

“The Effect Of Quench Temperature On Silicon Containing Low Carat Investment Casting Alloys.”

by

**Stewart Grice, Metallurgical Manager,
Cookson Precious Metals Ltd.,
Birmingham, England.**

It is well documented how silicon additions can influence the properties of carat gold casting alloys, improving fluidity and surface finish. Increased additions can however lead to brittle failures in castings. There are commercially available low carat casting alloys that contain additions of up to 0.5% silicon, the benefits of which are increased scrap recycling rates however a higher incidence of casting failures can result. This study will investigate the effect of quench temperature on a 9ct yellow casting alloy with various silicon additions and will determine if this is related to failures typically seen. The optimum use for low carat high silicon alloys will also be discussed.

INTRODUCTION.

There are numerous alloys available to the jewellery investment caster in both carat gold and silver. These range from additive-free "clean" alloys - which appear to be experiencing a resurgence in popularity at present - to those containing small additions of certain elements to aid the casting process. This study is concerned with the latter, in particular low-carat casting gold alloys. 9ct alloys are utilised for the majority of the U.K. jewellery industry and their metallurgy is similar to the equivalent 8ct alloys used in Europe and 10ct alloys used in North America. One element commonly added to an alloy to aid casting performance is silicon, which not only provides bright, oxide-free castings but also increases flow characteristics. An overview of casting alloys revealed that of those found to contain silicon, additions varied significantly from 0.005% to 0.7% depending on carat and intended use. An overview of the levels of silicon added to 9ct casting alloys in the U.K. revealed additions ranging from 0.05% to 0.7%. These alloys are all relevant in today's market and have their specific uses, however their performance will vary significantly. Alloys that may be classed as "high-silicon" - for the purposes of this study "high" being $>0.2\%$ - are generally used for specific applications:

1. For use in operations where intensive recycling occurs. As a general rule it is not recommended to use casting charges with a scrap to new metal ratio greater than 50%, however in practice this can and does occur, in some instances charges of 100% scrap being used. The potential for failures then increases significantly. A "high-silicon" alloy will allow a more aggressive scrap recycling programme to be employed before the alloy becomes "silicon-exhausted".
2. For use as master alloys. The situation may occur - particularly in the smaller workshop - where scrap from other areas of the manufacturing process - e.g. wire, sheet or tube - may be used to make up the casting charge. These alloys - intended for wrought applications - will almost certainly have no silicon present and as such additions of a high-silicon grain will aid the casting process. The

silicon content of the master alloy will be diluted by the scrap/grain ratio i.e. if the master alloy contains 0.5% silicon and is mixed 50/50 with other processing scrap the overall silicon content of the charge will be 0.25%.

3. For use in "high abuse" environments. These alloys can be used to good effect with processes where there is no temperature measurement or control, or where there is ineffective or non-existent melt protection. There are operators who, whilst they are extremely knowledgeable on the practicalities of the casting process, do not understand the significance of certain aspects of the process and as such change or ignore these without fully understanding the implications and consequences of their actions.

The effects of silicon on the performance of casting alloys has been widely documented and is well understood by the majority of the world jewellery manufacturing industry. This study will concentrate on a specific phenomenon encountered when using this element. As higher silicon levels are approached, detrimental as well as the positive effects may occur, including failure both during and after the casting operation. The study will evaluate the effect of quench temperature on a standard 9ct yellow casting alloy with varying silicon additions and will document any best practice determined. It is not concerned with alloy development, the alloys used being commercially available or close to commercially available compositions, but will concentrate on determining the effects encountered during and optimisation of the casting process. Determination of any change in mechanical properties of castings will be of secondary consideration to failure resistance during the casting process.

BACKGROUND.

A study of the binary phase diagrams of silicon show that it is insoluble in zinc, undergoes limited solid solubility in gold and silver and forms a series of single and two-phase solid solutions with copper (figures

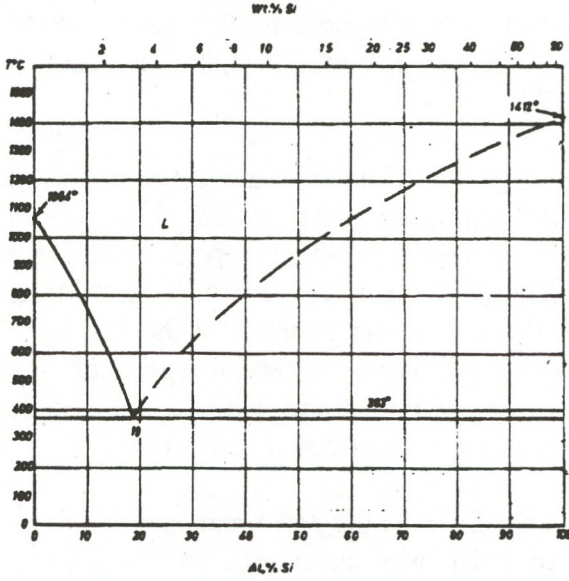


Figure 1a. Au-Si phase diagram.

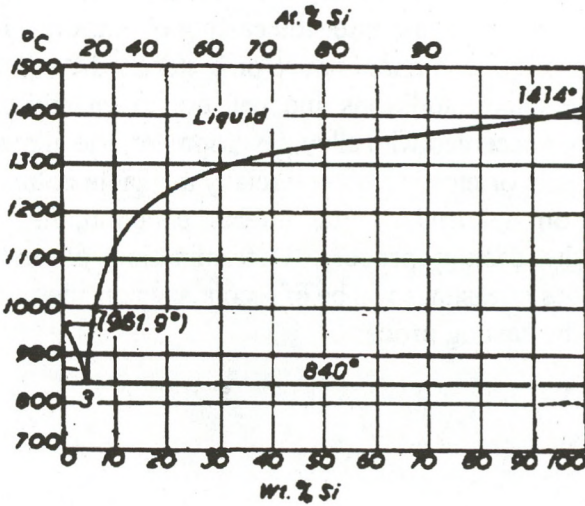


Figure 1b. Ag-Si phase diagram

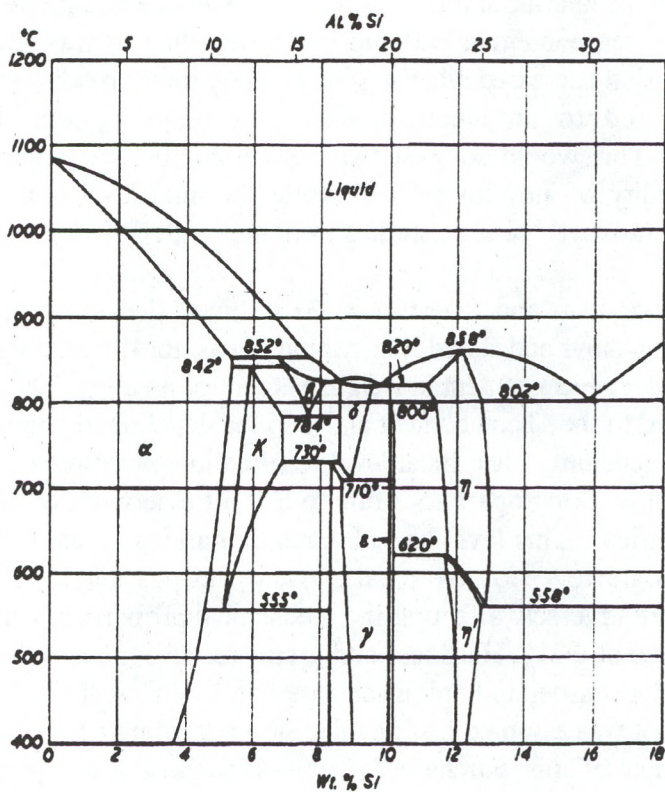


Figure 1c. Cu-Si phase diagram.

1a-1c). There have been numerous papers previously published outlining the effects of silicon on casting alloys and carat gold alloys in general. Ott (1) stated that the form filling capabilities of an alloy were dependant on several factors, two being the surface tension - the force that forms liquids into spheres - and the interfacial tension - which prevents a liquid wetting a solid surface. A decrease in either will improve form filling. It was noted that the interfacial tension decreased when casting an alloy under oxidising conditions when compared to an identical alloy cast under a protective argon atmosphere. This would suggest that silicon additions decrease the form filling capability of an alloy by increasing the interfacial tension through deoxidation, however various studies have met with differing results (2,3).

Normandeau and Roerterink (3) outlined the effect of silicon on various casting alloys and stated that caratage was not the limiting factor but the total (gold + silver) content in weight percent of an alloy. This factor was directly related to the silicon content and a critical level of silicon was defined (Figure 2). Exceeding this critical level resulted in embrittlement and failure on subsequent working operations due to a "brittle network of silicon at the grain boundaries". This level had obvious limitations when looking at the higher carats, however for low carat alloys it was possible to tolerate 0.5% silicon without adversely affecting the mechanical properties, with increases in fluidity noted at 0.1%. Hardness and grain size also increased with silicon addition, and an associated colour change noted. This will not be discussed in this study - it was assumed that any decision regarding alloy colour will be taken at the time of grain purchase. Jackson (4) suggested that levels of 0.4% silicon in 9ct alloys gave rise to embrittlement on soldering due to the formation of a low melting point silver and silicon-rich eutectic phase. Other references note the importance of grain boundary silicon-rich phases leading to embrittlement (5,6,7) however all were concerned with embrittlement in cast pieces subjected to post-casting exterior forces and not during the actual casting process. The latter area is the purpose of this study.

As a brief summary, it may be stated that silicon additions in low carat casting alloys will:

Gold + Silver
Weight %

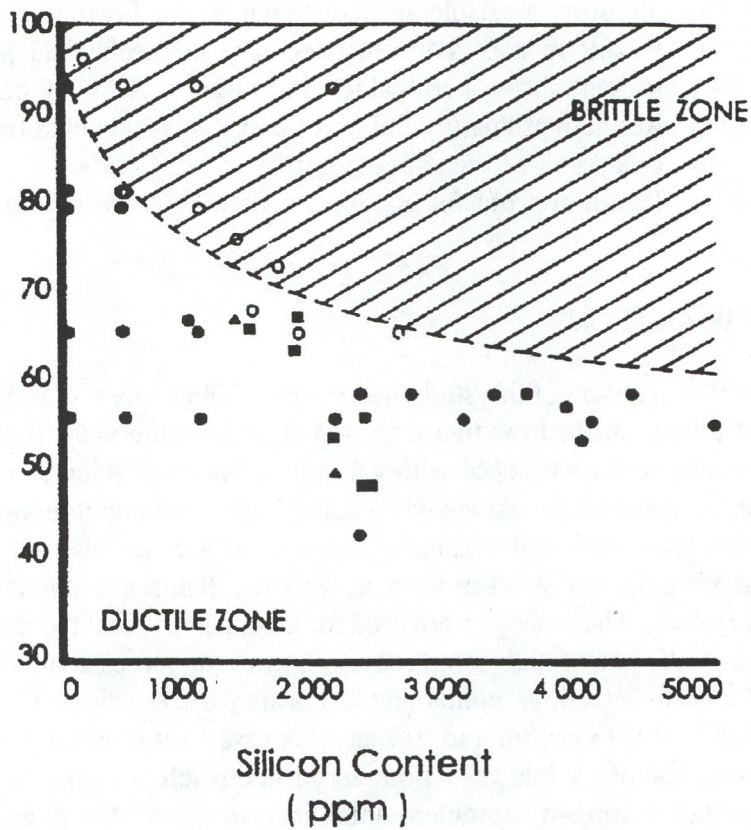


Figure 2.

- Deoxidise the melt.
- Result in bright oxide-free castings.
- Decrease the surface tension of the liquid alloy resulting in increased fluidity.
- May or may not improve the surface finish of cast items - the literature available gives different results for this effect.
- Result in a catastrophic decrease in mechanical properties when present above a critical level for a given Au + Ag content.
- Result in premature failure of cast items subjected to external forces as a result of the above point.
- Result in problems encountered during soldering operations.

OBJECTIVES.

The aim of this study was not to develop a new casting alloy or range of alloys but to investigate certain effects on the properties of an alloy of existing composition but with varying additions of silicon. It had been noted on a number of occasions when using high silicon containing alloys that, for what were described as standard conditions, a caster may achieve full, partial or virtually no success with a cast, the failures becoming evident after devesting. These alloys were used for a number of reasons, the most common being the use of high scrap recycling rates, an increase in which were noted between 9ct alloys containing 0.1% and 0.2% silicon (8). If these alloy systems were considered further, there was not only the possibility for the formation of a brittle grain boundary silicon-rich phase but also the potential for hot tearing if complete solidification during the quenching/devesting process was not achieved. The potential for these phases to remain in the liquid or partially liquid state at the time of quenching was, for the higher level of addition, considerable, possibly resulting in failure due to hot tearing as well as brittle fracture. It was necessary to determine if phases were grain boundary in nature or precipitated as distinct phases throughout the structure - i.e. a multi phase system as opposed to a single phase system with a grain boundary impurity present. To this end the study was primarily concerned with the investigation into failures that occurred during the casting process,

mechanical and physical properties already having been documented to some degree as a function of silicon content, if not quench temperature, on standard alloys.

Alloy choice.

For the purposes of this study the parent alloy chosen was 9ct DF, a general purpose alloy with approximate 3N colour and used throughout the U.K. industry. It has the nominal composition:

37.5% Au, 10.0% Ag, 44.5% Cu, 8.0% Zn

which places it safely within the ductile zone as described previously (figure 2). This alloy is used for all types of manufacturing processes and sold as casting grain with various elemental additions present. The alloy has an Ag' value of 18% and as such is moderately age hardenable (9). The phases $\alpha^1(\text{Au-Ag}) + \alpha^2(\text{Au-Cu})$ are precipitated when slowly cooled to equilibrium at room temperature.

When determining the range of silicon additions to be assessed, a study of the most popular casting alloys purchased was undertaken. This suggested additions of 0.1%, 0.25% and 0.5% silicon by weight, with control alloys at zero and 1.0%.

Designation	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5
Silicon (%)	0.00	0.10	0.25	0.50	1.00

The inclusion of the 1.0% silicon alloy may appear unusual however this provided an upper limit, no reference to a jewellery casting alloy containing such a high addition being found. Although the 0.5% silicon alloy may also be considered high, it was noted that approximately 10% of the 9ct yellow casting grain purchased was of an alloy with this addition, hence its' inclusion. Boron was added to the alloy to help clean the melt during graining and to increase the surface tension resulting in spheroidal grains with minimal

“stringers” of alloy - a problem often encountered when graining high-silicon alloys. Boron additions are usually lost during the graining process or on remelting by the customer and as such will not effect the fluidity of the alloy during the investment casting process. Care has to be taken on the level of boron addition due to its high affinity for elements such as iron to form hard iron boride particles (iron is often present as an impurity in copper/silicon master alloys). Measurements by Normandeau (7) suggested the level of boron remaining after the graining process to be typically of the order of 5% of the original addition.

Tree design.

To correctly assess the casting trials, several standard tree patterns were used to ensure maintenance of identical conditions for all casts. The three standard trees employed in these trials consisted of:

1. A selection of common designs ranging from thin lightweight rings through heavy rings to complex brooch designs. A degree of emphasis has been placed on thin section lightweight designs since these generally dominate the U.K. casting market. Heavyweight items are commonplace but do not approach the quantity of lightweight items produced (figure 3).
2. A selection of test pieces to determine mechanical properties, porosity, surface finish, degree of ring sizing tolerated and solderability (figure 4). These are all standard test pieces employed in numerous other casting studies.
3. A mesh design for measuring fluidity.

Trials.

For each of the five alloys tree No.3 was cast at 120°C superheat into a flask at 650°C and quenched at 450°C (measured at the button). For all alloys trees No.1&2 were cast at 120°C superheat and quenched at

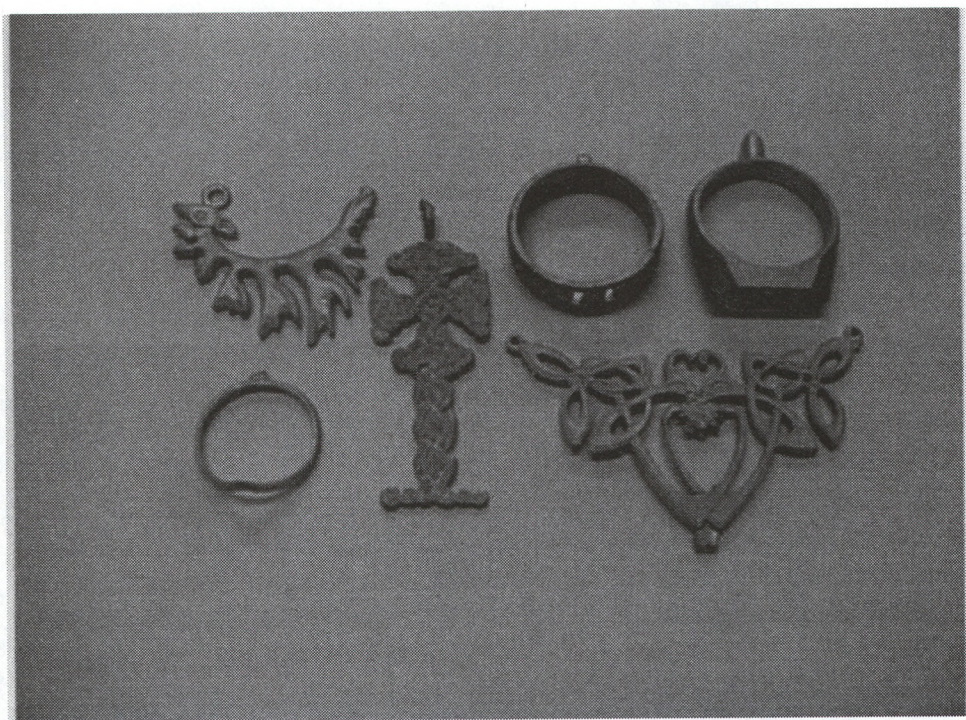


Figure 3.

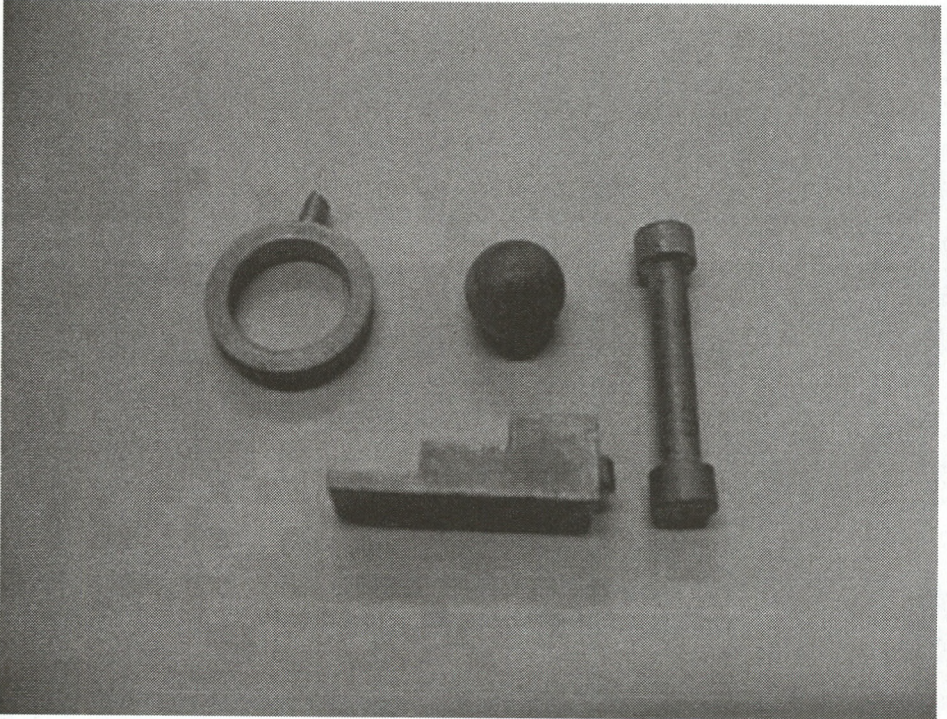


Figure 4.

temperatures of 600°, 550°, 500°, 450° & 400°C (measured at the button). Analysis was then performed, where necessary as a function of quench temperature, for each alloy.

EXPERIMENTAL.

Grain production.

All grain used in this study was produced on an Inresa graining unit in 2500g batches. The plant consisted of an induction melting unit utilising a six-hole bottom pouring crucible and a pneumatically operated stopper rod releasing the liquid metal into a water quench tank positioned below the crucible. Nitrogen was used as a cover gas over the melt surface and also over the water surface, ensuring the liquid metal was protected at all times during processing. The temperature of the charge was determined by immersion thermocouple (type R). Each alloy batch was grained using 100°C superheat.

Investment casting procedure.

All flasks underwent an identical investing and burnout cycle to a final temperature of 650°C. The casting machine used was a Galloni VCM vacuum assist static caster with an argon gas cover. Standard weight charges of 100% grain were used for each type of tree and heated to 120°C above the liquidus, held for 1 minute and then cast. Each casting was held under vacuum for 2½ minutes (3 minutes for alloy 5) then removed and placed on an insulated plate where temperature measurements were taken. At the quench temperatures (measured at the button) all flasks were quenched in water, cleaned by power-wash and pickled in a sulphamic acid solution for 10 minutes. Samples were then assessed for investment adherence, further pickling completed if required and failures assessed.

Analysis.

Chemical analysis was performed using standard techniques by the Analytical Chemistry Department at CPM on random grain samples. The melting range of each alloy was determined from a grain sample by thermal analysis using a Rheometric Scientific STA 1500. Temperatures were determined using type K thermocouples, the cast button from a surface contact probe, the middle and bottom tree castings from probes through pre-formed holes in the investment. Fluidity was assessed by the degree of fill for the mesh pattern and stone setting prongs for each alloy. Surface finish was assessed under a stereo microscope using x10 magnification. Metallography was carried out on microsections prepared by standard techniques using a metallurgical microscope. Further analysis was performed on a scanning electron microscope using both qualitative and semi-quantitative techniques. Two environmental tests were performed on cast "doughnut" rings that had been polished to simulate finished product:

- Exposure to sulphur dioxide as specified in BS 6670 part 2. Samples are suspended above a solution of sodium thiosulphate pentahydrate and sulphuric acid for 24hrs at 25°C. The test gives an indication of resistance to discolouration - often noted in the U.K. by both the wearer and retailer due to everyday pollutants present in the local environment.
- Exposure to an alcoholic ferric chloride solution. Castings were immersed for 24 hrs in the ferric chloride solution and an assessment of the degree of surface attack made. The test is important since it will assess resistance to stress corrosion.

Ultimate tensile strength, 0.2% proof stress and elongation after failure were determined from standard dumbbell type tensile cast samples. All UTS and 0.2% PS values were averaged from six samples to the nearest 5 MN/m², all elongation values from six samples to the nearest whole percent. Vickers hardness values were determined using a 5kg load. Six indentations were made on the side face of a wedge shaped casting and an average hardness determined. Grain size was determined from identical ring castings using a linear intercept method, taking an average of three tests per casting.

The degree of ring sizing tolerated was assessed by sizing-up doughnut ring castings using a Benzinger ring stretcher. Similar castings were cut by fretsaw and soldered using a 9ct easy cadmium-free solder then the above test repeated.

RESULTS & DISCUSSION.

Compositional analysis:

Silicon and oxygen contents of grain and castings were determined:

Alloy	Nominal Si (%)	Grain Si (%)	Casting Si (%)	Grain O2 (ppm)	Casting O2 (ppm)
1	0.00	0.00	0.00	6	38
2	0.10	0.075	0.02	9	24
3	0.25	0.20	0.10	8	33
4	0.50	0.50	0.50	4	85
5	1.00	>0.75	>.50 <.75	6	85

The decrease in silicon content from nominal after graining in alloys 2&3 was probably due to the presence of oxygen in the molten charge. The low oxygen levels in the grain would either confirm there was no original oxygen present or the silicon was deoxidising the melt. The method used for determining oxygen content will detect both free and combined forms in the alloy. The silicon and oxygen detected may be combined and residual in the casting, the decrease in silicon from nominal being associated with any "lost" by deoxidation and slagging-out in the crucible. The boron content for the grain was detected as <10ppm - this was the limit of resolution for the analytical method used.

Melting range:

The melting ranges for each alloy were determined and may be viewed in graphical form (figure 5).

Alloy	1	2	3	4	5
Solidus (°C)	880	805	784	755	675
Liquidus (°C)	900	890	880	870	830

Whilst the increase in silicon addition reduced the liquidus considerably, the solidus was influenced to a far greater degree, expanding the melting range of the alloy. This was undoubtedly due to the formation of major low melting point silicon-rich phase(s). It must be noted that the precipitation of any phases in grain and castings may differ due to the dissimilar solidification conditions. This will have an effect on the melting ranges determined.

Temperature measurement:

All temperature measurements discussed were taken from tree No.2. All flasks remained under vacuum soak for 2½ minutes (3 minutes for the 1.0% silicon alloy) prior to removal for cooling. Measurements were taken every 30 seconds after 3½ minutes had expired (1 minute of cooling after removal from the chamber).

Analysis of the data generated revealed a significant difference in button temperature after 1 minute of cooling for any given alloy. For identical hold and cooling times the button temperature ranged from:

Alloy	Button Temperature after 1 minute (°C)	Cast Temperature (°C)
1	550 - 625°C	1020°C

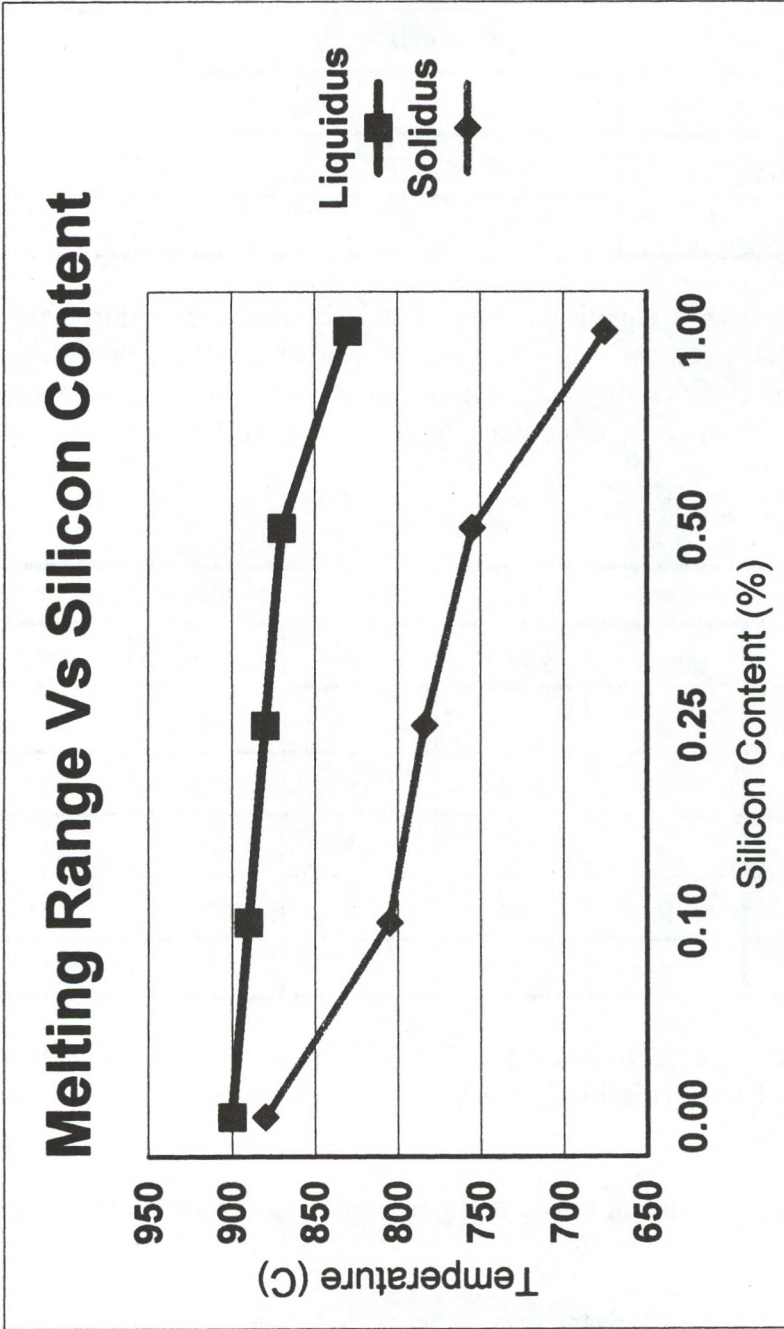


Figure 5.

2	630 - 790°C	1010°C
3	670 - 770°C	1000°C
4	635 - 815°C	990°C
5	690 - 735°C	950°C

There was a significant difference in button temperature ranges between the alloys - those containing silicon being much higher than alloy 1, even though lower casting temperatures were used. This must be directly associated with the rate of cooling for each alloy. Further analysis of the results revealed:

Alloy	Time (mins) to Temp.				
	600°C	550°C	500°C	450°C	400°C
1	2	3	3	9	---
2	3	10	18	22	20
3	6	8	16	25	23
4	9	13	17	27	33
5	5	7	11	15	22

This data may be seen in graphical form (figure 6) and for a single temperature of 450°C (figure 7). Again, alloy 1 exhibited the fastest cooling rate.

The cooling rate of the casting trees will be governed by three major factors:

- the rate of heat quantity flowing between the alloy and the investment

Cooling Rate Vs Temperature

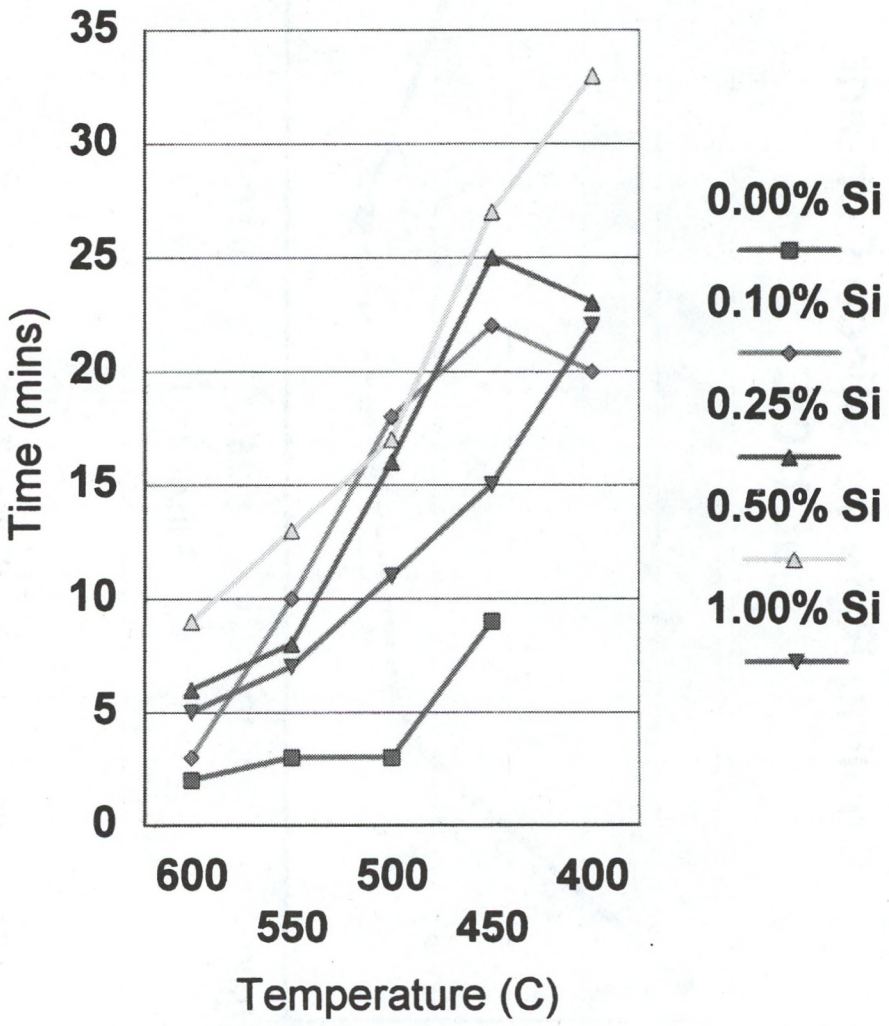


Figure 6.

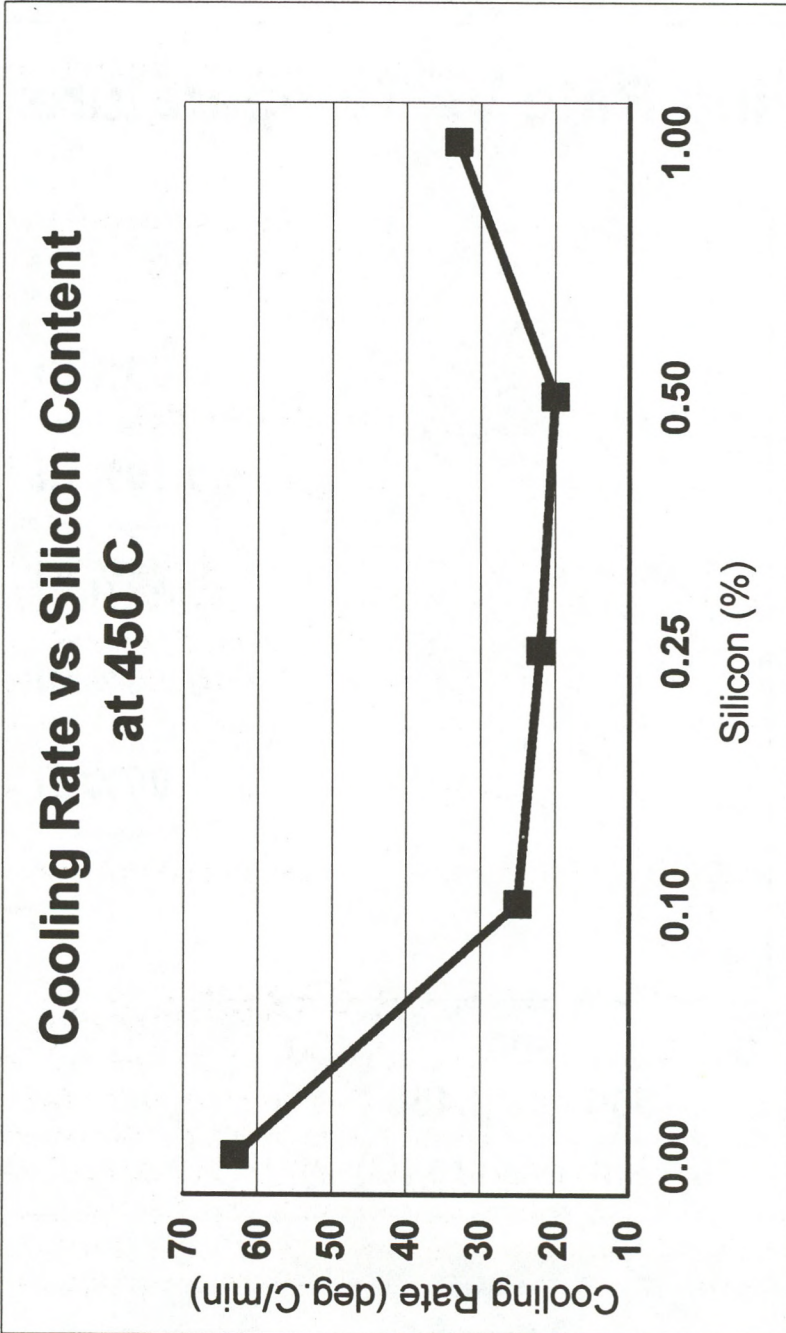


Figure 7.

i.e. the conductivity of the investment,

- the amount of heat energy radiated from the alloy by the button, and
- the specific heat capacity of the alloy.

The rate of heat loss from the alloy to the investment will be governed by the equation:

$$Q = Ct$$

where Q = heat quantity flowing per second through a unit area
 C = conductivity of the body
 t = temperature difference between the faces

This relationship demonstrates that as temperature difference between an alloy and the investment decreases so a corresponding reduction in the rate of heat flow will occur - i.e. the cooler an alloy becomes, the slower it cools. The rate of heat loss for the open surface of the button is governed by the Stefan-Boltzmann law of radiated energy:

$$E = \sigma T^4$$

where E = radiated energy from a black body per unit area per unit time
 σ = Stefan-Boltzmann constant
 T = absolute temperature of the body

The amount of heat energy radiated is dependant on the absolute temperature to the fourth power therefore the rate of decrease will be influenced significantly by relatively small decreases in temperature - again, the cooler an alloy becomes, the slower it cools. Both of the above factors will be influenced by the emissivity of the alloy, this being defined as the amount of heat energy lost by a surface due to conduction, radiation, convection and the radiation received from surrounding bodies (10). Note that emissivity must not be confused with emissive power, which applies to

radiated heat energy only. Since the rate of cooling decreases for the silicon-containing alloys, which are at a higher temperature than alloy 1, the assumption may be made that the "satin" finish of the castings contributes significantly to the cooling rate by lowering the emissivity. The increase seen for alloy 5 over the others may be a result of the lower casting temperature used, a change in the emissivity due to the coarser, dendritic surface generated or a combination of both. The surface of alloy 1 was smooth but dull, again suggesting that the surface condition was affecting the cooling rate by raising the emissivity. Typical emissivity values quoted are:

Lampblack - 1.00
Dull copper - 0.79
Polished copper - 0.48
Polished silver - 0.02

This does not create a true picture since the rate of heat loss will also be complicated by shrinkage. If the alloy has a high thermal coefficient of expansion the shrinkage rate will be high, giving rise to an air gap between the casting and investment. Below 600°C the rate of heat loss due to radiation is negligible compared to that of conduction. Air is a more efficient insulator than investment resulting in an overall decrease in cooling rate due to conduction and radiation effects. The cooling rate of each alloy will also be effected by its' specific heat capacity. Any increase in the specific heat capacity will result in a corresponding decrease in the cooling rate under identical conditions since more heat energy must be dissipated per °C reduction. At the time of writing the variation of specific heat capacity between the alloys tested was not known and will require further work to establish.

This summation may be proved incorrect by future work however based on the evidence available here it is a logical conclusion. It must be noted that whatever the reason behind the change in cooling rate, it is extremely significant. For a given time after casting to quench, the silicon containing alloys may have phase(s) present that remain in the liquid or semi-

liquid state. Direct temperature measurement is essential; both sets of results indicate time is not a good indication for quench temperature.

Data taken from T1, T2 & T3 (button, middle and bottom of the tree) have been compared (figure 8), this being a typical cooling cycle. T1 was measured directly on the alloy surface, T2&T3 assumed to be within a small distance of the castings. It must be accepted that there is a significant decrease in temperature moving down the tree. The metal at the bottom of the tree was the first to come into contact with the relatively cold investment will have cooled to a greater degree at any given time. The metal at the top of the tree - in particular the button - will be the last to flow into the flask and therefore at a higher temperature as a result of superheat from the remainder of the tree and reduced time in the flask. The button will also experience a reduction in heat flow due to radiation from the open surface below 600°C decreasing significantly. The presence of low melting point phases would have a marked effect on the solidification characteristics of the alloy. In different tree positions at any given time, castings nearer the bottom half may have undergone full solidification whilst castings near the top half may still contain liquid or semi-liquid phases. As a result the potential for hot tearing will exist.

Time to temperature will be affected by the factors outlined above, but also by the size of tree, the charge weight and tree content. These will influence cooling rates drastically and may result in the problems noted when using high silicon alloys.

Fluidity and surface finish.

All alloys filled the mesh pattern and ring settings completely indicating no measurable difference in fluidity from this test. It must be considered that differences may be noted if more demanding patterns were used however since this study is primarily concerned with the effect of quench temperature on silicon addition and not silicon addition per se, no further work was carried out in this area.

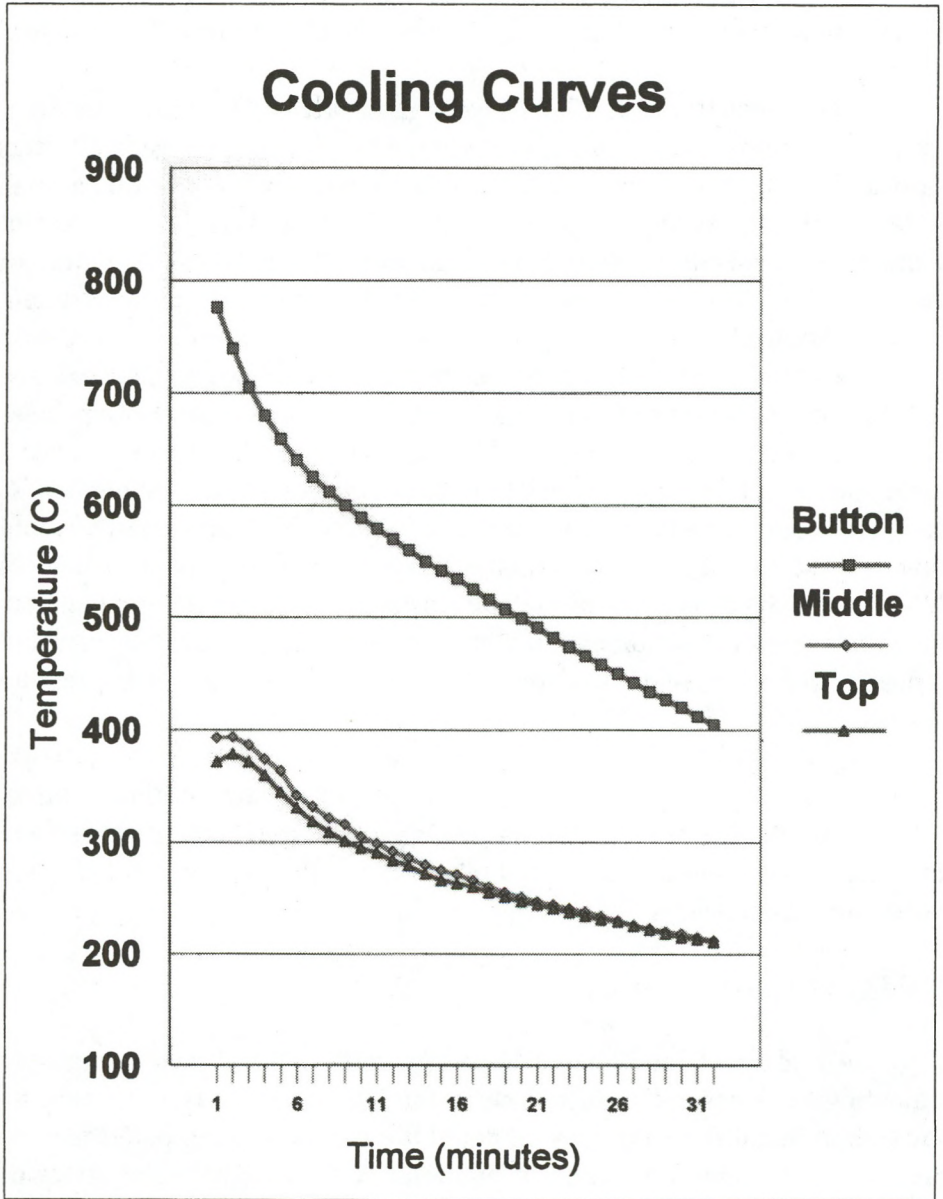


Figure 8.

Castings were examined under the stereo microscope at x10 magnification. Alloy 1 exhibited a smooth surface finish for all quench temperatures with evidence of dendritic formation being negligible. The surface, although smooth, had a dull texture. Alloys 2&3 exhibited a similarly smooth surface finish for all quench temperatures with evidence of dendritic formation again being negligible; the surfaces had a satin texture. Alloy 4 exhibited a smooth surface finish for all quench temperatures, however evidence of dendritic formation was marginally increased over the previous alloys; the surface had a satin texture. The surface of alloy 5 exhibited a random dispersion of satin and dull textures for all quench temperatures. There was evidence of dendritic formation, this decreasing with decreasing quench temperature. Castings from this alloy exhibited the roughest surfaces of the study.

All alloys - apart from alloy 5 - were unaffected by quench temperature and gave similar results regardless of silicon content. The results for alloy 5 suggest a relationship between quench temperature and surface finish, with higher quench temperatures preventing filling of inter-dendritic spaces. It has been well documented that higher silicon additions increase the potential for heavy dendritic growth (2,3). Since this alloy was introduced to the study as a control only and there are - to the best of the authors knowledge - no commercially available alloys with this level of silicon addition, no further investigation was carried out. For acceptable surface finish, the alloying limit may be considered as 0.5% silicon and the marginal decrease in surface quality accepted.

Failure analysis.

The quenched and devested trees were subjected to an initial examination prior to pickling. Only alloy 1 exhibited dark areas of copper oxide - all casting surfaces were grey/black. Alloys 2, 3 & 4 all exhibited a "satin" surface finish, alloys 2 & 3 being superior. Alloy 5 had an intermittent satin finish with "dull" areas however there were no indications of any oxides present. Trees were then pickled in a solution of thiosulphamic acid for 10 minutes, re-examined, and the amount of residual investment noted. For a

given alloy, this increased with decreasing quench temperature, however this fact will be no revelation to the investment caster and was expected. The amount of residual investment was also substantially higher for alloys 1&5 when compared with alloys 2 & 3, which were investment-free. Residual investment was present in minor quantities on the surface of alloy 4. This is a direct consequence of the satin finish generated by the silicon additions being resistant to investment adherence.

For failure analysis, castings from tree design No.1 were examined - these were actual work pieces and as such more relevant to the caster than tensile and wedge castings. Each tree contained 20 castings. Failure rates were determined as:

Alloy No.	600°C	500°C	400°C
1	1	1	1
2	1	2	1
3	6	2	0
4	13	5	1
5	15	10	3

These results can be seen graphically (figure 9).

The failed castings from alloys 1&2 occurred at random positions on the trees. Metallographic examination confirmed these to be associated with areas of shrinkage porosity. For the remaining alloys, failure was predominantly at the top (button) end of the tree, those with a high incidence having failures move down the tree with increased quench temperature. Only with alloy 5 quenched at 600°C were there failures at the bottom of the tree. It was also noted that failures in castings from the lower section of the trees or when few failures were identified were generally in the sprue area of the casting, i.e. the part expected to be hotter and last to solidify. This confirms

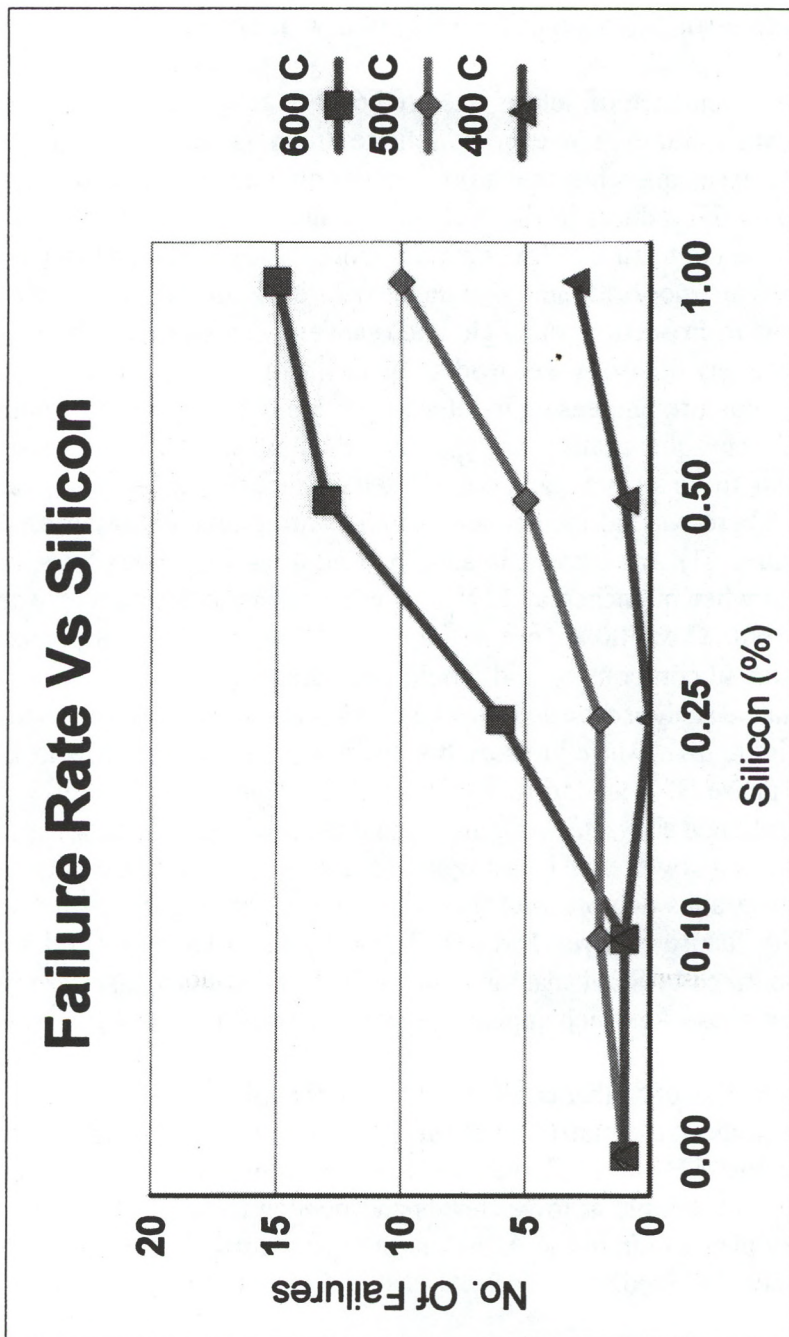


Figure 9.

a relationship between tree position and failure potential and suggests the theory regarding solidification and cooling rates was correct.

A high incidence of failure was predicted in alloy 5 when quenched at higher temperatures, however a definite trend existed suggesting a relationship between quench temperature and silicon content. Metallographic examination of the failures in the high silicon alloys confirmed the failure mechanism to be hot tearing of low melting point phases in conjunction with liquation pores and not brittle inter-granular failure (figure 10). Two phases were evident in microsection, one light and one dark - categorised as phases A & B respectively. Phase A was evident in all silicon containing alloys and was random in nature, increasing in intensity with increasing silicon content (figure 11). Semi-quantitative analysis by scanning electron microscope confirmed this to be a silver-rich, copper depleted silicon containing phase (figure 12). There was no incidence of failure with phase A only present. Phase B (figure 13) was present in alloy 5 at all quench temperatures, but only marginal when quenched at 400°C. It was present in alloys 3&4 when quenched at 600°C & 500°C, but not at 400°C. The incidence of phase B increased with silicon content and would only precipitate within phase A. Semi-quantitative analysis revealed it to be a gold-rich phase with high levels of silicon (figure 14). All failures by hot tearing were coincident with the presence of phase B. A silicon-rich grain boundary phase was identified at high magnification in alloys 3&4 (figure 15) and resulted in some minor grain boundary cracking however all catastrophic failures were associated with hot tearing. Micrographs demonstrate the difference in appearance of the two phases during failure (figures 16&17). The smooth surface detected was phase B - confirmed by SEM analysis - with failure taking place also through the silver-rich phase A, which appears to be more tensile in nature.

Examination of further castings confirmed that phase A was randomly dispersed throughout the matrix of all silicon containing alloys at all quench temperatures. Phase B was insoluble in high silicon alloys at elevated quench temperatures but soluble at lower levels and quench temperatures; it only existed as a duplex within phase A. At the time of writing neither phase had been positively identified.

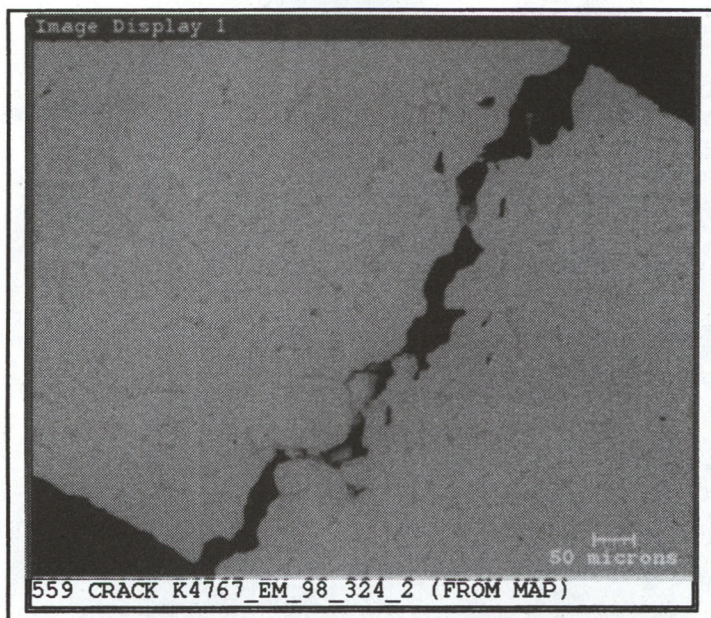


Figure 10. Failure in alloy 4.

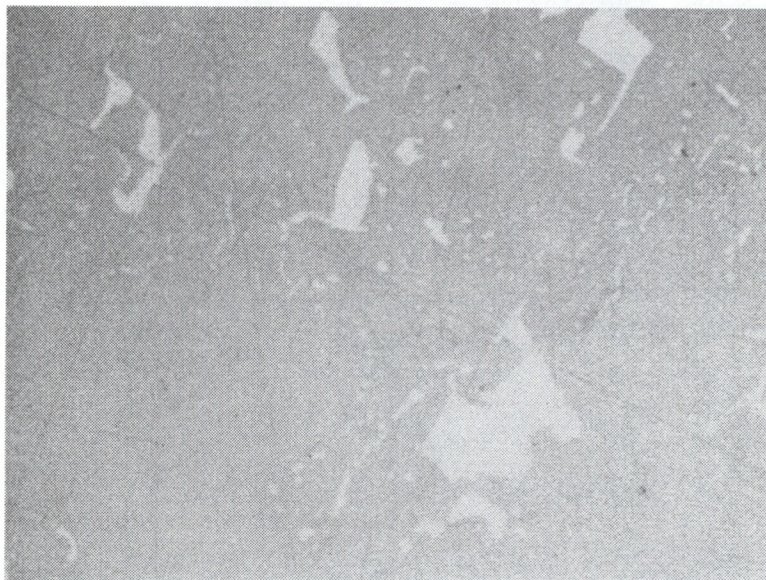


Figure 11. Phase A. Magnification x 700.

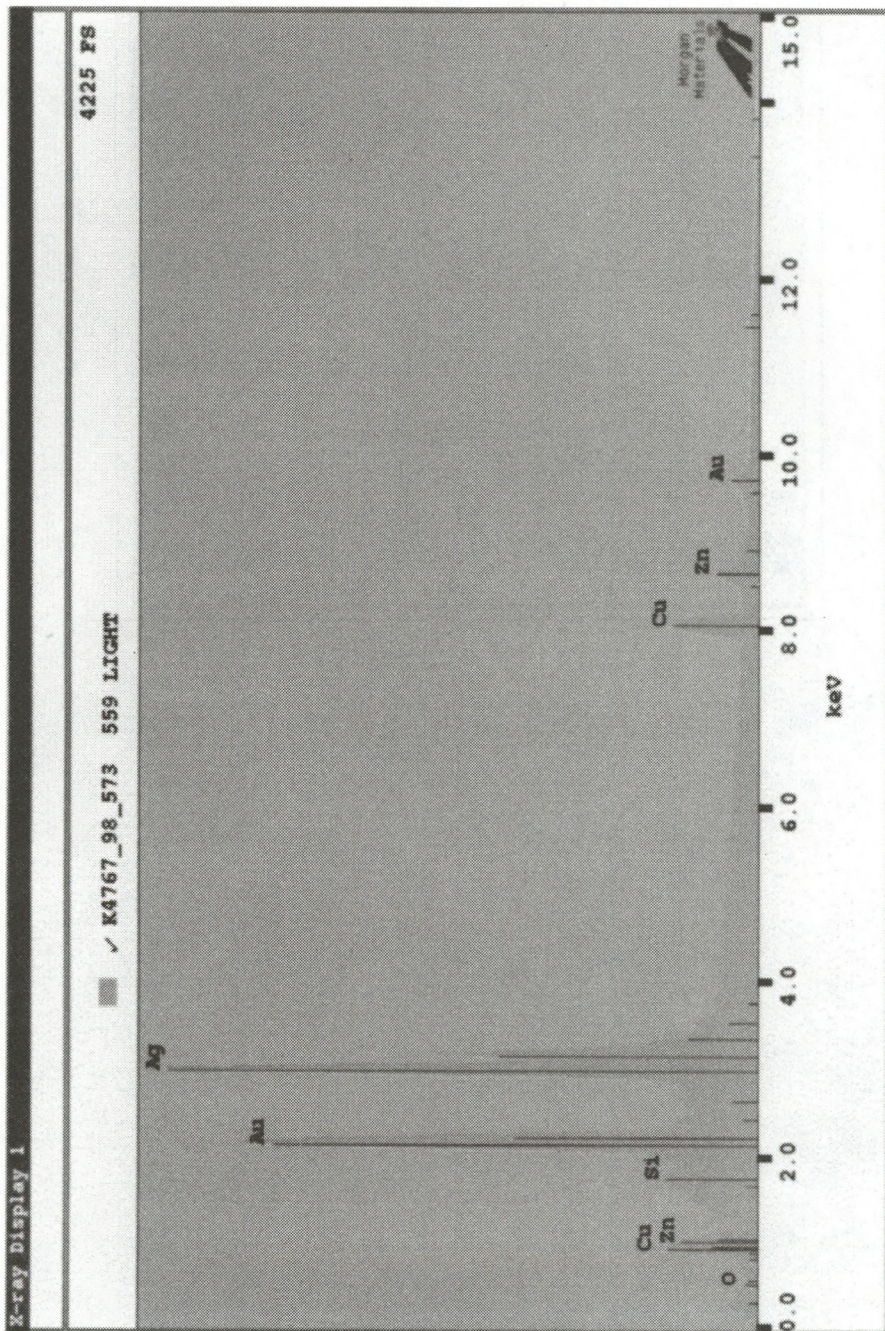


Figure 12 - Phase A analysis

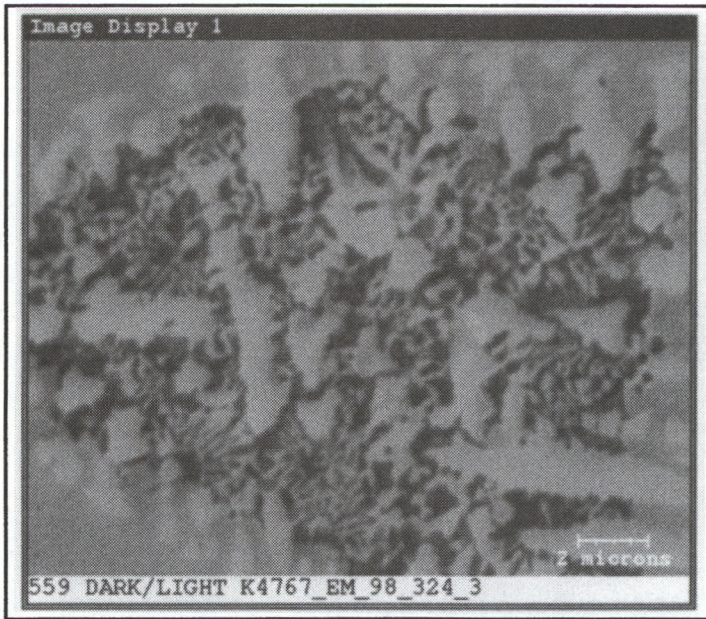


Figure 13. Phase B.

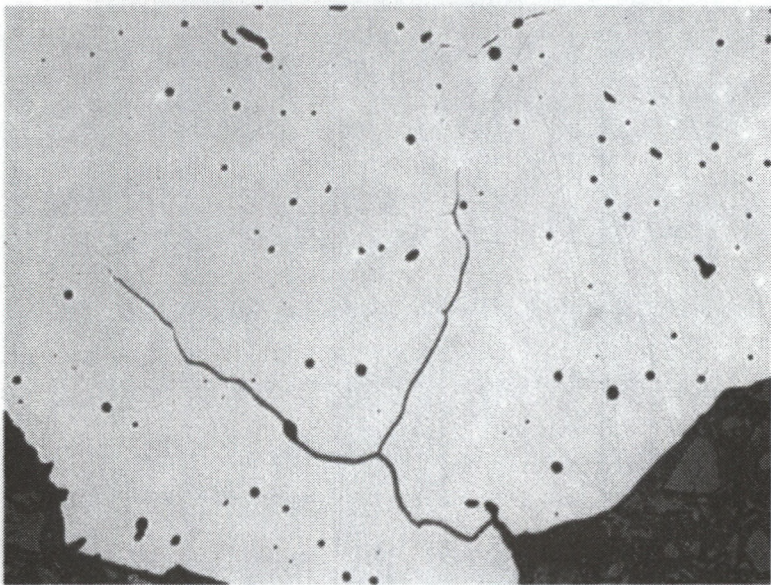


Figure 15. Grain Boundary Crack. Mag'n x 140.

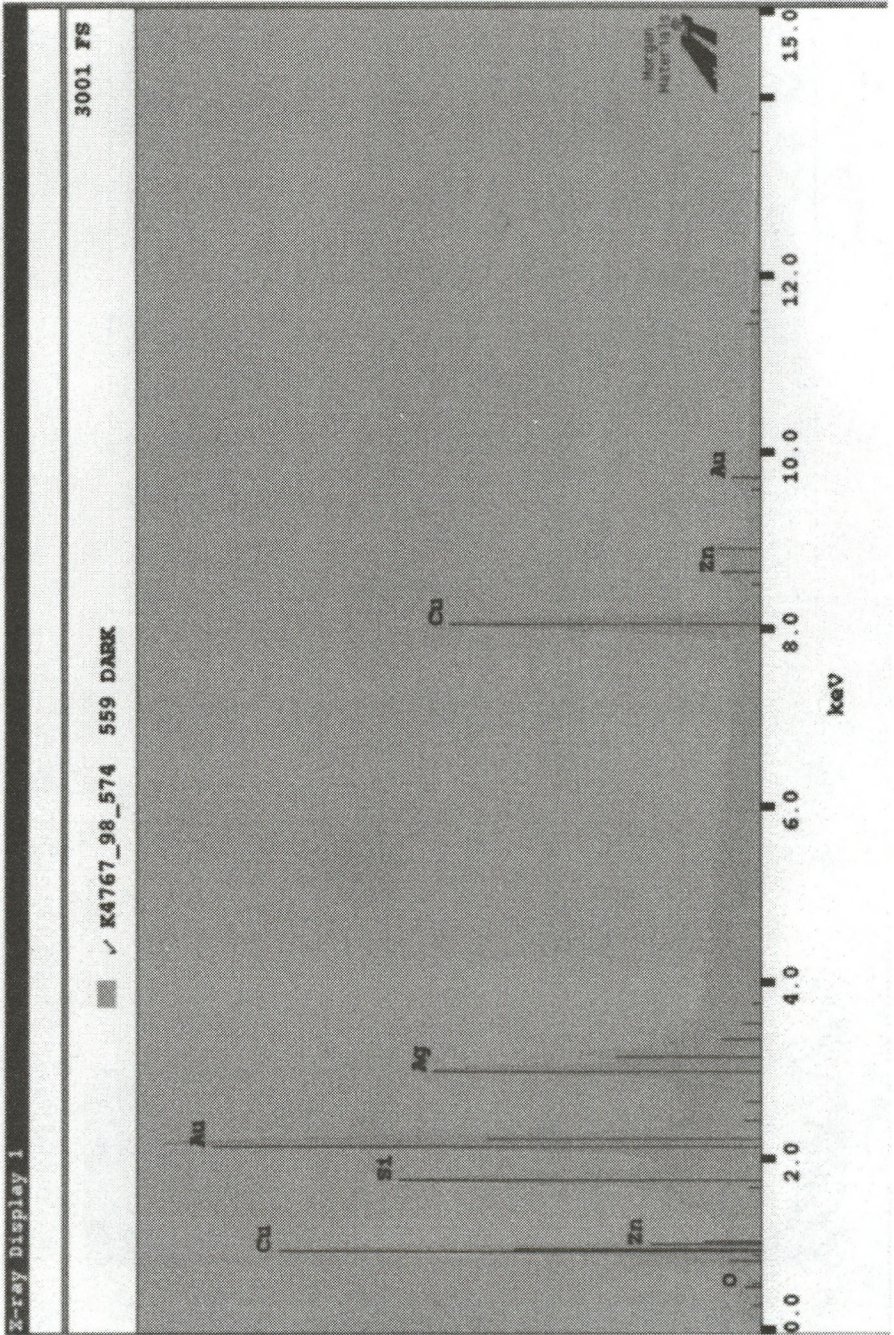


Figure 14 - Phase B analysis

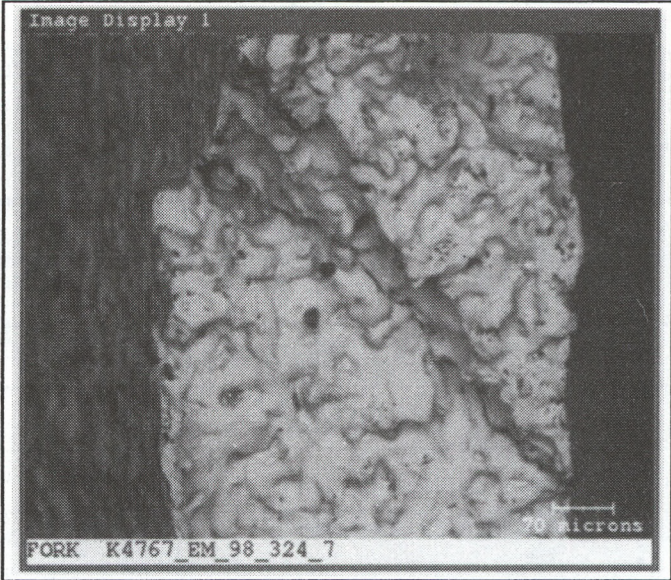


Figure 16. Phase B on crack face.

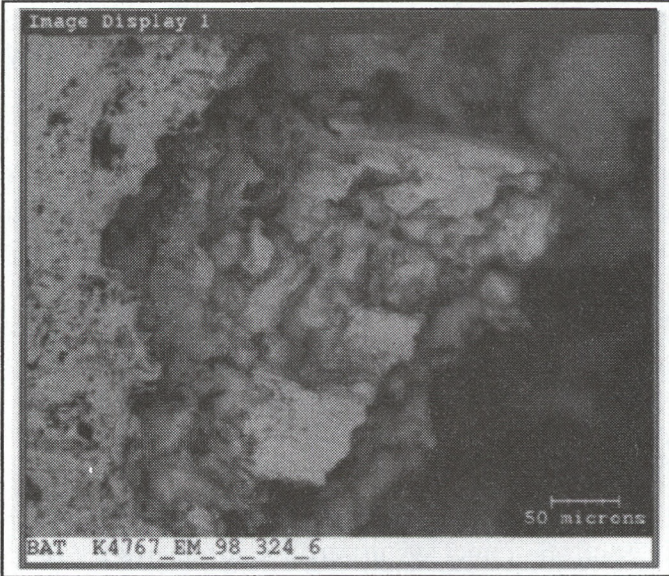


Figure 17. Phases A & B on crack face.

Environmental analysis.

After exposure to sulphur dioxide the following observations were made, using a scale of 1 - 10 where 1 is high resistance and 10 high susceptibility to corrosion:

Alloy	600°C	550°C	500°C	450°C	400°C
1	3	3	3	3	---
2	3	3	3	3	3
3	4	4	4	4	4
4	4	4	4	4	4
5	8	8	7	6	6

Alloys 1&2 had a relatively high resistance, being only marginally discoloured (figure 18). As the silicon content increased through alloys 3&4 so the resistance decreased, however the difference was marginal. Up to this point there was no correlation between reaction and quench temperature. Alloy 5 had a marked increase in reaction at the surface, all samples exhibiting a blue/green precipitate (figure 19). Analysis by scanning electron microscope confirmed this to be predominantly copper sulphate, with silicon and oxygen also present. This reaction susceptibility decreased marginally with quench temperature. The higher degree of reaction was possibly associated with the formation of phase B, high levels of silicon being detected in the corrosion products. It must again be noted that this was the control alloy and due to time restraints on the author, any investigation into the corrosion mechanism was postponed until a later date. For resistance to attack by sulphur dioxide it may be stated that 0.5% silicon was an acceptable limit.

The samples immersed in ferric chloride were examined however there was no discernable correlation between quench temperature or silicon

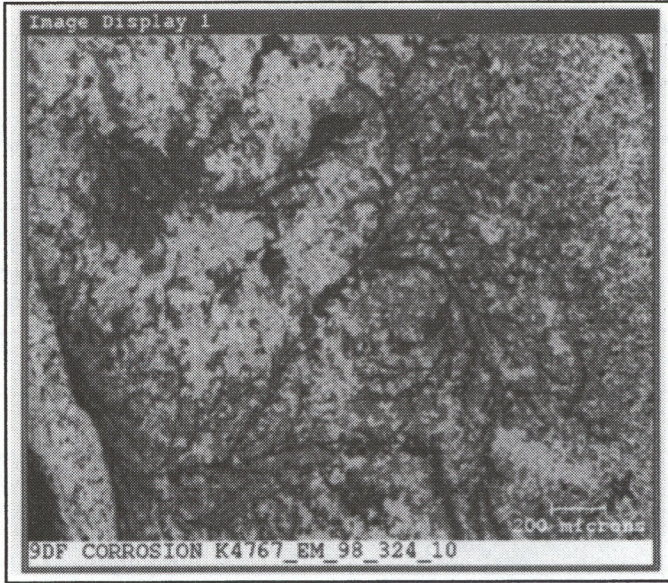


Figure 18. Discolouration of ring surface.

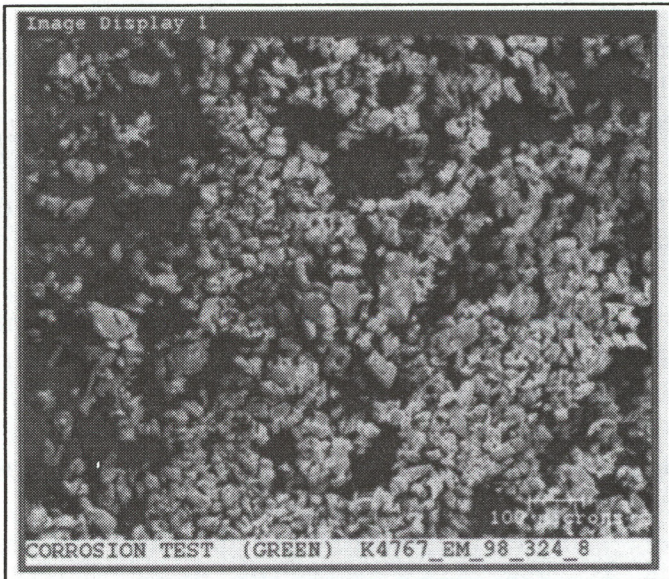


Figure 19. Blue-green surface precipitate.

content and resistance to attack by ferric chloride. Microsections of samples did not exhibit any signs of stress corrosion failure or inter-granular cracking.

Alloy	600°C	550°C	500°C	450°C	400°C
1	4	1	1	1	---
2	1	1	1	8	1
3	1	2	2	3	1
4	2	1	5	5	2
5	1	1	10	8	6

Mechanical properties.

The mechanical properties for each alloy as a function of quench temperature have been compared (figures 20 - 23). From the data measured there appeared to be no correlation between the quench temperature and UTS, 0.2% proof stress, elongation and hardness. This was probably the result of the erratic nature of the segregates formed. Increasing the sample rate may yield data that is more representative and negate any anomalies. It has been observed in previous publications that an increase in silicon addition will change the mechanical properties, increasing the UTS, hardness etc. This was confirmed however for alloy 5 the elongation decreased considerably, fracture surfaces appearing brittle.

Quenching 9ct alloys above 390°C results in the generation of a homogeneous solid solution α (Au,Ag,Cu). The two phase region in the silver-copper binary results in the generation of an immiscibility curve below 390°C in the ternary system. If the alloy is slowly cooled below this temperature, the phases α^1 (Au-Ag) and α^2 (Au-Cu) will precipitate. This may be complicated further by the decomposition of α^2 into the ordered phase AuCu³ - from the Au/Cu binary system (11,9) - resulting in some degree of hardening in the alloy. Samples were etched in a solution of 1/1 10%

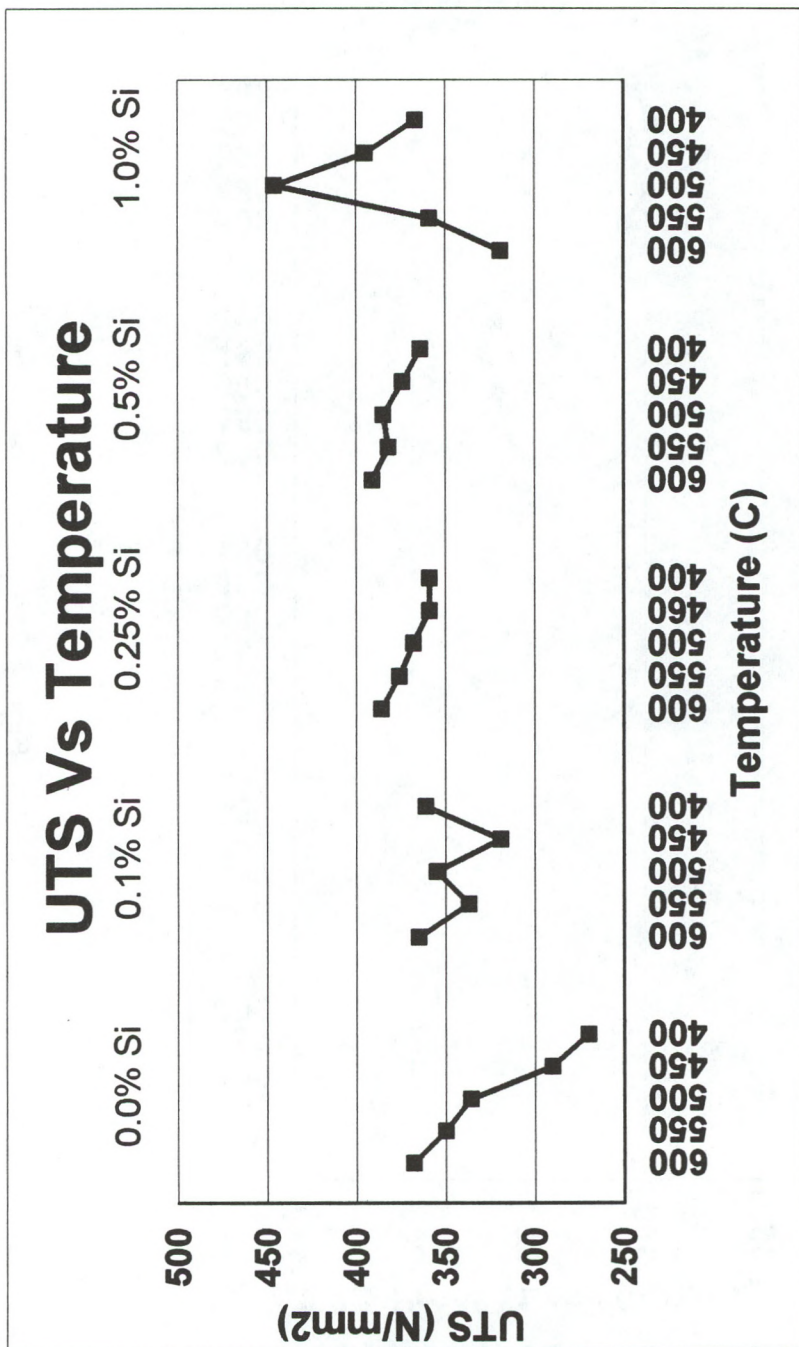


Figure 20.

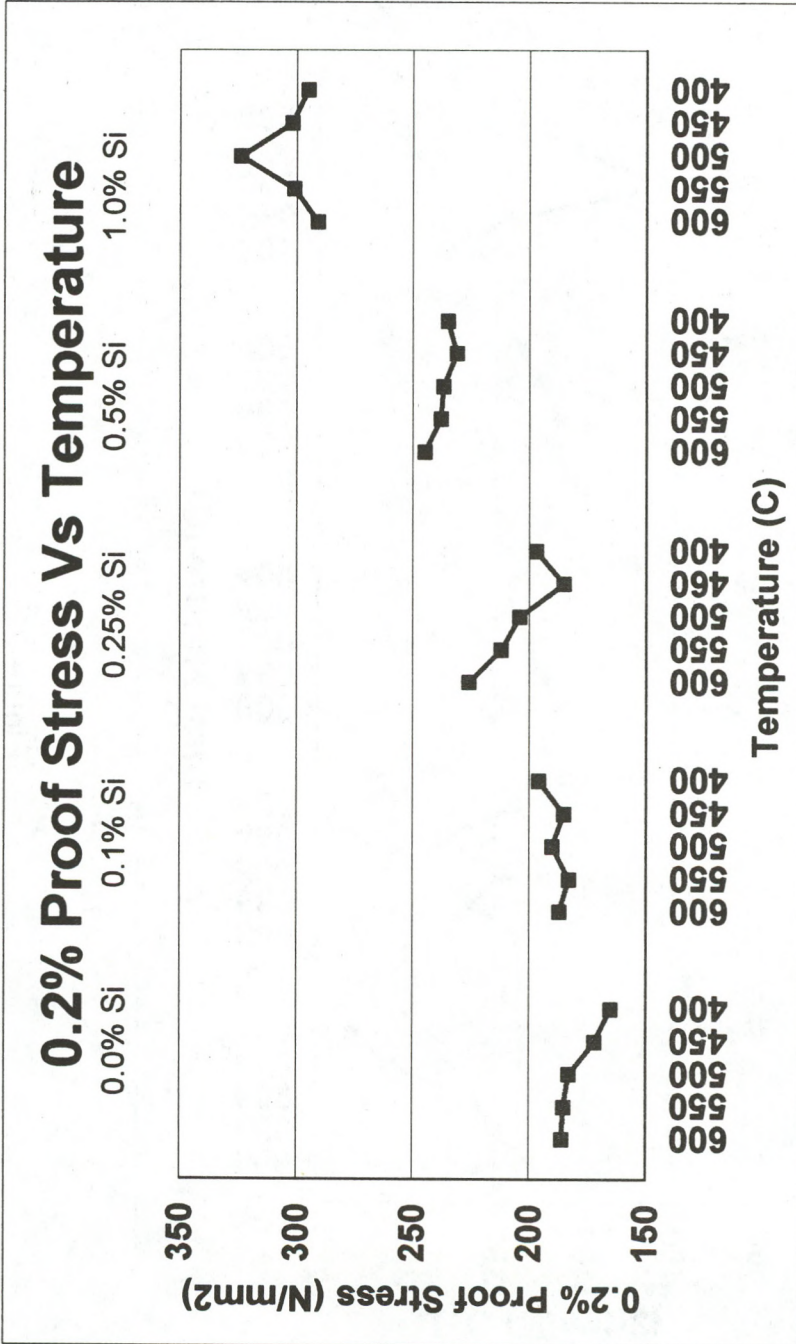


Figure 21.

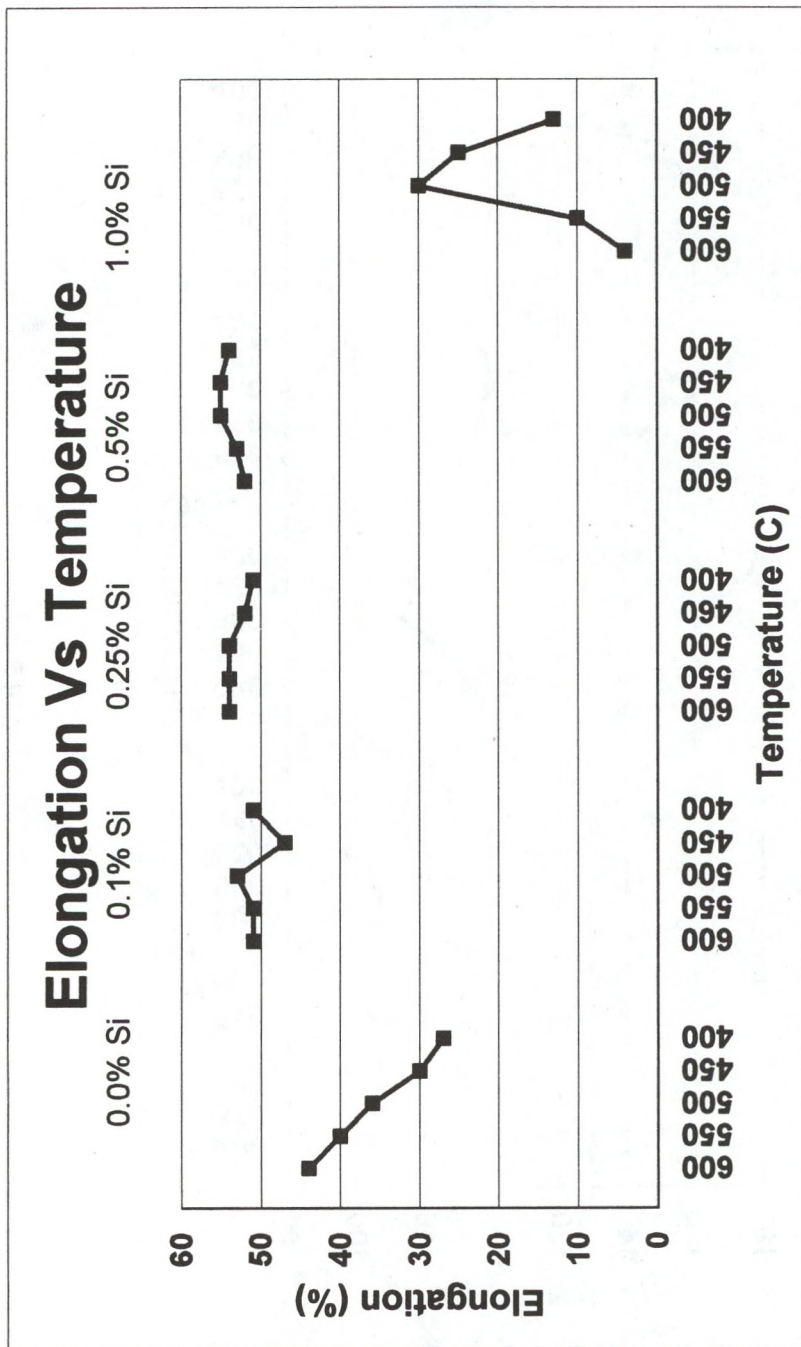


Figure 22.

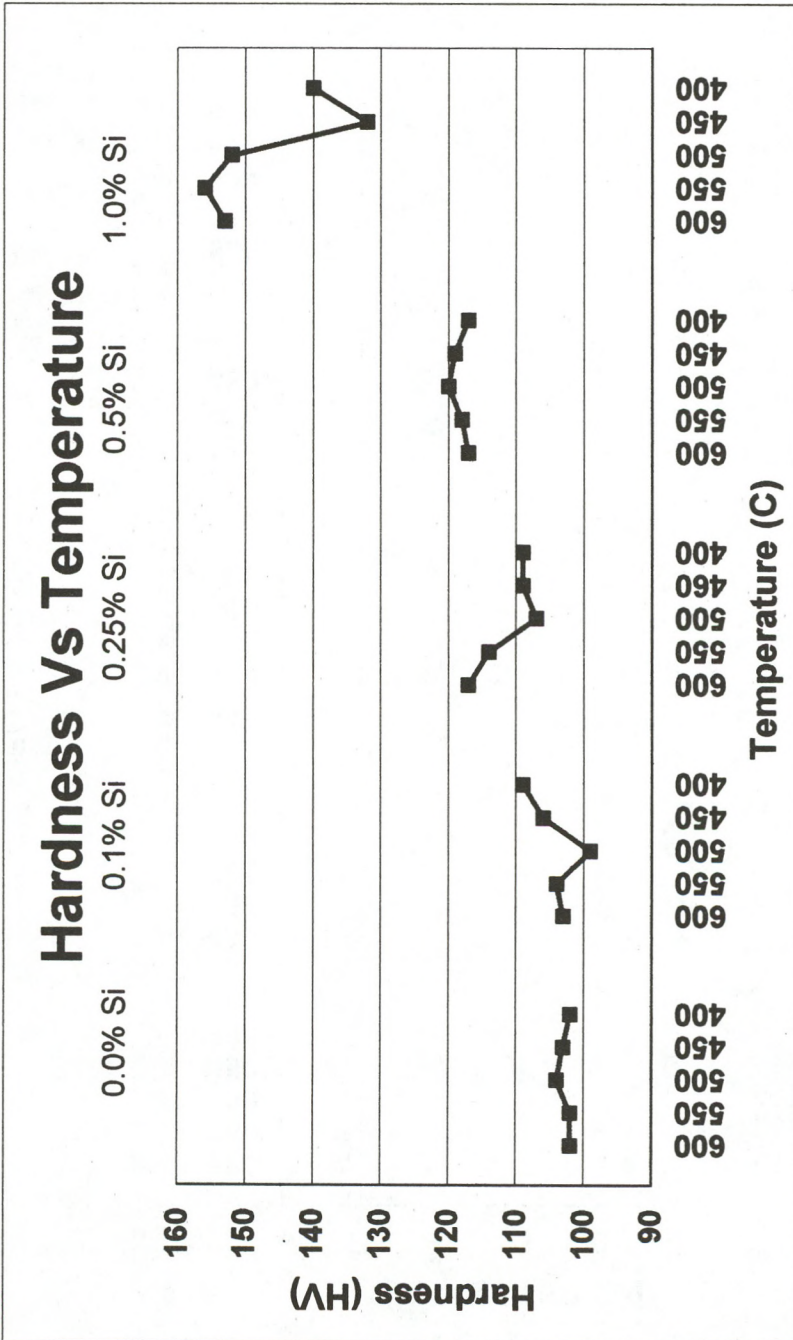


Figure 23.

potassium cyanide/10% ammonium persulphate and any precipitation noted. The level of ($\alpha^1 + \alpha^2$) increased with decreasing quench temperature as expected, however the increase in silicon content also resulted in an increase in precipitation around the silicon-rich phases (Figures 24 - 28). X-ray diffraction of samples quenched at 400 & 450°C for alloy 4 revealed the presence of AuCu_3 as a major (>10%) phase. This will contribute to the hardening identified with increased silicon content due to an increase in α^2 precipitate and as such AuCu_3 . This would suggest a corresponding increase in hardness with decreasing quench temperature, but this was not detected. Further work is required to confirm the levels of ($\alpha^1 + \alpha^2$) precipitated and to determine the rate of formation of AuCu_3 as a function of both quench temperature and silicon addition. A comparison between the degree of hardening due to ordering from the above two functions is also required.

The confirmed presence by XRD of AuCu_3 indicated the castings tested were quenched below 390°C. Although the button quench temperature was 450°C, the casting temperature was below this due to the temperature difference related to tree position.

Grain size analysis.

No significant change in grain size as a function of quench temperature was noted for any of the alloys tested. Alloy 1 exhibited a minor increase from 0.8mm when quenched at 600°C to 1.0mm at 400°C, however this was not considered significant. The remaining alloys tested all exhibited similar average grain sizes of 2mm regardless of silicon content or quench temperature. All of the alloys tested here, in particular the silicon-containing alloys, would benefit from some degree of grain refinement. The generation of a fine grained cast structure would improve surface finish, corrosion and crack resistance. Grain refining may also influence the performance of these alloys during quenching - a finer grain structure may offer some degree of control on the otherwise erratic formation of the silicon-rich segregates identified, and as such improve quench strength. Refinement by homogeneous nucleation with either iridium or cobalt is suggested, however the tendency for iridium and silicon to form hard agglomerations may prevent its' use in

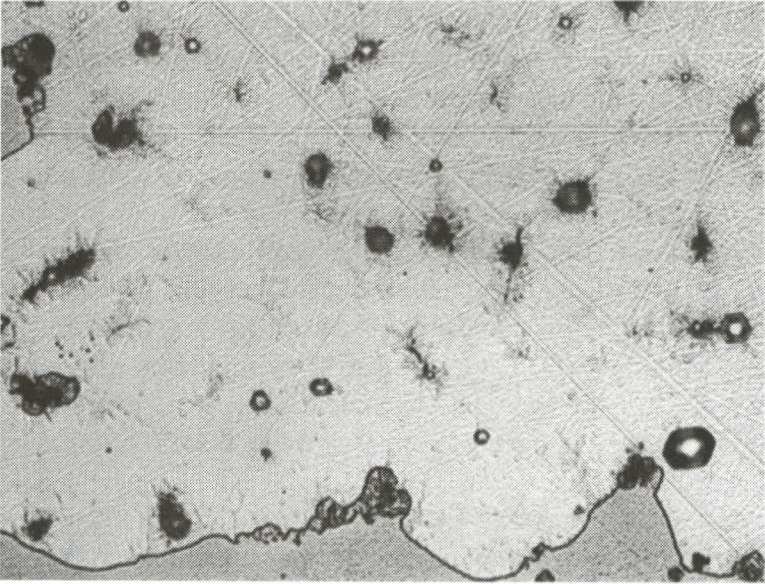


Figure 24. Alloy 1 quenched at 400°C. Mag'n x 280.

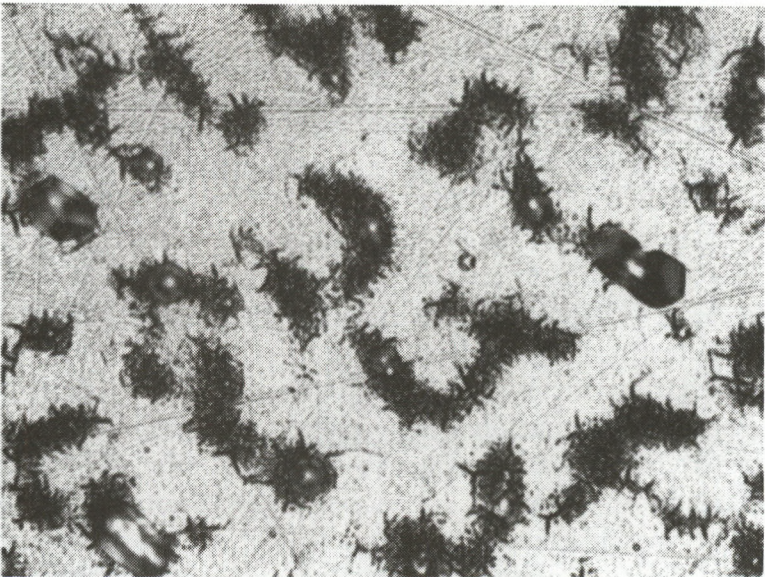


Figure 25. Alloy 2 quenched at 400°C. Mag'n x 280.

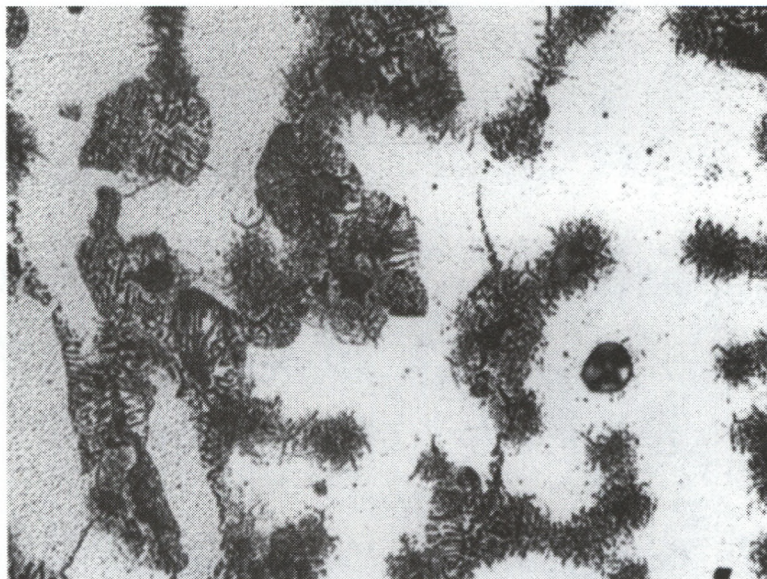


Figure 26. Alloy 3 quenched at 400°C. Mag'n x 280.

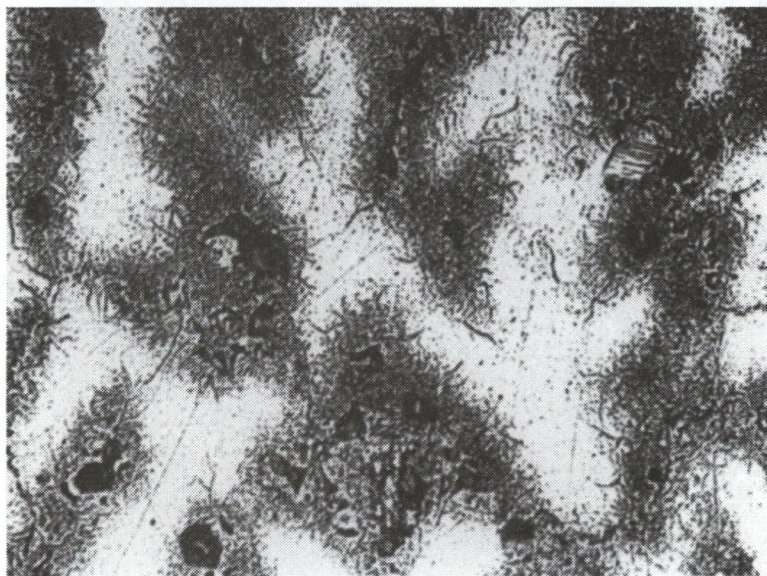


Figure 27. Alloy 4 quenched at 400°C. Mag'n x 280.

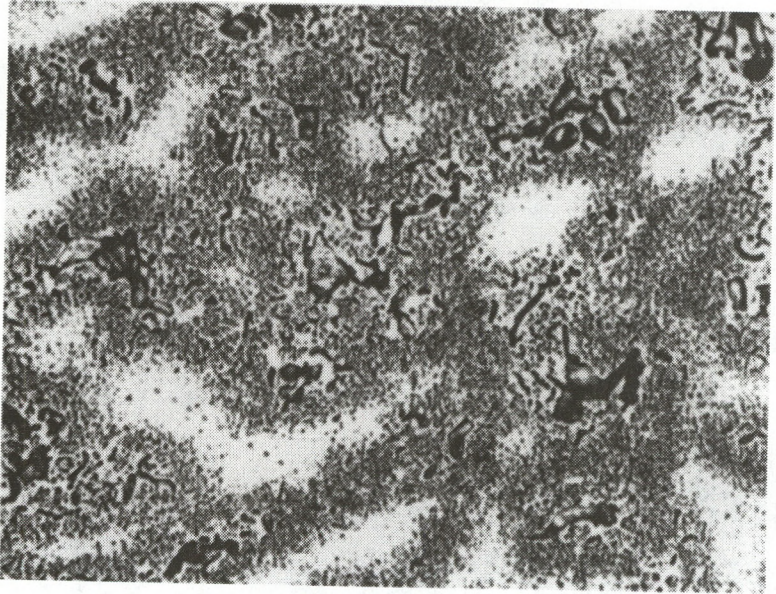


Figure 28. Alloy 5 quenched at 400°C. Mag'n x 280.

higher silicon alloys.

Ring sizing and solderability.

Unfortunately due to time constraints on the author, ring sizing and solderability trials were not performed or analysed at the time of writing. These tests will be carried out and included in the presentation at the Santa Fe Symposium in May 1999.

CONCLUSION.

Analysis of the data generated in this study confirms susceptibility to failure during devesting increases with silicon addition for a given temperature. At levels of 0.25% silicon and above care must be taken when determining quench temperature to ensure complete solidification has been achieved. It was confirmed that the major mechanism of failure during devesting was not brittle fracture through grain boundary phases but hot tearing through low melting point silicon-rich phases. These were randomly dispersed throughout the alloy matrix.

The following factors were also determined:

- Low carat alloys may fall within the safe (Au+Ag) limit for a given silicon addition as determined by Normandeau & Roeterink and have acceptable post-casting properties but fail during devesting if a critical quench temperature is exceeded.
- The presence of the silicon-rich grain boundary phase often noted in higher carat alloys was negligible, precipitation in low carat alloys being into two randomly occurring irregular phases.
- Silicon additions of 0.1% and over precipitated a random irregular silicon containing silver-rich phase. This increased in intensity with addition however was not affected by quench temperature. The

presence of this phase alone was insufficient for failure to occur and evidence suggested it was ductile in nature.

- A second silicon-rich phase was identified under certain processing conditions. This was insoluble in the first at higher quench temperatures. It was the presence of this phase that resulted in the failures during devesting.
- The extent of ($\alpha^1 + \alpha^2$) precipitate increased with silicon content for a given temperature. The silicon-containing phases appeared to act as nucleation points for precipitation.
- The formation of the ordered AuCu_3 phase was noted in high silicon alloys at low quench temperatures. This contributed to the increase in hardness associated with increasing silicon content however further work is required to study this phenomenon fully - time and budget constraints resulted in XRD analysis of two samples only during this study.
- The cooling rate of an alloy varied significantly with silicon content due to a number of factors outlined in the text.
- Time after casting was confirmed as an unreliable measure for quench temperature.
- Direct measurement of the button was established as the most reliable indication for temperature. It was noted that this was not necessarily a true reading of temperature for all castings - this decreased moving down the tree. Calibration of cooling rate for high-silicon alloys may be required to establish the quench temperature limit below which failure will not occur.
- The corrosion susceptibility increased with increasing silicon content. This was possibly related to the increased precipitation of copper rich phases noted previously. All alloys below 0.5% silicon were

determined to have similar corrosion resistance to the silicon-free alloy.

- Mechanical properties as a function of quench temperature were erratic for any given alloy. This was possibly a function of the erratic nature of the silicon-containing phases formed.

Overall, the use of alloys containing 0.5% silicon or less was determined to be acceptable provided certain production parameters were adhered to. Temperature measurement should be taken as a direct reading from the button and not as a function of time after casting - this was confirmed as unreliable. A learning curve may be necessary when using high-silicon alloys enabling the caster to become familiar with an alloy and to have a measure - albeit subjective - for when the alloy has undergone complete solidification. There are several disadvantages when using high-silicon alloys however these are not catastrophic and their use is perfectly acceptable under the correct circumstances. It is suggested that a maximum level of 0.5% silicon be used in low carat alloys - no advantage can be seen for any increased addition. If a high-silicon alloy is not specifically required it is suggested that one of lower content be used - 0.1% silicon offers a full range of beneficial properties with no disadvantages over the silicon-free alloy.

This study has raised a number of unanswered questions that will require further work to resolve.

FURTHER WORK.

It has been noted on several occasions within this study that time constraints have prevented full analysis of the results and trends determined and that there are further avenues for investigation. Further work is proposed and will be presented at the Santa Fe Symposium in May, 1999 and for publication thereafter.

- The degree of ring sizing tolerated and the resultant surface finish of

the casting as outlined in the experimental section of this study.

- The performance of each alloy after soldering as outlined in the experimental section of this study.
- Phase analysis to identify the silicon containing phases A&B.
- Determination of the limit of silicon required for the formation of phases A&B.
- Grain refining all the alloys in the study and repeating specific tests to determine the effect on failure susceptibility, mechanical properties, surface finish and corrosion/tarnish resistance.
- Phase analysis to determine the rate of precipitation of ($\alpha^1 + \alpha^2$) as a function of silicon content.
- Analysis to determine the rate of generation of the ordered AuCu_3 phase and its effect on hardening as a function of quench temperature and silicon content.
- Determination of mechanical properties at elevated temperatures. This will yield further information regarding performance at various temperatures inside the mould cavity and during quenching. The hot strength of phases A&B will give an indication of the critical quench temperature above which failure will occur.
- Increased accuracy in the determination of cooling rate at different parts of the casting tree and the factors influencing this. This will include determination of the specific heat capacity, the linear coefficient of thermal expansion and an investigation into why button temperatures differed for a given alloy between casts. This will enable the hot tensile data to be used to full advantage.
- Further investigation into the factors influencing the corrosion and

tarnish resistance of the alloys.

- An investigation into the effects of silicon on other 9ct alloy compositions - specifically white and red alloys.

ACKNOWLEDGEMENTS.

The author would like to thank the following for their help in this study:

Peter Rotheram, Technical & Development Director, Cookson Precious Metals Ltd.

Bruce de Kocks, Casting Manager, CPM Dublin.

G. Normandeau & R. Roeterink for the use of the "silicon content in carat gold alloys calibration curve".

Morgan Materials Technology Ltd. for the SEM, XRD and thermal analysis.

REFERENCES.

1. Ott, D., "Metallurgical and Chemical Considerations In Jewellery Casting", Santa Fe Symposium, 1987, Met-Chem Research Inc., 1988.
2. Carrano, R.V. & DeRohner, J., "The Effects Of Common Additives On The Cast Properties Of 14 Karat Alloys", Santa Fe Symposium, 1988, Met-Chem Research Inc., 1989.
3. Normandeau, G. & Roeterink, R., "The Optimisation Of Silicon Alloying Additions In Carat Gold Casting Alloys", Gold Technology, No.15, April 1995.
4. Jackson, R.S., "An Improved 9ct Yellow Gold Casting Alloy", Gold Bulletin, 1978, 11(3).
5. Ott, D., "Influence Of Small Additions And Impurities On Gold And Jewellery Gold Alloys", Santa Fe Symposium 1997, Met-Chem Research Inc., 1997.
6. Kinneberg, D.J., Williams, S.R., & Agarwal, D.P., "Origin And Effects Of Impurities In High Purity Gold", Santa Fe Symposium, 1997, Met-Chem Research Inc., 1997.
7. Normandeau, G., "The Effect Of Various Additives On The Performance Of An 18 Karat Yellow Gold Investment Casting Alloy", Santa Fe Symposium, 1996, Met-Chem Research Inc., 1996.
8. Bacon, J.A., "9ct Yellow Casting Golds", Johnson Matthey internal report, October 1979.
9. McDonald, A.S. & Sistare, G.H., "The Metallurgy Of Some Carat Gold Jewellery Alloys - Part 1 - Coloured Gold Alloys", Gold Bulletin, 1978, 11(3).
10. Duncan, J. & Starling, S.G., "Text-Book of Physics", Macmillan & Co. Ltd., 1948.
11. Grimwade, M., "Getting Increased Strength In Carat Gold Jewellery", Gold Technology, No.14, November 1994.