER

## 2.1 Phosphorus

Archbutt[1] gives a solid solubility for phosphorus in copper of 0.5% at 200°C. A Cu-$Cu_3P$ eutectic melts at 707°C. and $Cu_3P$ contains 8.27% phosphorus. Smart[4] investigated the effect of phosphorus on an otherwise very pure copper in concentrations of up to 200ppm. He reports that this level of phosphorus remains in solution at all temperatures in the range 300°C to 800°C. Phosphorus in solution decreases conductivity by 0.73% for each 10ppm up to 60 ppm and increases the softening temperature by 110°C for a 60ppm addition.

Smart[4] also reports that phosphorus is used as a deoxidant for electrolytic copper at three levels. (1) just sufficient phosphorus is added for deoxidation so as to have negligible effect on conductivity, or (2) a part of the phosphorus present is in the oxidised condition and the remainder is present to influence conductivity and other properties, or (3) all the phosphorus present is in solid solution and the alloy is essentially free of oxides. Adding oxygen to a phosphorus containing material by diffusion from an oxide scale caused the phosphorus to be converted to an insoluble oxide. He presumes the oxide to be $P_2O_5$ but adds that this has not been demonstrated.

Phillips[16] reports that phosphorus is a very powerful deoxidant which will not co-exist with $Cu_2O$ in the melt, it is presumed that $P_2O_5$ which is formed by reduction of $Cu_2O$ escapes as a gas and the surplus phosphorus remains in the melt.

Punshon[13] has examined electron beam welds in phosphorus bearing OFHC copper for phosphorus segregation. He found no evidence of phosphorus depletion in the welds. This suggests that phosphorus remains in solution and it is not removed during welding by evaporation or zone refining.

Bingley[8] examined electron beam welds in ten grades of copper including 3 PDO, 2 TP, and 2 OFHC. and one high purity material. Gross porosity was usually observed in the roots of partial penetration welds Best results, in this respect, were obtained with super pure material and the worst were obtained with PDO. In this case the defects were attributed to high phosphorus level in the PDO material.

Foulger[14] reports that phosphorus may be instrumental in controlling grain growth in commercial alloys. Kee[15] on the other hand compares PDO and OFHC coppers and reports that whilst phosphorus raises the recrystallization temperature it also promotes grain growth. He explains the raising of the recrystallization temperature through its deoxidising effect, which leaves trace elements in free solution rather than precipitated as oxides. In solid solution they are each able to exert their individual effect on recrystallization temperature. The effect on grain growth is not explained although it might be suggested that the absence of oxide particles in grain boundaries were important. Sundberg[17] refers to the work of others in reviewing the effects of impurities in OF copper. He refers to work reported by Takuno[20] in which Secondary ion mass spectrometry (SIMS) was used to examine OF and PDO and TP coppers for sulphur segregation. Their failure to find segregation in PDO copper (which had 4ppm sulphur) in either the as continuously cast or annealed conditions is interpreted by the authors and by Sundberg as evidence that phosphorus influences the segregation of sulphur in copper. There is no direct evidence to support this assertion.

Henderson[12,22,23] explored the effects of phosphorus on creep ductility of OFHC copper used in the SKB development programme for nuclear waste containers. Her work demonstrates that creep ductility is sensitive to the creep failure mechanism. A so-called creep ductile mechanism which is observed in OFHC at temperatures below

145°C and in OHFC with 50ppm phosphorus added at 215°C. Fracture strains under this mechanism are more than 15%. A creep brittle mechanism, which is observed for OFHC at temperatures exceeding 145°C, is associated with intergranular failure at strains of order 10%. A second brittle intergranular failure mechanism is associated with sulphur segregation to grain boundaries and failure strains of less than 1%. The second brittle mechanism is extremely undesirable in the canister that is under development for disposal of nuclear waste by SKB.

The addition of phosphorus to OFHC copper is shown at least to delay the onset of the creep brittle mechanism with increasing temperature[22]. Following the early work[12] there was speculation[12, 17] that phosphorus in some way interfered with the segregation of sulphur to grain boundaries or with its embrittling effect. The later work demonstrated that the embrittlement is associated with sulphur contents in excess of 6ppm and/or coarse grains. In fact the phosphorus bearing material which had been used in the early work had 6ppm sulphur and fine grains.

A very careful study by Forsberg[30] on material taken from creep studies conducted by Henderson[12, 22,23] concluded that there was no evidence to support a suggestion that phosphorus influenced the segregation of sulphur in OF copper to which 50ppm of phosphorus had been added or that phosphorus segregated to grain boundaries. This is the expected result and the speculation of Sundberg should be rejected.

## 2.2 Sulphur

Smart and co-workers [2,4] consider the solubility of sulphur in otherwise pure copper. They estimate that solubility is 2ppm at 600°C, 10ppm at 700°C and 20ppm at 800°C. Saavarita[24] confirms Smarts figures and adds 25ppm at 850°C and 36ppm at 950°C. He estimates that the solubility at the eutectic temperature of 1067°C is between 64 and 76 ppm. This is consistent with the report by Archbutt[1] that sulphur does not cause hot shortness during rolling, since all the sulphur will be in solid solution at rolling temperature.

Saavarita[24] observed that excess sulphur present in cast materials occurs as $Cu_2S$, which appears as spherical particles in the grain boundaries. These particles redissolve on heating above the solvus and reprecipitate in grain boundaries and grain interiors on subsequent slow cooling. No evidence is provided to support the suggested composition of these particles. Saavarita reports that material with more than 18ppm sulphur is exhibits hot shortness during rolling. The report of Archbutt[1], the results of Smart[4] and the solubility information given above, suggest that this should not happen in homogeneous material, it might be a segregation effect.

Smart[4] demonstrated that the presence of oxygen at saturation level at temperatures up to 800°C had no influence on the solubility of sulphur or the effects of sulphur in solution in the ternary material.

The large change in solubility of sulphur in the temperature range 800°C to ambient indicates that sulphur should dissolve during hot working and reprecipitate during cooling. Punshon[13] provided clear evidence of sulphur rich particles, up to 1µm diameter, precipitated in grain boundaries of parent (hot rolled) material and in welds from the SKB canister program. This material contained 6ppm sulphur.

Material containing sulphur segregated to grain boundaries has been reported to be cold short[1] (susceptible to grain boundary cracking during cold work or under the influence of internal stresses) after welding for instance).

Henderson[12, 22,23] has studied the creep priorities of OFHC copper and OFHC copper with 50ppm of phosphorus added. She has shown that creep failure may be transgranular or intergranular depending on the test temperature, the test stress, the grain size of the material and its composition. For failures occurring by the intergranular process an embrittling mechanism can lead to unacceptably low fracture strains (<1%). This mechanism is associated with segregation of sulphur to grain boundaries it has been observed when the sulphur content is as low as 6ppm. As it is dependent on segregation of sulphur to grain boundaries the critical sulphur level above which it can happen is grain size dependant. There is no evidence of an interaction between sulphur and phosphorus but in the tests that have been conducted on phosphorus bearing materials the transgranular failure process has been favoured over the intergranular failure process.

Smart[2] states that in deoxidised copper it is difficult to develop grain growth after cold rolling and annealing when the material contains more than 3ppm of sulphur whist in sulphur free copper no such difficulty is experienced. Bowyer and Crocker[31] also reported difficulty in achieving grain growth by the strain anneal method in material from the SKB programme. These observations suggest that sulphur have the ability to pin grain boundaries during recrystallization when it is present at very low levels. That requires either oxide particles to combine with sulphur to neutralise its effect on grain size or, elements released by deoxidation to combine with sulphur to provide grain boundary particles that act as pins.

Phillips[16] considers solidification and cooling of alloys containing sulphur, oxygen and hydrogen. He reports serious alloy concentration of sulphur during solidification. In a 5ppm-sulphur material the last material to solidify was 500ppm sulphur, this is well above the eutectic composition.

Myers and Blythe[18] measured the mechanical properties of cast materials containing oxygen and sulphur at various levels and carried out microscopical examination of fracture surfaces. They observed that under all conditions of oxygen content 4ppm of sulphur led to embrittlement at 950°C. Since all the sulphur should be in solid solution in these specimens at equilibrium it must be concluded that the alloy concentration effect reported by Phillips[16] must have been active in these cases and led to gross segregation. Myers[18] also reports the work of Clough and Stein in which Auger spectroscopy had been used to detect significant (12%) levels of sulphur in the grain boundaries of embrittled OF copper with a nominal sulphur content of 12 ppm. These observations on segregation in castings strongly suggest that sulphur should be readily zone refined out of copper.

Myers[18] also refers to the work of Bigelow and Chen which suggests that a low melting point (less than 900°C) Cu-O-S eutectic forms when sulphur levels are as low as 14ppm. This would lead to hot shortness.

The work of Punshon[13] on electron beam welding of phosphorus bearing copper OFHC copper with 6ppm sulphur, reports clear evidence of sulphur segregation to grain boundaries in the parent material and in the weld. Particles in the parent material must have developed during solidification and hot working but those in the weld had formed during cooling from the welding operation indicating a high mobility of sulphur atoms in the copper and a high driving force for precipitation and that zone refining did not occur.

Suzuki et al[21] carried out very careful experiments on an 8ppm atomic (~2ppm by weight) oxygen copper. They demonstrated that trace additions (<10ppm atomic) of transition elements, Titanium, Zirconium or Vanadium combined with residual sulphur in the copper when the sulphur content was 4ppm atomic (2ppm by weight) or less, caused reductions in recrystallization temperatures and in electrical conductivity. They provided evidence of combination of all three elements with sulphur in the melt and of combination between zirconium and titanium with sulphur on annealing at 800°C.

## 2.3 Oxygen

Archbutt[1] reports a copper-oxygen eutectic containing 3.4% oxygen, which forms at1064°C. This of course is a copper-copper oxide eutectic. Solubilities for oxygen in copper of 0.015% at 1050°C and 0.007% at 600°C. with excess oxygen present as $Cu_2O$ are also reported.

Cold shortness was reported in alloys containing 0.02% oxygen and hot shortness was observed at oxygen contents exceeding 0.36%. Consideration of these high oxygen levels is beyond the scope of this work.

Smart[3] confirmed that a very small concentration of oxygen remains in solid solution in otherwise pure copper using conductivity measurements.

The effect on conductivity was however very small. Smart[2] reports that the effects of $Cu_2O$ in copper, is to limit grain growth in the normal annealing temperature range. This is presumably a grain boundary pinning effect. $Cu_2O$ is also reported to adversely affect both hot and cold workability, and to reduce electrical conductivity by 0.126% for each 0.01% of oxygen.

The highest quality OF and OF (E) coppers are produced by remelting of cathode copper in a reducing environment. This is usually by induction melting under a protective graphite surface and is followed by continuous casting through a water-cooled graphite mould. The specifications for these coppers and for the cathode have been summarised in table 1.

Maximum impurity levels in the specification for cathode may be as high as 90ppm excluding oxygen, which may be as high as 200ppm. Total impurity level in the specification for OF and in OF (E) may be as high as 500ppm and 100ppm respectively. In current practice total impurity levels are very much lower than these values Outokumpu claim 100 and 30 ppm for their OF and OF (E) grades respectively. Oxygen levels claimed by Outokompu are 3ppm for OF and 1.5ppm for OF (E). The solubility levels referred to above suggest that these levels of oxygen would certainly be in solid solution at hot working temperatures and probably at cold working temperatures. Oxygen or $Cu_2O$ would certainly cause no negative effects on hot or cold workability. The effect on electrical conductivity would also be small enough to be neglected.

Pops[19] considers commercial material; he points out that the highest quality copper is used by the magnet segment of the wire industry. Grade one cathode is used and oxygen is added to the melt. This reduces the effects of impurities on annealing temperature and workability even when they are present at the levels found in the highest-grade materials. Chia et al25, Yea7, Smets et al27 and Young28 also report this benefit of oxygen.

Smart[2, 4,5,6] and Archbutt[1] have studied the effects of many single elements at impurity levels in copper and the effects of addition of oxygen to the binary alloys. Table 1 below has been compiled from their work.

## Table.2 The effects of oxygen on impurity elements in copper.

| Impurity Element | Effect |
|---|---|
| Arsenic | Soluble at impurity levels at all temperatures[1]. Unaffected by oxygen in ternary alloy[1]. Complex oxides formed in commercial materials, e.g. Forms complex oxide with lead and Bismuth. Beneficial in limiting hot shortness due to Bismuth or Lead. |
| Iron, Tin, Zn, Si, Al | Soluble at all temperatures when present at impurity levels. Is completely converted to oxide at 850°C when oxygen is present. Coarsening of $SnO_2$ particles happens very rapidly. |
| Antimony and Cadmium | Both elements exhibit similar behaviour. Soluble at impurity levels at all temperatures[1]. No effect on hot or cold shortness. Complex behaviour with oxygen. An oxide (probably $Sb_2O_3$) forms below 700°C but rate of reaction is slow, reversion occurs very rapidly at 800°C. A different oxide precipitates at temperatures above 800°C, (probably $Cu_xSb_yO_Z$). The oxide phases have no effect on working properties when Sb levels are within the normal impurity ranges. Sb counteracts the effects of Bi. |
| Bismuth and Lead, | Very low solubility, separate during hot working, cause hot shortness, and cold shortness[1], oxidise below 700°C.[1], As or Sb counteract the effects on hot and cold shortness. Occur as films in grain boundaries[1] |

The behaviour of many elements at impurity levels in copper is modified by the presence of oxygen. Specifically, Iron, Tin, Zinc, Silicon and Aluminium at the impurity levels are all removed from solution as stable oxides when oxygen is present. This eliminates the negative effect of these elements on conductivity and softening temperature and gives some control of grain size during mechanical working due to the presence of the second phase particles.

Antimony and cadmium form at least two oxides that are stable. These oxides occur as precipitates that may be formed or redissolved in specific and different temperature ranges. There are no negative effects of these oxides at the impurity levels and their formation or solution may be controlled by control of heat treatment and mechanical working procedures. Removing Sb and Cd from solution as oxide improves electrical conductivity and the oxide particles may contribute to control of grain growth during annealing after cold work.

Bismuth and Lead both form low melting point films or globules during cooling after casting or mechanical work. Such low melting point phases lead to hot shortness and their low strength leads to cold shortness. These negative effects are much reduced by oxidation and by the formation of complex oxides with other impurities such as Arsenic.

Phillips[16] offers confirmatory evidence for the effects oxygen on iron in solution in the copper and adds that iron oxide is usually uniformly distributed in the copper because when increased oxygen becomes available due the decrease in solubility on solidification iron is oxidised in preference to copper. He also confirms the very slow rate of precipitation of antimony as the oxide by decomposition of $Cu_2O$.

In the grade of copper specified for the overpack material none of these oxidations will occur owing to the high level of deoxidation arising from the phosphorus addition. The effects of Bismuth and lead on hot and cold shortness will be maximised and the benefit of arsenic in reducing their effect will not occur. The formation of oxide particles, which could assist in controlling grain size, will not occur.

## 2.4 Hydrogen

Yea[7] has examined the number of wire breaks per ton of material processed for coppers at a range of oxygen contents by examination of production records. The relationship shows a clear minimum at 380ppm oxygen. The material was tough pitch copper and the range of oxygen contents was from 150ppm to 600ppm. Yea attributes the wire breaks to the presence of oxide particles and to the presence of porosity caused by the steam reaction. The reason for the minimum is unclear.

Harper[9, 10] studied embrittlement in OFHC copper and TP copper with oxygen contents of <1ppm and >200ppm oxygen respectively. He demonstrated that all tough pitch coppers were embrittled by heat treatment in a hydrogen atmosphere at temperatures up to 400°C. The embrittlement was much more rapid at temperatures exceeding 374°C, the critical temperature for steam formation in copper. At temperatures up to 650°C the rate controlling step for embrittlement was absorbtion of hydrogen at the surface whilst at 700°C the rate controlling step was diffusion of oxygen in the copper. It was demonstrated that the hydrogen embrittling reaction could not be induced in OF coppers.

## 2.5 Elements that are soluble at all temperatures when present at impurity levels.

Arsenic[1,2,4], silver[1,2,6], nickel[1,2,5], manganese[21], chromium[21], iron[1,2,5,16,21], tin[1,2,6], zinc[1,2], silicon[1,2,], aluminium[1,2], antimony[1,2,6] and cadmium[1,2,6] are all soluble at impurity levels at all temperatures of interest when present in binary alloys. Information on the cases where they are present in combination is limited but their effects on conductivity and annealing behaviour are not additive. Whilst it is possible that they may be concentrated by zone refining, the observations by Punshon[13] strongly suggest that the conditions in electron beam welding are not conducive to zone refining. It seems very likely that effects due to these elements in canister material will be undetectable.

## 2.6 Elements that have limited solubility when present at impurity levels.

Sulphur[1,2,4,16] selenium[1.2,4,16] and tellurium[1,2,4,16] all have rapidly decreasing solubility with decreasing temperature. They all form $Cu_2X$ phases when they are rejected from solid solution. These phases tend to concentrate in grain boundaries and cause embrittlement. The specific effects of sulphur have been dealt with in section 2.2. Whilst there is no specific statement in the literature examined that selenium and tellurium have similar behaviour, it is reasonable to suppose that they will. However the levels of selenium and tellurium are much lower and closer to their solubility limits in the specifications and in commercial materials. Their effects on ductility will therefore be much less apparent. There is no information relating to additive effects

from these elements when they are present together. Pops[16] reports that they form further intermetallic compounds such as $Ag_2Se$, PbSe, and PbS.
The effects of sulphur in canister material have been referred to above, and their magnitude is grain size dependent. Selenium and tellurium contents are not likely to significantly exceed solubility limits and therefore they would not be expected to have a grain size sensitive effect.

## 2.7 Elements which are insoluble in copper through the hot and cold working ranges

Bismuth[1,2,26,14,15] and lead[1,2,14,27] are both separate from copper during hot working. Smart[2] gives solubilities of 100 and 400ppm for bismuth and lead respectively at 800°C but adds that this reduces almost to zero at 500°C. Both separate as low melting point films in grain boundaries and lead to hot and cold shortness. Their effects are more serious as grain size increases.

# 3. CONCLUSIONS

1. The impurity elements most likely to influence the working and durability properties of the OFP alloy selected by SKB for the corrosion resistant liner of the disposal canister for high level nuclear waste are, sulphur phosphorus bismuth and lead.
2. The addition of approximately 50ppm phosphorus to the otherwise OF material ensures very low oxygen content in the product.
3. Arsenic, nickel, manganese, chromium, iron, tin, zinc, silicon, aluminium, antimony and cadmium may all be present as impurities but the levels will be below the solubility limit at all temperatures of interest. The absence of oxygen will ensure that they remain in solid solution. Their presence in solid solution should not have any effect on properties that are important during production or service.
4. Sulphur, selenium and tellurium may all be present in amounts that are soluble at high metal working temperatures but insoluble at service temperatures. They all separate as grain boundary particles or films that cause embrittlement.
5. A constraint is applied on the specified levels for selenium and tellurium at <3ppm max. combined. This should ensure that their effects are negligible.
6. The constraint on sulphur content <8ppm is well above the solubility limit and it will not prevent segregation of sulphur to grain boundaries. Such segregation will cause embrittlement under certain conditions. The seriousness of this segregation will increase with increasing grain size.
7. There is some evidence that sulphur will combine with other impurities such as vanadium, zirconium or titanium even when it is present at very low (2ppm) levels.
8. The available evidence suggests that the addition of phosphorus have no influence on the mode of segregation of sulphur.
9. There is clear evidence that at 215°C and under specific stress conditions 50ppm phosphorus causes a transgranular rather than an intergranular creep failure mechanism to be favoured in the fine grained OF material. The intergranular mechanism can, in the presence of sulphur, lead to unacceptable creep strain to fracture levels. This effect is accentuated in coarse-grained material.
10. Bismuth and lead both have very low solubility at metal working temperatures and both separate as low melting point grain boundary films. In this state they may be responsible for hot and cold shortness.

11. Whilst sulphur and phosphorus may be removed from copper by zone refining, the evidence suggests that conditions which apply in electron beam welding of copper are not conducive to zone refining and neither element is concentrated by the process.

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# 5. REFERENCE SUMMARIES

5.1. Archbutt et al Effects of impurities in copper British non ferrous metals research association Monograph 1937

This is regarded as the classic work on the subject even though it is sixty-three years old. It summarises the results of a large body of work conducted by scientists working in the fifty years before its publication together with work conducted by the authors starting in 1921, that is before production of OF copper without deoxidisers was commercially realised. The authors combine controlled scientific method in their experiments with a practical awareness of the significance of the experiments to products prepared in an industrial environment. In their own work they considered the effects of eight elements (O, Fe, Bi, As, Sb, Ni, Pb, P) used one at a time, six pairs of elements (As-O, Bi-As, Bi-O, Ni-O, Pb-O, As-Sb, Bi-Sb), three groups of three elements (Bi-As- O, Ni-Sb-O, Ni-As-O), one group of four elements (Bi-Ni-Sb-O) and one group of seven elements (Pb-Bi-Sb-As-Ni- Fe-O). In their discussion they compared their own results with results reported by other workers. Their interest was in alloys of copper or copper with impurity levels that were significantly higher than are of interest in this work and was mainly directed to rolling behaviour and mechanical properties. With this in mind the following notes are prepared in a highly selective way from their text.

Their material was prepared from selected cathodes, crucible melting was used throughout with very careful control of melting and alloying. They start with a gas-fired furnace and progressing to a vacuum induction furnace. Hot rolling was at 850 to 900°C with annealing at 700°C for 30 minutes followed by air-cooling. Hot rolled material was pickled using 30% nitric acid before cold rolling to 5/8 in diameter bar. Certain alloys were cold rolled as cast, cropped top and bottom, annealed at 850°C for 1hour in air, surface machined to1.11/32 inches diameter and cold rolled to 5/8 inches in 20 passes. Strip was produced by flattening with the hammer followed by cold rolling.

The analysis of the cathodes used was according to the table overleaf.

The copper content of untreated cathodes of that time was between 99.92% and 99.97 %

OFHC of that time was 99.98 % copper

The effects of each element and some combinations are detailed below.

## OXYGEN

Present as $Cu_2O$ when the solubility limit is exceeded.

0.015% soluble at 1050°C, & 0.007 at 600°C, eutectic contains 3.4% $Cu_2O$ and melts at 1064°C.

Analysis of cathodes used as stock material

| | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Oxygen ppm | 166 | 88 | 143 | 40 | 100 | 60 |
| Iron ppm | 42 | 69 | 38 | T | 30 | 20 |
| Nickel ppm | T | T | T | nil | - | - |
| Sulphur ppm | - | - | - | nil | 0 | - |
| Lead ppm | - | - | - | - | 40 | T |

Hampe showed increasing oxygen makes copper first cold short 0.02 % then hot short 0.36%.
In general modest additions of oxygen improved mechanical properties but some reduction of toughness and fatigue strength was noted for contents exceeding 0.016 %
In castings increasing oxygen content to 0.36% led to increases in density owing to reduction in hydrogen content and consequent reaction unsoundness.
During fire-refining, overpoling reduces oxygen level so far that, (1) it no longer has any beneficial effect due to oxidation of Bismuth and other deleterious impurities and (2) the hydrogen level rises leading to reaction unsoundness.

## HYDROGEN

Leads to unsoundness due to reduction in solubility at the melting point during cooling.
When oxygen is present leads to reaction unsoundness after solidification.

## SULPHUR

Causes cold shortness at the level of 0.05%
Far from hot short at 0.5%

## IRON

Solubility at 800°C close to 0.3% and rises very rapidly with temperature, does not age harden probably due to excessive grain growth which occurs during solution treatment. Additions of iron up to 2 % are generally beneficial to mechanical properties.

## PHOSPHORUS

Added as deoxidant
$Cu_3P$ formed as a eutectic melts at 707°C contains 8.27% P
Solubility 0.5% at 200°C
Generally beneficial effect on mechanical properties little age hardening effect.

## SILICON

6.7% soluble at 750°C
4.0% soluble at 400°C

## BISMUTH

Present in many ores, difficult to remove, insoluble, forms films in grain boundaries, low melting point 271°C causes hot shortness.

Early workers found 200 ppm causes hot shortness and 500 ppm causes cold shortness

Roberts and Austen showed that 20 ppm had a damaging effect on strain to fracture.

Johnson noted 100ppm affected malleability at red heat.

Hampe found that Bi is not so detrimental if oxygen is present.

NPL investigation showed solubility less than 20 ppm at 980°C.

With minor amounts of oxygen present (1120-210 ppm) 90 ppm caused hot shortness and cold shortness

20 ppm caused poor mechanical properties after cold rolling from cast state, presumably because no redistribution of Bi occurred as a result of hot work

In hot/cold rolled material 100 ppm appeared to have no adverse effect

## LEAD

Insoluble in solid copper.

Appears as films or globules, similar in effect to Bismuth but not so severe.

NPL work indicated 10 times as much lead required bringing about the same effect as Bismuth-though the reason for this is not clear.

Hampe found that hot shortness did not occur until the level of lead reached 0.3% 0.4% and above was very hot short and cold short.

Oxygen alleviated the effects of lead even at these levels.

Johnson found hot shortness at 0.18% lead after considerable poling.

He states that 0.1% lead in the absence of oxygen makes copper unworkable but it is harmless in tough pitch copper containing arsenic at the 0.3 % level. Indications point to a benefit on the effect of lead if both oxygen and arsenic are present suggesting that the combined arsenic lead oxide is less of a problem than lead oxide and that even lead oxide is a problem.

NPL work used cathode containing 180 ppm oxygen 1000 ppm oxygen and a tough pitch analysis with 900 ppm oxygen for manufacture of lead bearing alloys,

Hot rolling was light but 920 ppm lead with 90 ppm or 130 ppm oxygen was OK.0.2% lead alone was hot short

Lead reacted with cuprous oxide to reduce the effects of $CuO_2$ on toughness; such alloys are cold short however.

## ARSENIC

Soluble at the level of 7.25% at 650°C. No damaging effects on workability hot or cold.

Can neutralise the effects of bismuth

## ANTIMONY

Soluble in solid copper up to 10% at 450°C. 0.1% does not impair hot or cold working properties, when oxygen is available this level increases to at least 0.3%, higher levels lead to hot shortness.

Suggested that antimony additions at the appropriate level may be used to offset the adverse effects of bismuth and, that Sb is more potent than As in this respect but if used in large quantities will itself cause hot shortness.

Oxygen combines with Sb and reduces hot shortness and Sb reduces the cold shortness, which arises from high oxygen contents. Can be used together with arsenic to reduce the effects of bismuth

NICKEL

Complete solid and liquid solubility. Combines with antimony and eliminates its beneficial effect with respect to bismuth

SILVER

Soluble at 8% level at eutectic temperature of 778.5°C falls to zero at ambient temperature.

## 5.2 J S Smart Jr. The effects of impurities in copper, Butts A (Ed) Copper, Rheinhold Publishing Corp NY 1954 Ch 19 pp410

Sb and Cd oxides are unstable above 700ºC thermal histories below 700ºC are such that they remain partially in solution. Bi behaves in a similar way but the temperature of oxide stability is not given. In oxygen free coppers the rate of decrease in conductivity for individual impurities with impurity level is higher than for oxygen bearing coppers. This is simply the result of oxidation and precipitation of oxides on the residual levels in solution.

Ag, As, Ni, Se, Te, and S do not form stable oxides when they are present at less than 0.05% (i.e. 500ppm which is far above the concentration of interest to SKI). Se, Te and S have very limited solubility above 650ºC but they will stay in solution on rapid cooling from above this temperature. However rapid cooling in this range will not be achieved in the components of interest to SKI. Retention of impurities in solution by quenching increases the softening temperature of rolled products during subsequent annealing. Similarly oxygen free material will have a higher softening temperature due retention of impurities in solution rather than precipitation as oxides.

Grain growth in high purity coppers occurs readily with increasing annealing temperatures but usually a non-uniform grain size is produced. In oxygen bearing (TP) coppers grain growth is very limited at normal annealing temperatures owing to the effects of $Cu_2O$ particles. Deoxidised or OF commercial coppers with limited amounts of impurity precipitates behave more like high purity copper but they produce a more uniform grain size on annealing. This picture is clouded however by the statement that, “the observations are only valid for products which are deoxidised by practice which was normal at that time” (1954) and that, “ if such material were melted and solidified under extraordinary reducing conditions, such as may be achieved by prolonged contact of the molten metal within a closed graphite system, grain growth may be almost completely inhibited, even at annealing temperatures in excess of 800ºC”. First we have a picture in which reducing oxygen content leads the material to behave like an high purity copper which is susceptible to grain growth and subsequently we have a statement that conditions which are highly reducing during holding in the molten state lead to inhibition of grain growth. Smart adds that this inhibition only occurs in the presence of sulphur and it is not affected by other impurities when they are present in normal amounts.

In 1954 when the paper was written the continuous casting process for copper had not been developed in commercial operations. Now it is almost universally used and it usually uses a graphite mould. Thus for large slabs or ingots a condition of contact with a reducing environment whilst molten is employed. The product might therefore be resistant grain growth after annealing. Our experience (Bowyer and Crocker 1996[31]) is that grain growth was almost impossible to achieve by cold work and annealing of plate material taken from the SKB programme, however hot rolled material almost invariably exhibits a coarse and mixed grain size in the section sizes used by SKB. Material of similar composition extruded (at 600-650ºC) to 50mm bar for tube production exhibits a uniform fine grain size and tubulars produced by SKB with 50mm wall thickness also have uniform fine grains.

The development fine uniform grains in an almost pure hot worked material by using a high degree of reduction and a controlled working temperature is easy to understand. The difficulty of implementing this approach to the canister problem by hot rolling and relative ease of implementing it by extrusion is also well understood. The observed difficulty in development of controlled large grain sizes by cold working and annealing[31], is consistent with the observation reported by Smart for a heavily deoxidised material. It suggests that grain boundary energy is low or that grain boundaries are strongly pinned. Smart states that difficulty in developing grain growth in the cold rolled and annealed material does not occur in sulphur free copper, it does occur when the sulphur content exceeds 3ppm and it is not influenced by other impurities when they are at normal levels. This suggests that in heavily deoxidised material, such as that used in the SKB programme, sulphur at the very low level of 3ppm is capable of diffusing to and pinning grain boundaries during recrystallization. Other impurity elements do not have that capability when they are present at normal levels.

The decline in the effectiveness of other elements with reducing oxygen could be a solution effect but it is implicit in the report that sulphur only becomes effective in controlling grain growth when the oxygen levels are very low. This suggests, either,

1. that the sulphur becomes effective at pinning grain boundaries only when other impurities are available in solution (that is not associated with oxygen), or
2. that the effect of sulphur in pinning grain boundaries is inhibited by the presence of oxygen and other impurities, or
3. that the effect of sulphur is inhibited by the presence of oxygen alone.

The latter option is rejected because sulphur does not compete for oxygen with other impurities in solution. The inhibition of the effect of sulphur by the presence of oxygen and other elements requires that some form or forms of oxy-sulphide forms to tie up the sulphur. The first option requires a direct association of sulphur and one or more impurity elements, which may be released by deoxidation, to form grain boundary particles. That is to say either oxide particles combine with sulphur to neutralise its effect on grain size or, elements released by deoxidation combine with sulphur to provide grain boundary particles which act as pins.

All this could be consistent except that the earlier observation that reducing oxygen content causes grain growth during annealing after cold work to occur more readily. This reported increasing ease of grain growth occurs as the oxygen content declines but in the presence of sulphur and the other low-level impurities. It is suggested by Smart that the presence of the low level of oxygen together with other impurities leads to some degree of grain boundary pinning by oxide particles and that this explains why such materials develop a more uniform grain size than pure copper during annealing after cold work. This is a realistic interpretation of the observations but the added observation on heavily deoxidised material suggests that there is a grain boundary pinning effect of sulphur that is inhibited by the combined effects of oxygen and other impurities.

The observations on material used for the canister suggest that they are most compatible with the heavily deoxidised material described by Smart and that sulphur has an important role in pinning of grain boundaries. There is nothing to suggest that this mechanism operate during hot working when the sulphur would be in solution.

Ag, Au, Ni and As are soluble irrespective of oxygen content when present as impurities.

Cd and Sb will partially oxidise and precipitate at temperatures below 700°C. Have no effects on hot or cold workability when in the impurity levels.

Fe, Sn, Zn, P, Si and Al soluble but form stable oxides in the presence of oxygen. Have no deleterious effect on workability.

Se, Te, S and $O_2$ form $Cu_2x$ compounds, which are generally brittle. Decrease hot and cold workability.

Bi and Pb very low solubility, in OF copper, separate during hot working when at impurity levels. Solubility at 800°C, 100 and 400 ppm respectively but negligible at 500°C. Cause serious hot working problems unless well below solubility limits. Bi forms grain boundary films that are embrittling. Embrittling effect depends on grain size and thermal history. Practical limit for Bi in OF copper 20 ppm. Effects of Bi are alleviated by additions of P, Cd and Sn.

Safe limit for lead in OF copper is given as 200ppm, as it separates as globules. Globules are good for machinability. Both Bi and Pb form oxides below 700°C. And oxides are less harmful than the elemental material.

## 5.3 Smart JS, Jr et al. Preparation and some properties of high purity copper. Trans AIMME. 143, 272 (1941).

This paper describes the preparation and some properties of copper, which was prepared in order that,

1. no impurity would be present in an amount sufficient to have a detectable effect on the properties studied, and
2. Even the minor effects caused by the addition of extremely small amounts of individual elements could be measured without significant interference from contaminants.

A three-step purification process is described. Step 1 involves electrolysis through a purified $CuSO_4$-$H_2SO_4$ electrolyte, this removes all impurities except Sulphur. The second step removes Sulphur by surface blowing molten metal in a clay/graphite crucible using induction heating. The melt from this stage is cast in the form of anodes for step 3. Step 3 is electrolysis through a purified $Cu\ (NO_3)_2$ solution to remove contaminants picked up during blowing. Nitrates present after stage 3 are removed by remelting under nitrogen in a high purity graphite crucible, oxygen bearing casts were directly cast through air into graphite crucibles but oxygen free casts were made by continuous casting through a graphite die (in 1942). State of the art spectrographic methods of that time indicated that none of the impurities which could be spectrographically detected were present above the 1ppm level.

Oxygen free material was remelted with small additions of $SiO_2$ and it is claimed that the $SiO_2$ was reduced and that Si entered solid solution to form an alloy. The same alloy removed oxygen from commercially pure hydrogen at 850°°C by formation and precipitation of $SiO_2$ in the copper. At the same temperature, hydrogen removes oxygen from otherwise pure copper. The authors give this as evidence that the nominally oxygen free material really was oxygen free. Whilst they are unable to give the exact levels of purity of this material owing to the recognised limitations of analytical methods, no impurities were detected and they claimed less than 10ppm total. This claim appears modest in the light of the evidence presented.

As cast high purity material was reported to be too coarse grained for many applications but capable of withstanding an unlimited amount of cold work. Intermediate anneals during drawing schedules enabled grain refinement to be achieved. Variation of annealing temperature between 300ºC and 800ºC had no effect on properties other than grain size.

Oxygen bearing rod of otherwise nominally pure copper were prepared by allowing the oxygen free material to absorb oxygen by diffusion, to the point of saturation at 850ºC. Conductivity measurements on wires drawn from the rods indicated that oxygen in solution does cause a slight reduction in conductivity. The magnitude of the effect was small and correlation of the amount of oxygen in solution with the magnitude of the reduction in conductivity was not possible. The significance of this observation is that in almost all other works on the effects of oxygen an increase in conductivity is reported. The reason for the increase is usually attributed to removal of other impurities from solution by oxidation and precipitation.

## 5.4 Smart JS, Jr et al. Effects of Phosphorus, arsenic, sulphur, and selenium on some properties of high purity copper Trans AIMME. 1166, pp144 (1946).

Phosphorus is added to many coppers as a deoxidant. If an excess of phosphorus is added over and above that required for deoxidation the residue enters solid solution and has the effect among other things of reducing conductivity. Alloys are produced from electrolytic copper in which,

1. just sufficient phosphorus is added for deoxidation so that there is a negligible effect on conductivity,
2. a part of the phosphorus present is in the oxidised condition and a remainder is in order to influence conductivity and other properties, and
3. All the phosphorus present is in solid solution and the alloy is essentially free of oxides.

Up to 60ppm phosphorus reduces conductivity at a rate of 0.73% per 10ppm. Similarly 60ppm of phosphorus increases the softening temperature by 110ºC. The authors results indicate that all the phosphorus in their experimental range (up to 200ppm is taken into solid solution and remains in solution after cold work and annealing at all temperatures in the range 300ºC to 800ºC. Addition of oxygen to all alloys by diffusion from an oxide scale was effective in converting all the phosphorus in solution to an insoluble oxide and completely restoring the conductivity and softening temperature properties to those of pure copper. The oxide has been presumed to be $P_2O_5$ but this has not been demonstrated.

The properties of alloys containing up to 465ppm Arsenic, with and without oxygen were compared. For material cold worked and annealed for 30 minutes at temperatures in the range 300ºC to 800ºC annealing temperature had no effect on measured conductivity. Conductivity was continually reduced and softening temperature was continually increased by increasing As content within the range examined. Addition of oxygen to these alloys had no effect on either conductivity or softening temperature. These results indicate that As is soluble up to the highest composition examined for all temperatures in the range. Further they indicate that the

As is unaffected by the presence of oxygen in the ternary copper alloys in the composition range explored. The authors are careful to point out that there is no reaction between As and oxygen in the ternary alloys, however it is known that complex oxides may be formed in commercial alloys. For example addition of lead to arsenical copper leads to the formation of a complex oxide containing arsenic.

The effects of sulphur contents in the range zero to 100ppm were examined in oxygen free and oxygen bearing materials. The results suggest solubility for sulphur in oxygen free material of less than 3ppm at 600ºC and amounts of sulphur in excess of the solubility limit form $Cu_2S$. At temperatures of 700ºC and 800ºC the solubility of copper for sulphur exceeds 3ppm. The presence of oxygen at saturation level has no effect on the sulphur. The authors estimate that solid solubility of sulphur in copper might be 2ppm at 600ºC, 10ppm at 700ºC and 200ppm at 800ºC.

Oxygen free and oxygen bearing alloys containing additions of selenium in the range zero to 500ppm were examined. Conductivity tests indicate increasing solubility through the temperature range 300ºC to 800ºC. Values of 2ppm at 500ºC, 30ppm at700ºC and 150ppm at 800ºC are suggested with the remainder being present as $Cu_2Se$.

## 5.5 Smart JS, Jr et al. Effects of iron cobalt and Nickel on some properties of high purity copper Trans AIMME. 147, pp48 (1942).

Considers composition range up to 500ppm. Measured effects on conductivity and softening temperature. Softening temperature is defined as the temperature at which the half hard condition is achieved during a one hour anneal after cold reduction of 75% by drawing. Test samples were produced by continuous casting to 5/16 in. diameter rod, followed by cold drawing to 0.162 in. with three inter-anneals of 30 minutes at 600ºC. The final cold reduction to 0.081 was 75 %. Specimens were annealed at 100ºC intervals in the range 300ºC to 800ºC for one hour followed by quenching into a 10% $H_2SO_4$ pickle bath.

Iron contents varied from 0.7 to 500 ppm. The loss in conductivity was 0.8% per 10 ppm. of iron, for iron contents up to 100ppm at all annealing temperatures. This indicates solid solution behaviour across this composition and annealing treatment range. Other work quoted by the authors reports a solid solubility limit for iron at 300ºC of 4ppm and the authors suggest that after prolonged annealing times some precipitation of iron would occur and that the conductivity would therefore rise. In this work however the specimens containing 500ppm of iron showed less reduction in conductivity after annealing at 300ºC and 400ºC than after annealing at higher temperatures. This suggests to the writer that the full 500ppm is soluble at 500ºC and above but that at less than 500ppm is soluble at 400ºC and below.

A series of the iron bearing specimens were saturated with oxygen by diffusion at 850ºC and then subjected to conductivity checks. The precipitation of iron as $Fe_2O_3$ proceeded to completion at very low oxygen contents with full restoration of conductivity save for the very slight reduction arising from the solution of oxygen and the presence of iron oxide. Iron present in solution at the 100ppm level increased softening temperature by 20ºC and, present as oxide 500pm was required to produce this effect. Thus it is concluded that at residual levels the effect of iron on softening temperature is marginal at best.

Copper-nickel alloys form a complete solid solution, this work shows a marginal effect of nickel on conductivity with a loss of 0.09% for each 10ppm up to 200ppm. Above 200ppm the rate of loss of conductivity decreases with increasing nickel content. The effects on softening temperature are even less marked with no detectable effect for up to 500ppm. Oxygen bearing nickel alloys prepared by diffusion of oxygen at 850ºC demonstrated no change in conductivity or softening temperature compared with oxygen free alloys. Incorporation of larger amounts of oxygen, up to 190ppm by remelting and casting through air produced effects on conductivity equal to the effect expected from the corresponding volume of $Cu_2O$, i.e. 0.136% for each 100ppm. There was no evidence to suggest the formation of NiO even though excess O is available. When the nickel master alloy (containing 1900ppm nickel) was exposed to the oxygen diffusion process at 850ºC before being made into test specimens for conductivity, the results showed that after 168 hours diffusion treatment 600ppm of nickel was converted to oxide whilst 1300ppm remained in solution. The kinetics of the change indicated that the system was very slowly approaching equilibrium. It is concluded that the reaction between nickel and oxygen is reversible and that the amount of oxide that forms is dependent on concentration, time, and temperature. The reaction does not proceed to an appreciable extent at the concentrations found in electrolytic coppers.

Cobalt is rarely found in commercial coppers. Its effects resemble that of iron when it is present. In the absence of oxygen it has a strong effect on conductivity and softening temperature. When oxygen is present the effect on conductivity is removed but the effect on softening temperature is retained.

## 5.6 Smart JS, Jr et al. Effects of certain fifth period elements on some properties of high purity copper Trans AIMME. 152, pp103 (1943).

Considers Ag, Cd, Sn, Sb and Te present at impurity levels. Specimens for conductivity and softening temperature tests were prepared as in the previously reported work.

The effect of silver on conductivity is extremely small and difficult to detect when the concentration is less than 340 ppm. Up to 30ppm has negligible effect on softening temperature but between 30ppm and 343 ppm the softening temperature increases almost linearly from 150ºC to 300ºC. Above 340ppm the rate of increase of softening temperature with increasing silver content reduces rapidly. Thus silver as an impurity has little effect on softening temperature or conductivity but it is an ideal alloying element for increase in softening temperature alone.

The solid solubility of antimony in copper increases from 2% at 200ºC to over 11% at 650ºC. according previously published work quoted by the authors. This previous work and other work on the effects of Sb on various properties had been conducted on oxygen bearing material, with oxygen present in varying amounts. This work has paid particular attention to the effects of Sb in oxygen free and oxygen bearing materials with controlled amounts of both elements. In oxygen free material with Sb levels up to 600ppm the Sb appears in solid solution and has pronounced effects on both conductivity and softening temperature.

For oxygen bearing materials conductivity values were corrected for the effects of $Cu_2O$ by adding 0.136% for each .01% (100ppm) of oxygen present. Actual oxygen contents varied from 300 to 1300ppm. In the presence of oxygen the effects of Sb on conductivity varied through the range of annealing treatments employed. They reached a maximum after the 600ºC anneal and they reached a minimum after the 800ºC anneal.

This temperature sensitive effect suggests that precipitation of Sb occurred at the lower temperatures but resolution occurred at higher temperatures. A detailed investigation of annealing behaviour revealed that up to 87 hours was required to achieve maximum improvement in conductivity at 500ºC but maximum loss of conductivity occurred in less than one hour at 800ºC. The authors suggest that the precipitating phase is $Sb_2O_3$ and that this becomes unstable as the temperature is increased. The rate of precipitation will depend on concentration of the reactants and temperature. Resolution is more rapid owing to the increased temperature. The experiments provided evidence of a further precipitation reaction occurring at 800ºC or higher. This precipitate was assigned the general formula $Cu_xSb_yO_z$. This precipitation reaction is very slow and reversible, although reversion has only been observed on remelting. The reaction product once formed is stable at lower temperatures.

Rolling experiments were carried out on the oxygen bearing materials in order to check the effects of Antimony on workability. No hot shortness was observed on specimens containing less than 200ppm of Sb. Samples containing 600ppm of Sb usually developed small cracks on cooling to dull red heat. Methods for controlling this cracking were demonstrated and the authors conclude that whilst antimony in solution has no influence on workability, the oxide which forms below 700ºC can lead to hot shortness.

The effect of cadmium on conductivity is so small that at least 100ppm is required for any effect to be detected, in the presence of oxygen this figure is raised to 500ppm. The oxidation behaviour of cadmium is apparently similar to that of antimony.

In oxygen free copper with up to 500ppm of tin, losses in conductivity are a linear function of tin content at 0.9% per 100ppm of tin. The addition of oxygen completely restores the conductivity. Tin also has a strong effect on softening temperature in oxygen free material but in the presence of oxygen this effect is lost. During annealing at high temperature coarsening of $SnO_2$ particles occurs. It is suggested that this is through dissociation of fine particles of the compound, diffusion of the Sn and O atoms and reformation of the oxide at the surface of the coarser particles. Further experiments suggest that free tin will not co-exist with free oxygen in copper at high temperatures.

Annealing and conductivity test results indicate that the solubility of tellurium in copper is very limited. Values of 75ppm at 800ºC, 15ppm at700ºC, 4ppm at 600ºC and less than this at lower temperatures. The reduction in conductivity was measured at 0.23% per 10ppm within the solubility range. Oxygen addition had no measurable effect on these results and it was concluded that in the composition range up to 500ppm tellurium, tellurium and oxygen do not combine to any appreciable extent. It was assumed that the tellurium not in solution was present as copper telluride. The influence of tellurium on softening temperature is very strong in spite of the low solubility. In material quenched after annealing at 850ºC the effect on softening temperature was much stronger than it was in material quenched from an annealing temperature of 600ºC. This indicates the increasing solubility of Te with increasing temperature.

## 5.7 Yea-Yang Su Analysis of the factors affecting the drawability of copper rod Wire Journal January 1992 pp 74

The author correlates oxygen content with number of wire breaks per ton processed. The relationship shows a clear minimum at 380 ppm oxygen. Whilst the rising trend for oxygen contents above 380 ppm is discussed the falling trend from 0 to 380 ppm is not. Oxygen Free High Conductivity copper is included in his test series and these coppers show more wire breaks per ton processed than the material containing 380 ppm oxygen. Wire breaks in the high oxygen material are related to oxide inclusions. Oxide inclusions are also observed in the oxygen free material and are identified as a possible cause for wire breaks. It is difficult to explain the initial fall in the trend of breaks per ton processed on this basis alone and it seems likely that, as has been suggested in other work, combination of available oxygen with otherwise damaging species may be responsible.

## 5.8 Bingley MS et al Electron beam welding copper and dilute copper alloys BNF Report 608/7

Ten grades of copper were examined, 3 PDO, 2 Tough pitch, 2 OFHC, 1 Copper Chromium alloy and 1 special high purity copper (as cast).

All except the last one was supplied as 75 mm wide x 15 mm thick bar stock. Eight were extruded and drawn whilst the ninth was hot and cold rolled.

Whilst some casting defects were apparent in the as cast materials, none were apparent after mechanical working.

All materials were analysed by BNF, some were checked by Pori-copper.

Oxygen and hydrogen levels were measured in as cast, as extruded and as welded bars. In the latter case checks were carried out on both the matrix surrounding the weld and the weld metal.

Electron Beam Processes of Chertsey England carried out the welding using 1. A 13.5 kW and 2. A 6 kW machine. The first was medium vacuum $5\times10^{-2}$ Torr and the second was high vacuum $5\times10^{-4}$. The second machine was only capable of partial penetration welds.

Pressure in the welding chamber was constantly monitored but the point is made that the pressure seen by the weld exceeds the pressure in the chamber owing to,

1. The pressure generated by the electron beam
2. The pressure due to vaporisation of the weld metal, and
3. The metallostatic head of the molten metal in the weld.

These factors may produce pressures in the weld of up to 0.05 atmospheres, (78 Torr) (TWI has used 80 kW and partial vacuum for lid welds, with higher vacuum and lower power for seam welds.)

The types of defects seen in association with welds were,

1. Superficial cracks, particularly in the weld root
2. Root porosity in partial penetration welds
3. Blowholes, and
4. Internal porosity.

The bottom surfaces of full penetration welds always contained pinholes and sometimes minor cracks. Wells were formed on the back surface and it is acknowledged that this defect can be controlled using a backplate.

Usually gross porosity was observed in the roots of partial penetration welds. The best results in this respect were obtained with the super-pure ingot, closely followed by the OFHC. Results were much worse with PDO. Control of welding speed eliminated this defect in the OFHC material.

Blowholes form on the top surface, they have the width of the weld and in this work they frequently extended to the weld root. They occurred in every material examined in varying degrees and apparently at random.

At the high chamber pressure ($3\times10^{-2}$ Torr) the effect was least for OFHC (3.4/m). In partial penetration welds made at lower pressure $5\times 10^{-4}$ Torr, OFHC had the highest frequency of blowholes (109/m). Formation of blowholes was also sensitive to welding speed and power but chamber pressure was by far the dominant control parameter.

Weld quality was assessed. Radiography was only capable of clearly detecting major defects, mainly blowholes and root defects but there were some indications of porosity, few welds were defect free of weld root or blowholes and none were free of porosity.

Metallography confirmed the radiographic results. Pores were circular in cross section suggesting that they were due to gas evolution. In many cases the pores were in clouds, usually at the weld/matrix interface, but in the case of OFHC some were seen in the parent metal, larger pores were up to 0.3 mm in diameter.

All the defect types were found in all materials but the frequency of all types were lowest in super-pure and OFHC grades.

The Authors relate blowholes to instability in the electron beam, they comment that quality depends on run length and whilst short runs of weld (200 mm) may appear perfect longer runs may be impossible to achieve. Attempts to repair blowholes by rewelding failed. They also comment that material composition has an effect on the frequency of blowholes but they do not relate material composition to stability of the electron gun.

The authors refer to work by others on gas porosity and quote solubility products for various gasses at 1100$^{o}$ C. They reiterate that the pressures seen by the weld may be in the range 8-40 Torr and suggest that average chamber pressure may be neglected when considering the gas reactions in the weld. Consideration of the solubility products and the measured concentration of gasses in the starting materials indicated that under the welding conditions used for the OFHC, $H_2S$, $SO_2$, CO, $H_2$ and $O_2$ are unlikely to form. $H_2O$ however was likely to form. They conclude that the most likely cause of porosity is the steam reaction. Best results were on OFHC with <2ppm oxygen and <0.2 ppm hydrogen.

The analyses carried out by BNF and pori-copper differed somewhat in their results from samples of the same material. For OFHC material BNF quote a total impurity level of <64 ppm. Whilst pori copper quote <33 ppm. Some of this discrepancy may be accounted for by the difference in lower limits of detection claimed by the two groups, but this can not be the full story. BNF are lower on Sulphur than pori-copper, 3 ppm compared with 7 ppm and higher on Tellurium 30 ppm compared with <3 ppm. This highlights the problems associated with analysing for such low levels of impurities. It is believed that at the time in question analytical standards were supplied to pori-copper by BNF.

## 5.9 Harper et al. The embrittlement of tough pitch copper windings in Hydrogen cooled electrical generators. JIM 1961-62 Vol. 90 pp 414

Tough Pitch Copper (oxygen contents 0.02-0.053%) and OFHC copper (oxygen content < 0.0001%) were examined. Strip specimens were heat treated in hydrogen atmospheres at 1 and 7 atmospheres pressure. No embrittlement of OFHC coppers was detected after heat treatments of up to one month at temperatures up to 400$^{o}$C. All tough pitch coppers were embrittled after heat treatments throughout this range. Embrittlement is much more rapid at temperatures exceeding 374$^{o}$C, the critical temperature for steam formation in copper. Heat treatment at 700$^{o}$C of specimens previously heat treated in hydrogen at temperatures below 374$^{o}$C leads rapidly to increased embrittlement. Embrittlement follows the reduction of cuprous oxide and oxygen in solution in the lattice by hydrogen. The rate-controlling step for this reduction below 400°C is the rate of permeation of hydrogen through the lattice and permeation rates are calculated from published data. Above 400°C the rate controlling step is the rate of absorption of Hydrogen at the copper surface. Below 400°C water forms as a result of the reduction reaction, the pressure exerted on the lattice by water is modest and embrittlement is delayed until fissures are formed in grain boundaries. The mechanism of fissure formation is obscure; it does not appear from rate estimates to be creep or vacancy diffusion controlled. Above 400°C the pressure exerted by steam is sufficient to cause cavities to be generated spontaneously and embrittlement is rapid. The authors assert that in their experience whenever experimental evidence of deoxidation is observed embrittlement follows.

## 5.10 Harper et al. The embrittlement of tough pitch copper during annealing or preheating. JIM 1961-62 Vol. 90 pp 423

This paper is a sequel to 2 above and it deals exclusively with tough pitch copper. It shows that at temperatures in the range 400°C to 650°C on the rate controlling step is absorption of hydrogen at the surface whilst above 700°C outwards diffusion of oxygen has a significant effect.

## 5.11 Ye Y. et al Fiz. metal. metalloved, 44, No 2, 1977 pp 323 Influence of the matrix structure and dispersed oxide particles on the hydrogen embrittlement of copper.

This paper describes a study in which the properties of internally oxidised copper aluminium alloys are compared with those of pure copper (9x$10^{-4}$% oxygen) after annealing in a hydrogen atmosphere.

Hydrogen annealing of pure copper at temperatures in excess of 600°C leads to significant reductions in strength and in reduction in area of tensile specimens. Vacuum annealing has no effect. No reduction in area is noted for annealing at lower temperatures or for vacuum annealing at any temperature. Voids appear in the structure of copper and the copper alumina alloy after annealing at temperatures above 550°C. It is proposed that these voids arise from the reaction of hydrogen with oxygen dissolved in the copper to form steam. The presence of voids is observed to have no embrittling effect when the grain size is small, however annealing at temperatures in excess of 600 °C causes significant grain growth in the nominally pure copper.

## 5.12 Henderson PJ. et al. SKB technical report 92-04 Low temperature creep of copper intended for nuclear waste containers

This is a very early paper from Henderson and co-workers. They looked at the creep ductility of several alloys including OF copper and OF copper with 50 ppm of phosphorus added. Both were fine-grained (45 microns). Chemical analyses were not given but later work[22,23] on specimens of the same material reveals that the phosphorus-free material contained 10ppm sulphur whilst the phosphorus bearing material contained 6ppm sulphur. The work provides convincing evidence that OF copper with fine grains and 10ppm sulphur exhibits a creep elongation to failure of less than 1% when tested at temperatures of 180 °C and above. A coarse-grained phosphorus free material with only 6ppm sulphur also exhibited the very low (<1 %) fracture strains when tested at 215°C.

A phosphorus bearing material (50ppm) which was fine-grained had an improved creep strain to failure compared with a non-phosphorus bearing material with a similar grain size and a similar sulphur content. However neither of these two materials had the extreme low creep strain to fracture of less than 1%.

Variations in sulphur contents between batches were not examined in this work. Consequently the difference in sulphur contents between the fine-grained phosphorus free material referred to above and the fine grained OF material which had less than 1% strain to fracture was not apparent.

Consequently it was not apparent to the investigators that the very low creep strain to fracture values were linked to testing temperatures exceeding 145°C and, either sulphur levels of 10ppm with fine-grains or sulphur levels of 6ppm with coarse grains. The improvement in ductility which was observed between the two fine-grained materials having 6ppm sulphur was rightly attributed to the effects of phosphorus but it was not explained. In a later paper[22] Henderson pointed out that two different failure mechanisms occurred in the fine grained materials with 6ppm and 10 ppm sulphur, both were intergranular but one was assisted by segregation of sulphur (the 10ppm case) and the other was not. The former resulted in failure strains of less than 1% and the latter resulted in failure strains of order 10 %.

With these observation in mind it would be very surprising if the phosphorus bearing material did exhibit the less than 1% strain to fracture, it was fine grained and had 6ppm sulphur.

The fact that the strain to fracture in this phosphorus-bearing material, was higher than a fine-grained 6ppm sulphur and phosphorus free material, still needs to be explained however. In fact the values measured 15% to 70% for fine grained phosphorus bearing material overlaps the range (15% to 35 %) [22] for the fine grained phosphorus free material tested at lower temperatures (i.e. up to145°C).

Henderson[22] suggests that two transitions in ductility occur in the phosphorus free material. At the higher temperatures there is a transition from creep ductile (Transgranular) failure, to creep brittle (intergranular) failure. The second is due to sulphur embrittlement. This affects intergranular but not transgranular fracture and ductility falls to less than 1%. This suggestion fits well with the observations. It is also reasonable to suggest that phosphorus addition has had the effect of raising the temperature for the creep ductile to the creep brittle behaviour. This would explain the higher ductility observed for the case of the phosphorus bearing materials.

As the transition from transgranular to intergranular failure is dependant on the relative strengths of grain boundaries and grain interiors it is to be expected that it will be influenced by, temperature, solid solution elements, precipitates, grain size, grain boundary segregates and the applied stress (rate of strain).

### 5.13 Punshon C. et al. Examination of ambient temperature mechanical properties and segregation effects in reduced pressure electron beam welds in oxygen free low phosphorus copper SKB Project report number 94-3420-04

This work was carried out to determine whether or not phosphorus added to OF copper to improve creep resistance is depleted in the weld region by segregation or evaporation, and whether or not this has an effect on mechanical properties. The report includes room temperature mechanical properties on parent metal and on welds. No adverse effects of welding are observed. It also gives good grain size information measured in three directions in the weld and in the parent material. The parent material was equiaxed with a grain size of 150 -180 microns. The weld region had plate like grains with dimensions up to 3 mm. There was no evidence of depletion of phosphorus in the weld region but there was clear evidence of sulphur segregation to grain boundaries in the parent material and in the weld. His detection method was EDAX on the SEM and the analyses of the particles are totally convincing. The particles detected and photographed by the SEM were large (1µm) and the sulphur peak in the x-ray analysis was very clear. The failure to zone refine is interesting and it suggests that the temperature gradient in the weld must have been such that homogeneous nucleation of new crystals occurred ahead of the solidification front leading to trapping impurities rather than carrying them along in the molten zone. Such temperature gradients are not conducive to zone refining but they would be very likely to occur in electron beam welding of copper.

### 5.14 Foulger RV et al, Influence of composition and microstructure on mechanical working properties of copper base alloys. Metals technology, August 1976, pp 366.

This is a very general paper but it does discus copper along with alpha alloys. It is written by a works metallurgist. He states that brasses other than alpha brasses are easy to hot work. In general alpha alloys (of which pure copper is the extreme case) are difficult to hot work and require lower impurity levels. Impurities cause embrittlement in hot work even when they are present in very small quantities. Lead and Bismuth are cited as impurities likely to be involved in hot shortness and it is suggested that phosphorus may be instrumental in controlling grain growth. It does not give conditions for the control of grain growth but quotes other work. The first is referred to brass ingots and the second is dated 1932. (Cook and Miller JIM 1932, 49,247.)

### 5.15 Kee W. The control of properties and structure in the hot and cold rolling of copper and copper-base alloys. JIM 1953/54, vol. 82 pp 307

Another very general paper by a practising works metallurgist. The limit of lead content which affects the hot workability of copper is dependant on oxygen content. In oxygen free copper the most important factor is hot working temperature as lead in solid solution has little embrittling effect. For example for rolling above 800°C, 0.04 % lead can be tolerated but at 700°C this is reduced to 0.02 %. Antimony resembles lead in its behaviour in hot rolling; Bismuth forms a low melting point grain boundary film, which leads to hot shortness. The presence of oxygen arsenic or phosphorus diminishes the effect of bismuth. Impurities also affect recrystallization temperature. Curves are presented to show the effects of annealing temperature on UTS Elongation and grain size in electrolytic, OFHC and PDO coppers. The information indicates that phosphorus increases the recrystallization temperature as expected. The unexpected observation (to the writer) is that phosphorus also promotes the onset of grain growth. The effect on recrystallization temperature is explained as an indirect effect of the reduction of oxygen. This leaves impurities in solid solution and this raises the recrystallization temperature. No explanation of the reduction in temperature for the onset of grain growth is given but the evidence is very clear, rapid grain growth in PDO starts at 550 $^{o}$ C whilst in OFHC it is delayed to 650 $^{o}$C.

## 5.16 Phillips AJ. Gas and other impurity reactions in copper Metallurgical Transactions Volume 4 August 1973 pp1935

This paper is mostly concerned with the reactions of oxygen hydrogen and sulphur, during the solidification and cooling of copper. It gives equilibrium constants for hydrogen-oxygen and hydrogen-sulphur reactions in liquid copper as a function of temperature. The effect of alloy concentration of sulphur during solidification of a copper melt is mentioned. For a sulphur content of 5 ppm at 100% liquid, the concentration in the last liquid to solidify is 500 ppm. The significance of this is that such a segregation effect suggests that a strong zone refining action might be expected to occur in electron beam welds.

The paper is mainly concerned with the effects of gas metal reactions on the “set” of tough pitch copper. It contains useful references to work on the effects of other alloying elements.

Iron oxide in solid copper is uniformly distributed because iron is present in the melt in an uncombined form. The increased availability of oxygen on solidification leads to oxidation of the iron before the Cu-$Cu_2O$ eutectic is reached and no iron is left in solid solution.

Nickel in the range found in refined copper is present in solution and probably does not precipitate as the oxide during solidification or cooling to ambient temperature.

All the Antimony in refined copper remains in solution during freezing and only precipitates as room temperature is approached probably by the reaction.

He does not comment on oxygen free material.

Arsenic does not react with $Cu_2O$ either on freezing or on cooling to room temperature.

Phosphorus, on the other hand, is a very powerful deoxidiser and will not coexist with $Cu_2O$ in the melt. It is presumed that $P_2O_5$ escapes as the gas and surplus phosphorus remains in solution in the solid.

Lead is known to influence overpoled (over-deoxidised) copper, it is believed that lead and sulphur combine to form lead sulphide, this buffers the sulphur to <1ppm and causes the solid lead sulphide to precipitate instead of the liquid lead.

## 5.17 Sundberg R. Influence of impurities in oxygen free copper. SKB Project report 98-3420-32

Sundberg points out that impurities reduce electrical conductivity and increase recrystallization temperature. The grade of copper specified for the copper canister has all impurities except silver below 10ppm and therefore the effects on conductivity are very limited. Elements present at greater than 1ppm are sulphur, arsenic lead, antimony, and tellurium plus phosphorus that is added. All these elements may influence recrystallization temperature but they have a negligible effect on mechanical properties at the concentrations present. Sundberg refers to work commissioned by SKB which indicates that creep ductility has been seen to be reduced to 0.25 % in OF (E) grade copper with no phosphorus added (Henderson et al 1992[12]). He goes on to

refer to the work of Takuno et al[20] to demonstrate the effects of phosphorus. The Takuno paper refers to work by others on OF, PDO and ETP coppers containing 9,15 and 16 ppm of sulphur respectively. This work measured the reduction in area of tensile test specimens as a function of test temperature in the range 20ºC to 700ºC. The reduction in area of the OF material showed a severe minimum at 350ºC, in the TP copper the minimum was much less pronounced and in the PDO it was almost absent. The material was in the extruded condition and testing was in air but no further details are available. The work of Myers et al [18] is also referred to. That work clearly indicates that sulphur present in concentrations greater than 4ppm reduces ductility of cast copper specimens when they are tested at 950ºC.
On the basis of this evidence Sundberg concludes that it is likely that the presence of sulphur is mainly responsible for the reduction in creep strain to failure seen by Henderson et al and that addition of phosphorus improves creep ductility. There is no explanation of the likely mechanism or consideration of other possible explanations of the observations. The author does not claim that the suggestion is proved or that the addition of phosphorus will eliminate the low creep to fracture problem for the SKB canister case.

## 5.18 Myers and A Blythe. Effects of oxygen sulphur, and porosity on mechanical properties of cast high-purity copper at 950 $^{o}$C- Metals technology May 1981 pp165.

The authors very briefly refer to work by others, of particular interest was their reference to observations by Stark and Marcus that low levels of sulphur caused grain boundary decoration in steel and their prediction that a similar effect would be observed in copper. In addition Clough and Stein had reported that a sulphur content of 12 % had been detected using Auger spectroscopy in grain boundaries of embrittled oxygen free copper which contained only 24 at ppm (12 wt. ppm) of sulphur.
In their own work they worked with high purity starting materials (no impurity present at >1ppm). They cast test bars from 72 melts with sulphur contents that varied from 1 to 50 ppm and oxygen contents that varied from <1 to 1500ppm. Cast specimens were subjected to tensile testing at 950ºC and reduction in area was used as a measure of ductility.
They report that electron probe microanalysis was used to examine second phase particles in sulphur bearing specimens. Unfortunately the sulphur contents and the oxygen contents of the specimens in question are not disclosed. However it was observed that sulphur was concentrated at the oxide particle locations. The specimens were as cast and no homogenisation treatments had been used. It is therefore likely that segregation of sulphur would have occurred on solidification. The authors propose that oxide particles act as “sponges” which absorb sulphur and prevent the formation of grain boundary films. They refer to other work by Bigelow and Chen that suggests that a Cu-S-O eutectic may form at temperatures below 900ºC. This requires at least 14ppm sulphur but they point out that under conditions of non-equilibrium cooling, segregation of sulphur could well result in this level being reached locally. However the authors conclude that whilst this association between sulphur and oxide particles has been detected the effects of the interaction were not discernible in their experiments.
The surprising result of the work was that under all conditions of oxygen content and porosity in the castings, sulphur levels exceeding 4ppm led to embrittlement at 950ºC. The authors predict that if this is due to the formation of grain boundary films then the

critical sulphur level will be dependant on grain size. That is to say finer grained material would have a higher critical level. Porosity is also shown to have a negative effect on ductility at 950°C when sulphur levels are below 4ppm.
The authors predict that in alloys of this type the effects of porosity will be more pronounced in coarse-grained material.
They describe the presence of an intergranular liquid phase such as the low melting point copper-oxygen-sulphur eutectic as a classic cause of hot short cracking. The significance of this is that hot short cracking during hot rolling can lead to oxidation of the cracks and this in turn leads to strings of oxide particles penetrating from the surface to the interior of the finished product.

## 5.19 H Pops. Copper rod requirements for magnets, Wire journal international May 1987 pp 59

Pops states that the highest quality copper being produced today is usually channelled towards the magnet segment of the wire industry. He points out that there are no existing specifications that adequately meet the demands of the user and that there is a need to replace subjective opinions with meaningful parameters that can be measured. He attempts to meet that need.
A low recrystallization temperature and rapid annealing kinetics are identified as a key factor in the quality of magnet wire. The classical studies on effects of impurities in copper were conducted 40 years ago and they were made by doping high purity copper with single impurity elements. Most elements cause increases in recrystallization temperature at very low concentrations but their effects are not linear with concentration nor are they strictly additive owing to interactions between impurity species. Nevertheless the table below is produced for the influence of impurities at typical levels on recrystallization temperature.

| Element | Level ppm | Annealing temperature | |
|---|---|---|---|
| | | °C/ppm | Increase (°C) |
| S | 10 | 8.3 | 83.3 |
| Se | 2 | 8.3 | 16.7 |
| Te | 2 | 5.6 | 11.1 |
| Pb | 8 | 3.3 | 26.7 |
| Bi | 1 | 8.3 | 8.3 |
| Sb | 4 | 1.7 | 6.7 |
| As | 4 | 1.7 | 6.7 |
| Sn | 4 | 2.8 | 11.1 |
| Fe | 10 | 0.6 | 5.6 |
| Ni | 5 | 0.6 | 2.8 |
| Ag | 15 | 0.6 | 8 |
| Total | 65 | | 187 |

.
Possible interactions of impurities listed are oxidation reactions, copper metal intermediate phases (such as $Cu_2Se$, $Cu_2S$ and $Cu_2Te$) and metal-metal (such as $Ag_2Se$, PbSe, PbS).

The ASTM and LME specifications for grade 1 cathode copper are given (90 ppm total impurity and 65 ppm total impurity respectively). It is pointed out however that progress in the production of copper cathodes has resulted in most product being considerably better than the ASTM or LME standards. For wire applications high quality cathode is used and oxygen is added to the melt. This has no direct effect on annealing temperature but it reduces the effect of other impurities by forming insoluble oxides. It is claimed that it also has a beneficial effect on ductility and it might be interpreted that this is due to a reduction in the tendency to hot shortness. The use of oxygen to reduce hot shortness is specifically mentioned and a photomicrograph of a deep oxide defect arising from “hot cracking” is presented. Rod surface defects are in two main categories, one from the casting/rolling process and the second through mechanical damage. Defects arising from casting/rolling processes include rolled in oxide scale, hot cracks overfills and holes. Hot cracks frequently extend very deep into the rod and are sometimes visible to the unaided eye. They are considered to be among the most harmful of defects, particularly when a network of branched oxide particles fans out from the original crack.

In a section on softness Pops reports that annealability of rod can be improved significantly by decreasing the rolling temperature from 900°C to 650°C, thereby causing impurities to precipitate from solid solution.

## 5.20 Takuno N. et al. The analysis of grain boundary segregation of sulphur in commercially-pure coppers. Jnl of the Japan copper and brass research association. Vol. 35 1996 pp204

Only the abstract, the tables and some figure captions appear in English in this paper. Auger electron spectroscopy (AES), Electron probe microanalysis (EPMA) and Secondary ion mass spectrometry (SIMS) were used to search for sulphur segregation in as continuously cast and as cast annealed specimens of oxygen free (OF), phosphorus deoxidised (PDO) and tough pitch (TP) coppers. The OF and PDO coppers had 4ppm sulphur and the TP copper had 5ppm sulphur.

AES and EPMA failed to detect sulphur segregation in all specimens; it was detected by SIMS but only in annealed OF copper and in TP copper in both the annealed and as cast conditions. The authors present this as evidence that oxygen and phosphorus influence the segregation behaviour of sulphur in copper.

It is unfortunate that the whole paper is not available for reading in English. In the absence of the detail that may be contained in the text, the writer with scepticism views the conclusions of the work. The very low sulphur levels in the specimens will render any sulphur segregate hard to find and failure to detect does not indicate absence. SIMS should be the best method for detection owing to the high sensitivity of its detector. It is likely that in the OF and PDO materials the sulphur would remain in solution as cast and precipitate on annealing. The results for the OF and PDO cases are therefore not surprising. Smart[4] has shown that there is no reaction between sulphur and oxygen in the copper–oxygen-sulphur ternary system, so it is unlikely that oxygen alone is responsible for a difference in segregation characteristics between as cast OF and as cast TP coppers. The role of phosphorus is problematical. SKB present the results of this paper as evidence that phosphorus limits the segregation of sulphur which may cause an adverse effect on creep ductility. However the sulphur levels considered in this work are substantially below the 6ppm at which sulphur segregation has been reported to be a problem, and clear evidence of sulphur segregation in SKB material containing phosphorus has been provided by Punshon[13] using Scanning electron microscopy.

A more satisfactory explanation of the results reported in this paper may be that, at the very low sulphur levels considered, segregation is very difficult to detect. The fact that it was detected in some specimens and not in others may be pure chance.

### 5.21 Susuki et al. Effect of a small addition of transition elements on annealing characteristics of cold-worked pure copper. Trans Japan IoM, Vol26, No1 (1985), pp69.

Experiments were carried out on electrolytic copper (40 ppm impurity level) with additions of up to 1000ppm (atomic) of Ti, Zr, Hf, V, Cr, Mn, or Fe. Oxygen levels were close to 8ppm (molecular). Ingots were vacuum cast, homogenised at 800ºC, quenched scalped and cold rolled to sheet. Alternative specimens were similarly homogenised and cold drawn to wire. Reductions in the two cases were 94% and 96%. After cold working specimens were stored in dry ice. The 1mm thick sheet specimens were isochronal annealed for 3 minutes at temperatures in the range 100ºC to 500ºC, wires were isothermally annealed at 150ºC. Hardness and conductivity measurements were made on annealed specimens.

Trace additions of each element had the effect of reducing the recrystallization temperature in each case.

To explore this further, three types of wire specimen were produced by adding 30ppm (atomic) of Ti, Zr, or V to the following coppers,

1. the original base copper,
2. two purified versions of 1. (1) by further electrolysis in $H_2SO_4$-$CuSO_4$, and (2) As 1 with subsequent second electrolysis in $HNO_3$-$Cu(NO_3)_2$ (to remove sulphur) and
3. material purified according to (2. (2)) above with additions of S or S together with Ti, Zr, or V.

The half-softening temperature ($T_H$) decreased regularly to a minimum with increasing amounts of Ti, Zr, or V. The minima occurred at 13ppm, 21ppm and 16ppm (atomic) respectively. The greatest reduction was 65ºC for the Vanadium case. Additions beyond the minimum caused increases in $T_H$ with the strongest effect in the zirconium bearing material and the weakest in the vanadium bearing material.

Resistivity was measured as cold drawn, and as quenched after annealing on the original group of materials. Both measurements increased linearly with increasing amounts of added element up to 100ppm for each element except Zr, Hf and V. For these additives both curves deviated from straight lines when concentrations of 200,300 and 600ppm (atomic) was reached respectively. These concentrations correspond to the solid solubility limits for the elements at 800ºC.

When Ti, Zr and V were examined in low concentrations it was revealed that for additions of several ppm no changes occurred in the resistivity as drawn or as quenched.

Both the recrystallization and the resistivity results suggest that each additive is reacting with an impurity in the copper.

When the purified coppers were compared it was observed that, during annealing, the rates of change of resistivity with time were identical for the base copper and the first purified version and both were much slower than the second purified version. It was suggested that recrystallization temperature of nominally pure copper might increase as sulphur content is reduced from 4ppm to <1ppm. To confirm this the third type of specimen composition, (double purified by electrolysis, with sulphur and other elements added) was explored. Rate of recrystallization at 150ºC was fastest in the pure material. Additions of sulphur at the 2.0, 2.6 and 13 ppm levels caused continuous reductions in rate of recrystallization but addition of 41ppm of Ti to the 13ppm sulphur bearing material returned its rate almost to that of the pure material. Similar results were obtained when the effects of sulphur and Zr and sulphur and V were examined. SEM studies on the specimen materials revealed the presence of inclusions that were shown to contain sulphur and Ti, Zr or V for the respective cases. The work concludes that trace additions of each transition metal enhanced the softening of cold worked commercially available pure copper. For the cases of Ti, Zr and V recrystallization was most enhanced when the addition amount was about 10ppm or less. This is a result of combination of these elements with sulphur dissolved in the copper which takes both elements of the compound out of solution. They further conclude from thermodynamic considerations that the sulphides could form in the melt and point out that their spherical shape suggests that this may have happened. However they also provide strong evidence that some combination of sulphur and Zr or Ti occurs during annealing at 800ºC.

The authors point out that their specimens contained around 8ppm (molecular) of oxygen but they give no evidence for reaction between the oxygen and the added elements or for an effect of oxygen on recrystallization behaviour.

## 5.22 Henderson PJ. et al. Low temperature creep ductility of OFHC copper, Mat Sci and Eng A246 (1998) 143

Three batches of OFHC copper from Outokompu were examined. Two batches had 10ppm sulphur and the third had 6ppm sulphur. Batch one was fine grained material (60µm) from forged bar. Batch two was coarse grained material (350µm) from the SKB canister development programme stock and batch 3 was fine grained (45µm) from hot extruded bar. Creep tests were carried out on all materials at 215ºC and the results were compared with previously reported results for batch one material at a range of temperatures from 75ºC to 250ºC.

Batch two had much lower creep lives than batch one and batch three had much longer creep lives than batch one. This suggested that both increasing grain size and increasing sulphur from 6ppm to 10ppm had adverse effects on creep life.

Creep strain to fracture on batch three specimens (low sulphur-fine grains) tested at 215ºC was always close to 10%. On batch one specimens (high sulphur-fine grains) strain to fracture at 75ºC and 110ºC lay in the range 10% – 40%. Batch one material tested at 145ºC gave strain to fracture values in the range 5%–11%. Batch one material (low sulphur-fine grains) tested at 215ºC and 250ºC and batch two material (high sulphur-coarse grains) tested at 215ºC all gave strain to failure values in the range 0%-1%. These low fracture strains are attributed by the authors to segregation of sulphur to grain boundaries. This view is supported by observations of sulphur on intergranular fracture surfaces using Auger microprobe analysis on creep specimens and on specimens fractured at room temperature in the Auger microscope.

The authors conclude that OFHC copper is not suitable for the disposal canister under development in the Swedish nuclear waste disposal programme. They also comment that alternative copper alloys, in particular those containing silver and phosphorus do not have the limitations of OFHC.

## 5.23 Henderson PJ. et al Creep testing of oxygen-free phosphorus copper and extrapolation of the results. Swedish Institute for metals research, Report No IM-3197 Feb 1995

This work is an extension of the work described in 22 above. Two further copper batches are considered, batch 4 was in the form of extruded rod and batch five was in the form of hot rolled plate. Batch four had a grain size of 45µm and batch five had a grain size of 115µm. Both had phosphorus additions of 50 ppm. Sulphur contents were not given but were said to be "close to the levels in batch three of the earlier work"(6ppm). The observation that increasing grain size reduced creep strength made in the earlier work was confirmed for the phosphorus bearing materials in this work. It was also clear that the phosphorus addition had resulted in a considerable improvement in creep strength and in creep strain to fracture. All specimens tested had creep failure strains in the region which would be considered safe. It should be recognised however that the sulphur content in the phosphorus bearing material was at or below the 6ppm which has been considered the safe level for prevention of the low creep strain to fracture problem. Both batches of specimens which displayed the low strain to failure problem in the earlier work had 10ppm sulphur. One was fine grained and one was coarse grained.

An interesting feature of both pieces of work is that failure strain in creep tests increases markedly with initial applied creep stress. This is an indirect result of the fact that the low strain to fracture failures which have been observed are in the higher temperature tests. Henderson[22] pointed out that this is a result of, one the transition from transgranular to intergranular failure that occurs on increasing the test temperature and two, the weakening of grain boundaries by sulphur segregation.

No mechanism is proposed for the improved creep performance of the phosphorus bearing material but Henderson observes that very little grain boundary damage was observed in the phosphorus bearing materials. In the earlier work[22] extensive grain boundary damage was reported. It is attractive to conclude therefore that the presence of phosphorus elevates the temperature of transition from transgranular to intergranular failure. If this were the case then additions of phosphorus would reduce if not eliminate the likelihood of low creep strain to fracture in these materials.

This is not firmly established however. Indeed the established role of phosphorus in increasing recrystallization temperature and increasing proof stress may be considered to act in the opposite direction. It is clear that the responsible mechanism for the extreme loss of ductility is influenced by grain size, stress level, temperature and sulphur content. Henderson and her co-workers[22, 23] point out that further work is necessary to further understand the effects of these variables.

## 5.24 Saarivirta MJ. Behaviour and effect of Sulphur on Oxygen Free High-Purity copper. Trans ASM 57, 1964 pp133

Saarivirta confirms the value of 20ppm for the solubility of sulphur in copper at 800ºC and measures values of 25ppm and 36ppm at 850ºC and 950ºC respectively. He estimates that at the eutectic temperature of 1067ºC the solubility lies between 56ppm and 74ppm. Metallographic observations indicate that excess copper in as cast material is present as spherical $Cu_2S$ particles which are normally found in the grain boundaries. Some $Cu_2S$ particles decompose on heating above the solvus and on subsequent slow cooling, reprecipitation occurs both in the matrix and in grain boundaries. In trials at 900ºC it was observed that specimens containing more than 18ppm sulphur were subject to surface cracking during rolling.

## 5.25 Chia and Adams The metallurgy of Southwire`s Continuous Rod JOM Feb. 1981 pp68

The Southwire`s Continuous Rod (SCR) system was made commercial in 1965. The system enables continuous casting rolling and cleaning of copper rod. The casting stage is achieved using a mould in which a rotating grooved wheel runs against a continuous and moving steel band. Contact between the **steel** band and the wheel extends over 250° starting at 35° to the vertical. Thus the mating groove and the flat band forms the mould cavity, molten copper is supplied at the initial point of contact of the wheel and the band and the solid continuous rod emerges at the final point of contact. Tough pitch copper is used with an oxygen content in the region 200-500 ppm. This produces 4 to 12 percent $Cu/Cu_2O$ eutectic in the cast structure. The undercooling of the metal as it first meets the mould wall results in solute rejection ahead of the solidification front and to the development of columnar grains. Some equiaxed grains form in the centre where solute is concentrated by the grain multiplication mechanism. The proportion of equiaxed grains in the structure depends on initial superheat and achieved cooling rate with low superheat and high cooling rate producing a higher proportion of equiaxed grains. Eutectic is the last material to solidify and it is found in the interdendritic spaces, with larger oxide particles close to the copper /eutectic boundaries. This is explained in terms of constitutional supercooling thus low oxygen contents result in a higher proportion of coarse oxide particles to fine oxide particles (since growth of particles at the advancing solidification front continues for a longer interval before eutectic solidification of the remaining liquid starts).

After the caster the rod is cleaned before continuous hot rolling through 12 passes to the final dimension. The first pass takes a 35% reduction to yield a recrystallized equiaxed structure with a grain size of approximately 60 microns (after quenching) in which the oxide particles are well distributed (that is no longer segregated to grain boundaries). Subsequent passes result in further grain size reductions to a final value of 20 microns. It is explained that the progressive reduction in grain size is a result of the decreasing temperature as the material progresses through the mill (945°C to 650°C) and the decreasing time interval between passes as the speed of the material through the mill increases. Full recrystallization appears to occur after each pass but the reducing temperature and time between passes limits grain growth.

It is pointed out that the high oxygen content is beneficial to processing because it ties up impurities which otherwise might cause hot shortness or high temperature recrystallization problems. The latter are not explained.

## 5.26. DW Davies Bismuth in copper and copper base alloys: A literature review. CDA report 7012-009

This is a substantial document prepared in response to the proposal that Bismuth might be used as a replacement for Lead in free cutting brasses. Since Bismuth is added as an alloying element in these cases levels of bismuth considered are well above the levels occurring as impurities. For this reason a highly selective approach has been used in abstracting information from the work.

Several workers have investigated the solubility of bismuth in copper and there is uncertainty owing to a lack of strict comparability between experiments. It appears however that at least 0.015% is soluble at 920°C and that there is a rapid loss in solubility as the temperature is reduced below this level possibly to a value as low as 0.001%at 600°C. On cooling from 900°C bismuth is precipitated both in grain boundaries and grain interiors depending on cooling rate and concentration. In supersaturated solid solution the element at low levels has no adverse effect on ductility, after precipitation very low levels of bismuth cause severe embrittlement. It was recognised as early as 1904 that 20 ppm of bismuth made oxygen free copper hot short and cold short. Subsequently it was recognised that this shortness could be alleviated by addition of oxygen. When bismuth contaminated tough pitch copper was rapidly cooled from 900°C it could be cold rolled but in subsequent annealing at 400°C embrittlement occurred at the annealing temperature and persisted after cooling to ambient. This embrittlement could be removed by further annealing for long time periods. This suggests that oxidation of the Bismuth does not occur at 900°C in tough pitch copper, that it stays in solution during rapid cooling and that it subsequently precipitates as metallic bismuth during annealing, oxidation to harmless $Bi_2O_3$ then occurs on prolonged or higher temperature annealing. Arsenic is effective in counteracting the embrittlement caused by bismuth in oxygen free and oxygen bearing materials and roughly 5 parts of arsenic are required to counteract the effect of one part of bismuth. In low oxygen material the improvement arises through a change in the morphology and composition of the precipitates from pure bismuth films in grain boundaries to dispersed globules. When the oxygen content is higher a mixed Cu-As-Bi oxide is formed.

### 5.27. Smets and R Mortier- The influence of oxygen during hot rolling and drawing of continuous cast rod Wire Journal International November 1984 pp80

The authors claim that a disadvantage of oxygen free copper is its high recrystallization temperature. This is because, in oxygen free copper, there is an increased tendency for impurities to stay in solid solution and there is no thermal treatment to solve this. In oxygen bearing copper certain impurities combine with oxygen and precipitate as oxides, in this state they promote recrystallization (presumably through an influence on nucleation).

They point out that in the days when reverberatory furnaces were mainly used for melting and refining the molten pool was frequently uncovered in order to all allow oxygen pick up and this led to a reduction in hot shortness. With shaft furnaces hot shortness increased and in 1970 the Olen company investigated the effect of oxygen content. They concluded that the oxygen content should normally be maintained above 50 ppm in the launder and 190 ppm in the bar stock.

In 1979/80 the company were using continuous casting (contirod-lines), and it was time to look at hot shortness again.

A base composition with the following impurity levels was investigated,

Pb 30 ppm, Sb 4.5 ppm, Bi 0.2 ppm, Fe 5 ppm, Co 0.5 ppm Ag 11 ppm. I.e. total declared impurity excluding silver and oxygen 40.2 ppm.

A 120 tons charge was cast in two 60 ton batches with the first containing 170 ppm of oxygen and the second containing 535 ppm of oxygen. Bend tests on as cast material showed severe cracking in the low oxygen material and considerably less cracking in the higher oxygen bearing material.

Evidence is presented to support the conclusion that re-solution of impurities during annealing influences the recrystallization temperature and therefore the recrystallization temperatures of materials from different sources differ. Unfortunately the sources of the materials used and their compositions are not revealed.

### 5.28. Young S K. Improved copper rod through tighter operating and testing controls Wire Journal International March 1985 pp 59

This is a general paper on quality control at Magma Copper Co which includes a section on metallurgy. A major requirement for customers of that time was and presumably still is consistent annealing characteristics in order that full annealing could be achieved during an enamelling process. The company exerted close control of composition in order to achieve this. They use their own cathode to feed a continuos wheel rod caster. Two cathode standards are quoted as below.

| Cathode Specification | Element ppm | | | | | | | | | | | Grand Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Se | Te | Bi | Sb | As | Pb | S | Sn | Ni | Fe | Ag | |
| ASTM B115-82 Grade 1 | 4 | 2 | 2 | 5 | 5 | 8 | 25 | 10 | 8 | 12 | 25 | 90 |
| Group total | 5 | | | | | | | | 15 | | | |
| LME Proposed Higher Grade | 2 | 2 | 2 | 4 | 5 | 5 | 15 | - | - | 10 | 25 | 65 |
| Group total | 3 | | | 15 incl. Cr, Mn Cd, P | | | | 20 incl. Si, Zn, Co | | | | |

Oxygen content after casting is controlled to 186 ppm with a standard deviation of 26 ppm.