HANDBOOK ON CASTING AND OTHER DEFECTS

In Gold Jewellery Manufacture

THE SANTA FE SYMPOSIUM

WORLD GOLD COUNCIL

gold

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In Gold Jewellery Manufacture

by Dieter Ott

WORLD GOLD COUNCIL

Publication Date: November 1997
Reprinted 2001

Published by World Gold Council, Industrial Division,
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Originated and printed by Trait Design

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It is always important to use appropriate and approved health and safety procedures.

PREFACE

Gold has an image of preciousness - colour, rarity, indestructability, value, etc. - and this is reflected in the ever growing desire to own gold jewellery. Thus, the consumer's perception of gold as a unique, attractive and valuable metal should be reflected in their expectation of a quality-made jewellery product. As manufacturers of gold jewellery are well aware, this expectation is not always so easily fulfilled in practice and production of gold jewellery, as in all metal fabrication, is prone to the occurrence of defects which can be difficult and expensive to rectify. Many progressive jewellery manufacturers are refocusing their businesses to a Total Quality approach. The old maxim 'prevention is better than cure' has strong economic benefits for the producer. In an increasingly international and competitive industry, high quality at low cost is essential.

Investment casting is now the dominant mass production process in gold jewellery manufacture and is especially prone to defect formation. The nature and causes of such defects are generally not well understood in the industry and thus their prevention during manufacturing is not easily attained. In recent years, however, much light has been shed on these problems and we now have a good scientific understanding of the principal defects and their causes; this knowledge has been translated into manufacturing 'best practice' which, if followed, should lead to a significant reduction in the probability of defect formation.

World Gold Council provides technical support to the gold jewellery industry in terms of disseminating technical information on manufacturing technology and 'best practice' through its journal, *Gold Technology*, its International Technology Symposia held annually in Vicenza, Italy, and through a series of local symposia and technical seminar programmes held in the major jewellery production centres worldwide. Increasingly, these latter are being supported by a series of technical publications. The *Technical Manual* is a practical basic guide to manufacturing best practice and this is supplemented by more specialised publications on specific aspects such as Investment Casting and Finishing. This *Handbook* complements these and describes typical common manufacturing defects, their causes and ways to prevent them. It is the first major publication on this topic and takes a systematic, user-friendly, technology-based approach and, I believe, it will prove to be essential reading for all serious jewellery producers interested in quality.

Inevitably, a Handbook such as this cannot cover all defects that can and do occur in jewellery manufacture but we believe that most of the common ones are listed. Much of the material in this Handbook is based on a comprehensive case history study of actual production defects carried out at the German Precious Metals Research Institute, FEM, in Schwäbisch Gmünd, supported by the Santa Fe Symposium on Jewelry Manufacturing and World Gold Council. It was our concern that this valuable reference information source should be available to the industry in a practical and useful way; hence, the production of this *Handbook*. We would like to continue to add to this 'defect database' and FEM would be pleased to receive other defects in jewellery for investigation to provide further information that can be shared with others.

Chris Corti

Christopher W. Corti
Manager, Technical Information & Development, World Gold Council.

CONTENTS

INTRODUCTION

Just as in any production process, jewellery fabrication can give rise to defects which lead to rejects and customer dissatisfaction. The defect rate depends strongly on the type of production process. The focus of this Handbook is on investment casting, which is known to be a critical process. This might be explained by two facts:

a) Investment casting is widely used for the production of a great variety of jewellery items in an equally large number of casting shops with levels of equipment, expertise and experience that vary widely.
b) Investment casting is a complex set of processes which is determined and influenced by numerous physical, metallurgical and chemical factors. Mastering and controlling all of the process steps is difficult, if not almost impossible.

Of course, other production methods are also susceptible to defect formation, such as wire-drawing, rolling, heat treatment and surface treatment. Corresponding cases are also included in this Handbook.

Naturally, if a defect occurs, measures have to be adopted to eliminate its cause and prevent its repetition. Of course, this is only possible if the defect can be identified and its cause determined. Therefore the following procedure should be followed:

- identify the nature of the defect
- seek the cause
- develop procedures to prevent the cause from recurring.

The first step is not as easy as it seems. Some types of defects may appear almost identical although they have completely different causes. A good example is porosity. Pores visible on the surface of a polished jewellery item may look very similar, independent of their origin.

The problem can only be solved by a two-pronged approach:

- exploring the 'history' of the defective item
- performing a metallurgical and/or chemical investigation.

Identification of the nature of a defect is at least half the way towards finding its cause. Understanding the cause is the first and most important step towards avoiding repetition of the defect in future. This Handbook will provide some help in performing these tasks.

Part A is a structured survey of defect types which, with the aid of diagrams and photographs, should act as an orientation guide. The visual appearance of a defect, together with some simple information, should guide the user of the handbook to case descriptions which might fit the actual case. However, confirmation by extended investigation will be necessary in most cases.

A number of case histories of actual production defects have been investigated and are described in **Part B.** A rough classification is made in terms of causes and types of defects. It is not unambiguous.

The description of each defect case follows a constant pattern. Firstly, the defect is described as it appears with visual inspection (use of a magnifying glass or a stereomicroscope can help a lot). Photographs support the description as far as possible. Additional information is mentioned in “Alloys” and “Manufacturing method” (so far as necessary and available).

Unfortunately, it is generally not possible to identify the type and the cause of each defect only by visual inspection. Frequently, additional investigation is necessary. We are conscious that this may constitute a disadvantage for the straight use of this Handbook in the workshop. However, there is no easy way to overcome this difficulty. Therefore, in addition, other parts which follow the defect description (“Influence on properties”, etc) present the results of such metallurgical investigation. The “Brief explanation” provides initial information about the kind and cause of the defect. Additionally, more technical and metallurgical information is provided in “Extended explanation”, where appropriate. Last but not least, advice on preventing the defect is given under “Recommendations for avoidance”.

More information on the metallurgical and technical background to the processes and causes of defects is supplied in **Part C**. The purpose of this part is twofold:

a) To improve the understanding of the investment casting process and, through this, help to avoid defects.

b) Many defects have a very similar metallurgical background; to explain in one place saves much repetition. In each case history, a reference to the relevant section is given under “Further reading”.

‘Part C: Basic aspects of metallurgy’ focuses primarily on the investment casting process and some other common problems in jewellery fabrication. It is *not* a textbook about metallurgy in general or precious metals in particular. It is an effort to produce an understandable manual for practising craftsmen and technicians who have not been technically trained in metallurgy or chemistry.

One very important aspect has been disregarded: alloy phase diagrams. Understanding phase diagrams needs a more extended explanation which is not appropriate in this chapter.

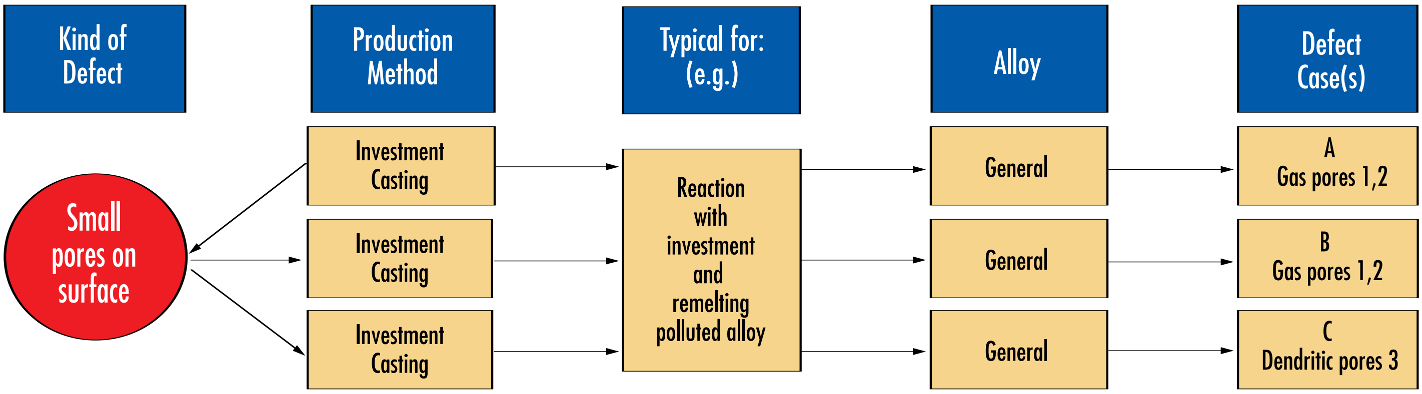
Hopefully, this Handbook will help jewellery producers to improve the quality of their jewellery fabrication. However, it cannot be completely comprehensive as it is based on the investigation of a limited number of jewellery defects submitted to the author, mainly through the auspices of the Santa Fe Symposium, with support of World Gold Council.
The author would like to continue to add to our defect database and requests that jewellery producers continue to send him their defects for investigation. Hopefully, a supplement to this Handbook can be published at a later date.

Dieter Ott
Schwäbisch Gmünd
October 1997

PART A:

SURVEY OF DEFECT TYPES

Surface defects



Kind of Defect

Production Method

Typical for: (e.g.)

Alloy

Defect Case(s)

Small pores on surface

Investment Casting

Investment Casting

Investment Casting

Reaction with investment and remelting polluted alloy

General

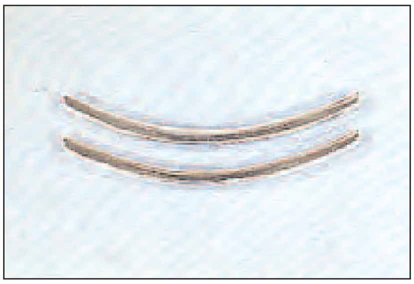
General

General

A Gas pores 1,2

B Gas pores 1,2

C Dendritic pores 3



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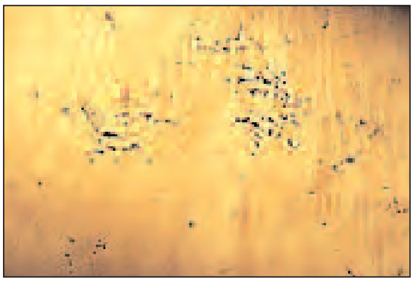
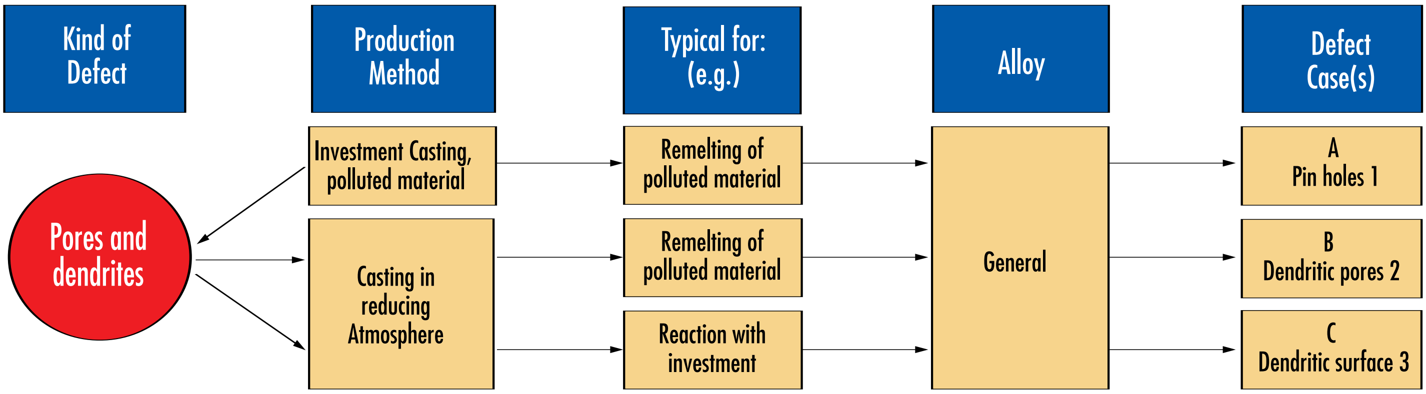


C

Surface defects



Kind of Defect

Production Method

Typical for: (e.g.)

Alloy

Defect Case(s)

Pores and dendrites

Investment Casting, polluted material

Casting in reducing Atmosphere

Remelting of polluted material

Remelting of polluted material

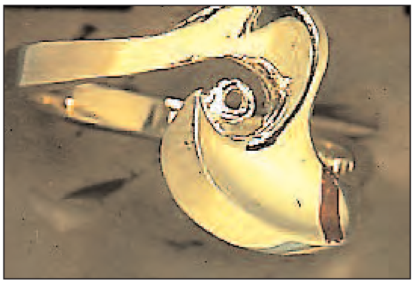
Reaction with investment

General

A Pin holes 1

B Dendritic pores 2

C Dendritic surface 3



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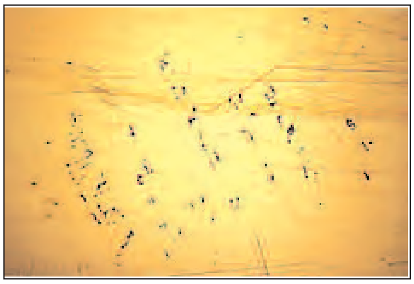
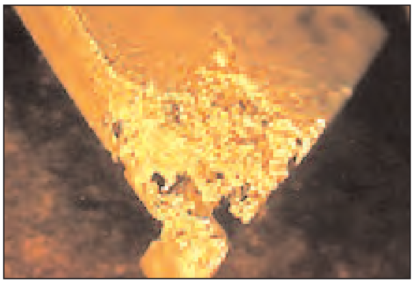


B

C

Surface defects

Kind of Defect	Production Method	Typical for: (e.g.)	Alloy	Defect Case(s)
Irregular surface structure	Investment Casting, melting procedure	Polluted crucible, too much flux	General	A Slag ('cauliflower')13
	Investment Casting, melting procedure	Remelting polluted metal, oxidation	Zinc containing alloys	B Inclusion of zinc oxide ('crow's feet') 12
	Investment Casting, burnout cycle	High heating rate at burn-out	General	C Wrinkled surface 9



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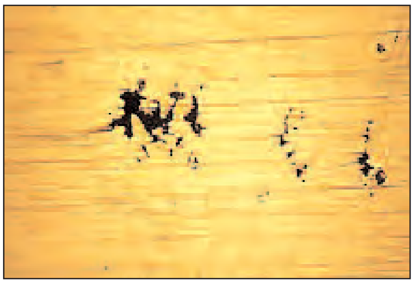

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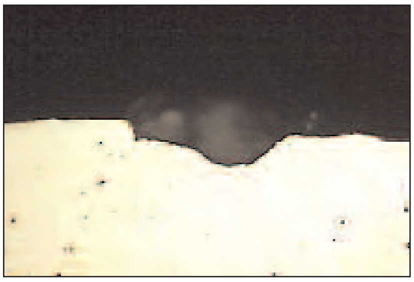
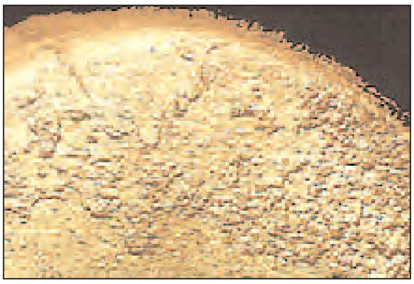


C

Defects caused by investment or investing process

Kind of Defect	Production Method	Typical for: (e.g.)	Alloy	Defect Case(s)
Rough surface	Quality of investment powder, investing procedure, Centrifugal casting	Investment was too weak	General	A Sandy surface 7
				B Fins 7
	Investing procedure	Wrong investing procedure		C Water marks 8



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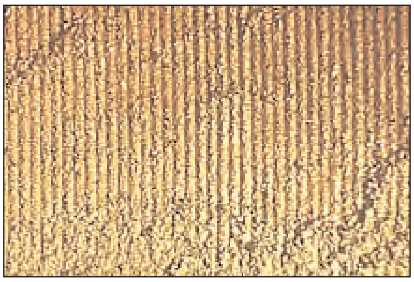
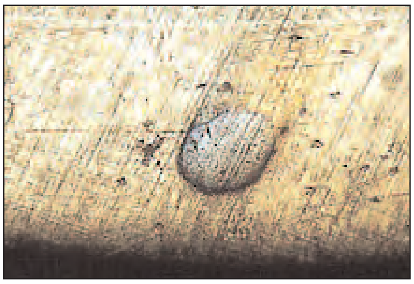


C

Inclusions

Kind of Defect	Production Method	Typical for: (e.g.)	Alloy	Defect Case(s)
Hard spots	Investment Casting	Inclusions of grain refiner	Abundant if grain refiners are used	A 20
	Rolled sheet	Nests of grain refiner		B 20
	Rolled sheet	Impurities in gold	Bad quality of gold used for alloying	C 20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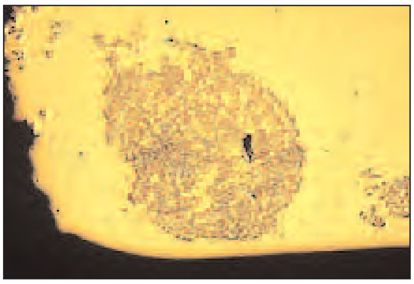
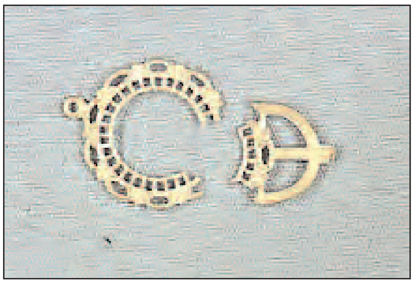

B


C

Fracture

Kind of Defect	Production Method	Typical for: (e.g.)	Alloy	Defect Case(s)
Brittle fracture	Casting, alloy composition	Low melting components	Yellow gold with Silicon	A Brittle silicon phase 17
	Casting in reducing Atmosphere	Reaction with investment	Jewellery alloys in general	B Formation of sulphide 19
	Heat treatment, Soldering	Age hardening in red/pink gold	Red and pink alloys	C Embrittlement by soldering 24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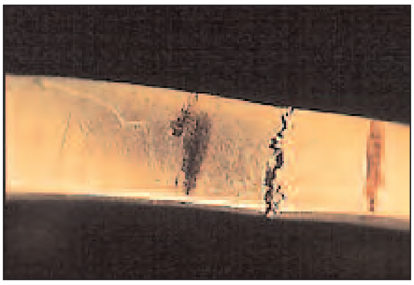
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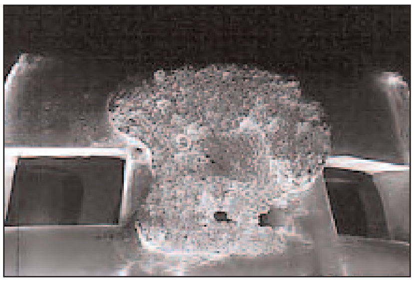
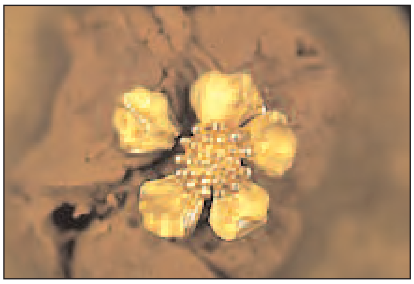

C

Fracture

Kind of Defect	Production Method	Typical for: (e.g.)	Alloy	Defect Case(s)
Fracture, material separation	Investment Casting	Shrinkage Porosity	General, 14ct alloys are more critical	A 4
	Investment Casting	Cold shuts	General	B 6
	Ingot casting, rolling	Lamination caused by ingot pipe		C 16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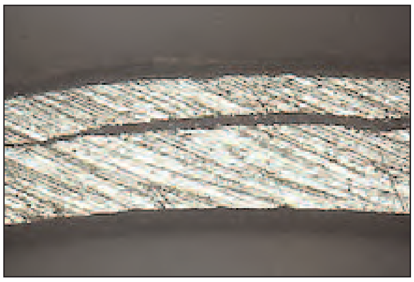
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PART B:

CASE HISTORIES: DESCRIPTION OF DEFECTS

NOTE: The photographs in this section have been reproduced from slides and are magnified by approximately 150%. Therefore, where magnifications are given, they are not exact but should be considered as approximate.

1 INVESTMENT CASTING

INTRODUCTORY REMARKS

Investment casting is a very useful technique in medium- to large-scale jewellery production. However, it can also be a source of many defects, with up to 10 - 20% of defective items not unusual.

A large proportion of rejected items is due to porosity. There are two different types of porosity - shrinkage and gas porosity - which, in their most characteristic shape, can normally be distinguished easily. However, in practice their appearance can vary widely, and all intermediate shapes between small spherical holes (gas porosity) and dendritic pores (shrinkage porosity) are possible.

The origin of porosity is also variable. Shrinkage porosity is caused by a purely physical process (the decrease in metal volume at solidification) whereas gas porosity was thought originally to be caused solely by chemical decomposition of the mould investment, either directly or via sulphide formation (see Part C: Basic Aspects, section 3). Whilst often the case, other causes can also lead to gas porosity, such as oxidised and contaminated metal.

In the following case histories, several defects are illustrated that have similar origins but different appearances.

Another common cause of defects arising during investment casting is connected to the investing process, which commences with slurry preparation and ends with the flask (mould) burn-out process. Poor quality investment powder may add some extra difficulties.

Incomplete form-filling (mould-filling) is another common defect that should be mentioned but which is often not well understood or properly investigated. The causes of poor form-filling can be detected relatively easily.

Other reasons for defects in investment casting are not so common. Cracks and fractures can often be related to porosity or alloy properties. Such defects induced by alloy properties or alloyed impurities are reported in chapter 3.

1.1 POROSITY

CASE 1: PIN HOLES ON THE SURFACE - CAUSED BY GAS POROSITY

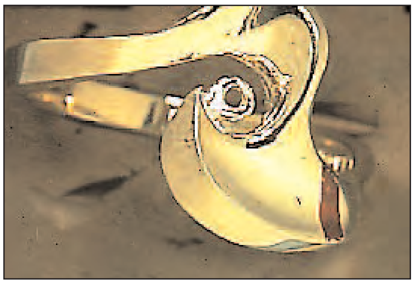


Fig. 1.1 The polished surface

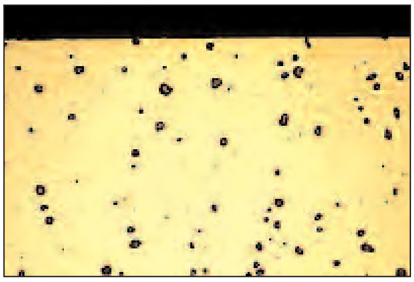


Fig. 1.2 Microsection through a piece of jewellery with gas porosity. 50 x

Similar to
Cases 2 and 3

Key Words
Gas porosity; static casting; contaminated/polluted material

Description of Defect
The polished surface of a flat jewellery item shows numerous, uniformly distributed round pores.

Visual Appearance
The pores are like *pinholes* and rather randomly scattered on the surface. The type of porosity and its origin cannot be identified only by its visual external appearance. Examination of a micro-section is necessary.

Alloy: 18ct yellow gold (AuAgCu).

Manufacturing Method: Static casting in argon atmosphere, starting pressure 0 bar, final pressure 2-3 bar.

Influence on Properties

Surface Quality
The pinholes are detrimental to the quality of a polished surface. In most cases, they cannot be removed by extended grinding or polishing; on the contrary, even more pinholes (lying below the surface) will be exposed.

Mechanical Properties
Pinholes usually have little influence on the strength of the item, in contrast to other types of porosity which can result in fracture.

Microstructure
Typically, the gas pores are roughly spherical and are often situated in a discrete layer just beneath the surface, indicating their origin from reaction of the investment at casting. Alternatively, as in this case, they may be distributed across the entire cross-section, indicating their likely origin as a reaction of contaminated (polluted) alloy. The gas pores are small but abundant. Only a few pores are exposed and visible on the surface. Obviously, attempting to remove these pinholes by polishing them away is unrewarding because other, subsurface pores will then become exposed.

Brief Explanation
The almost homogeneous distribution across the cross-section and the smooth surface indicates that, in this particular case, the porosity is probably not caused by reaction (decomposition) of the investment during pouring of the melt into the flask. More probably, the substance producing the pores is introduced with the metal. In the present case, the use of remelted scrap material containing sulphides, together with new metal (made from fine gold and a master alloy), is responsible. The master alloy contained copper oxide which reacted with the sulphide to form sulphur dioxide gas, resulting in this typical gas porosity. Note that contaminated material can also cause porosity with a different appearance (for example, see Case 3)

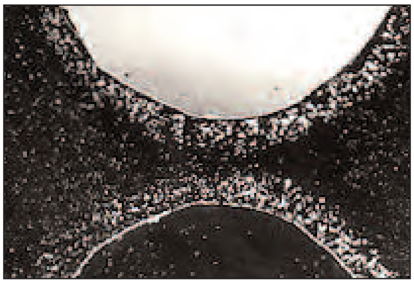


Fig. 1.3 Typical layer of gas pores just beneath the surface 9 x

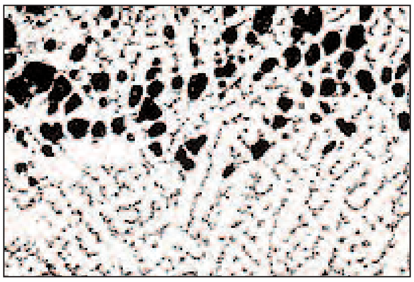


Fig. 1.4 Detail of fig.1.3, gas pores at higher magnification 50 x

Recommendation for Avoidance

Two measures should be taken to prevent the occurrence of the defect:

a) Use oxide-free, clean master alloys (or oxygen-free silver and copper) for preparing a new alloy melt. Note: Fine silver can have a high oxygen content. It can be removed by melting the silver separately under reducing conditions prior to alloying.

b) If used alloy scrap such as feeders is remelted, it must be thoroughly cleaned to remove any mould investment material as this can react with the alloy, leading to the formation of sulphides. Used alloy from castings with severe porosity should not be remelted again but refined.

Extended Explanation: *Copper oxide(s) can exist in pure copper (use oxygen-free 'high conductivity' copper for preference) and in silver-copper master alloys up to a high concentration. Silver can also contain significant amounts of oxygen. In yellow carat gold alloys, any copper oxide present can be reduced to copper with formation and release of oxygen gas under certain conditions. Sulphides of silver and copper can be formed on remelting dirty scrap from casting when remains of the old investment are present. The gypsum (calcium sulphate) binder in the investment can be decomposed, reacting with copper and/or silver during remelting to form sulphides. When sulphide and oxide (or oxygen) are present at the same time, they can react chemically during melting with the generation of sulphur dioxide gas, thus causing gas porosity.*
(The simultaneous presence of sulphide and oxide has been proved in several investigations).

When the gas porosity only extends to a layer below the surface, the cause is more usually due to the decomposition of the gypsum binder during pouring of the molten metal. The temperature at which this occurs is lowered in the presence of carbon (hence the need for a clean burn-out).

Another Example

This example, figs 1.3,1.4, of a discrete layer at the surface of a 14 carat yellow gold is more typical of gas porosity due to reaction of the investment.

Further Reading

Part C: Basic Aspects, section 3.2, Gas porosity.

CASE 2: GAS POROSITY - CAUSED BY IMPURITIES (A FURTHER EXAMPLE)

Similar to

Case 1

Key Words

Investment casting; surface porosity; contaminated/polluted material

Description of the Defect

Numerous small pores on the surface of rings

Visual Appearance

The surface looks as if it is perforated by small pores and holes. This appearance is typical for any kind of gas porosity and also for shrinkage porosity. Polishing evens out the typical differences in the appearance of both kinds of porosity. Hence, for reliable information on type and cause of porosity, microsections have to be prepared.

The pinholes are small. Without use of a microscope, the defect often looks like cloudy spots. At higher magnification, the irregular shape of pores can be recognised.

Alloys: Independent of alloys. Examples are shown of 10ct and 18ct yellow gold alloys.

Manufacturing Method: The main source for this type of porosity is remelting contaminated metal (see below). Melting and casting under oxidising conditions are another reason. These defects are often seen when casting is done in an open system without a protective atmosphere.

Influence on Properties

Microstructure

The structure shows severe porosity, fig 2.5. The pores, which are close to the surface, are of two types of pores: small, almost spherical gas pores and irregularly shaped larger pores. At higher magnification, small inclusions are visible which are probably copper oxide (CuO). Again caused by impurities, the mixture of spherical gas pores and irregular pores, resembling shrinkage porosity, can be recognised. Most cases with really severe porosity are caused by this type of defect.

Brief Explanation

Several cases of defects involving severe porosity have been found which could not be attributed unambiguously to just shrinkage or gas porosity. The porosity comprises both smooth spherical shaped pores, typical of gas porosity, and very irregular, large ones. This kind of defect is often found in cases where oxidised metal has been used and/or no precautions taken to prevent uptake of oxygen during melting. Typically, oxide inclusions are found in the microsections.

The cause of this type of defect is not well understood. A possible explanation is that abundant inclusions of copper oxide decompose when the melt is about to solidify, releasing oxygen and forming gas pores. Whether other factors such as the presence of reducing agents (old investment/sulphides) play a role is not clear. Further study is necessary.

Fig. 2.1

Fig. 2.2 Another example of the same kind of defect

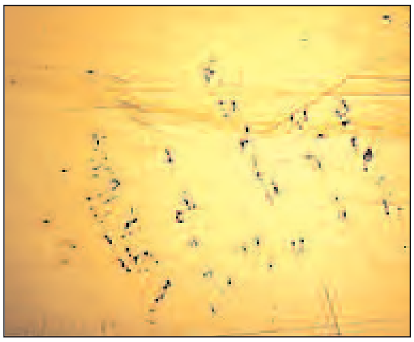


Fig. 2.3 Typical example at higher magnification 100 x

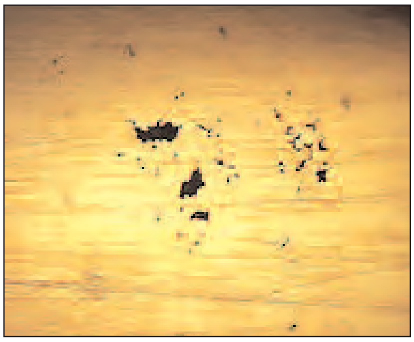


Fig. 2.4 Another example at higher magnification 100 x

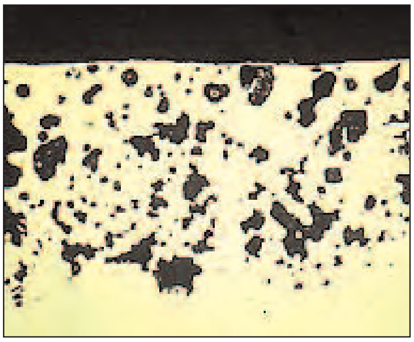


Fig. 2.5 Microstructure of a ring with a porous surface. 50 x

Fig. 2.6 Another example. 200 x

However, it can be stated for certain that polluted, oxidised material plays a major role in this defect type.

Recommendation for Avoidance

This defect can be avoided if only clean, unoxidised material is used and the casting conditions are controlled to avoid extensive oxidation. The amount of scrap used in a new melt charge should be limited - normally up to 30 - 40%, depending on the quality (cleanliness) of the metal. Continued re-use of scrap will also lead to a build-up of deleterious impurities in the alloy.

Extended Explanation: *The explanation given above is not yet fully proven and is based on practical experience. In the system gold-copper-oxygen-(silver), the stability of copper oxide is temperature dependent. In alloys strongly contaminated with oxides, the equilibrium between copper in solid solution, oxygen and copper oxide will change during solidification causing evolution of gaseous oxygen.*

A distinction between this kind of porosity and that caused by sulphide inclusions (from reaction with investment) is very difficult.

Further Reading

Part C: Basic Aspects, section 3.2, Gas porosity.

CASE 3: NESTS OF SMALL PORES ON THE SURFACE

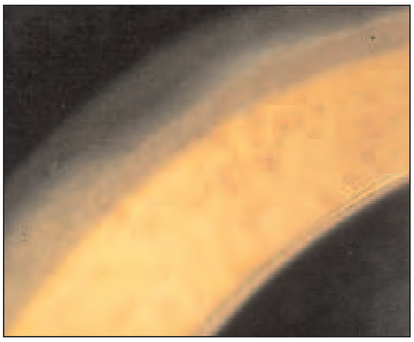


Fig. 3.1 9 x

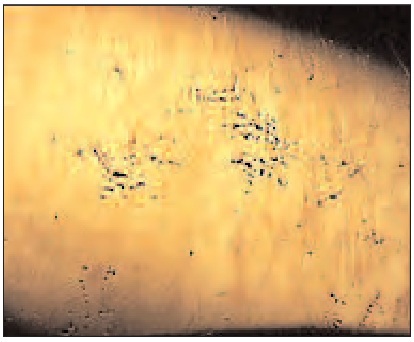


Fig. 3.2 50 x

Fig. 3.3 200 x

Similar to

Cases 1 and 2.

Key Words

Surface defect; dendritic porosity; contaminated/polluted material

Description of the Defect

A ring shows nests of pores on the surface. The shank is covered with dark brownish spots. The surface cannot be improved by stronger polishing. It is a characteristic feature of this kind of defect that extended polishing tends to increase the incidence of the defect rather than improve the surface quality.

Visual Appearance

The shank shows many dark spots. Distinct pores can be recognised, using a pocket magnifying lens. The defect is not restricted to critical places such as necks, or transition zones between thick and thin cross-sections, etc.

Alloy: 14 ct yellow gold

Manufacturing Method: Only a few details were given about the investment casting conditions. However, some very important details were noted: (1) the casting temperature was in the range 980 - 1010°C and (2) a melt charge comprising 40% new metal/60% scrap was used.

Influence on Properties

Mechanical Properties

There was no actual complaint about fracture. However, fracture might occur if the ring was to be expanded (“sized”).

Microstructure

Both micro-graphs show the cross-section of the shank at different magnifications. At low magnification, nests of dendritic pores are visible, randomly distributed all over the cross-section. Only a few of them reach the surface, causing dark spots on the polished shank. The microsection makes clear that further polishing would not improve the surface; on the contrary, more pores would be exposed.

At higher magnification, some interesting details are revealed: the pores are a mixture of roughly spherical, small gas pores and dendritic porosity. Real shrinkage porosity can be excluded as a cause; another explanation has to be found.

Brief Explanation

Several instances have been investigated showing defects similar to those shown in this case which, at first sight, appear to be attributable to dendritic shrinkage porosity. However, more detailed examination leads to the conclusion that the main cause is impurities, probably copper oxide, introduced by use of dirty scrap material or improper melting methods (for further explanation, see Cases 1 and 2).

In this case, the use of 60% of recycled metal in the new charge is

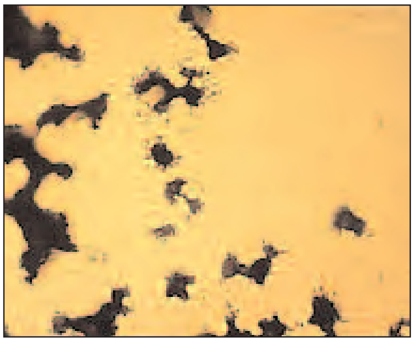


Fig. 3.4

relatively high. Such a high proportion can only be acceptable if the reused scrap is very clean. Otherwise, in the course of the time, impurities (oxides, inclusions, embrittling metals, etc.) will accumulate to damaging levels.

The other critical point is the comparatively low metal casting temperature. Depending on the casting method, this temperature is probably sufficient for form-filling. However, if impurities (especially oxides) are present, they are unlikely to be separated from the melt at low melt temperatures and short melting times. Increasing the melt temperature to 1050 - 1100°C would help to minimise the defect.

Recommendation for Avoidance

The only safe way to avoid this kind of defect is the use of clean materials and melting in a clean crucible under protective gas. The proportion of (clean) recycled scrap material should be restricted to no more than 30-40% of the total melt charge.

Sometimes, increasing the casting temperature will also help to remove oxides (if melting is performed in a protective atmosphere).

Another example

The connection between oxide inclusions and porosity can be demonstrated with the following example, a broken 18ct item.

The microstructure, fig 3.4, shows heavy porosity. The pores are partly filled with oxides (identified as copper and zinc oxides). Around these pores, many small inclusions of oxides are visible.

Further Reading

Part C: Basic Aspects, section 3.2, Gas porosity

CASE 4: FRACTURE - CAUSED BY SHRINKAGE POROSITY

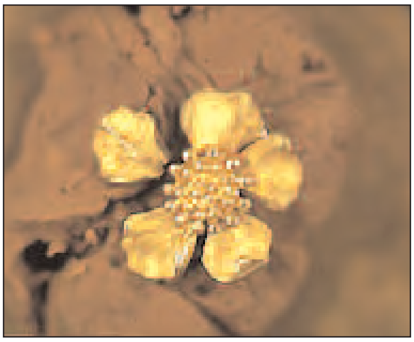


Fig. 4.1

Key Words

Fracture; shrinkage porosity

Description of the Defect

A petal of a flower-like jewellery item broke off after final polishing. The fracture occurred at a low applied stress. The fracture surface looks brittle and oxidised.

Visual Appearance

A flower was cast in 18ct. yellow gold. One of the petals broke off when the item was bent by a very small amount. No deformation of the material is visible. The only remarkable detail is a brownish ('oxidised') discolouration of the fracture surface (which is not revealed on the photograph). Visual inspection does not disclose the cause of the defect. Examination of the microstructure is essential (see figures 4.2 and 4.3)

Alloy: This particular defect was observed in 18ct yellow gold alloy (75.0 Au, 15.0 Ag 9.3 Cu, 0.7 Zn). However, the same defect can also occur in other jewellery alloys.

Manufacturing Method: The flower was vacuum cast; casting and flask temperatures are not reported. In another example, fig. 4.3, casting of a 14ct alloy was by a combined vacuum and pressure assisted method with a very low flask temperature (200°C) and a high melt casting temperature (1200°C).

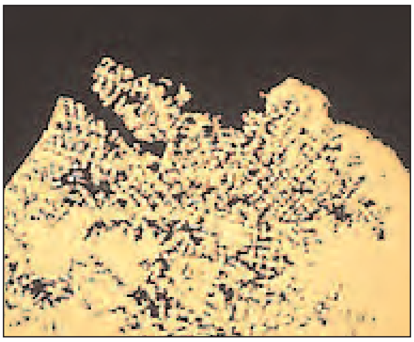


Fig. 4.2 50 x

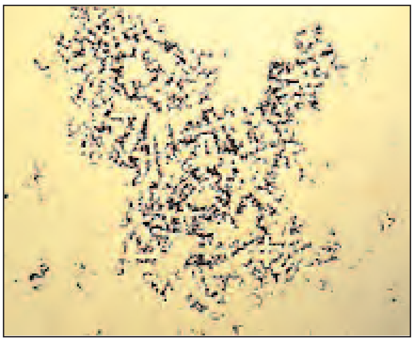


Fig. 4.3 50 x

Influence on Properties

Microstructure

A microsection through the fracture of the petal (ref. fig. 4.1) discloses a typical morphology. The petal, with its relatively thick cross-section, is connected to the calyx of the flower by a thin neck. The fracture has occurred at this neck, the thinnest part of the item. Only in this region, a spongy structure of dendrites is formed, with voids inbetween.

This example shows the microstructure of the centre of a cast ring in 14ct yellow gold. The spongy shape of the structure is identical with the example shown above.

Mechanical Properties

It is evident that such a spongy porous structure in a critical narrow connection will drastically reduce the strength locally. The part will break off with only a little force.

Others

The same defect can also be manifested at the surface. The dendritic structure to the pores should be recognisable. However, if the surface is sand blasted or tumble polished, the typical appearance is masked and examination of microsections is necessary to reveal the true nature of the porosity. As before, any attempts to remove the pores by polishing will not be successful.

Brief Explanation

The defect is a exemplary case of shrinkage porosity in terms of appearance and the cause. It must be noted that liquid (molten) metals shrink on solidification, causing a contraction in volume, and that heat is lost from the molten metal through the mould walls.

At the beginning of solidification, solid ‘crystallites’ grow in the melt in the typical dendritic form (it can be compared with the structure of branches of a fir tree). With continued solidification, the dendrites will grow and eventually meet each other; the spaces between them arise from the shrinkage on solidification and should be filled with solidifying material, if liquid metal can continue to be fed into these voids.

In this case, solidification starts and proceeds faster at the thin walled neck (since heat is more quickly extracted here) compared to the adjacent thicker parts. The flow of liquid metal to the thicker petal to feed the voids arising from solidification shrinkage becomes difficult due to the resistance to flow in the spongy neck region and any remaining liquid in this region is sucked into the petal region, leaving the neck with shrinkage porosity.

The situation with the ring is somewhat different. Here, solidification started very quickly at the surface due to the low flask temperature, as did the gate and other thin walled parts of the item. These parts completely solidify while the core of the ring is still liquid and so interrupting further supply of liquid metal to the core region. When the core starts solidifying, the supply of melt necessary to compensate the shrinkage in the core is no longer possible.

Extended Explanation and Further Reading

See Part C: Basic Aspects, section 3.1, Shrinkage porosity.

Recommendation for Avoidance

In the case of the flower, the best and safest method for avoiding the defect is changing the design. Thin necks between adjacent thicker parts are always a likely cause of such problems and should be avoided, where practicable. Alternatively, repositioning of the gates or the addition of extra gates to feed the thicker regions may overcome the problem.

Another approach for reducing the shrinkage porosity is to change flask and/or casting temperatures. However, which direction to change them to yield improved results is difficult to predict. In the present case, it is probable that increasing the flask temperature will improve the quality.

In the case of the ring, however, a way to effect an improvement is much easier to predict. The flask temperature is definitely too low and should be at least 400°C (still relatively low) and the casting temperature should be decreased.

1.2 FORM-FILLING

CASE 5 SHRINKAGE POROSITY - CAUSED BY IMPROPER GATING

Key Words

Shrinkage porosity; surface defects; gating, sprueing

Description of the Defect

A part of a tie clip shows small pores on the surface which are concentrated on the tapered end of the item. At higher magnification the dendritic structure of the pores is revealed, figs. 5.2, 5.3. Polishing does not remove these defects. Some of the cast items broke near the porous end.

Fig. 5.1 Tie Clip

Visual Appearance

The pores, which are concentrated on the tapered end, are too small to be visible in this figure. With the naked eye they appear as dark clouds.

At higher magnification, the dendritic structure of the surface defects can be recognised.

Alloys: This particular defect was observed in a 14ct yellow gold alloy (58.6 Au-17.0 Ag-19.5 Cu- 0.5 Zn). However, the same defect can occur with other jewellery alloys.

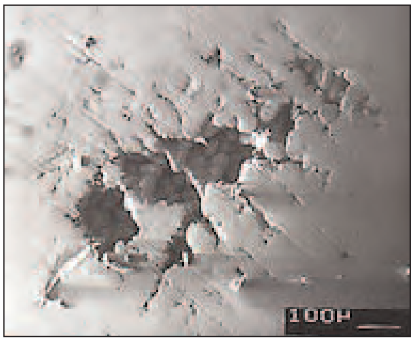


Fig. 5.2

Manufacturing Method: The clip was cast by the combined pressure and vacuum assisted method. An important detail is the 'gating' of the item (often erroneously called 'sprueing'). Fig 5.4 shows the wax model together with the gate which attaches it to the central sprue. Note that the gate itself is relatively thick and short. It is attached to the hook-shaped end of the tie clip.

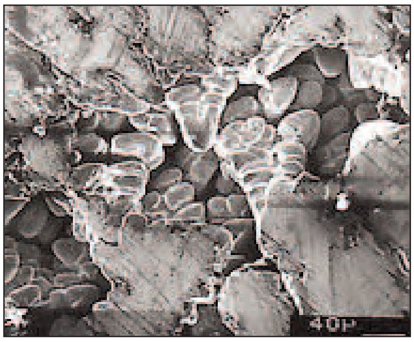


Fig. 5.3

Influence on Properties

Microstructure

A microsection through the porous end of the clip, at the opposite end to the gate, fig 5.5, discloses a typical dendritic appearance of the pores, resulting in a spongy metal structure with dendritic pores.

Mechanical Properties

Such a pronounced dendritic porous structure drastically reduces the strength.; the part may break with little effort.

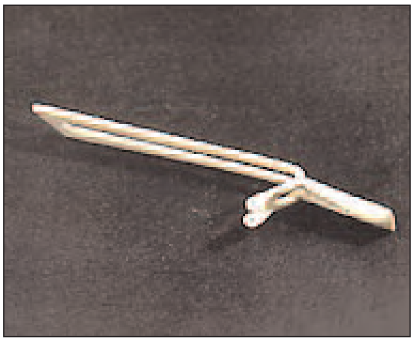


Fig. 5.4 Wax model with attached gate

Brief Explanation

The defect is an other exemplary case of shrinkage porosity. However, in this case, the gating of the wax is a critical point. The gate itself is short and sufficiently thick for supplying melt during solidification. However, the positioning of the gate on the wax model has to be criticised. The molten metal, fed to one end of the clip, has to be transported through thin bridges to the other, thicker end. The melt freezes on its way through the thin cross-sectioned part, resulting in an insufficient supply to the other end of the clip and, hence, severe shrinkage porosity occurs there.

The gate might be better attached to this thicker part of the clip, thus alleviating this problem. However, there is a high probability that shrinkage porosity will now occur at the opposite end for the same reason. There is

Fig. 5.5 80 x

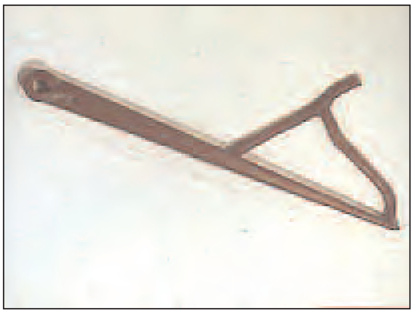


Fig. 5.6 Wax model of a needle with two branches on a sprue.

no ideal solution for gating. A forked gate with two branches attached at opposite ends of the clip will help. However, in practice the branches would be of considerable length. A positive effect cannot be guaranteed.

Fig. 5.6 shows a similar case with a divided gate. Of course, a good result was not achieved in this way. Many trials in this case resulted in the use of a three branched gate (fixed to both ends and the middle) whereby the diameter of gate was almost the same as the needle itself. Shrinkage porosity could be avoided with this method, but material consumption is large.

Recommendation for Avoidance

The design of the clip is very unfavourable for investment casting. There is no place for applying a single gate to ensure an item free of shrinkage porosity. A solution would be the use of a two branched gate, attached to each end but the branches must have such a sufficient diameter that a practical appliance will not be realistic. Two separate gates might be a preferred solution.

Experimenting with melt and flask temperatures might give a limited possibility to reduce shrinkage porosity. However, no firm recommendation can be given in this case.

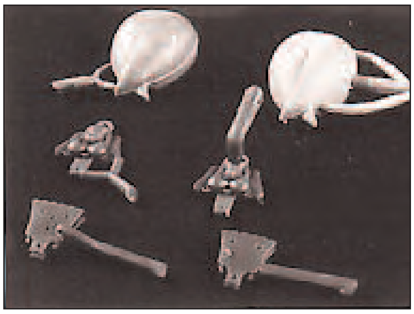


Fig 5.7

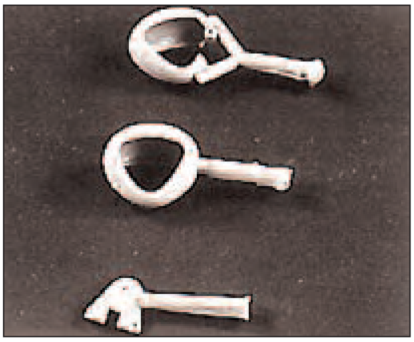


Fig. 5.8

More about gating

Figures 5.7 and 5.8 show favourable and unfavourable ways of gating. The subjects on the left hand side show wax models with gates designed and positioned by the jewellery designers; these resulted in incomplete filling of the mould. Those on the right hand side demonstrates what the casters did in repositioning and sizing the gates to improve the quality, i.e. to achieve good form-filling.

A part of a brooch (fig. 5.7, top) is an excellent example. The left side model has extremely thin gates. Of course, removing the gates from the cast item can be done with a minimum of work, but porosity would be a serious problem in this case. The problem is solved using a three branched, relatively thick gate (shown on the right side).

The dog's head (middle, left) is gated on the thinnest part of the item. Even if the gate is sufficiently thick and short (as in this case), premature solidification in the thin parts interrupts melt supply and causes shrinkage porosity. The solution is seen on the right side.

The gate on the item, left bottom, is fairly long and somewhat tapered towards its end; it is fixed to the wax model in a way which produces problems in cleaning the casting. On the right side, the gate has been shortened, but has a neck. Necks should be avoided if possible. Investment particles can break off in these places, obstructing melt flow. The best way of attaching the gate would be midway between these extremes.

The three examples in figure 5.8 show a good gate design, with regard to length and diameter. However, the gate of the ear-ring (top) is not attached properly. The tangential fixation of both branches provides only a small connection area, similar to a neck. As already mentioned necks should be avoided.

Further Reading

Part C: Basic Apects, section 3.1, Shrinkage porosity.

CASE 6: COLD SHUTS - CAUSED BY LOW MELT AND/OR FLASK TEMPERATURES

Fig. 6.1

Key Words

Cold shut; investment casting; form-filling.

Description of Defect

The surface of a flat thin piece shows traces which resembles cracks. However, in contrast to cracks, they have smooth edges and the surface in the surrounding of the traces is slightly wrinkled.

Visual Appearance

The defect was observed on a segment of a gramophone record used as a test specimen for testing casting conditions. The thin flat shape of the record is very susceptible to cold shuts. Grooves and a wrinkled surface structure are characteristic of a defect called a '**cold shut**':

Alloy: This defect can happen with any alloy

Manufacturing Method: Cold shuts can occur with any casting method. Low casting or/and flask temperature usually are crucial factors.

Influence on Properties

Mechanical Properties

Cold shuts can become cracks when stress is applied to the jewellery piece.

Surface quality

The surface is severely disrupted. Polishing or even grinding will not help to produce a good finish.

Microstructure

The microsection reveals that, in the defective region, the material is partly separated. Two flows of melt met without fully fusing together.

Brief Explanation

The melt enters the hollow space of the mould with some turbulence. Usually, the turbulence 'disappears' during solidification with no sign of it visible in the solid state. Sometimes, however, the 'tongue' of the turbulent melt solidifies on the mould wall before filling is complete. The turbulent structure is 'frozen' and the subsequent molten metal filling the mould cavity does not fuse into it, causing the formation of a cold shut. Several filigree pieces on the same tree may be reproduced incompletely.

A very similar defect can occur in zinc-containing alloys. Zinc oxide, formed during melting and casting, can form a thin membrane that floats in the melt and prevents the adjacent parts of the melt from fusing together on solidification.

Recommendation for Avoidance

Formation of cold shuts can be avoided by increasing the casting and/or the flask temperatures but restricted to the minimum amount necessary to avoid the occurrence of other kinds of defects (e.g. resulting from reactions with the investment). Material separation by films of zinc oxide can only be avoided by using clean material and a protective atmosphere.

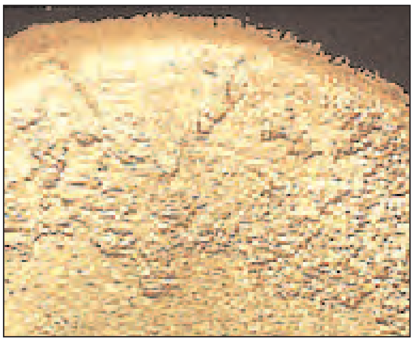


Fig. 7.1 Sandy surface on a relatively heavy test piece.


Fig. 7.2 Fins on a test tree.

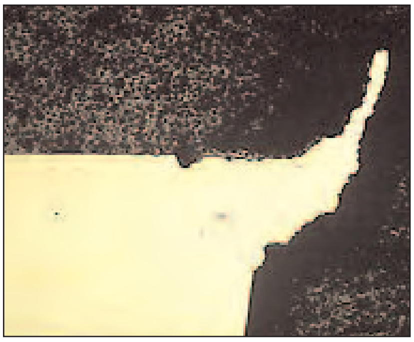


Fig. 7.3 Microsection through the edge of a piece with fins. 50 x

1.3 SURFACE QUALITY AND INVESTMENT

CASE 7: ROUGH SANDY SURFACE AND FINS - TYPICAL DEFECTS CAUSED BY WEAK INVESTMENT

Key Words

Investment casting; surface defects; sandy surface; fins; investment failure.

Description of Defect

This case includes two different defects with a common cause. They often occur together and more usually on large, heavy flat items. The surface of the casting appears rough and ‘sandy’. It seems as if a wet surface has been gritted with fine grained sand. On the edges of cast items, thin ‘fins’ may be formed. Fins are thin foils of material with irregular shape adhering to the edges of the casting.

Commonly, both types of defect are obvious after removing the investment from the cast tree. Sand blasting can partially remove the defects and alter the appearance. In this case, it is more difficult to identify the type and origin of the defects.

Visual Appearance

Centrifugally cast, the part of the tree most affected by this defect was at the flask bottom (opposite end to the melt button). Small fins can also be seen.

Typically the fins occur on edges of heavy cross-sectioned parts, at the flask bottom (opposite end to the melt button).

Alloys: In general, high carat alloys may have an increased propensity for this defect because of their higher density, placing a greater force on the investment.

Manufacturing Methods: The main cause of the defect is an incorrect investing procedure and/or a bad batch of investment (stored under the wrong conditions or for too long).

However, the casting method has also an influence. The higher the pressure in forcing the melt into the flask, the higher is the danger for getting fins or a sandy surface. With static casting, the pressure is limited by several factors. Centrifugal casting machines enable a much higher pressure to be exerted, depending on rotational speed. Thus, this kind of defect is more often reported when centrifugal casting is used.

Typically, the faults are more abundant at the bottom of the flask (end away from the melt button). The highest pressure exerted on the mould walls, in both centrifugal and static casting, occurs at the flask bottom.

Influence on Properties

Both types of defects are restricted to the surface. Neither mechanical properties nor microstructure are influenced. The main disadvantage is a higher level of rejects and/or a greater effort in finishing (polishing) the jewellery items. Deterioration of fine surface details causes rejects.

Brief Explanation

The main cause for both kinds of defects is a structural weakness of the mould investment. The investment cannot resist the pressure and abrasion of the incoming melt. A weak, friable mould surface, due to poor investment or, possibly, too rapid burn-out or casting conditions, leads to a rough, sandy surface structure after solidification.

In addition, on edges of heavy cross-sectioned parts, the investment breaks or cracks, allowing melt to penetrate the mould wall and resulting in the formation of fins.

The main reasons for the failure of investment are:

a) A bad batch of investment was used (investment powder too old or stored in humid surroundings - causing premature setting of the binder)
b) The investment was mixed with a too high a quantity of water.
c) Sometimes, accelerated heating of the flask in the burn-out cycle causes a break-down of the investment.

The tendency to induce the defect increases with increasing pressure during casting. Use of too high a speed of rotation in centrifugal casting is critical. In extreme cases, even sound investment can break. The force acting on the investment wall is highest in the case of large, thick walled items; therefore, the defects are more likely to be encountered with such jewellery items.

Recommendation for Avoidance

In the first place, the quality of investment powder and the correctness of the investing process has to be checked. The easiest way for doing this is measuring the ‘gloss-off’ time. After checking this point, the burn-out cycle has to be carried out in a correct, controlled manner as does the subsequent casting procedure, especially if using centrifugal casting. Static casting is not so critical.

The following schematic diagram shows the sequence of steps to be followed to determine the causes and, hence, the measures necessary for avoidance of the defect(s). Usually, quality of investment powder or/ and the investing process are the decisive factors. The burn-out cycle depends on the flask size, type and size of the furnace and the furnace filling. Therefore, any recommendations can only provide initial guidance. For safety, an additional hold at 450°C for 2 hours during burn-out should be included. The investment manufacturers recommendations should be followed.

Extended Explanation

The strength of the investment is, in the first place, determined by the quality of the binder, gypsum (calcium sulphate). Partially dehydrated calcium sulphate takes up water during the investing process and forms a network of (hydrated) gypsum crystals which bind the refractory silica (quartz and cristobalite) grains together. Investment powder can lose this binding property when it is stored in a humid atmosphere or for a long time (premature uptake of humidity). In a slurry with excess water, the gypsum needles cannot develop the bonding network, with the consequence that the investment has a reduced strength. During the burn-out process, gypsum looses a part of its water in a temperature range 190- and 200°C. The bonding strength can only be maintained if this process occurs slowly.

Decomposition of calcium sulphate also has to be avoided as this can also give rise to sandy surfaces. When mixed with silica, this can occur at

Fig. 7.4 Pendant in 14ct gold

temperatures as low as 750°C, especially when carbon is present (which can arise from incomplete burn-out of wax absorbed on the mould wall). These temperatures can be easily attained at the mould surface during pouring of molten metal. Higher caratage alloys and palladium white golds have high melting ranges.

Another example

In this case, there are at least three causes that have conspired to produce the defective pendant:-

a) The investing procedure was incorrect. Instead of an anticipated 'gloss-off' time of 12 minutes, a time of only 6 minutes was measured, probably due to an incorrect powder/water mixing ratio.

b) The burn-out procedure was wrong. The temperature-time cycle was programmed correctly. However, the furnace contained too many flasks. Some flasks were placed very close to the heating elements and were heated too fast on this facing side, resulting in a weak investment locally.

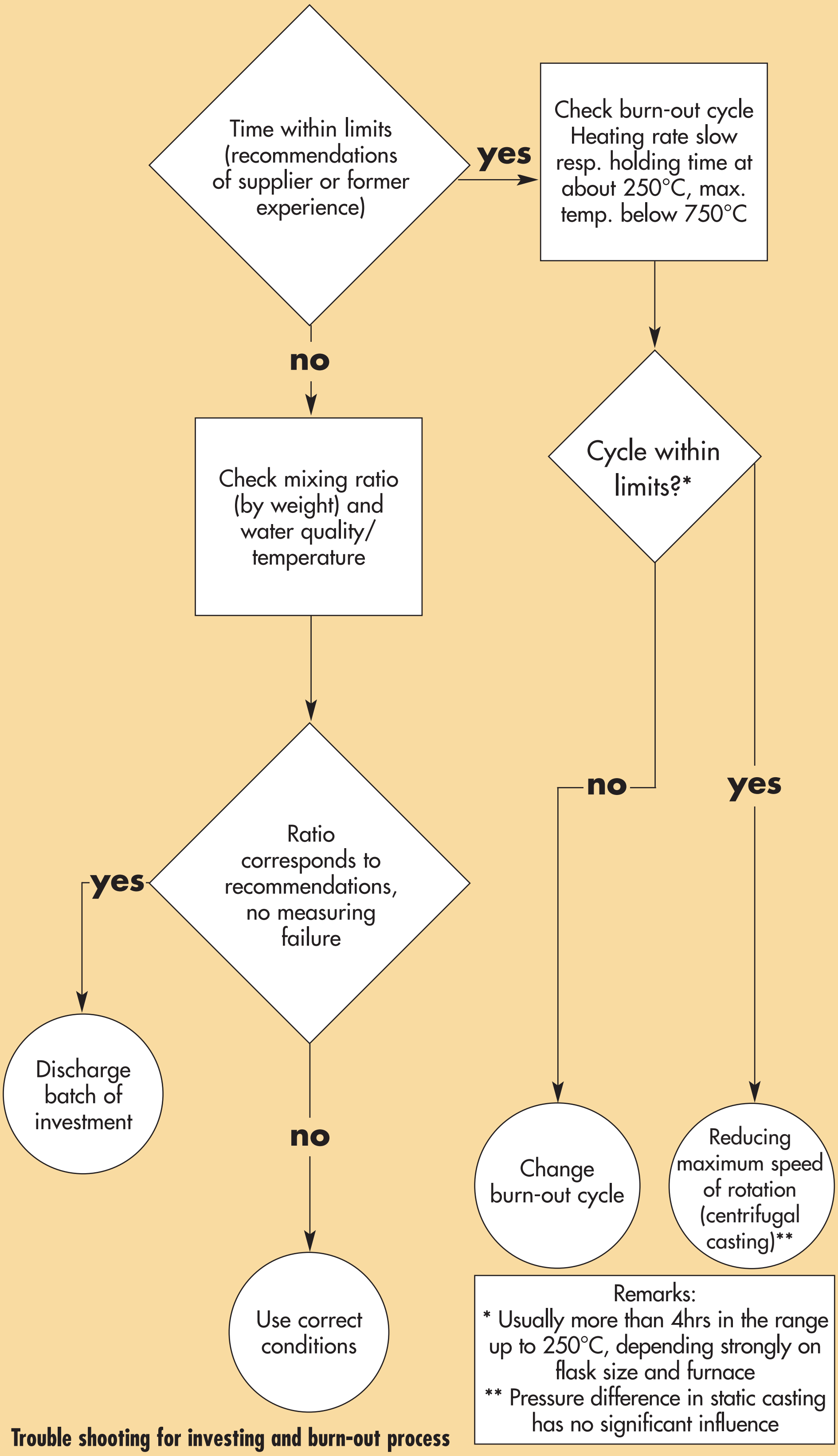
c) The burn-out cycle was interrupted during the night. The flasks cooled down to about 100°C and were re-heated to working temperature (350°C) the following day. *Cooling down the flask below approximately 250°C weakens the investment.*

A bad, rough sandy surface and the formation of fins on the edges of the flat pendant were the result of this mistreatment.

Further Reading

Part C: Basic Aspects, section 3.3, Influence of investment on casting quality.

Testing gloss-off time



Remarks:
* Usually more than 4hrs in the range up to 250°C, depending strongly on flask size and furnace
** Pressure difference in static casting has no significant influence

Trouble shooting for investing and burn-out process

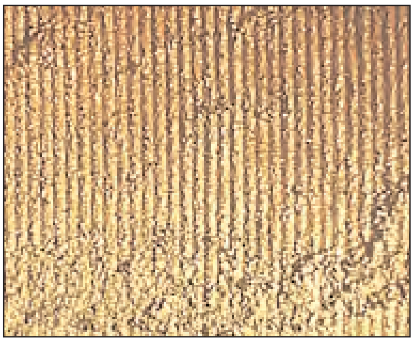


Fig. 8.1 approx. 20 x

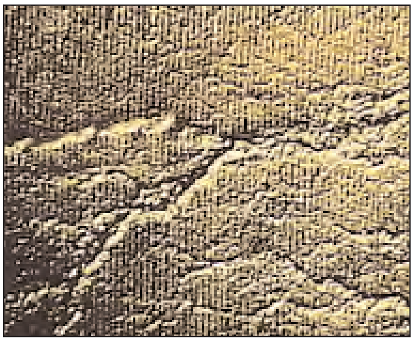


Fig. 8.2 Watermarks on test piece (piece of a record) approx. 10 x

CASE 8: ROUGH SURFACE AND ‘WATERMARKS’ - CAUSED BY INCORRECT INVESTING PROCEDURE OR BAD QUALITY INVESTMENT

Similar to

Case 7

Key Words

Investment casting; investing process; surface defects; watermarks.

Description of Defect

Raised traces are visible, particularly on flat surfaces. The orientation of the traces on the item run approximately from top to bottom of the tree.

Visual Appearance

The examples are severe cases. Not only raised traces are formed but also a complete destruction of the fine surface structure of the record has occurred.

Alloys: Independent of alloy composition.

Manufacturing Method: The cause is an incorrect investing process (as explained later). The casting method has little influence.

Influence on Properties

The only property affected is the surface quality. Slight traces on plain, flat surfaces can be removed by polishing (or gentle grinding).
More pronounced watermarks, especially on structured surfaces, are irrecoverable and should be rejected.

Brief Explanation

After mixing, the investment slurry contains an excess of free water. When the setting process commences, the water is taken up by the binder (partially dehydrated gypsum). If the slurry is left motionless for several minutes before setting starts, the water and solids can separate. Some of the separated water can collect on the surface of the wax models and may run together, forming the characteristic watermarks. The traces left by the water remain on the mould wall after dewaxing and are eventually reproduced on the casting.

Flat pieces are more sensitive to this fault than small, sculptured items. Such defects occur frequently when the slurry is made with too much water.

Recommendation for Avoidance

As a first requirement, the investment setting time has to be known. The best way to determine this is by measuring the ‘gloss-off’ time. A standard value is approximately 12 min. for most quality investments. However, this value can vary with brand of the investment and working conditions. The manufacturers recommendations should be followed.

The ‘working time’ is one or two minutes less than the gloss-off time. During the working time, the slurry should kept in motion. The working time is normally taken up by mixing, degassing, filling the flask, degassing again and vibrating. Where vacuum investing machines are used, a separate degassing is not necessary and filling the flask automatically is fast. Therefore, the mixing procedure has to be extended to keep the slurry in motion for a reasonable time to prevent separation.

Note: Mixing the investment slurry in vacuum investing equipment with a good vacuum can also have an adverse effect. Water evaporates in high vacuum very easily, the slurry can become too viscous and the working time is reduced. This has a detrimental influence on surface quality and even cracks in the investment can occur when the working period is longer than the reduced working time.

Note: At high altitudes, less water than the recommended amount is needed.

Further Reading

Part C: Basic Aspects, section 3.3, Influence of investment on casting quality

Fig. 9.1 Wrinkled surface of 14ct yellow gold ring 6 x

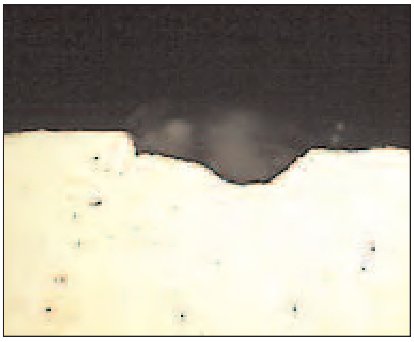


Fig. 9.2 100 x

CASE 9: WRINKLED SURFACE - CAUSED BY FAST HEATING DURING THE BURN-OUT PROCESS

Key Words

Investment casting; invest defect; burn-out process; surface defect.

Description of the Defect

The surface of cast items has a wrinkled, scarred appearance. The defect occurs only in small number of flasks out of a furnace fill. Often it is noticed only on pieces from one side of a flask.

Visual Appearance

The defect was restricted to some flasks of a 'furnace fill'. Furthermore, it appears mainly on parts positioned on one side of the flask.

Alloys: The defect is independent of alloy composition.

Manufacturing Method: The burn-out furnace was overfilled with flasks to the top. Some flasks stood very close to the furnace walls.

Influence on Properties

Mechanical Properties

Not influenced

Microstructure

The microstructure is not affected and no porosity or pitting is observed. The cross-section, fig 9.2, shows relatively flat surface irregularities.

Surface quality

For a smooth surface, more grinding and polishing has to be applied.

Brief Explanation

The burn-out furnace was overfilled with flasks, some stood very close to the heated walls of the furnace. The sides of these flasks facing the wall heated up very quickly and so the surplus water in the investment could not evaporate gently. Violent boiling occurred and the wax softened, causing the surface of the mould cavities to deteriorate; these defects were reproduced on the casting.

Recommendation for Avoidance

The burn-out furnace should not be filled to the top and close to the sides with flasks. This prevents uniform heat distribution. Depending on the furnace, the temperature within the chamber can vary widely (50 -75°C is not untypical). Usually, near the front door (and the back wall) the temperature remains low. Flasks in this position might not be heated sufficiently. In contrast, the heated side walls are usually the hottest places in the furnace. Flasks placed near them will heat up too fast. To avoid such problems, flasks should be positioned at a safe distance.

The heating rate should be sufficiently slow, at least up to 400°C, to allow water to evaporate away gently and allow phase transformations in the silica refractory to be completed without causing cracks. A holding time period at 250°C is recommended. Investment manufacturer's recommendations should be followed.

Further Reading

Part C: Basic Aspect, section 3.4.3, Burn-out cycle

CASE 10: DENDRITIC SURFACE - DUE TO SHRINKAGE AND REACTION WITH THE INVESTMENT

Key Words

Dendritic structure; investment casting; reaction with investment; flask temperature.

Description of Defect

The surface of heavy cross-sectioned items is rough with a typical dendritic structure. This structure often appears on the central sprue.

Fig. 10.1 Surface of central sprue

VISUAL APPEARANCE

The central sprue shows a typical rough structure. Even with the naked eye, the dendritic appearance can be recognised.

With higher magnification, the typical dendritic structure is better resolved. Removing any remaining investment from the tree by sand blasting hides the defect. Only a rough, irregular surface remains, with pores visible. The real reason for the defect is hidden.

Alloys: Any yellow carat alloy can show this kind of defect but 14ct alloys are especially sensitive to this surface structure.

Manufacturing Method: In general, the defect tends to appear on investment casting under a protective atmosphere and with a relatively high casting and/or flask temperature.

In one actual case, a 21ct alloy was cast with a flask temperature of 720°C and a melt temperature of 1150°C under a protective atmosphere. The reason for using such high temperatures was to obtain sufficient form-filling. Vacuum (static) casting was used under conditions where there was no great pressure difference.

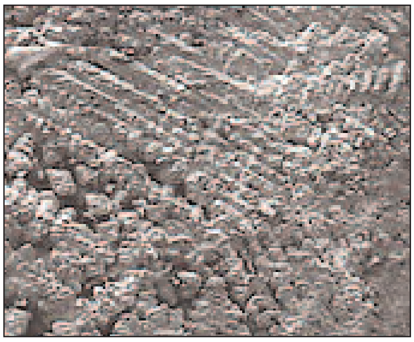


Fig. 10.2

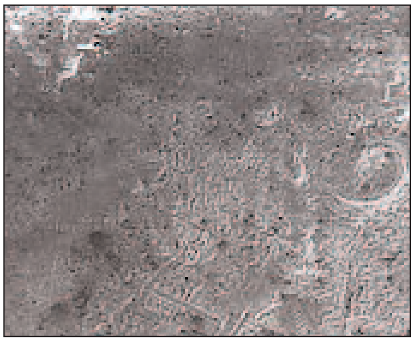


Fig. 10.3 The dendritic surface structure as revealed in a scanning electron microscope (SEM).

Influence on Properties

Mechanical Properties

In most cases, the mechanical properties are not significantly influenced, despite shrinkage porosity and porosity caused by some impurities.

Microstructure

The microsection, Fig. 10.4, shows a rough, degraded surface.
The structure itself is not affected and the casting shows no porosity.
In most cases, the defect is restricted to a small surface zone, as in this case. Sometimes, however, it will extend to include both shrinkage and gas porosity. A dendritic surface should be seen as a warning that porosity might have occurred too.

Other

The roughness of the surface is considerably increased, so extending the grinding and polishing necessary to obtain a smooth, polished surface.

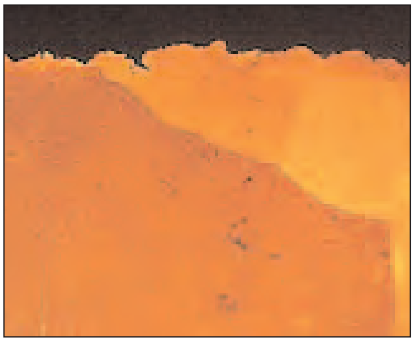


Fig. 10.4

Brief Explanation

Growth of crystallites at the onset of solidification manifests itself as a dendritic shape. The residual melt remains in the inter-dendritic space. If the melt does not wet the investment at the mould wall and decomposition of the investment gypsum binder causes the formation of sulphur dioxide gas, the residual melt is pushed away from the surface, leaving a skeleton of dendrites. Thus, the typical dendritic surface structure appears. These conditions are preferentially fulfilled in a neutral, protective atmosphere and with high casting and/or flask temperatures.

Usually, this defect is restricted to heavy cross-section parts or the central sprue. Both introduce a great quantity of heat, increasing the temperature on the surface of the investment and increasing the likelihood of gypsum decomposition. A dendritic surface is less likely when the casting is done in air. In this case, the wetting behaviour of the melt is enhanced by the formation of oxides.

Recommendation for Avoidance

If thick-walled items show this effect, the casting temperature and/or flask temperature should be reduced. However, the form-filling of any filigee items on the same tree, for example, may become worse. Improving form-filling by other methods (e.g. by increasing the pressure difference in pressure or vacuum assisted casting) should be done to compensate the negative effect of lower temperatures. Use of an alloy with small zinc additions should also reduce the roughness caused by the dendritic surface structure.

A dendritic structure on the central sprue is not necessarily a bad sign. In the case of casting thin-walled items, it can be neglected. However, if heavy parts are on the tree, a dendritic surface on the central sprue has to be taken as a hint that casting conditions are not optimum.

Further reading

Part C: Basic Aspects, section 2.1, Melting and solidification and section 3.5, Behaviour of gypsum-bonded investment during casting.

1.4 INCLUSIONS

Inclusions can be divided into two classes:-

a) Non-metallic particles, which do not originate in the alloy. Investment particles, eroded particles from worn crucibles, slags and oxides are examples and are caused by improper casting procedures and, therefore, are treated in the following chapter.

b) Metallic and non-metallic inclusions which originate from a contaminated (polluted) alloy. These include segregations of insoluble grain refiners but, for convenience, these are considered in chapter 3 on 'Defects caused by Alloy Composition', even though the defect may occur during investment casting.

CASE 11: PORES AND INCLUSIONS ON THE SURFACE - CAUSED BY INVESTMENT

Key Words

Investment Casting; surface defect; inclusion; investment.

Description of the Defect

Scattered, relatively large pores and inclusions are visible on the surface of a cast item. Usually, the defect is not visible until the jewellery is polished. Sometimes, attempts to remove the defect by grinding and/or polishing may be successful. However, in other cases the pores will be enlarged by this procedure.

Fig. 11.1

Visual Appearance

The pores are randomly scattered all over the surface. The pores can be empty or filled with obviously non-metallic material. Probably, an empty pore originally was filled by an inclusion which has been removed by the subsequent surface treatment, e.g. de-vesting, pickling, grinding and polishing.

Alloys: Independent of alloy composition.

Manufacturing Method: Investment casting in general, although centrifugal casting is more susceptible to this defect as the force acting on the investment is higher. More important factors are the quality of the investment, the investing procedure and the way of building up the tree (see later).

Fig. 11.2 40 x

Influence on Properties

Mechanical Properties

The mechanical properties are not usually affected.

Microstructure

Many pores are visible on the surface, fig 11.2, and just beneath the surface. Inclusions are not apparent; perhaps, the defects are too close to the surface and any inclusion was removed by surface treatment or sample preparation.

Figure 11.3 shows a pore at higher magnification. Only a small part of the defect volume reaches the surface. More polishing would enlarge the defect.

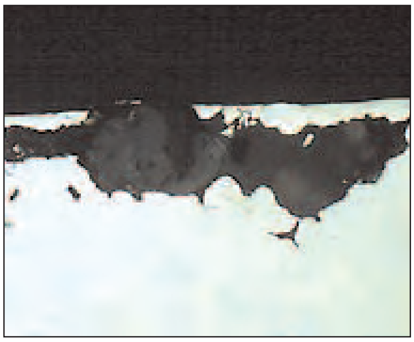


Fig. 11.3 400 x

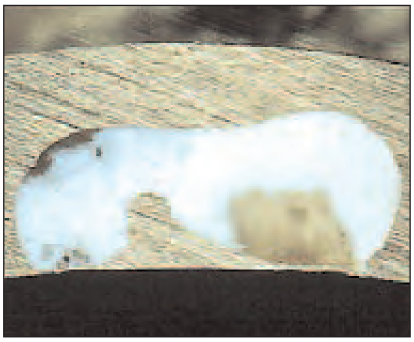


Fig. 11.4

An example from another defect case, fig 11.4, reveals an investment inclusion of considerable size. Such examples, with the inclusion completely retained after surface treatment and sample preparation, are not very usual.

Brief Explanation

The incoming flow of liquid metal during pouring breaks off parts of the investment out of the mould which then become entrained in the melt as it fills the mould cavity. These eroded investment particles (mainly silica) are the inclusions. They are frequently found near the surface of a jewellery item.

Reasons for this defect can be manifold: Firstly, a weak investment; the strength of the investment will be low if a bad batch - a batch too old or stored on a humid place - is used or if the powder/water ratio was wrong. Secondly, improper setting up of the wax tree. Sharp edges, especially at the connection of the wax model/gate to the central sprue, or elsewhere on the tree or in the design of larger jewellery items, can break when they are impacted by the melt as it is poured.

The danger of investment particles breaking off increases with increasing velocity of melt flow, particularly where the flow is turbulent. Thus, centrifugal casting tends to cause more of these defects than static casting.

Alternatively, inclusions may originate as eroded particles of graphite or ceramic refractory from old, worn melting crucibles, from old investment adhering to unclean recycled scrap or, simply, from airborne dusts.

Recommendation for Avoidance

Investment: The first step is the control of the investment quality and the investing procedure. If the ‘gloss-off’ time becomes unusually long, the danger for getting such (and other) defects increases considerably. Provided that the mixing ratio is correct, a bad powder quality is the cause. The powder originates from a bad supplied batch or the powder was stored for too long a time and/or in a humid place. Investment must be stored in an air-tight container.

Wax tree design: Make sure that wax model/gate-sprue joints are smooth and profiled and that larger cast items do not have sharp edges which can break off when impacted by the melt.

Casting: Do not use too high a speed or acceleration during centrifugal casting.

Other: Do not use old worn melting crucibles or unclean recycled scrap. The latter should be preferably remelted under a flux cover and grained.

Further information

Part C: Basic Aspects, section 3, Investment casting.

CASE 12: 'CROWS FOOT'-LIKE SURFACE DEFECTS - CAUSED BY ZINC OXIDE INCLUSIONS

Key Words

Investment casting; surface defects; porosity; inclusions; impurities.

Description of Defect

Porosity is claimed. The pores appear predominantly after finishing and polishing. In the case of low carat alloys, the area surrounding the pores is often tarnished.

Visual Appearance

The example shows a 10ct alloy which contains many oxide inclusions.

At higher magnification, figs 12.2, 12.3, the typical form of such 'crows feet'-like surface porosity can be seen. Unfortunately, sometimes shrinkage porosity has a very similar appearance. Identification requires detailed information on casting conditions and examination of a microsection taken at the site of the defect.

Alloys: Alloys with a higher zinc content. Generally, with few exceptions, 8 -10 carat alloys have a high zinc content. However, even 14 and 18 carat alloys can contain a considerable, high zinc content.

Manufacturing Method: The defect occurs with any casting method where there is not sufficient protection against oxidation. In the same way, use of remelted contaminated material is critical.

Influence on Properties

Mechanical Properties

In extreme cases, embrittlement can occur; the items break when a low force is applied if the structure is infiltrated by a large quantity of oxides.

Microstructure

Typically, zinc oxide forms inclusions in the shape of membranes or films. In microsections, the membranes are visible as filament-like traces, fig 12.4. Usually a high magnification and good metallographic preparation of the microsection are necessary to reveal the inclusions. Where the inclusions reach the surface (usually after polishing the jewellery items), pores in the shape of a 'crows foot' appear on the surface.

Other

Low carat alloys may be tarnished around the porous area. Chemical treatment, such as pickling, electrolytic stripping or cleaning, or under the influence of human sweat or other aggressive media such as sprays, the oxides will be etched away. Such aggressive media can remain absorbed in these micro-cavities, causing local corrosion and tarnishing.

Brief Explanation

Zinc is a good deoxidiser in gold alloys and readily forms zinc oxide in the presence of oxygen in preference to copper oxide formation, thus producing brighter castings. In contrast to copper oxide, it is not possible to remove zinc oxide by melting such contaminated alloy under reducing conditions. Unlike copper oxide, zinc oxide does not tend to float up to

Fig. 12.1 Surface porosity caused by impurities.

Fig. 12.2 Typical surface porosity caused by oxide impurities in a high zinc-containing alloy.

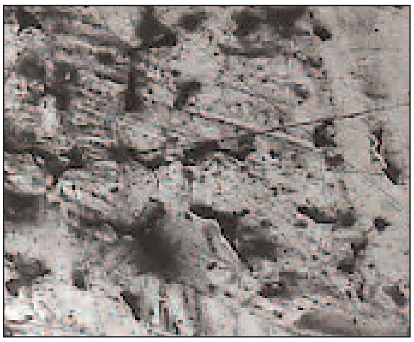


Fig. 12.3

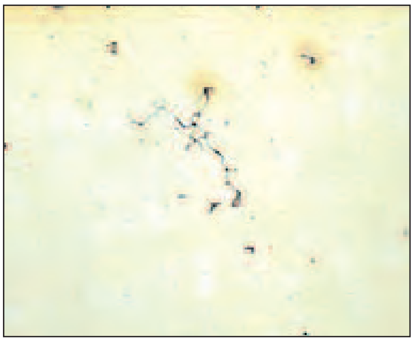


Fig. 12.4

the surface of the melt but remains within the bulk of the melt. After solidification, zinc oxide often forms thin membranes, situated mainly on grain boundaries (and appearing as filament-like inclusions in microsections). The result is that zinc oxide, once formed, persists in the material, causing porosity and surface defects.

The usual sources for zinc oxide inclusions are: a) Melting under oxidising conditions. Where melting is not done in closed chamber, shielding of the melt with a protective atmosphere is important. Purging an open crucible with a flow of argon or nitrogen may not be sufficient. b) Remelting contaminated scrap material. This is generally thought to be the main cause for the defect.

Recommendation for Avoidance

Avoid melting without a protective gas atmosphere. At the very least, the crucible should have a protective cover of gas (preferably ‘forming’ gas, blown on the surface of the melt). Where melting is done in a closed chamber, a clean oxygen-free neutral atmosphere such as nitrogen or argon is recommended

Scrap material used for remelting has to be clean. In contrast to copper oxide, zinc oxide, once formed, is very difficult to remove by melting procedures.

CASE 13: SURFACE ‘CAULIFLOWER’ DEFECTS - CAUSED BY SLAG INCLUSIONS.

Key Words

Investment casting; surface defect; inclusions; slag.

Description of the Defect

The cast item has a partly very rough surface with a cauliflower-like structure. Some inclusions are visible on surface.

Visual Appearance

The surface has a cauliflower-like structure caused by liquid slag or flux introduced into the flask with the melt. The slag collects on the surface and is mostly removed on removing the investment and cleaning the casting.

Alloys: This actual case is an 18ct yellow gold; however, the defect is independent of alloy composition.

Manufacturing Method: Investment casting by the vacuum assisted method, with bottom pouring from a ceramic crucible.

Influence on Properties

Mechanical Properties

The mechanical properties are not usually affected.

Microstructure

The alloy microstructure is not influenced by the defect. Inclusions near the surface can be frequently observed. In this actual case, different kinds of inclusions were found: Some had relatively sharp edges, fig. 13.3, which were identified as pure silica. Other particles had smooth edges and an apparently complicated structure, fig. 13.4, which analysis showed contained zinc, silicon and a small amount of nickel.

The sharp-edged inclusions, fig 13.3, were identified as silica particles. The relatively coarse size indicates that the inclusion did not come from the investment.

Fig 13.5 shows what is probably a slag particle with a maximum diameter of approximately 1mm. It can easily be detected and characterised with a magnifying glass as an irregular structure with rounded edges.

Other

It is not possible to obtain a bright surface by polishing. Inclusions tend to break out causing scratches.

Brief Explanation

The cause of the defect are external impurities introduced into the melt. At least some of the impurities were liquid (slag) at the moment of casting and are swept into the flask where some float to the surface of a cast item while the metal was still liquid. After solidification, this typical cauliflower-like structure of the metal surface remains, while the slag particles themselves are removed during the cleaning of the casting. However, not all the slag (or inclusions) collect on the surface. Some of it forms inclusions close to the surface. The shape of the inclusions and their analysis by SEM-EDX can provide reliable information on the origin of defect.

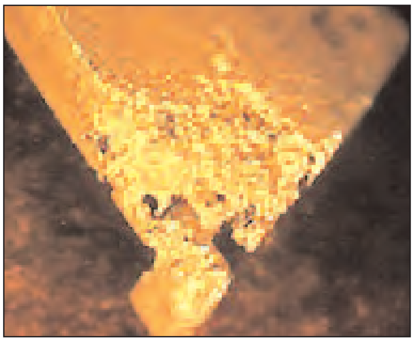


Fig. 13.1 8 x

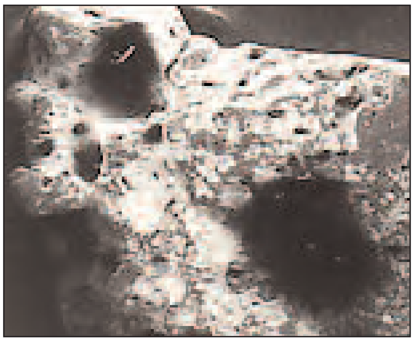


Fig.13.2

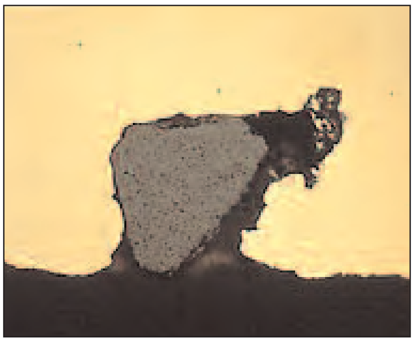


Fig. 13.3 SEM-micrograph

Fig. 13.4 Inclusion of slag with smooth edges, suggesting that the particle was probably liquid at the moment of casting

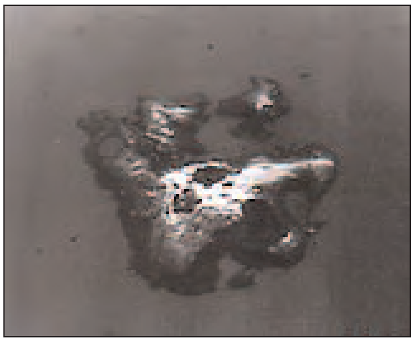


Fig. 13.5 Another example of a silicate inclusion.

The roughly spherical shape of the particles points to their origin as slag. It consists mainly of zinc silicate with a small amount of nickel oxide or silicate. These compounds can accumulate in the melt crucible if dirty scrap material, contaminated with some used investment, is remelted as part of a new melt. Boric acid, used as flux or for ‘conditioning’ the crucible, can also be involved. It decreases the melting range of the slag and increases the fluidity.

The fairly sharp-edged inclusion was introduced to the melt in the solid state. Size and shape exclude investment powder as a probable source. It could be a refractory particle from the crucible or possibly ‘dirt’ introduced from outside.

In summary, the evidence points to either a dirty, worn crucible with an excess of flux (used to ‘condition’ the ceramic crucible) or some ‘dirt’ from the bench as the cause of the defects.

Recommendation for Avoidance

Use only clean crucibles which are not worn out. Avoid too great an excess of flux, both in ‘conditioning’ the crucible or simply adding flux to the melt. In principle, the quantity of flux - if ever used - should be kept as small as possible.

CASE 14: POROSITY - CAUSED BY INCLUSIONS OF SLAG COMBINED WITH GAS PORES

Key Words

Investment casting; surface porosity; impurities.

Description of Defect

The surface shows a great number of pores.

VISUAL APPEARANCE

The surface is littered with irregular pores, fig 14.1.

Sometimes, shallow, flat hollows occur on a porous surface when slags are involved in the defect, fig 14.2.

Alloys: The example is an 8ct yellow gold alloy, although the defect can appear with other alloys, too. However, low carat alloys are more critical.

Manufacturing Method: Investment casting; the most important fact is that a great quantity of flux was used to prevent oxidation and collect any oxides, especially zinc oxide.

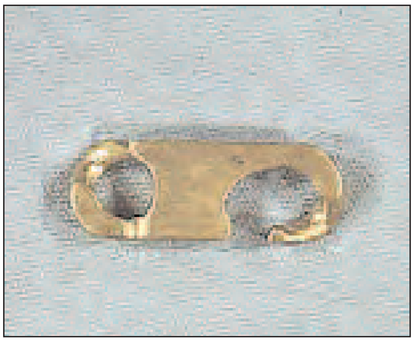


Fig. 14.1 A spring hook with surface porosity

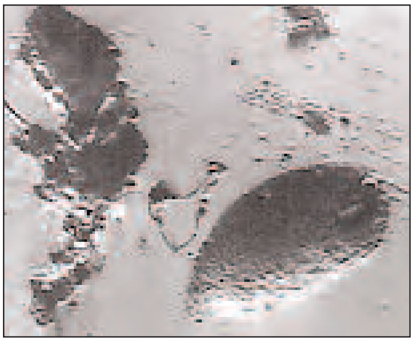


Fig. 14.2 Surface porosity on a 14ct yellow gold casting

Influence on Properties

Mechanical Properties

Fractures can be caused by excessive porosity in smaller cross-sectioned regions.

Microstructure

Irregular shaped large pores with dendritic edges are one of the characteristics of this kind of defect, fig 14.3. The pores are filled in part with a glassy substance which can be identified as slag.

This example, fig 14.4, shows large pores in a cast 14ct alloy. The thin lines between pores are a characteristic feature, caused by thin oxide membranes.

Fig. 14.3 200 x

Fig. 14.4 50 x

Brief Explanation

Sometimes material is melted and remelted in air (often in a worn-out clay-graphite crucible). To remove any remaining old investment and oxides and to prevent further oxidation during melting, a flux (e.g. borax) is added in considerable quantity. The flux forms a viscous surface slag and may accumulate with increasing number of castings performed with the same crucible, if the crucible is not sufficiently cleaned after each casting. Some of the slag containing oxides are poured with the alloy melt into the flask and form inclusions in the casting. Zinc oxide will form thin membranes and copper oxide is suspected of inducing severe gas porosity.

Even if the reaction mechanism which leads to such pronounced porosity is not completely understood, the appearance of this type of defect is a positive hint that it is caused by a considerable amount of impurities. In most cases, the defect occurs with zinc-containing alloys. Zinc oxide is readily formed and is not easily removed from the melt. Too much flux can exacerbate the defect considerably.

Recommendation for Avoidance

There are only a few, effective rules for avoiding this defect:

a) Only clean material should be melted.
b) The portion of used material should be restricted to about a third of the total quantity.
c) Any remaining used investment and other impurities must be completely removed.
d) Melting should be performed in a protective atmosphere, making addition of flux unnecessary.
e) Use of flux should be avoided in investment casting or, at least, reduced to a minimum. Any remaining flux and slag in the crucible should be removed after each casting, preferably whilst the crucible is still hot and the slag/flux is still pasty.
f) Avoid using an alloy with a high zinc concentration.

2 INGOT CASTING AND CONTINUOUS CASTING

Relatively few cases of defects have been reported that are attributable to these production methods. One reason might be that defects in a cast bar, rod or tube are only revealed many production steps later. Tracking back their causes to the origin is difficult, if not impossible.

2.1 CRACKS AND MATERIAL SEPARATION

CASE 15: CRACKS ON THE SURFACE OF A RING - CAUSED BY A BAD SURFACE ON A CONTINUOUSLY CAST TUBE

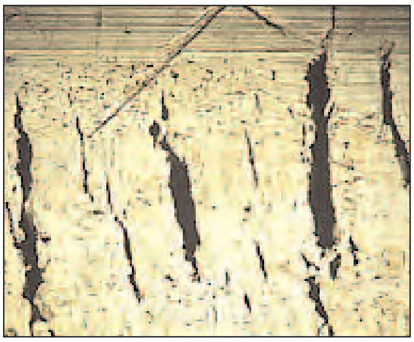


Fig. 15.1 Surface of the ring approx 20 x

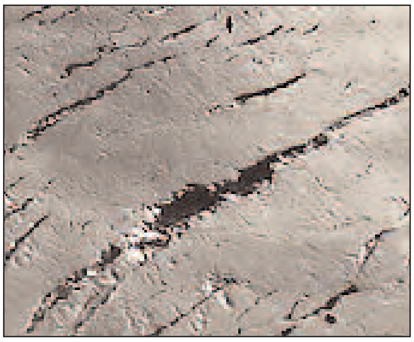


Fig. 15.2 SEM image of the surface

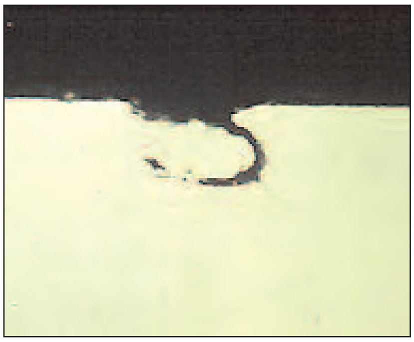


Fig. 15.3 250 x

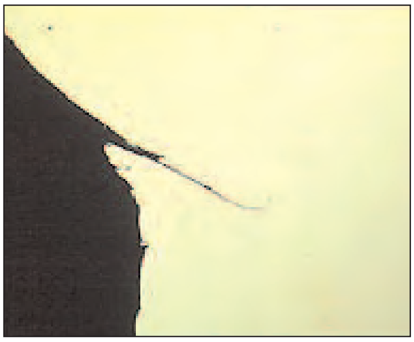


Fig. 15.4 250 x

Key Words

Continuous casting; surface defects; over-stressing; cracks.

Description of Defect

Small cracks are visible on the surface of a ring and are repeated. Apparently, the cracks are restricted to the surface.

Visual Appearance

The surface of the ring, fig 15.1, is split open in many cracks, some small. Despite the cracks, the ring has not broken.
The SEM photograph, fig 15.2, shows the cracks more clearly: the surface has a scaly structure. Apparently the scales or other surface defects have broken open.

Alloys: The defect appeared in a 14ct yellow gold containing 6% zinc.

Manufacturing Method: A continuously cast tube was put through a pilger mill and further reduced in diameter and wall thickness by drawing. Small ring blanks were cut off for ring manufacture.

Influence on Properties

Mechanical Properties

Whilst fracture of the rings was not reported, it could occur if a ring is enlarged by stretching.

Microstructure

Both figures 15.3 and 15.4 show incipient cracks. The cracks are not very deep and have the typical structure of laminations or laps. There is no sign of embrittlement. Impurities, e.g. segregations on grain boundaries or oxides, cannot be detected.

Surface Quality

The defect cannot be removed by polishing as the cracks are too pronounced.

Brief Explanation

The cause of the defect is probably a bad surface on the tube produced during continuous casting. The rough, scaly (laminated) surface of the cast tube will tend to be levelled when passed through a pilger mill, although the laminations are hidden beneath the new smooth surface. Subsequent drawing lengthens the laminations.

Subsequent rolling of the ring blank deforms the material in a radial direction. This deformation with the applied radial tensile stress causes the laminations to break up, resulting in cracks and flakes visible on the surface. Overstressing the material during rolling increases the defect considerably. Even small defects have a notch effect, causing cracks when the material is towards the end of its workability, i.e. in a severely work hardened condition. In the present case, the hardness was HV 260, a high value indicating that the material was highly strained by deformation.

Therefore, surface defects produced on continuously cast tube, followed by heavy deformation without any intermediate soft annealing, can be blamed for the occurrence of the defect on the rings.

Recommendation for Avoidance

In the first place, a good smooth surface should be achieved on the continuously cast tube. The melt should be clean and free from oxides and slag. A protective atmosphere will help to prevent oxidation and avoid the need for too much flux. The advance of the emerging tube during continuous casting and the cooling conditions should be perfectly matched to ensure a good surface. Any surface defects should be removed, e.g. by grinding, from the continuous cast tube before advancing to other production steps to avoid the occurrence of defects on the rings.

Furthermore, overstraining (excessive work hardening) must be avoided by an intermediate soft annealing of the material. Annealing is recommended after pilger milling the tube and before ring rolling.

Further Reading

See Part C: Basic Aspects, section 2.2, Deformation and mechanical properties and section 2.3.1, Soft annealing.

CASE 16: LAMINATIONS ON A RING

Key Words

Ingot casting; laminations; sink hole; primary pipe; shrinkage.

Description of Defect

Wedding rings show lamination or crack-like separations of the material on the side edges.

Fig. 16.1

Visual Appearance

The ring shows a crack-like defect on the side, fig 16.1. Several rings from the same batch have the similar defects. The length of cracks is variable; grinding or polishing does not remove them.

At higher magnification, fig 16.2, the material separation (lamination) is more obvious.

Alloy: The defect appeared in a 14ct yellow gold with 6% zinc, but is independent of alloy composition.

Manufacturing Method: The ring was punched from a rolled bar.

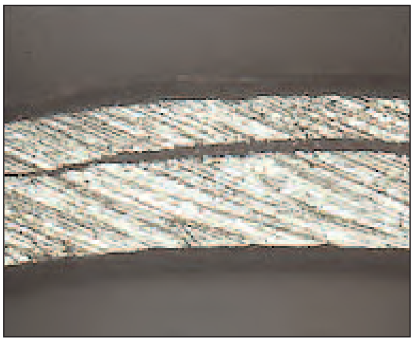


Fig 16.2 50 x

Influence on Properties

Mechanical properties and surface quality

The material lamination is permanent and can lead to complete separation of the ring into two pieces if it is further deformed to widen it.

Microstructure

The material separation is obvious, fig 16.3. Non-metallic inclusions (oxides, slag) are often seen accumulated on the parting plane.

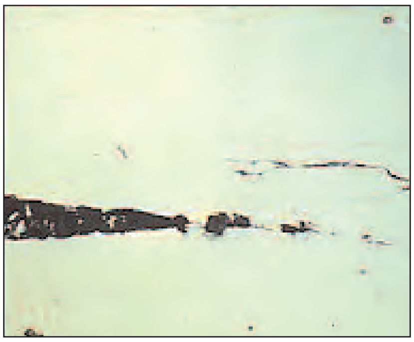


Fig. 16.3 200 x

Brief Explanation

On casting a bar vertically, a deep sink hole - or *primary pipe* - is formed on the top surface. In extreme cases, this sink hole can extend to a small and deep axial porosity - a *secondary pipe*. These pipes should be removed (by 'cropping' the ingot) prior to rolling the bar down to a smaller section. Otherwise, they can lead to a material separation in the rolled material. Even a small remnant of the pipe is extended to a considerable length during rolling and the defect remains undetected until final processing, e.g. by cutting or bending, deep drawing etc. Also, after rolling to plate or sheet, the material may split or delaminate into separate sheets.

The present case shows these separations on the cut edge of the punched wedding rings.

Recommendation for Avoidance

The only way to avoid this defect is by removing the pipe from the cast bar by cropping prior to rolling. Hidden axial porosity - a *secondary pipe* - might exist, which is not easily removed because of its depth, even if the primary pipe is small or virtually absent. To obtain a flat sink hole or pipe, the melt and mould temperature should be adjusted. Usually, an increased mould temperature will reduce the depth of the pipe.

Further Reading

Part C: Basic Aspects, section 3.1, Shrinkage porosity.

3 DEFECTS CAUSED BY ALLOY COMPOSITION

In this context, defects are considered that owe their origin primarily to the alloy composition, i.e. the consequences of deliberate alloying additions, and also to impurities insofar as they cannot be considered as non-metallic inclusions.

3.1 LOW MELTING IMPURITIES

CASE 17: CRACKS - CAUSED BY SEGREGATION OF LOW MELTING SILICON COMPOUNDS.

Key Words

Investment casting; cracks; low melting compounds, silicon.

Description of the Defect

A ring fractured during de-investing (or shortly afterwards) without being subjected to any significant strain or deformation. The fracture follows either a straight line or a jagged trace like a lightning path.

This and other very similar defects are now being reported more frequently, a consequence of the fact that silicon additions are now used more often to improve casting properties.

Visual Appearance

A 14ct yellow ring fractured during channel setting, the cracks occurring preferentially in the surrounding region of the hammered area. The ring has broken in a straight line. More jagged cracks like lightning paths are visible. Cracks of this shape invariably indicate that the material is brittle, i.e. it breaks without any visible deformation. In most cases, this happens with only a small force applied or even without any external stress.

In general, there are two reasons for the occurrence of such behaviour: the presence of either low melting alloying components or similar impurities. (Also, a special kind of corrosion causes a similar brittle defect in low carat alloys - *stress corrosion cracking*)

The figures 17.3 and 17.4 show another example. This item was cast in 18ct yellow gold with an addition of a silicon-containing 'grain refiner'. The castings were found to be already broken after removing the investment.

The brittle nature of the fracture is obvious.

Alloys: The defect is not strictly restricted to a particular caratage or fineness level, but the presence of some alloying elements or impurities is essential. Alloys of higher caratage and alloys with higher silver content are more sensitive to this kind of defect than lower caratage alloys with high copper content.

Manufacturing Method: The defect is not primarily a casting defect; the composition of the alloy is the decisive factor. However, it occurs almost exclusively with some specially formulated casting alloys.

Fig. 17.1

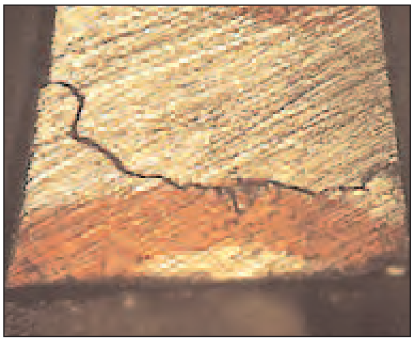


Fig. 17.2

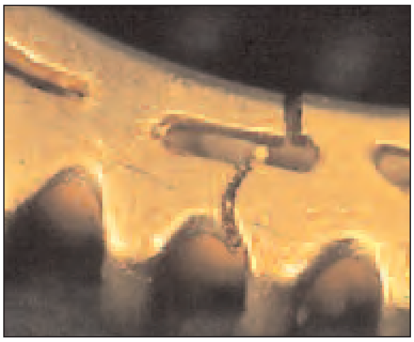


Fig. 17.3

Fig. 17.4 SEM of fracture surface

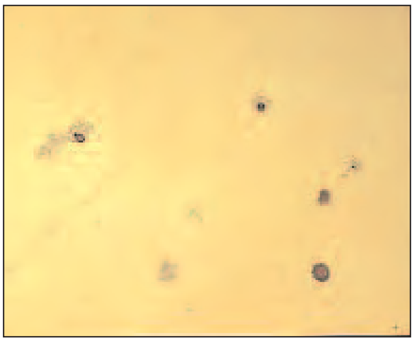


Fig. 17.5 Inclusions in a broken 14ct yellow gold sample

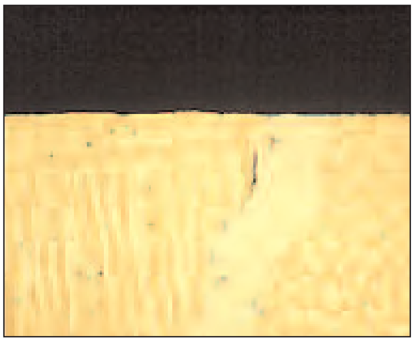


Fig. 17.6

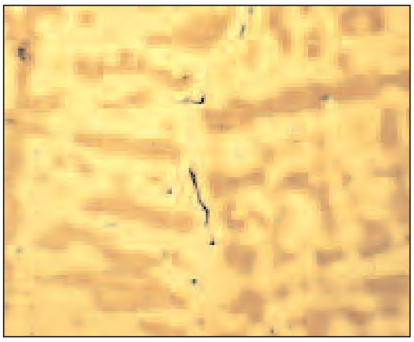


Fig. 17.7

Influence on Properties

Mechanical Properties

The material breaks easily without suffering any visible amount of deformation. A characteristic of this type of embrittlement is that it happens even if the alloy hardness is very low. In this case, the hardness was only HV 123, i.e. at the lower end of possible values for 14ct yellow gold.

Microstructure

At low magnification, only the path of the crack, along the grain boundaries, is visible whereas, at higher magnification (500x), greyish inclusions are revealed on the grain boundaries.

The grey inclusions, fig 17.5, were identified as a silicon-compound. Thin segregations of this compound along grain boundaries can cause embrittlement and cracks.

Figures 17.6 and 17.7 show the microstructure of a silicon-containing 18ct alloy. Two phenomena can be seen: the grain coarsening effect of silicon additions and very tiny segregations of a low melting phase on grain boundaries connected to cracks and crack-like pores.

Brief Explanation

Silicon additions, which cause the brittle behaviour, are used in 14ct yellow golds for preference to improve the castability of the alloy. However, silicon at too high a concentration forms a low melting component ('eutectic') which collects on the grain boundaries during solidification. This creates a brittle film on the grain boundaries which completely destroys the material's properties. Cracks can occur due to internal stresses generated during solidification or on cooling of the casting as well as later on further processing (polishing, setting etc).

Extended Explanation

Silicon has a negligible solubility both in gold and in silver. A low melting compound (eutectic) is formed. The solidus temperature in the binary Au-Si system is 363°C, and 830°C in the Ag-Si system. The low melting phase is brittle and collects on grain boundaries during solidification and weakens the material. The copper content of yellow gold enhances the solubility of silicon. For this reason, a small amount of silicon can be tolerated for improving castability.

The silicon concentration which can be used without causing problems depends strongly on the ratio Au/Ag/Cu and decreases with increasing (gold + silver) content. Thus, high carat golds are more susceptible to embrittlement than low carat alloys and, for a given caratage, silver-rich (pale) yellow gold will tolerate less silicon than a copper rich (pink) alloy.

In addition, silicon can cause a pronounced coarse grained structure which is not desirable. This multiplies the embrittling effect of even very small concentrations of silicon and other low melting compounds (see also figs. 17.8 - 17.10 below). Because of this fact, the critical level of a deleterious addition depends not only on the type of alloy but also on its microstructure.

Similar critical embrittling components include sulphur, lead, bismuth and phosphorus.

Recommendation for Avoidance

Silicon in yellow gold is a critical addition. To obtain the benefits of this element in the casting of carat golds without the danger of embrittlement and cracking, the concentration has to be strictly limited, according to the composition of the alloy. For example, a 14ct yellow alloy should not contain more than 0.1% silicon; an 18ct alloy can only tolerate 0.05% silicon at the most. Higher carat golds should not use silicon additions. However, the silver to copper ratio and any heat treatment has also to be considered.

Another example

In fig 17.8, the alloy is a 14ct white gold with 0.04% silicon and 0.001% boron additions. Silicon is considered as a 'grain refiner'.

The microstructure of this sample, figs 17.9 and 17.10, shows very thin traces of segregations on the boundaries of (large) grains. A very small concentration of a low melting compound is sufficient to form a brittle film on the grain boundaries in this coarse grained structure. The grains are effectively insulated from each other by this brittle substance. The detrimental effect of these compounds would be not so prominent in a fine grain structure (where the grain boundary area is much larger). The volume of the compound would probably not be sufficient to cover the increased surface area of the grains.

Further Reading

Part C: Basic Aspects, section 2.4, Low melting components

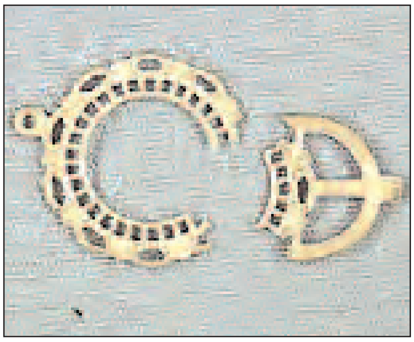


Fig. 17.8 A pendant, broken after devesting

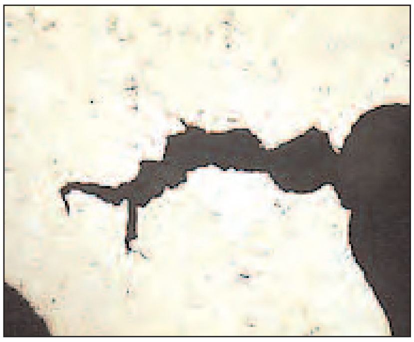


Fig. 17.9 100 x

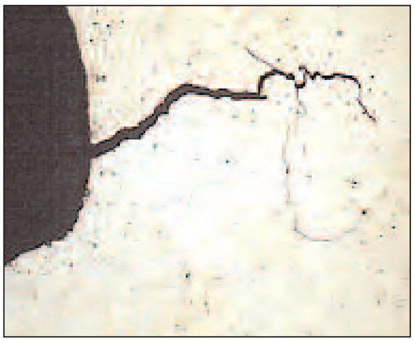


Fig. 17.10 200 x

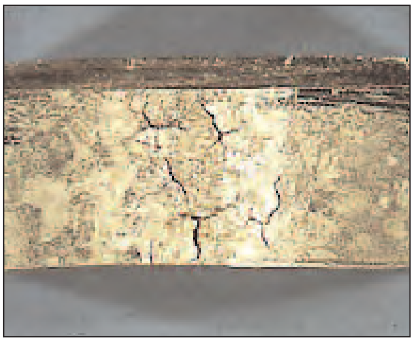


Fig. 18.1

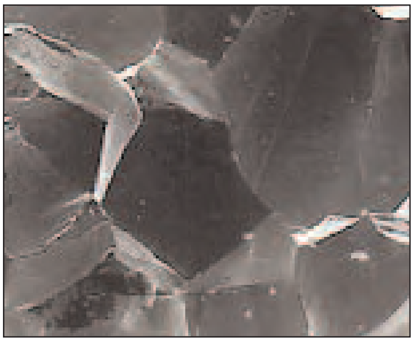


Fig.18.2 SEM: fracture surface of a lead-containing 18ct alloy

CASE 18: BRITTLE FRACTURE - CAUSED BY LEAD AS AN IMPURITY

Key Words

Embrittlement, fracture; lead.

Description of Defect

A piece of wire was completely brittle and fractured.

Visual Appearance

Alloy: 18ct yellow gold with a small impurity of lead (0.02%)
Manufacturing Method: The wire was manufactured in the usual manner without any difficulty. However, it was finally annealed at about 300°C. In this state the embrittlement occurs.

Influence on Properties

Mechanical Properties

The wire has broken with only a small deformation. It cannot withstand any strain; it is brittle.

Microstructure

The intergranular fracture (‘grainy’ structure), fig 18.2, is typical of a brittle fracture caused by impurities. The impurity, lead, segregated to the surface of the grains and degraded the bond between the grains (because the segregation itself has little strength) and resulting in the alloy fracturing along the weakened grain boundaries.

Brief Explanation

Lead is a dangerous impurity in gold alloys. Its solubility and, therefore, its critical concentration is very dependent on the composition of the alloy (components: gold, copper and silver). The higher the gold and silver concentration, the lower is the tolerable lead concentration. Furthermore, the detrimental effect of lead is also dependent on the alloy heat treatment. Annealing between 300 and 400°C is the most critical treatment. In this condition, even 0.02% lead can cause complete embrittlement of an alloy. This is well demonstrated in this case.
The alloy was ductile prior to this critical heat treatment, otherwise it would not have been possible to draw a thin wire. Only after annealing did the material become very brittle.

Recommendation for Avoidance

The only way to avoid the embrittlement is to use lead-free material. Sources for lead impurity include: a) recycling of old or scrap material repaired with soft solder (tin-lead alloy), b) the use of lead-containing (‘free-machining’) brass as a master alloy for zinc additions to the gold alloy (use 70/30 brass as brass with less 67% copper can contain some lead; brass with less than 60% Cu usually has more than 2% lead) and c) use of a lead support for working on jewellery items. Remnants of lead will diffuse into the material on subsequent annealing.

Further Reading

Part C: Basic Aspects, section 2.4, Low melting components

CASE 19: CRACKS - CAUSED BY SULPHIDE INCLUSIONS IN AN INVESTMENT CAST ITEM

Key Words

Investment casting; reaction with investment; cracks; sulphides; low melting components.

Description of the Defect

Rings cracked on one or both sides of the shank. The cracks were already present at the time of de-investing (removal of the investment).

Visual Appearance

The fracture occurred without any deformation. The fracture surface and the crack paths are jagged. The ring has fractured either during cooling after casting or whilst de-investing the tree. The alloy is a simple gold-silver-copper alloy and is not expected to be a problem. Only impurities can be the cause of such a fracture like this. In this actual case, sulphide (generated by reaction with investment) was found to be responsible.

Alloy: Conventional gold-silver-copper 18ct yellow gold.

Manufacturing Method: The investment casting was done by induction melting in a ceramic crucible and casting by the vacuum assisted method with bottom pouring. Forming gas (75% nitrogen, 25% hydrogen) was used as the protective cover.

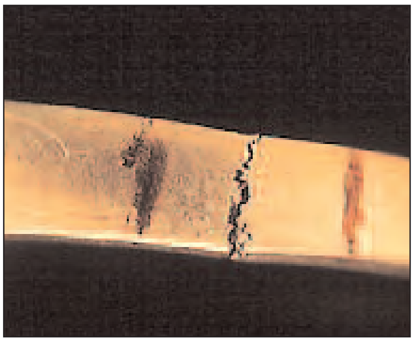


Fig. 19.1 A broken shank of an 18ct yellow gold ring

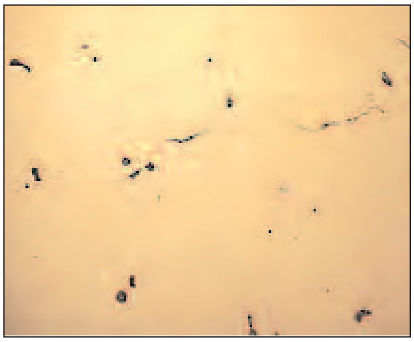


Fig. 19.2

Fig. 19.3

Influence on Properties

Mechanical Properties

The strength of the material is almost zero; the rings can be broken by hand with little effort..

Microstructure

The microsection reveals some interesting details. Numerous cracks and many gas pores are visible at low magnification. The 'cracks' are, in part, gaps on grain boundaries, fig.19.2. This becomes more clear at higher magnification in the SEM-micrograph, fig. 19.3. Another important detail is a small sulphide particle (analysed by EDX-microanalysis) in a 'boundary gap' (marked by a cross in fig. 19.3). A detailed search detected more tiny segregations of a grey compound, identified as sulphides, on grain boundaries.

Brief Explanation

The main cause of the defect was the formation of gas pores and sulphides at grain boundaries due to reaction of molten alloy with the investment. Probably, remelting of already contaminated, sulphide-containing scrap material played an active part in this case. The strong reducing atmosphere (protective gas with high hydrogen content) aided the reaction of melt with the investment to produce sulphides.

Extended Explanation

Gypsum (calcium sulphate), an important constituent of investment, can react with the melt to form both sulphur dioxide and sulphides of copper and silver. The sulphur dioxide dissolves and manifests itself as characteristic spherical *pores in the solidified metal. The sulphides constitute low melting components and collect on grain boundaries (together with gas pores). The alloy loses its strength completely and falls apart when only a very small load is applied. Remelting of material already poisoned with sulphides or with adhering investment will amplify the detrimental effect of investment reaction and should be avoided.*

Recommendation for Avoidance

For melting and casting in a closed system, the rule is: a) Never melt and cast gold alloys in a strongly reducing atmosphere like forming gas. Strong reaction between the melt and the gypsum-bonded investment will occur. Neutral gas like nitrogen or (more expensive) argon is recommended. A strong reducing atmosphere will do more harm than good. [Note: Forming gas can be used if the material is melted and cast in an open system (in air) for protecting the crucible and the melt from oxidation.]. b) Remelting of sulphur-contaminated material as well as scrap alloy with adhering remnants of old investment must be avoided.

Further Reading

Part C: Basic Aspects, section 3.2, Gas porosity and section 3.5, Behaviour of gypsum-bonded investment during casting.

3.2 INCLUSIONS

CASE 20: HARD SPOTS - CAUSED BY INCLUSIONS OF 'GRAIN REFINERS' AND GOLD IMPURITIES.

Key Words

Hard spots; inclusions; iridium; impurities;

Description of the Defect

Hard spots on the surface were detected whilst polishing the item. Visual inspection disclosed hard, brownish particles.

Visual Appearance

Figures 20.1–20.3 show typical inclusions in different alloys that resulted in hard spots. They can appear as single particles of significant size or as an agglomeration (nest) of smaller particles. Fig 20.2 is a surface of a rolled sheet, etched with a cyanide-containing solution.

Alloy: Any alloy with iridium (or other platinum group metal) used as a grain refiner, independent of caratage, or alloys made from impure fine gold.

Description of Manufacturing Method: The examples were found in both investment castings and in rolled material. The defect is independent of the manufacturing method.

Influence on Properties

Microstructure

The solubility of iridium in gold alloys is very low, even in the liquid state. The addition is not homogeneously distributed. Nest of hard iridium particles are formed, fig 20.4. They cause hard spots when they reach the surface or they produce cracks on deformation due stress concentration.

Workability and mechanical properties

An excess of grain refiner and, therefore, the formation of nests of particles decreases the workability of the alloy. The maximum degree of deformation is reduced to about 60-65% (depending on alloy and amount of addition), whereas an addition-free alloy can be worked to 70% or more reduction.

Wire drawing will be seriously affected by both single particles and nests of inclusions. Even very small particles will cause breaks on drawing a small diameter wire.

Polishing

A flawless surface cannot be achieved by polishing. In most cases, improper (excessive) use of grain refiners or the presence of similar kinds of impurities will be noticed by difficulties at polishing. Hard spots with a characteristic 'comet tail' appearance occur.

Brief Explanation

High melting point metals, such as some platinum group metals, with only a limited solubility in the solid gold alloy are sometimes used in very small amounts as grain refiners. Such small, finely dispersed particles act as nuclei in the liquid metal during solidification, hence producing a fine grained structure which has superior mechanical properties, useful, for example, for polishing or deep drawing. Other additions such as cobalt act to refine the grain size during annealing of cold worked material.

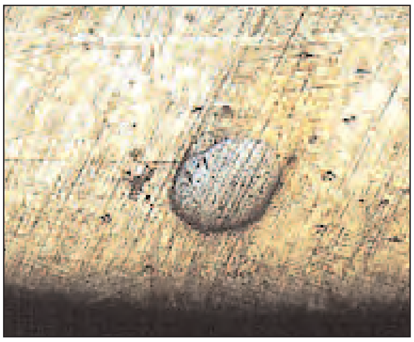


Fig. 20.1 14ct yellow gold with iridium as grain refiner.

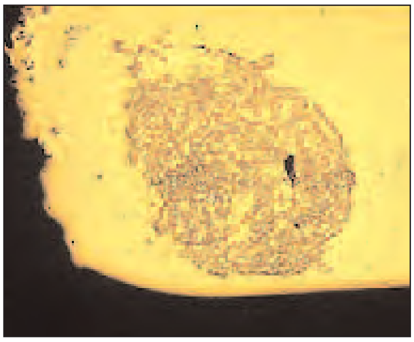


Fig 20.2 22ct yellow gold with 2% iridium 50 x

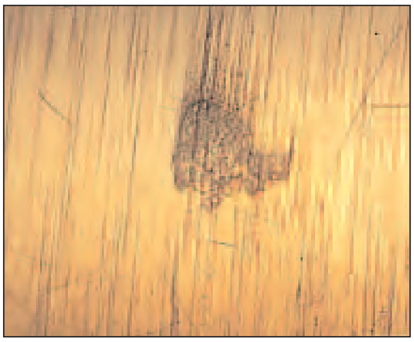


Fig. 20.3 14ct yellow gold made from contaminated gold

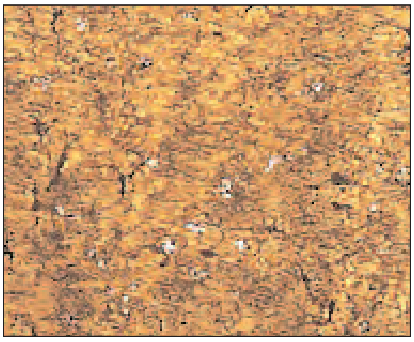


Fig. 20.4 Nests of iridium inclusions in a 21ct alloy

However, the addition of an improper compound or too high a concentration results in clusters of hard particles. Instead of improving the polishing procedure, a detrimental effect is caused.

Critical additions are iridium, ruthenium and - with a higher concentration - cobalt.

Sometimes, the same detrimental effect can occur when carat golds are made from fine gold ‘good delivery’ bars of 99.5% fineness. Some bars may contain small amounts of metallic compounds of, typically, iridium, ruthenium, tungsten and molybdenum. Such deleterious impurities can only be removed by electrolytic refining to 99.99% purity.

Heavy insoluble metals such as iridium tend to sink in the molten gold alloy under slow cooling conditions and agglomerate at the lower surface of the ingot, hence accentuating the hardspot problem at the surface of the finished jewellery.

RECOMMENDATION FOR AVOIDANCE

In the first instance, the effectiveness of a particular grain refiner in a particular alloy under your production conditions has to be determined. It makes little sense to add a grain refining element at will to any alloy just because it is known to have a grain refining in other gold alloys.
If any such grain refiners are used, the concentration has to be limited to about 0.01%. Melting needs some additional superheat and melting time should extended in comparison with addition-free alloys. The grain refiner has to be added as a master alloy, usually with copper.

As a general rule, if these conditions cannot be fulfilled with certainty, it is better to avoid the use of a grain refiner. The ensuing difficulties will outweigh the advantage of a grain refined alloy.

Extended Explanation

A grain refining effect in casting needs the segregation of extremely fine particles at the beginning of solidification which act as nuclei for the formation (and subsequent growth) of crystallites. An abundance of nuclei means a great number of growing crystallites and, consequently, a finer (smaller) grained structure.

The conditions for such a nucleation process are: a) The grain refiner should only have a very limited solubility in the solid alloy, but some solubility in the liquid melt, b) The grain refiner (or a compound formed from it) should have a relatively high solidus temperature and solidify before the main gold alloy.

The condition for a successful application of such a grain refiner is a complete dissolution in the melt prior to casting. The melting temperature has to be high enough and some time given for dissolution of the grain refiner. The most common additions used as ‘grain refiners’ in jewellery alloys are ruthenium and iridium. Both additions are difficult to use and should only be done using suitable master alloys. The grain refining effect of iridium can be variable.

In most defect cases involving hard spots, the ‘grain refiner’ was present in clusters of particles and very inhomogeneously distributed. In this state, no significant grain refining effect can be expected, but difficulties with hard spots on polishing will occur.

Further Reading

Part C: Basic Aspects, section 2.5, Grain refiners.

4 CORROSION, TARNISHING, DISCOLOURATION

4.1 DISCOLOURATION

CASE 21: TARNISHING - CAUSED BY THE LINING MATERIAL OF A STORAGE BOX.

Fig. 21.1

Key Words

Tarnishing; sulphide.

Description of Defect

Jewellery items stored in boxes showed discolouration. The tarnishing ranges from reddish brown to black. The intensity of discolouration is obviously influenced by the intensity of the contact which the jewellery had with the lining material of the box

Visual Appearance

A 10ct yellow gold ring tarnished while stored in a box containing sulphidic compounds. The colour varies between somewhat reddish to black, due to formation of silver or copper sulphide.

Alloy: 10 ct yellow gold

Description of Manufacturing Method: Tarnishing is independent of the manufacturing method with the exception of surface treatment by electroplating with high carat gold.

Influence on Properties

Only the brightness and the colour of the jewellery surface is affected.

Brief Explanation

Silver and copper react very easily with many sulphur compounds, with formation of sulphides. Very thin layers of sulphides can show a range of colour between yellow to reddish or brown and finally black when the layer reaches sufficient thickness.

Pure gold and high carat alloys (e.g. 18ct and higher) don't react with sulphur compounds and are, therefore, tarnish resistant. Usually, 14ct alloys also resist tarnishing unless subjected to a heavy attack of hydrogen sulphide.

Low carat alloys (10ct and lower) show similar behaviour to silver or copper and tarnishing is a naturally occurring phenomenon. Not only sulphur compounds can cause tarnishing; other compounds discolour the surface by oxidation.

Recommendation for Avoidance

The best way to avoid tarnishing is through use of higher carat gold alloys. Otherwise, a practical way to prevent low carat gold from tarnishing is by electroplating the pieces with fine gold or high carat gold with a sufficient thickness. This is not a permanent solution, however, as the electroplated layer will be eventually worn away. On storage, tarnishing can be prevented by keeping the jewellery pieces in a dry environment and avoiding contact with sulphur-containing boxes.

Fig. 22.1 A gold chain with discolouration.

Fig. 22.2 This example shows the stained surface in more detail

Fig. 22.3

Fig. 22.4

CASE 22: DISCOLOURATION OF YELLOW GOLD RING - BY ACCIDENTAL AMALGAMATION WITH MERCURY.

Key Words

Discolouration; amalgamation; mercury.

Description of the Defect

The surface of a yellow gold jewellery item is discoloured. The colour varies between brownish and dirty white or grey.

A customer complained about the defect after wearing the jewellery for some time. No details have been provided about the circumstances. Investigation, using SEM-EDX analysis, showed that mercury was present and the cause for the discolouration.

Visual Appearance

The surface should be yellow, but it’s colour has changed to a dirty white and brownish hue.

Alloys: All gold jewellery alloys will be sensitive to this defect.

Manufacturing Method: Manufacturing method is not important. The defect is typically produced by the customer.

Influence on Properties

Mechanical Properties

Strength is often degraded. Sometimes, mercury can initiate a stress corrosion fracture.

Microstructure

The dark spotted edge in the micro-section, fig 22.3, indicates that mercury has penetrated into the gold alloy and covers almost the entire cross-section. Sometimes, preferential segregation of the mercury amalgam on grain boundaries can be detected, too.

Others: Colour

The main cause for rejection by the customer was discolouration. There is a broad range of colours. The colour may vary between silver white/grey and brownish.

Brief Explanation

The discolouration is caused by uptake of mercury which is liquid and readily forms an alloy with gold (gold amalgam) even at room temperature. At a low gold concentration, the amalgam is liquid at room temperature. At higher gold concentrations, it is solid. When gold or gold alloys come into contact with mercury, a thin layer of amalgam is formed on the surface causing a silver white or grey appearance. Thus, yellow gold turns into a dirty ‘white gold’. Where only a small amount of mercury is available, only a slight, somewhat brownish discolouration takes place.

Mercury can penetrate into the material preferentially along grain boundaries, decreasing its strength significantly.

The growth of amalgam crystallites on the surface of gold can be easily observed in the scanning electron microscope (SEM), fig. 22.4

The SEM photograph shows amalgam crystallites grown on the surface of 18ct yellow gold jewellery. How the jewellery came into contact with mercury is not known; a broken thermometer is often the source.

Recommendation for Avoidance

This defect is not a problem of the manufacturer. It can only occur when the jewellery comes into contact with mercury, normally an accident by the customer. The source for mercury might be a broken thermometer or mercury used in dentistry (dental amalgams).

Recovery of an amalgam-covered piece of jewellery is sometimes possible by gently heating it up, preferentially under a vacuum, until the mercury is evaporated off [safety note: ventilate well and extract fumes via a fume hood; mercury vapour is very poisonous]. However, in the case of jewellery alloys, a dull or even brownish surface can remain which has to be polished off.

In the present case, with a deep penetration of mercury into the material, successful recovery is unlikely. The item should be sent for refining.

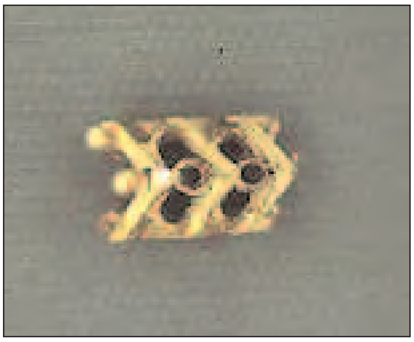


Fig. 23.1 Fractured 14ct gold ring

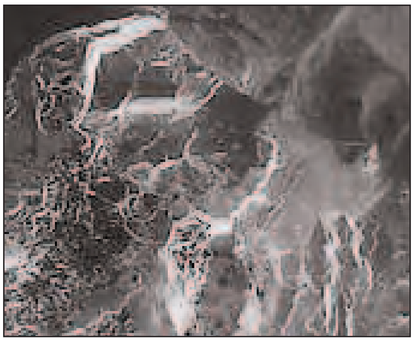


Fig. 23.2

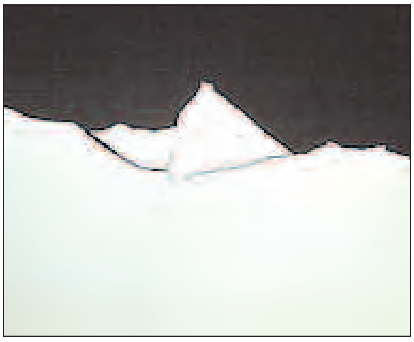


Fig. 23.3

4.2 STRESS CORROSION AND INTERGRANULAR CORROSION

CASE 23: CRACKS - CAUSED BY INTERGRANULAR CORROSION IN A SILICON-CONTAINING 14CT ALLOY.

Key Words

Investment casting; cracks; low melting components; silicon, intergranular corrosion.

Description of the Defect

A 14ct cast ring is broken in the stone setting area. The fracture is brittle. The defect was reported by a customer after approximately 7 month service.

Visual Appearance

One of the prongs is broken without any deformation (brittle fracture). The fracture is situated at a place where two relevant factors occur together, i.e. stress is applied and cleaning is difficult.

At higher magnification, fig 23.2, the fracture surface is intergranular, i.e. shows a grainy structure, indicating that fracture took place along grain boundaries. On the left edge of the figure, a dark coating is visible which consists of silicon and some remnants of a medium (chloride, potassium, calcium) which is presumed to have had a corrosive effect.

Alloys: 14ct yellow gold with additions of silicon, boron and iridium. The defect might also occur on alloys with even higher gold content if the quantity of silicon addition lies in a critical range or other low melting components are present. All low carat golds with such additions are susceptible.

Manufacturing Method: Investment casting with vacuum assisted static machine. However, the defect is presumed to be independent of manufacturing method.

Influence on Properties

Mechanical Properties

The material has lost its strength. Low stress applied to areas, e.g. by stone setting, causes cracks and fracture. The defect needs time to develop and the influence of a corrosive medium.

Microstructure

A cross-section through the fractured prong clearly discloses the nature of the fracture, fig 23.3. The alloy has cleaved along grain boundaries and the material has fallen apart without any deformation.

This appearance is typical for two special kinds of corrosion: stress corrosion and intergranular corrosion.

Brief Explanation

The influence of low melting components (silicon phase) and of intergranular corrosion lead to embrittlement. The fracture has occurred at a place where cleaning is difficult and impurities will tend to collect. Usually, 14ct yellow gold is fairly resistant to corrosion from sweat, cleaning agents, soap, salt water, etc. However, if additions cause segregations of less noble compounds on grain boundaries, even relatively weakly corrosive agents can attack these compounds preferentially. For disintegration of the complete item, only the dissolution of this thin grain boundary layer is necessary. Any applied stress accelerates the process.

In the present case, corrosion took place at a location where a corrosive medium could remain for a longer time and where the material (prongs) is stressed.

Recommendation for Avoidance

The only safe way to avoid this defect is to change the alloy composition to prevent segregation of undesirable compounds to the grain boundaries. (A thick layer of electroplated high carat gold will also help, at least for a limited time).

Extended Explanation

Stress corrosion and/or intergranular corrosion, leading to cracking along grain boundaries, is one of the most common reasons for complaints with low carat gold alloys (10ct and below). In gold alloys, the two mechanisms cannot be separated unambiguously.

The principal mechanism can be explained as follows:

Grain boundary segregations have a different electrochemical behaviour (in relation to the more noble gold-rich grain itself) and this forms the basis for a voltaic (or galvanic) cell, where the presence of a corrosive medium (e.g. sweat, sea water, cleaning fluids, etc) results in an electrochemical/galvanic corrosion process. In the very small anodic area on grain boundaries, the less noble material is preferentially dissolved. The corrosion current is concentrated on this small area, and therefore the dissolution of this region is very fast.

Stress (tensile stress) can increase the corrosion rate to a significant extent. The initial progress of intergranular corrosion forms notches which expose new areas to corrosion, further extending the depth of notches and increasing the concentration of stresses on the base of the notches and so it continues. (This explanation of stress corrosion is somewhat simplified and cannot be applied unmodified to other metal alloys.)

This kind of corrosion can be expected particularly in low carat alloys. It is much less frequent in 14ct alloy. Known exceptions are the long term attack by hydrochloric acid (used for removing an aluminium core from a hollow jewellery item) or a corrosive attack on an alloy with less noble precipitation on grain boundaries. Differentiating between intergranular corrosion and stress corrosion in gold jewellery alloys is very difficult. The mechanisms are not yet completely evaluated for this type of alloy.

5 SOLDERING

5.1 FRACTURE

CASE 24: FRACTURE - DUE TO MELTING OF LOW MELTING COMPONENTS DURING SOLDERING.

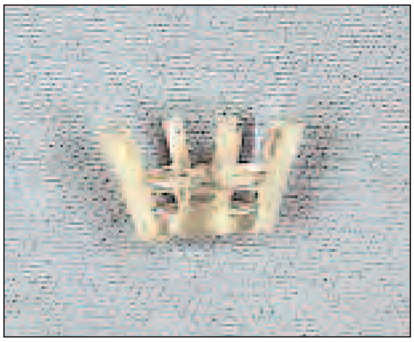


Fig. 24.1 Broken prong on a white gold finding

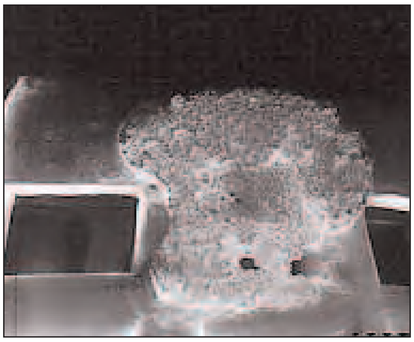


Fig. 24.2 SEM image of the fracture surface

Key Words

Soldering; brazing; fracture, white gold, low melting components.

Description of Defect

A prong has broken on a white gold finding. The fracture is located at the junction of prong and bridge. Obviously, some soldering has been done on the item.

Visual Appearance

The prong was broken without deformation. The fracture looks dendritic. Remnants of solder are visible

At low magnification, the structure resembles a honeycomb, fig 24.2. This image is not so easy to interpret; sometimes, severe gas porosity can cause a 'fracture' with a similar appearance.

Alloys: 14ct white gold, based on gold-copper-nickel-zinc with additions of silicon and boron. The solidus temperature is very low; melting range is 845° - 885°C (1550°F - 1625°F).

In principle, the defect can occur in any alloy containing low melting components (e.g. silicon)

Manufacturing Method: The finding was produced by vacuum assisted, static investment casting under normal conditions. The setting had been soldered to a shank.

Influence on Properties

Mechanical Properties

At the place where the fracture occurred, almost no physical connection between the two soldered parts existed. Applying a very low stress has lead to the fracture.

Microstructure

The investigation of the fracture surface in the scanning electron microscope (SEM) reveals a dendritic structure; the dendrites have smooth edges, suggesting that they have been molten.

The constituents of the solder used - cadmium, gold, silver and copper - were found on the fracture surface.

Brief Explanation

The soldering temperature was too high and, probably in this case, an additional problem is the presence of low melting components in the alloy (mainly due to the silicon content). The low melting silicon phase melted and became liquid in the space between the dendrites of the cast structure, inhibiting the flow of solder into the gap which was only partly filled with a small quantity of solder, insufficient to produce a solid bond.

Sometimes, the appearance (morphology) of this defect is very similar to fracture arising from stress corrosion or intergranular corrosion. A distinction between these types of defects is difficult and can only be done with certainty if related information is provided about the history of the defective item.

Recommendation for Avoidance

The soldering temperature has to be decreased by applying less heat and/or use of a lower melting solder, where possible. If this is not possible, then another alloy composition should be used which is free of (or has reduced amounts of) low melting components.

Further Reading

Basic Aspects, section 2.4, Influence of low melting components.

6 HEAT TREATMENT

6.1 AGE HARDENING

CASE 25: CHANGE IN SIZE OF A RING AND FRACTURING - DUE TO UNWANTED AGE HARDENING.

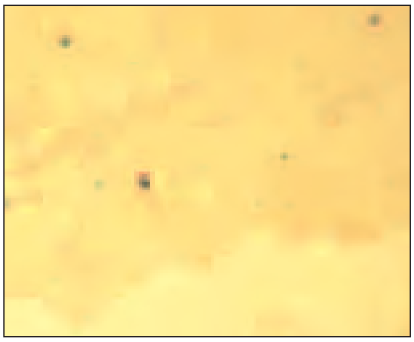


Fig. 25.1

Key Words

Cracks, fracture, age hardening.

DESCRIPTION OF THE DEFECT

The ring grew in size during soldering and finally cracked with a brittle fracture. The same effect happened while annealing the same material at 360°C. (The material had been pre-treated by soft annealing at about 700°C.)

Alloy: 18ct pink gold (gold-copper-silver)

Manufacturing Method: Investment casting, soft annealed at 700°C, soldered, and age hardened at about 360°C.

Influence on Properties

Mechanical Properties

The alloy is embrittled and has very low ductility.

Microstructure

The grains are very large, fig 25.1. A single grain covers almost the whole cross-section of the ring shank. The grains show an internal structure of series of parallel ribbons, a microstructure that is characteristic of age hardened material.

Brief Explanation

Copper-containing gold alloys of 18 carat or lower have a very special property. Soft annealed material (that is, material which has been annealed at about 700°C), if slow cooled, changes its microstructure by an ‘ordering’ effect in which the gold and copper atoms are no longer distributed randomly in the crystal (grain) lattice but are arranged in a well defined order. The beneficial effect of this behaviour is substantially increased hardness and improved wear resistance. The disadvantage is reduced ductility leading to brittleness and a physical change in size during the hardening process. The end result can be a change in size of the jewellery item, important if it is a ring, for example, or even cracks and fracture as can be seen from the present example.

This phenomenon can be controlled and used beneficially in jewellery production by rapid cooling (water quenching) the alloy from the soft annealing temperature (this retains the soft condition and the ductility) and, as a final pre-polishing process, ‘ageing’ the alloy at a low temperature, typically 260-360°C for 1 hour.

Both binary gold-copper alloys and gold-copper-silver alloys are sensitive to the age hardening phenomenon. The extent of age hardening depends strongly on the copper/silver ratio and the caratage. Pink and red gold alloys with high copper contents are especially sensitive. Note: High carat golds (21/22 carats and higher) are not affected by this phenomenon.

Fig. 25.2 6 x

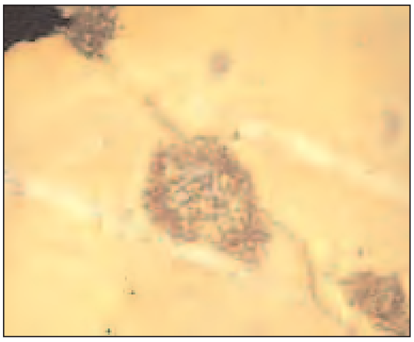


Fig. 25.3 1000 x

Recommendation for Avoidance

Age hardening can be avoided by water quenching the material as fast as possible from a temperature higher than 500°C, preferably 600-700°C. There are potentially some difficulties if subsequently soldering the material, causing parts to be heated up in the range 300-400°C, since ageing will occur at these temperatures. A safe solution to this problem doesn't exist. The best way would be to cool down the alloy from a temperature above 500°C to room temperature as slowly as possible (in a furnace) to enable the ordering process to occur, then carrying out soldering which should avoid formation of any cracks. To soften (ductilise) the material again (if desired) soft annealing at about 600°C should follow - *but* only if the melting range of the solder lays well above this temperature!

Extended Explanation and Further Reading

More detailed information is provided in Part C: Basic Aspects of Metallurgy, section 2, Age hardening. It is strongly recommended to read this chapter if difficulties with red or pink gold occur. See also the 'Technical Manual for Gold Jewellery', chapter 6, published by World Gold Council.

Another example

The edge of a stone setting on class ring is cracked and a piece has broken off, fig 25.2. The ring was only worn for a short time. The bezel of the ring was soldered on the shank. The yellow gold alloy contains silicon.

Very small segregations are visible on grain boundaries, fig 25.3. The investigation revealed two relevant facts, both contributing to the failure: a) The ring is age hardened with a hardness of HV 275, a high value for a yellow gold alloy; embrittlement is the natural consequence. The age hardening occurred during soldering. b) The material shows segregation on grain boundaries which are very small, but they can cause embrittlement.

6.2 BLISTERING

CASE 26: BLISTERING AND POROSITY - DUE TO HEAT TREATMENT IN A HYDROGEN-CONTAINING ATMOSPHERE.

Key Words

Blistering; gas porosity; intergranular cracking; hydrogen embrittlement; surface exfoliation.

Description of the defect

Annealed thick sheet and watch case pressings showed surface exfoliation of grains. In some instances, the (originally bright) surface had a 'milky' appearance. Close inspection under a low power microscope showed surface blisters.

Visual appearance of the defect

Figures 26.1 and 26.2 show protrusion and exfoliation of whole grains from the polished surface of 18ct yellow gold (3N) strip after annealing in a cracked ammonia atmosphere at 780°C. In other cases, the surface has a 'milky' appearance which, on inspection under a microscope, is revealed to be a blistered surface.

Alloys: The defects have been observed in several conventional gold jewellery alloys: 14ct yellow gold, 18ct yellow gold (Au-Ag-Cu, 3N and 2N) and 21ct alloy.

Manufacturing method: Continuously cast and rolled strip which was interstage annealed in a hydrogen-containing atmosphere, cracked ammonia, at a relatively high temperature of 650°C for 30 mins. Subsequently blanked and stamped with a final anneal at 780°C in cracked ammonia. Alloys were made from 4-9's purity gold, electrolytic silver and high purity, electrolytic copper.

Similar defect observed after soldering (brazing) of carat gold in a hydrogen-containing atmosphere.

Influence on Properties

Mechanical properties

Mechanical properties usually are not significantly influenced by this type of defect.

Surface quality

As already described, the surface structure is degraded by blistering and exfoliation of grains. Polishing does not normally succeed in removing the defect because new blisters and pores are continually revealed.

Microstructure

In these cross-sections of an 18ct (3N) yellow gold, figs 26.3 and 26.4, the incidence of widespread porosity and intergranular cracks throughout the section thickness is evident. The porosity is spherical and appears predominantly at grain boundaries and is similar to gas porosity seen in castings. The alloy is known to have had high oxygen contents, up to 40-50 ppm.

Spherical gas pores in brazed joints of a pen made of a high carat alloy, fig 26.5, are also found in the wrought material which was not molten

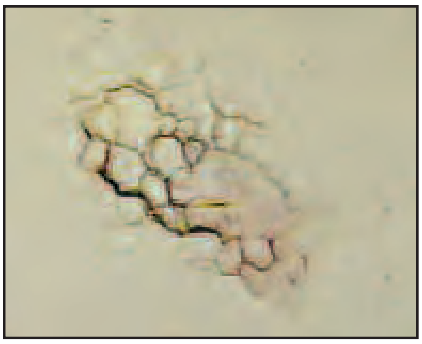


Fig 26.1 Polished and annealed surface, 18ct yellow gold 200 x

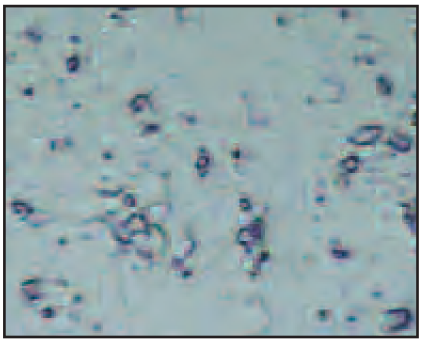


Fig 26.2 Polished and annealed surface, 18ct yellow gold 200 x

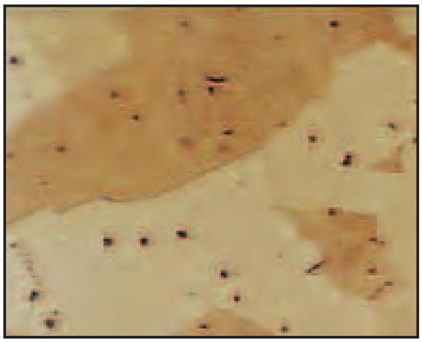


Fig 26.3 Watchcase, cold pressed and annealed (650°C, 30 mins) 200 x

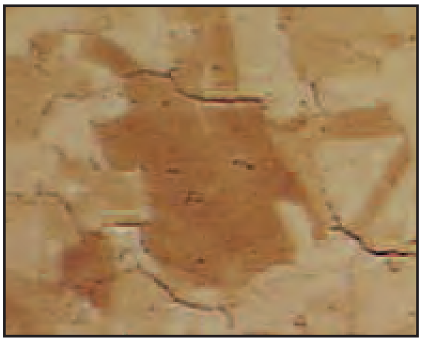


Fig 26.4 Watchcase, cold pressed and annealed (650°C, 30 mins) 100 x

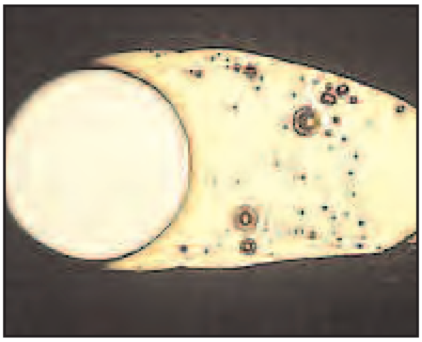


Fig. 26.5 Brazed joint of a pen made in a high carat gold

during brazing. Obviously, the pores were formed after rolling the material since any sphericals void would be flattened by rolling. The only possibility for the generation of gases is during brazing (soldering) or during the heat treatment connected with brazing.

Brief Explanation

Blistering and porosity are characteristic of gas formation and similar effects are common in copper and silver alloys. Coupled with particularly high annealing temperatures in hydrogen-containing atmospheres, the evidence is strongly suggestive of the ‘steam reaction’ whereby hydrogen diffuses into the alloy during annealing, preferentially along the grain boundaries, and reacts with oxide or dissolved oxygen to form steam (water). As the water molecule is relatively large, it cannot diffuse out and so remains and creates an internal gas pressure within the alloy, causing porosity within the bulk and blisters at the surface, as well as grain boundary cracking. At the surface, this grain boundary cracking results in exfoliation of whole grains.

The less pure grades of copper often contain residual copper oxide and is the reason why they should not be used in carat gold manufacture. However, in this case, high purity electrolytic copper was used, implying that oxide was unlikely, although relatively high dissolved oxygen levels were found. It may be that this oxygen is present in the form of very small copper oxide particles, which would tend to be found at grain boundaries, and arise during continuous casting.

Thus two factors are responsible for the occurrence of these defects: a) annealing in hydrogen-containing atmospheres at high temperatures and b) high oxygen levels (possibly as fine oxide particles) in the wrought alloy. These combine to allow the steam reaction to occur. Investigations where carat golds with low (<10ppm) oxygen contents were processed by the same route, including the same annealing schedules, did not result in the formation of defects.

In the case of the brazed joints, examination of microsections at high magnification revealed a great number of very fine particles, probably copper oxide. This is consistent with analysis which measured 20-40 ppm oxygen (by weight).

Recommendation for Avoidance

If the oxygen content is low or there is no hydrogen, then clearly, no steam reaction can occur. If the annealing temperature is reduced, then the diffusion of hydrogen into the alloy is markedly lowered.

Thus, there are three factors which, individually, should lead to avoidance of this defect. The first - and preferred - is the use of a low oxygen (oxide free) copper and silver for alloying (and clean, oxide-free scrap, if recycling) and to ensure that the conditions for producing the cast gold alloy result in a low oxygen content (preferably <10ppm). The second is to avoid use of hydrogen-containing reducing atmospheres where possible (use neutral atmospheres such as nitrogen or argon). If this is not possible, then the third factor is to perform annealing at lower temperatures for longer times. For 18ct (2N, 3N) alloys, the recommended annealing temperature is 550°C, 30 mins. Lower annealing temperatures also reduce the risk of excessive grain growth which can manifest itself as 'orange peel' surfaces in subsequent forming and bending.

Extended Explanation

Diffusion of gases in solid metals is well known. Importantly, the rate of diffusion is very strongly temperature dependent. Among the precious metals, the diffusion of oxygen and hydrogen in silver or of hydrogen in platinum and palladium are well documented. Blistered silver sheet is the result of the 'steam' reaction of dissolved oxygen (or oxide) with hydrogen during annealing. Similar behaviour in gold alloys has not been previously described in the literature. However, several cases have been reported recently.

It seems that very small oxide particles, hardly detectable by examination of microsections are especially critical for causing blistering. These micro particles may be formed in continuous casting.

Another critical process is soldering (brazing) in a furnace in hydrogen-rich atmosphere (which of course is favourable for the soldering procedure) where, again, the temperature is relatively high and the diffusion rate of hydrogen strongly increased.

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PART C:

BASIC ASPECTS OF THE METALLURGY OF CARAT GOLDS AND THE INVESTMENT CASTING PROCESS

The following sections are intended to provide some additional, general information on the metallurgy of carat golds and the investment casting process as an aid to understanding the defect case histories described in Part B. The intention is not to provide a substitute text book, but merely to underpin the explanations given in Part B with some basic technology involved as a guide for those with little formal technical training in metallurgy or chemistry.

1 GENERAL PROPERTIES OF METALS

1.1 PHYSICAL PROPERTIES

Metals are crystalline substances with some extraordinary properties. The crystals (or grains) are formed by atoms lying in a regular array (crystal lattice) which share a common ‘cloud’ of negative electrons. This atomic construction is responsible for:

- optical reflectivity
- high electrical and thermal conductivity
- the unique working properties, ductility and work hardening

1.2 STRUCTURE

The structure of a metal crystal is, as in the case of any other crystalline substance, determined by the shape of the unit cell. This is the smallest, basic unit of a crystal, which when extended by the addition of many other unit cells, builds up to produce the overall crystal.

The unit cells contain only a small number of atoms in a relatively simple arrangement. The most common structures for metals are the ‘face-centred cubic’ (FCC) and ‘body centred cubic’ (BCC). These are cubes with atoms on each cube corners and in the centre of the face planes (FCC) or in the centre of the cube (BCC). Another common structure is the hexagonal prism. Other less frequently occurring types of structure can also exist with metals, but are not usually of concern with gold alloys.

Any crystalline body tends to form a regular and typical macroscopic ‘crystal’ shape, well known from minerals and gemstones. Metals are a little bit different. On solidification (see section 2.1), a number of crystals start to grow in the melt. These embryonic crystals are called ‘crystallites‘. The growing crystals (or ‘grains’) grow into and obstruct one another from building up the regular external shape of crystals whereas the regular inner atomic lattice structure is maintained. The result is a fine (small) grained polycrystalline metal whose structure is only revealed by examination of a polished microsection under a microscope.

The average size of the grains in a metal sample is called the ‘grain size’ and is normally expressed in mm (or inch) or simply by a number (the ASTM number). It is important as it influences the properties.

2 METALLURGICAL EFFECTS

2.1 MELTING AND SOLIDIFICATION

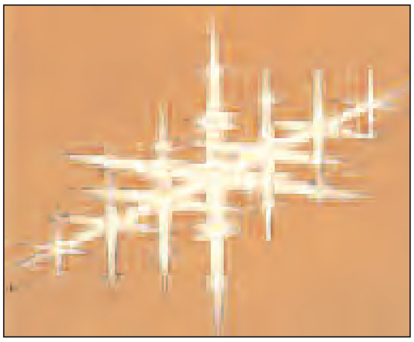

Figure 1. Schematic representation of a dendrite

Melting of a solid piece of metal is a procedure which is not difficult to understand. Increasing the temperature of a piece of solid matter causes an increasing vibration of the atoms. At a characteristic temperature, the vibrations are intense enough to overcome the atomic forces that hold them in a regular crystalline array. The atoms start to move relatively independently of each other, i.e. the material starts melting to become a liquid.

At this point, additional energy (heat) is needed to break the inter-atomic binding forces. The temperature of the material remains constant whilst the heating continues until all the solid has melted. An example is melting ice. The temperature of a water-ice mixture remains constant at 0°C as long as unmelted ice and water are present. The same behaviour is shown by pure metals. For example, pure gold melts at a constant 1063°C.

The melting behaviour of alloys [an alloy is a mixture of two or more pure metals] is a little more complicated. In general, all alloys melt within a melting *range* (with some specific exceptions). A more detailed explanation is possible using phase diagrams but is beyond the scope of this Handbook.

Solidification is the opposite of melting but more complex and is of greater practical importance. The basis for the properties of a piece of metal is laid at solidification.

The almost independent atoms of the liquid melt are not able to instantly rearrange themselves into solid crystals. The growth of new crystallites (the growing grains) starts from nuclei ('seeds'). These nuclei may be very small clusters of metal atoms or particles of impurities (e.g. oxides or other insoluble metals such as grain refiners). The nuclei may be initiated at preferred sites such as the roughness of the crucible or mould wall.

The crystallites do not tend to grow uniformly in all three directions of space until they meet adjacent growing grains, which would result in a polyhedral array of equi-sized grains. In most cases, directional growth of the crystallites along preferred crystallographic directions occurs. Primarily, needle-shaped crystals are formed, which branch again and again to produce the typical dendrite (see diagram, Fig. 1), a structure which we find in jewellery alloys. The orientation of the various dendrites in the melt vary, and they grow until they impinge on each other.

In actual alloys, the composition of the crystallites changes during solidification. The centre of the dendrites which is formed at the beginning of solidification has a certain composition (defined on the alloy phase diagram) and this gradually changes as solidification proceeds to completion. This is known as 'coring'. The average composition of the dendrite is as one would anticipate from the overall alloy composition. If solidification occurred very slowly, the different metal atoms would migrate and tend to equalise differences in concentration from dendrite centre to outside, a process which is called *diffusion*. Usually, solidification and subsequent cooling occurs too fast to allow adequate diffusion to equalise any differences in local dendrite composition.

Any type of crystal with defined composition range and atomic structure is considered as a phase. A metal or alloy which is built of only one kind of crystal is said to be single *phased*. An alloy can be single phase but may also consist of two or more phases:

a) Two or more metals may form a homogeneous solid solution: only one phase is formed which contains all atoms of the different constituents. (A similar example is the dissolution of salt in water. Salt water is only one phase which contains all constituents.). This means that if the metals are completely soluble in one another, the alloy is homogeneous and single phase.

b) Two and more metals may also form different phases e.g. phase α and phase ß which contain either (almost) pure metal ***A*** or metal ***B*** or both metals in different relations e.g. phase α: (high ***A*** + low ***B***), phase ß: (high ***B*** + low ***A***). In this case, both metals have no or only restricted solubility in one another. An alloy comprising a mixture of phase α and phase ß is two phased or heterogeneous. Depending on composition and temperature, some alloys can change from one crystal phase to another.

In summary: The number and kinds of phases existing in a given alloying system depend on composition, temperature and pressure (for practical purposes, the influence of pressure can be neglected).

There are some special kinds of heterogeneous alloys. Only one will be mentioned here. A 'eutectic' is a special defined composition in some alloy systems where melting or solidification occurs at a specific defined temperature rather than over a melting range. This eutectic temperature is normally much lower than either melting point of the constituent pure metals. A eutectic microstructure consists of a very fine grained mixture of at least two phases with no dendrite grains. A eutectic is formed in a number of alloy systems including silver-copper and gold-silver-copper jewellery alloys.

A particular case of a phase in an alloy system is the formation of an intermetallic compound, which resembles a real chemical compound formed between two elements with different characteristics. The atomic ratio of the constituent metals is fixed within a certain narrow range. For practical purposes, most intermetallics are brittle. Thus formation of intermetallic phases in an alloy may result in some embrittlement, i.e. loss of ductility. Gold-copper alloys can form intermetallic phases, and these can cause hardening of the alloy.

A final remark is necessary: The principles of alloying is one of the most important subjects taught in metallurgy as it is basic to understanding the resulting alloy microstructures and hence properties. The basis for understanding phase relationships are phase diagrams. As mentioned earlier, it is not possible to treat this subject in sufficient depth here; an appropriate text book should be consulted.

2.2 DEFORMATION AND MECHANICAL PROPERTIES

A pure metal or an alloy usually shows two kinds of deformation behaviour when a load (stress) is applied:

When a low load or force is applied (e.g. to a wire), a reversible elongation is observed, i.e. after releasing the load from the metal, it's original length is restored. The metal has been stressed in the 'elastic' range and the amount of deformation - or strain - is proportional to the stress applied.

When the stress is further increased, a limit for such elastic deformation is reached. Beyond this limit, part of the resulting deformation remains after releasing the stress. The material is permanently deformed and the deformation is said to be 'plastic'. The applied stress at the onset of plastic deformation is called the *yield strength*.

When the stress is increased further, further plastic deformation occurs. However, a maximum stress will be reached; beyond this value, the stress needed to maintain continued deformation decreases until eventually the metal sample breaks (fractures). The total plastic deformation at the moment of fracture can be determined by joining the two parts of the broken metal sample and measuring the increase in length compared with the original length. The maximum stress is called the *tensile strength,* the plastic increase in length at fracture is the *ductility* (or *elongation* in the tensile test).

Yield strength, tensile strength and elongation (ductility) are basic values for characterisation of the mechanical properties of a metal or alloy. It should be noted that *stress* is defined as a load per unit area applied to the original cross-section and the elongation is the increase in length related to the original length (in per cent, %). In practice, it is not always convenient or possible to perform tensile tests on a metal or alloy. The use of hardness measurements can serve as a rough substitute.

The principal of the hardness test is simple: An indentor of a given shape and high hardness (often a diamond) is contacted on the surface of the material to be tested. A load is applied for a specified time and the depth of penetration of the indentor is measured and from this a hardness value calculated. There are a number of hardness test methods. The most common are the Vickers and Brinell tests. The Vickers test is, perhaps, the most commonly used for jewellery alloys.

Vickers hardness uses a diamond pyramid with a square base as the indentor. The load applied to the test sample is selected to suit the alloy and sample size. The diagonal of the resulting indentation is measured, and a mathematical formula relates the indentation surface area and applied load to give a value called the Vickers hardness, abbreviated to HV. An example for a standard yellow carat gold is: 180 HV10; this is a hardness value of 180 measured at an applied load of 10 Kg. Often, it is just quoted as HV 180.

Influence of deformation on properties

Deformation (performed at room temperature) increases the tensile strength and hardness. The material is said to be 'work hardened'.

The ductility - or elongation (as measured with the tensile test) - is consequently reduced. The workability is reduced; the material becomes less ductile and will break if the deformation continues beyond a certain level.

The amount of deformation (called ductility) a metal or alloy can sustain is very dependent on the composition (and microstructure) of the alloy. For example, nickel-white gold has only a very limited ductility, whereas palladium-white gold can bear much more deformation, i.e. it is more ductile. Pure gold can be deformed with almost no limitation (and is the most ductile metal of all).

Influence of deformation on microstructure

The grains become elongated and thinner when the material is rolled or forged or a wire is drawn to accommodate the overall shape change. With a high degree of deformation, the grain structure is severely disrupted and appears to disappear completely. The microsection shows a 'fibrous' structure.

The mechanism of deformation at the atomic level of a metal crystal or grain is not easy to explain. The crystal lattice of a real metal crystal contains a number of faults ('dislocations'). At the beginning of deformation, the faults move along certain crystal planes to enable the planes of atoms to slide past each other, and this gives rise to an elongation of the grains (and therefore an overall elongation of the sheet or wire, etc.). Unfortunately, many more crystal faults are formed with progressive deformation which collect and intersect with each other and form 'knots', which, in turn, hinder movement of the faults, requiring more stress to produce further deformation. Thus, the material gets harder and the ductility decreases until the point is reached when no more deformation is possible and increasing the applied force further will break the item.

2.3 ANNEALING AND HEAT TREATMENT

2.3.1 SOFT ANNEALING

In most cases, annealing is carried out on work-hardened (deformed) material to restore the original soft, ductile condition as the cold worked material cannot be safely deformed any more. This is done by applying a heat treatment called soft annealing which causes recrystallisation of the deformed microstructure.

Increasing the temperature enables the atoms (and faults) in the deformed crystal lattice to move. At first, the internal stress is removed by this movement. This stress relief makes the item a little less brittle (and, incidentally, prevents low carat gold alloys from suffering stress corrosion cracking). When the temperature is increased further, a new process starts, which is very similar to the formations of grains (crystallites) at solidification. New crystallites are nucleated and grow into the deformed material until all deformed material is consumed, resulting in a microstructure of new equi-axed (i.e. uniform shape), undeformed grains. The material has recrystallised.

The size of the resulting new recrystallised grains depends on several factors:

a) The number of grain nuclei - the higher the **degree of deformation**, the more nuclei are initiated. Therefore, only heavily worked material should be soft annealed if a fine grain size is required. Preferably, the degree of deformation should be between 50 and 70% with normal carat golds. A critical deformation of about 15% is needed to initiate recrystallisation and will result in a very coarse (large) grain size.

b) Recrystallisation needs a certain minimum **temperature** to commence. Below this level new grains are not formed. However, exceeding this critical temperature to a significant degree causes the grains to grow rapidly and any smaller grains are consumed by larger ones which grow even larger. The result is a very coarse grained structure, one consequence of which is a rough surface on subsequent deformation such as deep drawing or bending - the so-called 'orange peel' effect. Removing this by polishing is costly.

c) Recrystallisation needs a certain **time** to be completed.
The nucleation of new grains is very fast (in the range of minutes) but some time is necessary for these grains to grow and consume all deformed material. The influence of time on the growth of grains is much more moderate than that of temperature. Therefore, it is recommended to vary the time and keep the temperature constant and to a minimum to effect control of the resulting mechanical properties and grain size. However, if annealing by a gas torch, such control is not easily attained.
The grain size obtained on soft annealing depends strongly on the type of alloy as well as the amount of cold work. Pure metals (e.g. fine gold) tend to result in a larger grain size as growth of new grains is more rapid, whereas alloys shows a smaller but broader variation in grain size. For example, pink or red golds usually have a significant larger grain size than yellow golds. The grain size can also be influenced by very minor additions of 'grain refiners' such as ruthenium, iridium and cobalt. These enhance nucleation of new grains, refining the resulting microstructure, if applied under correct conditions (see also 'grain refiners'). Additions of other metals such as silicon, iron and chromium have a coarsening effect.

2.3.2 AGE HARDENING (HARDENING BY HEAT TREATMENT)

Certain carat gold alloys containing copper, in the range 9-18 carat, undergo a hardening when slow cooled or heat treated.
This phenomenon can cause difficulties in jewellery fabrication but can be utilised to deliberately harden these alloys and improve strength, scratch and wear resistance of the finished jewellery. There are two hardening mechanisms relevant to gold jewellery making: a) precipitation hardening and b) hardening by ordering.

Precipitation hardening can be explained in a simplified way by means of an example: The solubility of copper in silver is limited and depends on temperature. Decreasing the temperature decreases the solubility. If an alloy containing sufficient copper is slowly cooled down (say from 700°C to room temperature), the surplus of copper precipitates from the silver-rich matrix as a second phase - a copper-rich solid solution - due to the decreased solubility for copper. If the alloy is rapidly cooled by water quenching, such precipitation is suppressed and a supersaturated (solid) solution with copper results. Subsequently, heat treating at a temperature of about 200 to 400°C enables precipitation of the copper-rich second phase in a very fine dispersed form which significantly increases the hardness. (This explanation is simplified, the real mechanism is more complicated).

This hardening process is not only restricted to silver-copper alloys but is also of importance in yellow-pink gold alloys (consisting of gold-silver-copper), especially 14ct alloys, where the precipitation of a copper-rich phase influences not only the hardness but also the colour.

Hardening by ordering is a special mechanism occurring in gold-copper alloys and in yellow golds where the copper content is relatively high. In the gold-copper system, a homogeneous solid solution exists at all concentrations above approximately 410°C. The gold and copper atoms are randomly distributed in the alloy crystal lattice. However, below this temperature, several ordered structures of intermetallic compounds ($AuCu$, Au_3Cu and $AuCu_3$) will be formed. The copper and gold atoms occupy fixed positions in the crystal lattice and the alloy is harder and less ductile.

The ordering process can be suppressed by quenching the material from a temperature above 500°C and the alloy retains its ductility and low hardness. This state is preferred if the material is to be further deformed. Heat treating this soft quenched material directly or after further deformation in the range between 200 and 400°C will cause age hardening by the ordering process. The material becomes harder and less ductile. The magnitude of this effect depends strongly on the gold-copper and copper-silver ratio. It is strongest in red and pink gold alloys in the 14-18 carat range. Hardness values of 300 HV can be easily obtained.
In some alloys, ordering cannot be suppressed completely by quenching, making the material difficult to work.

Particular difficulties can occur with irreproducible cooling conditions during investment casting. Subsequent annealing at about 700°C is recommended to avoid cracks in critical red gold alloys.

In gold-copper-silver yellow alloys, the process is more complicated. Prior to the ordering process, precipitation of a copper-rich phase from the silver-rich solid solution occurs. The subsequent ordering process mainly affects the copper rich phase.

2.4 LOW MELTING COMPONENTS

Low melting components occasionally occur in jewellery gold alloys either by **additions** made deliberately or by accidental **impurities**.
Two conditions have to be fulfilled for an addition or an impurity to form a low melting component: (a) the addition has a low melting temperature and a very limited solubility in the gold alloy, and (b) the addition/impurity forms small amounts of low melting compounds of

limited solubility with the main alloying elements (gold, silver, copper).

Typical low melting additions are silicon and gallium. Silicon is much more critical than gallium because of its small solubility in gold and its insolubility in silver. Typical impurities are lead, bismuth, sulphur and phosphorous. Lead can be introduced by: (a) gold alloy contaminated with soft solder (lead-tin) or (b) by use of lead-containing ('free machining') brass for alloying. Brass (copper-zinc) is usually used as a means of introducing zinc into gold alloys to reduce zinc loss by evaporation. [note: brass with less than 70% copper can contain lead; with less than 62% copper, brass generally contains lead.]

Sulphur, as a sulphide, is introduced during investment casting by the reaction of the melt with the investment or by the remelting of impure metal (see *Reaction with the Investment*). Phosphorous (as phosphide) rarely occurs, although it is sometimes used as a deoxidiser in silver.

Bismuth as an impurity in jewellery alloys may arise from use of soft solders.

Low melting components tend to segregate at grain boundaries, causing brittleness and fracture can occur with little applied force. Grain size can influence this effect through the grain boundary surface area available for such segregation; a fine grain size is preferable.

2.5 GRAIN REFINERS

Two kinds of grain refiners have to be considered: Those producing a fine grained cast structure (such as iridium and ruthenium) and those effective during soft annealing (e.g. cobalt). Only grain refiners used for casting are considered here because they are more frequently the cause of defects.

Principles of working mechanism

At the commencement of solidification, the formation of crystallites (grains) in the melt needs nuclei as starting points. The more nuclei that are available, the more grains that can grow at the same time and the smaller the resulting grain size of the dendritic structure. One method to increase the number of nuclei is by adding high melting elements or compounds to the melt. These should have no - or only a very small - solubility in the solid alloy and have to be present as a fine dispersion before the melt starts to solidify to be effective. For this reason, the best effect is obtained if the compounds are homogeneously dissolved in the melt and precipitate prior to the beginning of solidification.

The common grain refiners used are high melting metals of the platinum group, with limited solubility in gold alloys, and some very reactive elements which form intermetallic compounds or oxides or nitrides as the effective nuclei.

Figure 2 Schematic: Shrinkage cavity (primary pipe) on top of a cast ingot

3 INVESTMENT CASTING

3.1 SHRINKAGE POROSITY

All metals and most alloys show a sharp decrease in volume on solidification (solidification shrinkage) due to the closer packing of the atoms in the crystal lattice. Such shrinkage effects can lead to defects in gold jewellery alloys.

At first, consider the casting of a simple ingot: The solidification of an ingot starts from the mould wall, commencing from bottom to top. The centre of the ingot at the top is usually the last part which solidifies. Due to the shrinkage, there is insufficient melt to fill the remaining space on the top and a depression or funnel-shaped shrinkage cavity (pipe) remains, Fig. 2. Sometimes, a thin, deep cavity is formed (axial porosity, secondary pipe). Sheet made from such an ingot can suffer delamination and inclusions.

In investment casting, the situation becomes more complicated for several reasons: The size of the casting is relatively small and the shape complex; heat transfer is very dependent on the shape. A well-ordered progression of solidification from outside to centre and bottom to top (as in ingot casting) is not possible.

Early solidification of the gate (which connects the casting to the central sprue or feeder) and other small cross-section parts can prevent the supply of additional melt to compensate for shrinkage in the casting. Solidification takes place in a very short time - a few seconds. Heat transfer and growth of crystallites are strongly influenced by several factors.

Gold jewellery alloys (as with other alloys) start solidification by the formation of dendrites (see section 2.1 ‘Melting and solidification’ above). These dendritic grains impact and grow into each other, building a sponge-like structure and increasing the resistance to further melt flow needed to take account of solidification shrinkage. Therefore, the filling of inter-dendritic spaces by additional supply of melt is hindered, leading to interdendritic porosity with the typical dendritic shape.

Definite rules for avoiding shrinkage porosity are difficult to provide but guidelines include:

- Avoid pronounced changes in cross-section within an item.
- Provide a gate of sufficient diameter to avoid its premature solidification before the casting. Note: an extremely short and thick gate can also cause shrinkage porosity.
- Where practicable, place the gate on the thickest part of the jewellery item. If necessary, use two or more gates positioned to ensure feeding of liquid melt to thick sectioned areas.

The tendency to shrinkage porosity depends also on the type of alloy. Higher carat alloys seem to be less sensitive to this defect, especially if they have a higher silver content. Casting and flask temperatures have a significant influence, too. The relationships are complex and cannot be readily explained here. Reference should be made to other publications (see list at end). It is recommended that trials with varying temperatures should be performed to find suitable working conditions.

It is important to note that improvements in casting quality by optimising temperatures are only possible if items of similar size and cross-section are used for building up the wax tree. An optimum set of casting conditions cannot be achieved if the tree consists of a mixture of filigree and heavy parts, for example.

3.2 GAS POROSITY

Gases which are dissolved in the melt, or introduced with the flow of liquid metal or formed by chemical reaction, can produce a special kind of microporosity after solidification.

In its most typical appearance, the micropores are almost spherical (see Case 1). However, many other irregular or dendritic shapes are also possible (see Case 2). For this reason, a clear identification of the nature and origin of the porosity is not always possible.

In gold alloys, the most common source of gas porosity is the formation of sulphur dioxide by reaction of the melt with the mould investment. The presence of copper oxide in the melt can also cause gas porosity as it is believed that the oxide can decompose on solidification, releasing oxygen under some conditions. On the other hand, porosity generated by entrapped air or protective atmosphere is believed possible although not proven.

To avoid gas porosity, two rules should be observed:

- **Avoid conditions causing reaction of melt with investment**
  - The reaction of investment with the melt is covered later in section 3.5.
- **Use only clean material for preparing the melt.**
  - Use of too high a proportion of used/scrap material or recycling of ‘dirty’ casting scrap (e.g. central sprues), insufficiently cleaned, for remelting is potentially dangerous.

3.3 INFLUENCE OF INVESTMENT ON CASTING QUALITY

The quality of investment castings is strongly influenced by the properties and behaviour of the investment from which the mould is made. Properties which have to be considered include:

- setting behaviour of the slurry
- strength in the ‘green’ and the fired state
- gas permeability
- thermal conductivity
- chemical stability, i.e. the reaction of investment compounds with the molten metal.

For a better understanding, some remarks are made on the composition of investment powder; the investing procedure and firing process.

Composition of investment powder: Generally, the investment powder consists of fine grained mineral powder as the main component (‘body’) and a binder. The binder gives the strength and can be added as a solid directly to the dry mineral powder (as it is the case with gypsum-bonded investment) or as a liquid together with the water in preparing the slurry as is the case with phosphate-bonded investment. In gold jewellery casting, gypsum-bonded investment is normally used.

The main components are:

- silica (silicon dioxide) in two crystal modifications (quartz and cristobalite) as the refractory body,
- gypsum (Plaster of Paris) - calcium sulphate - as the binder,
- some additions e.g. detergents, for improving wetting behaviour of the slurry with the wax, and agents to modify setting time, thermal expansion and strength.

Whereas silica is relatively stable and does not lead to problems in casting of gold alloys, gypsum can cause many problems, depending on the alloy to be cast, flask and melt temperatures and working conditions.

Note: Gypsum-bonded investment is not recommended for casting palladium-white golds. Even with nickel-white golds, the use of gypsum-bonded investment can be critical. For good reasons, it is a material best suited for the casting of coloured carat gold alloys with relatively low melting ranges. Alternatively, phosphate-bonded investment can be used for casting jewellery alloys with a higher melting range (and/or greater reactivity). In this investment, phosphate compounds as used as the binder (in combination with magnesia) in place of gypsum; an organic silicate can also be used as the binder, producing another type of investment with similar properties.

The advantages and disadvantages of both types of investment are:

- Gypsum-bonded investment is convenient to handle and relatively cheap. However, the instability of calcium sulphate is the cause for many casting defects, as is discussed later.
- Phosphate- (and silicate-) bonded investment is not so easy to handle and more expensive. Its thermal and chemical stability in jewellery casting is excellent, but the subsequent removal of phosphate-bonded investment from the casting can be difficult.

Because of its dominant use in jewellery casting, only the behaviour of gypsum-bonded investment is considered in the following, especially with relation to casting defects.

3.4 THE INVESTING PROCESS (GYPSUM BONDED INVESTMENT)

3.4.1 SETTING TIME

The investing process starts with addition of water to the investment powder which must be mixed thoroughly. A reaction occurs, with the partially dehydrated gypsum taking up water and forming the stable hydrated state. At the end of the reaction, the investment slurry sets to a solid mass of 'green' investment of sufficient strength.

The time between the first contact with water and solidification of the investment is called the **setting time**. The setting time can be easily determined by observing the time to 'gloss off', i.e. when the setting process is almost complete, the glossy surface of the setting investment (visible on the top of the flask) becomes dull and matte. The setting time depends on:

- the brand/grade of the investment
- the mixing ratio, that is the powder to water ratio (e.g. 100:37 by weight)

- the temperature of the slurry
- the water quality (deionised, distilled or tap water which has a variable hardness)

A typical value is 12 minutes; however, the actual values should be checked in practice. Where the observed setting time differs significantly from the correct (manufacturers recommended) value, difficulties can be anticipated and defects are likely to occur on casting.

A **prolonged setting time** can be caused by:

- old (bad) batches of investment powder
- powder stored in a humid environment
- too much water added
- water and /or powder unusually cold
- changes in water quality

Result: investment is too weak. Cracks will occur, especially on edges of heavier parts and with centrifugal casting, and the cast item exhibits ***fins*** (Case 6). Melt can also penetrate into the surface of the weak investment, resulting in the cast item showing a ***sandy surfac***e (Case 6). Alternatively, the slurry can separate and release the excess of water, leading to the cast item showing ***water marks*** (Case 7).

A **shortened setting time** can be caused by:

- too little water (slurry is viscous)
- prolonged application of the vacuum in closed vacuum investing equipment (water evaporates more readily)
- a high water temperature (e.g. in unusually hot weather)
- a change in water quality

Result: investment tends to crack during handling and fine details of cast items are not well reproduced.

3.4.2 WORKING CYCLE

The working cycle comprises:

- Mixing
- Degassing
- Pouring into the flask
- Degassing the flask
- Vibrating the flask

The total time which can be used for performing this cycle is called the **working time**. The working cycle should use almost the entire setting time, less about one to two minutes.

Working time = Setting time minus one or two minutes

- If the cycle is completed a long time before setting occurs and the flask is left alone without any movement, water will separate from the slurry and collect on the surface of the waxes, causing typical ***water marks*** (Case 7) on casting. The danger of the occurrence of water marks increases with increasing water content.
- Where the working time is equal to or longer than the setting time, cracks can be caused.
- During the setting process, the flask should be still and not be

touched or moved.

- Degassing should be extended until the foam collapses. (Where the investment contains a significant detergent content, the foam does not disappear completely. Experience is required to find the correct time.)
- Pouring the slurry into the flask has to be done as gently as possible, not only to prevent breaking of fragile waxes but also to avoid uptake of an excess of air. In any case, additional evacuation of the filled flask is necessary to remove air from the setting slurry.
- Evacuation and subsequent vibration is essential to remove air bubbles from the wax surfaces. If this procedure is not performed properly, small spheres (‘pearls’) are visible on the surface of castings. Air bubbles form voids in the investment and the voids are filled with melt during casting.) This defect is named after its origin: **air bubbles.**

The procedure described above is typical for simple investing equipment consisting of a mixer and an evaporation and vibration table. With the more sophisticated closed automatic equipment, the danger of getting air bubbles is minimised because the introduction of air is avoided as the mixing and pouring is done in a vacuum. However, another problem may occur: prolonged evacuation at a relatively high vacuum results in a greater quantity of water being evaporated, with the result that the slurry becomes too ‘sticky’ and the setting time is reduced. The investment can crack. The water to powder ratio should be increased to compensate for this enhanced loss (follow manufacturer’s recommendation).

Altogether, the available working time should be split in a relatively long mixing period, with sufficient de-aeration and a moderate vibration time. The splitting ratio is very dependent on the equipment and needs some experience to optimise.

3.4.3 BURN-OUT CYCLE

Dewaxing

Dewaxing is also an important step to prepare the flask for a sound casting. The wax can be removed simply by heating the inverted flask to about 100°C. A great portion of the wax will flow out through the central sprue. However, a portion remains in the cavities. Where the investment is already relatively dry (by standing the flask for a long time between investing and dewaxing), the wax tends to be absorbed into the investment. The presence of water vapour, however, inhibits the uptake of wax by the investment and ‘pushes’ the liquid wax out. The subsequent burn-out process is considerably enhanced. A dry flask should be soaked with water again before dewaxing.

A more efficient method for removing wax is **steam dewaxing** which should be used wherever possible. The advantage of steam dewaxing is not only reduced wax retention in the flask; it also decreases environmental pollution (from combustion of the residual wax) and protects the burn-out furnace.

Removing water

This should be completed at about 150°C (a temperature higher than 100°C is necessary to remove the free water) as hydrated gypsum loses a part of its water in this temperature range.

Allow the flask to dry out for a sufficient time in the temperature range 150° - 250°C (furnace temperature), otherwise the investment will get a rough surface from violently boiling water.

Transformation of cristobalite

Cristobalite (a form of silica) transforms to quartz at about 400°C, with a consequent volume change. It is advised that this temperature should be passed through gently to avoid cracking.

Decomposition of calcium sulphate

Pure calcium sulphate decomposes at about 1200°C. However, in the presence of silica, the decomposition temperature is lowered towards about 780°C. Therefore, this temperature sets the highest temperature possible in the burn-out cycle. For safety, the maximum furnace temperature should not exceed 730 to 750°C. Other factors such as residual carbon can lower the decomposition temperature even further (see below).

Removing residual wax

Wax absorbed by the investment tends to resist relatively high temperatures until it is completely removed by combustion with oxygen. Air circulation within the narrow channels of a flask is inhibited, so adequate time needs to be given for wax residues to be fully combusted (oxidised). Normally, the maximum temperature in the burn-out cycle should be about 730°C, maintained for at least 2 hours (actual temperature within the flask, see later). Where gem stones are being cast 'in situ', such a high temperature cannot be applied without damaging the stones. Any carbon or wax residues may lead to defects. ***An indicator for an incomplete burn-out process is the presence of a greyish zone in the investment around cast items when the investment is broken up after casting.***

Additional to a sufficiently high temperature, an excess of oxygen has to be maintained. In a well insulated electrical furnace, overfilled with flasks to the top, or in a gas furnace, with reducing flame gases allowed to enter the muffle, this condition might not be fulfilled.

Low thermal conductivity of investment

Investment is a thermal insulator comparable with good insulating bricks, etc. For this reason, the actual temperature within the flask lags considerably behind the furnace temperature during the heating programme. To ensure a uniform temperature within the flask at maximum temperature and, later, at casting temperature, a minimum time of 2 hours at set temperature should be maintained (i.e. the time elapsing after the furnace has reached the set temperature). The time necessary to equalise the temperature depends strongly on flask size, furnace construction, filling of the furnace and position of the flask within the furnace. ***Filling the furnace to the top should be avoided. The flask should be positioned well away from the heating elements and door openings to avoid overheating or too low a temperature, respectively.***

Conclusions

Heating flasks through the temperature range up to 400°C has to be done very slowly; preferably, a holding time in the range 150° to 250°C should be included. In principle, further heating up to the maximum temperature can be done as fast as possible, consistent with the temperature within the flask following the rising furnace temperature. A **maximum temperature of 730 - 750°C must not be exceeded.** For complete removal of carbon residues, a holding time of 2 hours at maximum temperature should be included. After cooling down to the working (casting) temperature -in most cases about 600°C - an 'equalising' time of two hours should be provided, too.

3.5 BEHAVIOUR OF GYPSUM-BONDED INVESTMENT DURING CASTING

The most reactive component of the investment is gypsum (calcium sulphate). As mentioned earlier, pure calcium sulphate decomposes at about 1200°C to sulphur dioxide gas and calcium oxide, i.e.:

$$CaSO_4 \rightarrow SO_2 + CaO$$

Calcium sulphate → sulphur dioxide (gas) + calcium oxide

The presence of silica in the investment lowers the decomposition temperature substantially. Residual carbon from incomplete burn-out of wax residues also acts to enhance the decomposition of gypsum, effectively lowering the decomposition temperature significantly to the critical value of about 800°C. Even worse, the base metal alloying elements in jewellery alloys and their oxides can further enhance this decomposition of gypsum. Their detrimental effect increases from copper to zinc and nickel. Palladium as an alloying element is also critical. Of course, the relative influence of an element depends on its concentration in the alloy.

Another very critical factor is the casting atmosphere: a reducing atmosphere enhances the instability of gypsum, too. From this reason, casting in a closed chamber filled with forming gas (a mixture of nitrogen and hydrogen) should be avoided. Covering open casting equipment (crucible and flask) with forming gas may be advantageous if not too much gas is supplied but difficulties can be expected. Vacuum acts in the same way as a 'reducing atmosphere' and should be avoided. In closed vacuum casting equipment, the pressure has to be increased to atmospheric pressure (or even higher) with a neutral gas at the moment of casting. The recommended atmosphere for casting is a neutral gas such as nitrogen (preferable) or argon.

Not only gaseous compounds can be formed in the decomposition reaction. Especially with reducing conditions, compounds between sulphur, silver and base metals may be formed, leading to undesirable inclusions, typically sulphides, in the casting, for example:

$$CaSO_4 + 4Cu \rightarrow CuS + CaO + 3CuO$$

Calcium sulphate + copper → copper sulphide + calcium oxide + copper oxide

Thus, decomposition of gypsum can occur at temperatures close to or at the normal solidification temperatures of the alloys being cast. Hence, the need to keep both flask and melt temperatures to a minimum consistent with good mould filling. Temperature and heat transfer play an important role. The higher the casting and/or flask temperature, the more likely is the reaction of the melt with the investment. However, temperature alone is not the only decisive factor. The weight of an item to be cast is important, too. The quantity of heat transferred to the investment locally depends on it and determines the temperature reached at the adjacent surface of the investment. For example, it is possible to cast thin-walled, nickel-white gold items satisfactorily in standard investment whereas heavy cross-sectioned parts can cause serious problems.

A number of kinds of defect can be produced by the instability of gypsum. The most obvious defect is spherical gas porosity at and just beneath the surface (Case 1). The sulphur dioxide formed by the reaction cannot escape and stays in the liquid metal, thus forming pores in the cast metal. In most instances, the casting looks sound in the as-cast state, but pores are exposed during subsequent polishing. Sometimes, the porosity caused or favoured by sulphur dioxide shows a typical dendritic structure, similar to shrinkage porosity (see Case 2) and so it is difficult to determine it's cause from shape alone.

Another critical case appears when sulphide inclusions are formed. Sulphide inclusions are bluish-grey particles, only detectable in microsections using a microscope with high magnification. In many cases, the inclusions are randomly distributed within the structure as roughly spherical particles, causing little harm. Sometimes however, sulphides accumulate on grain boundaries and, in this instance, severe embrittlement occurs. The jewellery item can break with the application of very little force.

Another detrimental effect of sulphide inclusions is seen when remelting contaminated scrap material as part of a new metal charge since gas porosity can result. The remelting of used/scrap material - or adding such used material to fresh alloy - can be a source of many problems. Both sulphide-containing material as well as oxidised alloy can produce gas porosity. The worst case is where scrap material (e.g. sprues) contaminated with remnants of old investment are remelted: inclusions and gas porosity are likely to result.

Some rules for avoiding gas porosity and other defects resulting from reaction with gypsum bonded investment

- Keep the casting and flask temperatures as low as possible.
  - This is especially important for the casting of heavy items. This means also that casting filigree and heavy items on the same tree should be avoided.
- Never cast in a reducing atmosphere (e.g. forming gas).
  - A neutral atmosphere (e.g. nitrogen) is preferred.
- Phosphate-bonded investment is preferred for casting high melting alloys with reactive alloying additions (e.g. palladium white gold, '990' gold-titanium).
  - Nickel-white gold is on the limit for being cast in gypsum-bonded investment and only light/filigree items might be cast with success.
- Take extreme care if remelting used or scrap material.
  - It must be thoroughly cleaned of remnants of old investment, oxides, etc. and not contain sulphide inclusions.

FURTHER READING

There are relatively few good books on gold jewellery manufacturing that approach the subject from the technology and underpinning science rather than from a craft standpoint. Most are only available in English language editions and some are out of print, unfortunately.

Much useful and up-to-date information on gold jewellery manufacturing and materials technology and best practice has been published in the gold jewellery technology journal, *Gold Technology*, published by World Gold Council in several language editions, and in the proceedings of the Santa Fe Symposia on jewellery technology, published by Met-Chem Research Inc. Other useful conference proceedings and books are published by the International Precious Metals Institute, USA, and occasional technical articles appear in some of the trade press such as American Jewelry Manufacturer, published by MJSA, USA.

Back issues of *Gold Technology* are available from local offices of World Gold Council. World Gold Council also publishes a growing number of jewellery technology publications that complement this Handbook and which the reader will find invaluable. Increasingly, some of these are becoming available translated into other languages as well as English (contact your local World Gold Council office for information). At the time of printing, these include:-

1. ***Technical Manual for Gold Jewellery*** - A practical guide to gold jewellery manufacturing technology, published 1997
2. ***Investment Casting*** - A technical advisory manual for goldsmiths, published 1995.
3. ***The Assaying and Refining of Gold*** - A guide for the gold jewellery producer, published 1997.
4. ***Finishing Handbook*** - to be published 1998.

Information on these publications can be obtained from World Gold Council local offices worldwide or direct to:- World Gold Council, Industrial Division, 1st Floor, King's House, 10 Haymarket, London SW1Y 4BP, UK. Tel: +44 171 930 5171; Fax: +44 171 839 4314; E-mail: chris.corti@wgclon.gold.org. Internet: http://www.gold.org.

Some relevent articles are listed below.

Defects

1."Examples of typical defects in jewelry casting", Dieter Ott, Proc. Santa Fe Symposium, 1989, 297-310.
2. "Defects in jewelry - a new version of an old problem", Dieter Ott, Proc. Santa Fe Symposium, 1991, 171-197.
3. "Analysis of common casting defects", Dieter Ott, *Gold Technology*, no.13, July 1994, 2-15.
4. "Control of defects in casting", Dieter Ott, *Gold Technology*, no.17, October 1995, 26-35.
5. "Stress corrosion cracking in white golds", D.P.Argarwal, G.Raykhtsaum and Joann DeRoner, Proc. Santa Fe Symposium, 1990, 257-262.

6. “Stress corrosion cracking failure of wrought gold jewelry alloys”, G. Normandeau, Proc. Santa Fe Symposium, 1991, 323-352.
7. “Tarnish and corrosion of silver and gold alloys”, L.Gal-Or, Proc. Santa Fe Symposium, 1990, 19-36.
8. “An overview of tarnish in dental and carat gold alloys”, Mark Grimwade, Proc. Santa Fe Symposium, 1993, to be published.
9. “Residual stresses: their causes and how they can be minimised” (on stress corrosion cracking), Mark Grimwade, *Gold Technology*, no.8, November 1992, 9-13.
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ACKNOWLEDGEMENTS

The co-operation of many jewellery manufacturers in providing defective jewellery for investigation is gratefully appreciated; they are too numerous to name individually. Without such assistance and willingness to expose their problems, this Handbook would not be possible.

The author especially thanks the technical committee of the Santa Fe Symposium and World Gold Council for their support and encouragement to undertake the defects project and to publish the results. Thanks are also given to Eddie Bell and Valerio Faccenda for their contributions and especially to Christopher Corti for his many useful suggestions and the editing of the manuscript. Lastly, he would like to thank his colleagues at FEM for their support and practical assistance.