

A facile chemical screening method for the detection of stress corrosion cracking in 9 carat gold alloys

B. Neumeyer¹, John Hensler¹, Anthony P. O'Mullane^{2*} and Suresh K. Bhargava^{2*}

¹ Department of Chemical Engineering, ²School of Applied Sciences, RMIT University, GPO Box 2476V, Melbourne, VIC 3001, Australia

* Corresponding authors:

E-mail: suresh.bhargava@rmit.edu.au,
anthony.omullane@rmit.edu.au

Abstract

Stress corrosion cracking (SCC) is a well known form of environmental attack in low carat gold jewellery. It is desirable to have a quick, easy and cost effective way to detect SCC in alloys and prevent them from being used and later failing in their application. A facile chemical method to investigate SCC of 9 carat gold alloys is demonstrated. It involves a simple application of tensile stress to a wire sample in a corrosive environment such as 1-10 % FeCl₃ which induces failure in less than 5 minutes. In this study three quaternary (Au, Ag, Cu and Zn) 9 carat gold alloy compositions were investigated for their resistance to SCC and the relationship between time to failure and processing conditions is studied. It is envisaged that the use of such a rapid and facile screening procedure at the production stage may readily identify alloy treatments that produce jewellery that will be susceptible to SCC in its lifetime.

Introduction

Due to the softness of 24 carat gold, it is alloyed with other metals to modify its hardness, colour and ductility for the jewellery industry. The composition of low carat gold, in particular 9 carat gold, varies from ternary gold-silver-copper alloys to quaternary alloys where zinc is added to counteract the red colour induced by copper. Although alloys based on the gold-silver-copper-zinc formulation have been employed extensively in the jewellery industry, the specific compositions in general use are not well known (1) and few studies have been carried out on the relationship between the individual elements and the performance of the material. To date there are no analytical or performance standards for these alloys which are accepted for many other base metal alloys used in industry. Stress corrosion cracking (SCC) is a well known form of environmental attack in low carat gold jewellery (2). During the manufacturing process residual stress may be present in the alloy due to inhomogeneous deformation caused during working or from differential thermal expansion and contraction due to temperature gradients established in the article during the course of heating and cooling (3). In the presence of a corrosive environment, such as common cleaning products containing bleach and chlorinated water, SCC may occur which leads to in service failure.

SCC is the localised rupture of a metal or alloy that is under the combined effects of stress and corrosion at levels well below which they would cause failure if acting individually (4). During SCC the metal or alloy is virtually unaffected over most of its surface while fine cracks progress through it. The important variables affecting SCC are temperature, solution composition, metal composition, stress and metal structure. SCC is usually characterised by attack along grain boundaries (intergranular corrosion) under conditions of tensile stress, which progressively opens up the grain boundary positions to attack and leads to the formation of cracks and ultimate failure. Often when SCC occurs there is little evidence of corrosion products, distortion of the alloy and in many cases no external stress needs to be applied to produce failure (5). In some cases, however, transgranular cracking may occur in which the attack tends to focus at imperfections in the crystals.

The environmental corrosive attack of low carat gold jewellery arises from conditions such as contact with a humid atmosphere or wet conditions such as perspiration, seawater or chlorinated water. Recent studies have shown that even 18 carat gold is subject to SCC under the appropriate environmental conditions (2). Therefore, it is important to ensure that there is adequate relief of internal stresses in the alloy which occurs from the working of the alloy during manufacture. Typically these stresses are relieved by annealing, however in low carat gold alloys points of stress can still exist after commonly used stamping procedures (5) that re-introduce stresses by inhomogeneous deformation.

Table 1

Composition, treatment procedures and Vicker's hardness of the alloys used in this study

Sample no.	Composition (%)				Treatment	Vickers Hardness (HV2.5)
	Au	Ag	Cu	Zn		
1	37.60	10.57	42.86	9.07	Part drawn, annealed at 650°C, air cooled to 350°C and water quenched	129.0
2	37.70	5.90	46.70	9.94	Part drawn, annealed at 650°C, air cooled to 350°C and water quenched	148.5
3	37.60	6.00	51.00	5.40	Part drawn, annealed at 650°C, air cooled to 350°C and water quenched	134.0
4	37.60	10.57	42.86	9.07	Hard drawn – not annealed	177.5
5	37.60	10.57	42.86	9.07	Part drawn, annealed at 650°C and water quenched	146.2

Given that the gold jewellery industry uses around 2000 tonnes of gold per annum (2), it would be beneficial to develop a screening method to test the reliability of the alloy before it is sent to the market-place. Therefore, it is desirable to have a quick, easy and cost effective way to detect SCC in alloys and prevent them from being used and later failing in their application. Many studies to date have induced SCC using slow strain rate tests in a corrosive environment with the alloy under potential control (2, 6-11). Such studies in combination with electrochemical polarization techniques and potentiostatic electrochemical noise measurements (12) have given a fundamental insight into the mechanism of SCC in gold alloys. Electrochemical impedance spectroscopy is another powerful technique that has been employed to study the corrosion of alloys used in jewellery (13). However, the implementation of these experimental setups is costly and time consuming from an industrial viewpoint. Therefore, the need to develop a low cost and quick test to evaluate the performance of low carat gold alloys to a stage suitable for production control would be highly beneficial.

Experimental

Materials and chemicals

The alloys were supplied by Golden West in the form of 1.5 mm diameter wires. Three different compositions were provided which were treated as outlined in Table 1.

Each alloy was washed in acetone and methanol and dried with a flow of nitrogen prior to SCC experiments. The corrosive environments investigated were ferric chloride and cupric chloride and were used as received from Aldrich. All aqueous solutions were made up with water purified in a Millipore System (resistivity 18.2 MΩ cm).

Procedures and instrumentation

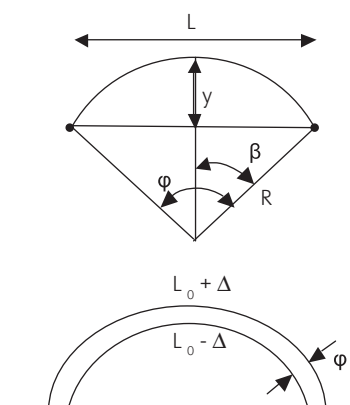
Perspex plates were manufactured with two holes at either end with the spacing between the holes varying over the

range of 30-100 mm. The alloy wires were then bent into an arc of a predefined height of 20 mm above the base of the plate so that the wires would be elastically deformed but would spring back when the ends were removed from the holes. Stresses were in the range from 700 to 3600 MPa. The plate was then immersed in an aqueous corrosive solution and the time to cracking at the top of the arc was measured.

A Hitachi S-520 scanning electron microscope was used for SEM microstructure observations. The Vickers hardness was measured using a hardness meter with a load of 2.5 Kg. The average of five measurements was taken for each sample.

Results and discussion

To produce a constant stress in a low cost and facile manner the following approach was taken. The gold alloy wire sample was simply inserted between two holes in a Perspex plate. The stress (S) depends on the distance between the holes (L), the original length of the wire (L_0), the height of the wire above the plate (y) and the radius of curvature (R) as illustrated schematically below.



The magnitude of the stress generated was calculated by applying elastic beam theory to the relevant dimensions of the bent wire. Stress will vary across the section of the wire. Taking,

$$L_0 = R\phi \quad (1)$$

$$L_0 + \Delta = \left(R + \frac{d}{2}\right)\phi \quad (2)$$

$$\frac{L_0 + \Delta}{L_0} = \frac{\left(R + \frac{d}{2}\right)}{R} \quad (3)$$

Therefore,

$$1 + \frac{\Delta}{L_0} = 1 + \frac{d}{2R} \quad (4)$$

where $\frac{\Delta}{L_0}$ is defined as strain.

If the stress applied remains elastic, i.e. the wire goes back to its original shape when the stress is removed, then

$$\frac{\Delta}{L_0} = \frac{S}{E} \quad (5)$$

where E = Young's Modulus for gold alloys (75×10^9 Pa), implying

$$S_{\max} = E \frac{\Delta}{L_0} = \frac{Ed}{2R} \quad (6)$$

R can be simply calculated from knowing y and L as

$$R = \frac{L^2}{8y} + \frac{y}{2} \quad (7)$$

Several combinations of L and L_0 were investigated to produce a range of stresses.

In this work Young's Modulus is taken as a constant. Although alloying gold does not change E as significantly as

its limit of elasticity (14) which is never exceeded during the testing procedure, the variance in E with composition must be considered. Given that mechanical test values for E are difficult it was not attempted in this work. Therefore only direct correlations between alloys of the same composition are investigated. It should also be noted that a tensile residual stress may be present on the surface of the samples which would be additive to the applied stress, however the wire samples used in this study are quite thin and it is therefore unlikely that a residual stress distribution has been set up through the wire section.

For SCC evaluation, the alloy wire samples were subjected to different stresses in a 10 % ferric chloride solution. It has been demonstrated by Graf that FeCl_3 is an effective medium for inducing SCC in low carat gold alloys (15). SCC is initiated by dissolution of components of the alloy in an electrochemical process. The nucleation sites at which this occurs have high energy and typically are microstructural features, such as stacking faults, dislocations or the intersection of the surface with grain boundaries (4). The dissolution of low carat gold alloys containing Zn and Cu is thermodynamically favourable since the standard reduction potentials of Zn^{2+}/Zn and Cu^{2+}/Cu which are -0.76 and 0.34 V vs SHE (Standard Hydrogen Electrode) respectively are lower than the standard reduction potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.77 V vs SHE). Initially Zn is assumed to dissolve to form ZnCl_2 which is followed by Cu dissolution given the 1.1 V difference in standard reduction potentials (2, 16). Subsequently, crack propagation occurs which continues under the applied stress which exposes fresh metal surface to the corrosive medium. Cracks may then follow grain boundaries, which are higher energy regions, resulting in intergranular SCC or across grains resulting in transgranular SCC. The cross sectional area of the wire is then reduced and the final cracking failure results entirely from mechanical action.

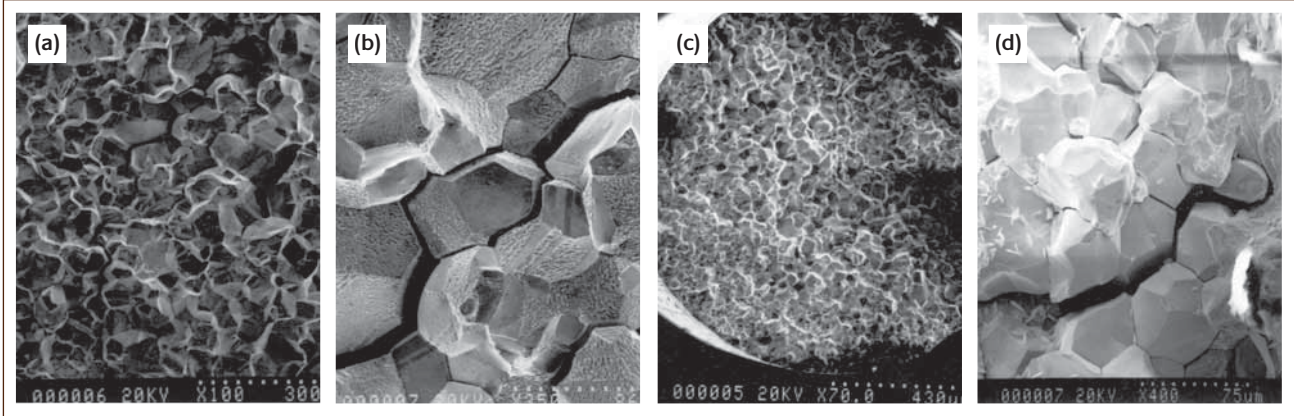
Illustrated in Table 2 are the times to failure for each sample. The failure mechanism is typical of intergranular SCC for samples 1, 2, 3 and 5 as demonstrated in Figure 1 which shows representative SEM images obtained of fractured surfaces of Samples 1 and 5. The fracture surface showed

Table 2

Time to failure in seconds for each alloy under stress in 10 % FeCl_3 . DNF = did not fail

Stress (MPa)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
3600	35	110	127	81	32
2813	36	113	128	115	38
2195	38	115	82	125	40
1731	46	74	82	160	41
1385	48	106	161	211	55
1125	88	87	237	215	40
928	114	185	140	281	72
776	115	155	DNF	291	100

Figure 1

SEM image of the fracture surface of sample 1 (a) and (b) and sample 5 (c) and (d) after immersion in an aqueous 10 % FeCl₃ solution

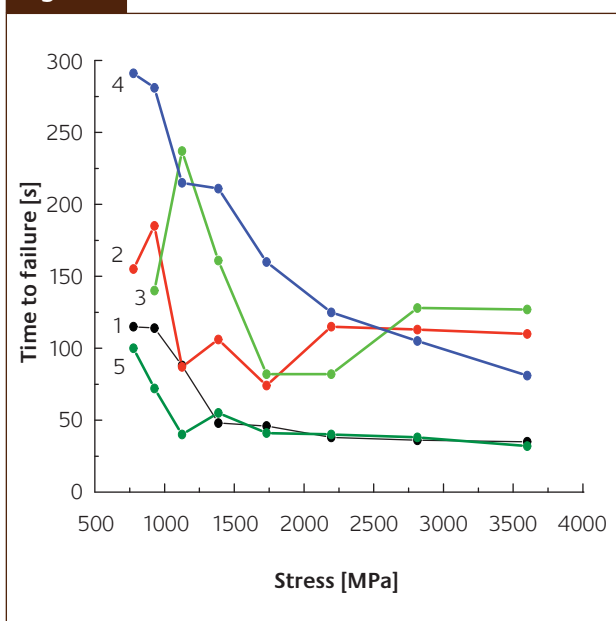
typical intergranular cracks where the polyhedral grains within the alloy can be seen clearly. Intergranular SCC has been observed previously for many types of Au-Ag based alloys (2, 4, 6, 8, 9, 17). Evidence of an electrochemical process is seen in Figure 1b which shows a fracture surface for sample 1. There are pinholes distributed over the surface which are indicative of a preferential dissolution process. Such a phenomenon was observed in all the above samples. There is also evidence of a precipitation product in the form of needles (Figure 1d) which may be copper. It is assumed these needles are metallic or conducting in nature as they do not charge during SEM imaging. Any dissolved copper induced in the presence of FeCl₃ in solution has the potential to oxidise Zn at open circuit potential. Such a reaction would

then result in the redeposition of copper at the point of Zn dissolution.

An important conclusion from this data when considering the same alloy composition but different sample treatments (Samples 1, 4 and 5) is that an annealing step followed by air cooling and subsequent water quenching does not inhibit SCC more than a single annealing step followed by quenching. Also the sample which was hard drawn and not annealed (Sample 4) demonstrated the highest resistance to SCC under these conditions. This may be related to the hardness measured for this particular sample (177.5 HV_{0.5}) which was significantly higher than the other two samples.

It can be seen from the plot of stress versus failure time in Figure 2 that each of the alloys behaved significantly differently under stress. For samples 1, 4 and 5 of the same composition the time to failure gradually decreased when the stress applied to the sample was increased. Samples 2 and 3 do not demonstrate such a strong trend and may be due to significant differences in the alloy composition. It must be emphasised that E , and therefore the applied stress which is directly proportional to E (Eqn. 6), will vary between samples with different copper contents. It is known that the E value for copper is approximately 50% higher than that of gold and silver which are very similar (18). Therefore, taking sample 3 as an example, which has the highest copper content, such a consideration would result in an 8% increase in E value and applied stress in comparison to samples 1, 4 and 5. However, some of the anomalously short times to failure under certain applied stresses cannot be accounted for by such an increase in the applied stress. In heterogeneous alloys the components of the sample are not completely soluble in one another and exist in separate phases. Therefore, there exists the possibility that significant differences in composition and distribution of elements in the alloy may be attributable to such a scatter in the data. However, it was noted that a large distribution of non-uniformly sized surface cracks were present at the surface of samples 2 and 3 which may result in significant differences in the crack initiation step

Figure 2

A plot of time to failure versus applied stress for sample 1 (—), sample 2 (—), sample 3 (—), sample 4 (—) and sample 5 (—) in an aqueous 10 % FeCl₃ solution

which is more likely to be the influencing factor on the time to failure for the same sample under different stresses than the alloy composition. Therefore, this method could also be used as a screening process against microstructural defects present in samples of the same composition.

Comparing the results for samples 1-3 which were treated in exactly the same manner but differ in composition of the alloy, a gradual increase in failure time was observed under 5 of the 8 applied stresses. It is difficult to draw a direct conclusion from this data given the difference in E values for each alloy as mentioned previously. However, it is interesting to compare samples 2 and 3 which have essentially the same amount of gold and silver but differ considerably in zinc and copper content. For 5 of the 8 applied stresses sample 3 shows more resistance to SCC than sample 2. This phenomenon may be related more to the zinc content of the alloy than differences in copper content. It has been reported that increasing the zinc content of Au-Ag-Cu-Zn ternary alloys can lead to greater risk of SCC. At low zinc contents, like that present in sample 3, the alloy tends to be duplex in character whereas with increasing zinc content (sample 2) the alloy becomes single phase and more prone to SCC (19).

From the data it was found that there is not a conclusive correlation between hardness and time to failure for these alloys as it is difficult to correlate hardness values between samples of different composition that have been treated differently. However, it can be concluded that sample 4 which

has the highest measured hardness (177.5 HV2.5) shows a marked improvement in SCC resistance. Illustrated in Figure 3 is a SEM image of the fracture surface. It can be seen that the morphology of this surface is significantly different to that observed for all other samples (Figure 1). The surface is rough and irregular and consists of many voids and dimples. It is typical of a ductile fracture surface as observed previously for 18 carat gold alloys (Au, Ag, Cu and Cd) subjected to slow strain rate tests in air (7). This suggests that this alloy may be in a different physical state to that seen for samples 1 and 5 of the same composition. The distribution of reactive components in the alloy, in particular zinc and copper, may have more importance than the actual composition of the alloy. It was previously demonstrated that production of 9 carat gold alloy resulted in a large degree of segregation of zinc and copper at the grain boundaries which was extremely susceptible to SCC. The same alloy treated in a different manner resulted in segregation of Ag at the grain boundaries generating a highly resistant material to SCC (4). It is therefore most likely that the distribution of components in sample 4 which was not annealed is significantly different to that in samples 1 and 5.

The influence of the corrosive electrolyte concentration and type was also investigated. Samples 1-3 were exposed to SCC tests in aqueous solutions of 1 and 5% FeCl_3 . Under every applied stress the time to failure increased significantly at lower concentrations of FeCl_3 for each sample. Taking sample 1 as an example the time to failure increased from 35s in 10 % FeCl_3 to 140s in 5 % FeCl_3 to 171s in 1 % FeCl_3 under an applied stress of 3600 MPa. From a manufacturing and screening viewpoint the use of the most concentrated FeCl_3 solution would be the most beneficial as failure times were always less than five minutes. 10 % CuCl_2 was also investigated as a corrosive solution to investigate SCC in these alloys. Samples 1-3 showed a decrease in failure time under the same applied stress when compared to an equivalent concentration of FeCl_3 . For example the time to failure for sample 3 decreased from 106 s in 10 % FeCl_3 to 66 s in 10 % CuCl_2 under an applied stress of 1385 MPa. Although this is a more attractive system from a rapid screening point of a view the cloudiness of the CuCl_2 solution did obscure the visibility of the wire in solution due to copper's affinity for oxygen to form $\text{Cu}(\text{OH})_2$.

It must be stated that low carat gold jewellery in its lifetime will not be exposed to aggressive corrosive solutions such as FeCl_3 . However, it is believed that rapid screening of alloys in such a simple manner at the production stage will identify manufacturing processes that result in alloys that are most prone to SCC. A future study in this area is to obtain accurate E values for alloys of different compositions to allow for more direct comparisons and also to relate the time to failure of gold jewellery in 10 % FeCl_3 to failure under conditions in which jewellery is exposed in normal wear such as household cleaning products, chlorinated water and perspiration.

Figure 3



SEM image of the fracture surface of sample 4 after immersion in an aqueous 10 % FeCl_3 solution

Conclusion

A facile chemical route to study SCC in 9 carat gold alloys typically used in the jewellery industry has been developed. The simple experimental setup consists of a Perspex plate with predefined holes into which a length of alloy in the form of a wire is placed. The stress applied to the alloy which is dependent of the length of wire and hole spacing in the Perspex plate can be readily calculated. Simple immersion of this apparatus into a corrosive solution such as 10 % FeCl₃ induces SCC and final failure in less than five minutes. From these studies it was concluded that a two stage annealing procedure did not significantly improve the resistance of the alloy to SCC over a one step process and that hardness is not a reliable indicator of SCC sensitivity. This is a simple but elegant method for measuring the effect of an applied stress on the SCC of low carat gold alloys and has value in determining the effect of sample treatment and variables such as structural defects on gold alloys of the same composition. The use of such a rapid and facile screening procedure at the production stage may readily identify alloy treatments that produce jewellery that will be susceptible to SCC in its lifetime.

About the authors



Suresh Bhargava is a professor and Chair of Industrial Chemistry in the School of Applied Sciences, RMIT University. His current research interests include surface modifications for developing sensors for air pollutants, tailored design of metallic and bimetallic surfaces for mercury sensing, biosensing and electrocatalysis and the formation and stabilisation of gold nanoparticles using biomolecules.



Anthony P. O'Mullane is a postdoctoral research fellow working in the materials group in the School of Applied Sciences, RMIT University. He obtained his PhD in Chemistry from University College Cork, Ireland in 2001. His current research interests are focused on the electrochemical synthesis and electrocatalytic properties of nanostructured noble metals, the formation of organic charge transfer complexes and probing electron transfer processes at the solid-solution interface.

John Hensler is a retired professor from the Department of Chemical Engineering, RMIT University. His work focused primarily on secondary metallurgy such as heat treatment, corrosion, surface engineering, casting, and welding.

B. Neumeier was an undergraduate student at the School of Applied Sciences, RMIT University.

References

- 1 R.S. Jackson, *Gold Bull.*, 1978, **11**, 88
- 2 C.C. Merriman; D.F. Bahr; M.G. Norton, *Gold Bull.*, 2005, **38**, 113
- 3 M. Grimwade, *Gold Tech.*, 1992, **8**, 9
- 4 J.M.M. Dugmore; C.D. DesForges, *Gold Bull.*, 1979, **12**, 140
- 5 W.S. Rapson, *Gold Bull.*, 1996, **29**, 61
- 6 M.G. Alvarez; S.A. Fernández; J.R. Galvele, *Corrosion Science*, 2002, **44**, 2831
- 7 G.S. Duffó; S.B. Farina; J.R. Galvele, *Corrosion Science*, 2004, **46**, 1
- 8 M.G. Alvarez; S.A. Fernández; J.R. Galvele, *Corrosion Science*, 2000, **42**, 739
- 9 I.A. Maier; S.A. Fernández; J.R. Galvele, *Corrosion Science*, 1995, **37**, 1
- 10 R.C. Newman, *Corrosion Science*, 2008, **50**, 1807
- 11 S.B. Farina; G.S. Duffó; J.R. Galvele, *Corrosion Science*, 2005, **47**, 239
- 12 B. Malki; A. Legris; J.L. Pastol; D. Corse, *J. Electrochem. Soc.*, 1999, **146**, 3702
- 13 I. Costa; H.G. De Melo; M. Saiki; O.V. Correa; S.O. Rogero, *J. Electroanal. Chem.*, 2003, **544**, 113
- 14 J.C. Wright; C. Corti, *Gold Technology*, 1998, **23**, 27
- 15 L. Graf, in: *Stress corrosion and Embrittlement*, W.D. Robertson, (Ed.) John Wiley and Sons: New York, **1956**
- 16 B.G. Ateya; G. Geh; A.H. Carim; H.W. Pickering, *J. Electrochem. Soc.*, 2002, **149**, B27
- 17 M.L. Montoto; G.S. Duffó; J.R. Galvele, *Corrosion Science*, 2001, **43**, 755
- 18 G.W.C. Kaye; T.H. Laby, in: *Tables of physical and chemical constants*, Longman: London, **1993**
- 19 W.S. Rapson; T. Groenwald, in: *Gold Usage*, Academic Press: New York, **1978**, 55