Investment Casting of Gold Jewellery

POROSITY IN CASTINGS, ITS CAUSES AND PREVENTION

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Porosity is one of the important causes for the rejection of jewellery items cast by the lost wax process. If it is of the shrinkage type, then there is a considerable reservoir of knowledge, arising from experience in the casting of dental gold and other gold alloys, which can be drawn upon to overcome the problem. If it is gas porosity, however, the caster is faced with the fact that there are special features in regard to its occurrence in carat gold castings about which there is still little information. This article addresses both these situations. It not only reviews available information on shrinkage porosity in dental gold alloys, but also presents an account of investigations carried out on certain hitherto unstudied aspects of gas porosity in carat gold castings. In particular it focusses upon the role played by reactions between the metals being cast and the calcium sulphate-bonded investments which are generally used for production of the moulds.

Very little has been published in regard to the manifestations, causes and prevention of porosity in jewellery gold alloy castings. This is in strong contrast with porosity in dental gold alloy castings which has been extensively studied and reported upon in the dental literature (1-21). It is also in contrast with the position in respect of porosity in castings of other metals and their alloys. A further anomaly is apparent when it is realized that the fabrication of gold jewellery is by far the largest industrial usage of the metal, more than 900 metric tons being consumed for this purpose world-wide in 1984. This figure can be compared with the estimated 120 metric tons and 56 metric tons used in the electronics and dental industries during the same period.

Because of the considerable differences in the sizes of the castings and the precise casting techniques used, and because of the inherent differences between the metals and alloys, and the investment materials used, it cannot always be assumed that knowledge which has been built up in one area is directly applicable in another. Nevertheless, the analogies which exist between the casting of dental and of jewellery gold alloys are so close that some consideration of porosity in dental gold alloy castings seems called for as an introduction to consideration of this effect in jewellery gold alloy castings.

Porosity in Dental Gold Alloy Castings

In the casting of dental gold alloys, a number of different types of porosity have been identified.

Shrinkage Porosity

This manifests itself in the form of irregularly shaped voids which can be either small and fairly evenly distributed throughout the castings (microscopic porosity) or larger (macroscopic porosity) and confined to certain parts of the metal. Shrinkage porosity of the first type does not pose serious problems. It tends to occur in castings of

small dimensions or in castings made using relatively low mould temperatures. Under both these conditions solidification occurs evenly and rapidly. Shrinkage porosity of the second type may cause rejection of castings. It tends to occur in larger castings whenever free flow of molten metal into any part of the solidifying casting in the mould is blocked.

Thus under *ideal* conditions, after the metal immediately in contact with the investment surface has solidified, the contraction which follows cooling and, in particular, crystallization of the rest of the metal should be compensated for by flow of further molten metal into the dendritic mass from the sprue and its reservoir. Such conditions are, however, not simply achieved.

In the early days of dental casting, shrinkage porosity near to the point of attachment of the sprue was not an uncommon defect in castings. It was the subject of a number of investigations which demonstrated that it was caused by solidification of the melt in the sprue cutting off the supply of melt to the main casting while it was still undergoing solidification and contraction. It could be avoided by appropriate attention to the melt temperature and to the design and dimensions of the sprue and its reservoir.

Even with sprues of good design, it was nevertheless found that localized shrinkage porosity still persisted in some castings near to portions of their surfaces. This subsurface porosity was ultimately found to be associated with slow cooling of the metal near certain areas of the mould surface. Such slow cooling apparently arises through selective heating of the surface of the investment over these areas, either because of the pattern of flow of molten metal into the mould during casting or — in centrifugal casting — owing to an increase of the rate of heat transfer to the investment over these areas as a result of selectively increased hydrostatic pressure of the melt (16). Under these conditions, pockets of molten metal persist in these areas after solidification elsewhere is complete, with the result that localized shrinkage porosity or sub-surface porosity develops.

In the case of shrinkage porosity, the pores may contain gases released from solution in the melt during its cooling and solidification. However, no account of any specific studies in this connection has been found, though the effects of hydrogen upon the shrinkage porosity of aluminium-copper and aluminium-silicon alloys have been studied (22).

Gas Porosity

This manifests itself in the form of gas-containing pores which are rounded or spherical in shape, and which have therefore clearly been formed in the melt prior to its solidification. It can arise in a variety of ways: for example, by release of gases from solution in the melt as it cools, as a result of 'back pressure' of gases in the mould if the investment is not sufficiently permeable, by inclusion as a result of turbulent flow of the melt while pouring, and by generation of gases either directly or indirectly as a result of reactions between the melt and the investment material. Although observed, it seems never to have posed acute problems in the casting of dental gold alloys.

Porosity in Jewellery Gold Alloy Castings

In modern practice, porosity in 18- and 14-carat gold-silver-copper alloy castings normally takes the form of microcrystallization voids (shrinkage porosity) or gas bubbles in the metal (gas porosity).

Figure 1 is a cross section vertical to the surface of an 18-carat gold alloy with typical crystallization voids of dendritic origin. Figure 2 is a scanning electron microscope picture of a fracture surface of the alloy. It shows the characteristic dendritic growth structure of the crystallites which results in the formation of microcrystallization voids. It will be apparent from the brief review above that knowledge of this type of porosity, and of methods for its prevention, is considerable and probably adequate for dealing with manifestations of it which arise in castings of gold jewellery. This is currently not the case in respect of gas porosity which is found, in particular, in castings with considerable strength in their outside layers and occurs frequently concentrated in a zone just below the surface of the casting (see Figure 3).

It may be responsible therefore — at least in part — for sub-surface porosity, (2, 10, 24, 25).

The understanding of the occurrence and prevention of gas porosity in cast gold jewellery has been made difficult by its sporadic and often non-reproducible appearance in castings made using both centrifugal and vacuum-assisted casting techniques. One widely held view is that the gas bubbles or pores are the result of the entrainment of air in the turbulent stream of metal when it is poured into the mould. Their appearance, however, does not accord with this view, since their surfaces are without exception unoxidized. Any direct contact with atmospheric oxygen is therefore excluded. Thus, a thorough investigation of the effect appeared necessary.

Fig. 1 Micro-crystallization voids in a cross section, taken vertical to the surface, of an 18-carat yellow gold casting
Magnification: 50x

Fig. 2 SEM picture of the fracture surface of the 18-carat yellow gold casting shown in Fig. 1 showing the characteristic dendritic growth structure

Fig. 3 Gas porosity in an 18-carat yellow gold casting as revealed in a section taken vertical to the surface
Magnification: 50x

Experimental

Centrifugal and vacuum-assisted casting techniques were used. Casting was also carried out in a sealed vessel. In the first two techniques, the molten metal could be blanketed in an inert atmosphere (argon, nitrogen or a mixture of nitrogen and hydrogen ('forming-gas')). The melting was carried out in carbon crucibles both with and without ceramic coatings. Each casting experiment was conducted using a casting tree made up so as to produce three tensile test pieces (DIN 50 1025 and 13906), one dumb-bell shaped casting and one stepped casting (see *Gold Bull.*, 1985, 18, (2), 58-68). The mass of the melt was 150 g in each experiment. For the preparation of the moulds, a commercially available calcium sulphate-based investment was used, as well as sulphate-free phosphate-bonded investment. The flask temperature was 600 °C.

The detection of gas pores was carried out using polished longitudinal sections of the dumb-bell casting. Quantitative measurements were also made of the density of the dumb-bell casting, and the tensile strength and elongation-at-rupture of the tensile test pieces. All specimens were studied without any prior heat treatment.

The effects of the following casting parameters were investigated:

- the maximum speed of rotation in centrifugal casting
- the quality of the casting alloy and the crucible
- the casting atmosphere
- the melting and casting temperatures

Effects of Casting Parameters on the Tensile Properties and the Density of Castings

Porosity lowers both the tensile strength and the elongation-at-rupture of castings, as a result of the reduction in the effective load-bearing cross section which it causes and because of notching effects. Pores of dendritic origin are more active in this respect than gas pores. Our experiments revealed that, with the casting procedures used, and the chosen arrangement of the tensile test pieces on the casting tree, hardly any dendritic-type cavities were formed in the portions of the test pieces subjected to testing. They did not display shrinkage porosity. In contrast, numerous gas pores were found when casting conditions were unfavourable. Figure 4 illustrates the normal fracture pattern of a sound test specimen with high tensile strength and high elongation-to-rupture. Figure 5 shows the fracture surface of a highly porous tensile test specimen which displays the characteristic features of brittle fracture and also the gas bubble cavities cut through by the fracture. In Figure 6, the porosity can be seen on a longitudinal polished section through the test piece close to the fracture zone.

Figure 7 illustrates the correlation between tensile strength and elongation-at-rupture. Within the scatter of the experimental data, a linear relationship between the values of these two properties can

Fig. 4 The fracture surface of a dense tensile test specimen

Fig. 5 SEM picture of the fracture surface of tensile test specimen showing many gas pores

Fig. 6 Longitudinal section through the fracture surface of a tensile test specimen showing many gas pores
Magnification: 50x

be perceived. The tensile strength of the dense castings lies between 340 and 360 N/mm² at an elongation of 40 to 45 per cent. There is also an approximately linear relationship between density and tensile strength (see Figure 8). This is remarkable, since density and tensile strength measurements were carried out on different test pieces located at different positions on the casting tree. Both these measurements can be used therefore to assess the quality of complete castings. Because of the large scatter in the elongation values (Figure 9), no clear relationship between the densities of castings and their elongation-at-rupture is evident.

The Effects of Material and Crucible Quality in Centrifugal Casting

In centrifugal casting, the maximum speed of rotation is a factor of critical importance in determining the porosity of castings. Whereas other properties, such as mould-filling, were affected by the initial acceleration at different casting and flask temperatures, a relatively high maximum speed of rotation is necessary if a dense casting, which is free from gas pores, is to be obtained. The reason for this is the hydrostatic pressure in the flask which is generated by the centrifugal force. This facilitates the escape of gas from the melt and so restricts pore formation. Because of the geometrical disposition of the crucible and the flask in the casting machine used in the investigations, the filling of the flask was virtually completed when the speed of rotation reached 100 min⁻¹. A rotation speed of about 200 min⁻¹ sufficed, in the absence of other negative influences, for the avoidance of porosity. An increase to 300 to 350 min⁻¹ was sufficient partly to offset other negative influences, but the surface roughness of the castings was increased as a result of the high pressures developed between the mould wall and the cast metal.

The influence of the quality of the cast metal and of the crucible material on the tensile strength, elongation and density of castings can be seen from Table I. The mean values ($\bar{X}$) and the standard deviations (S) were calculated. By the term 'old material' is meant material which had been repeatedly melted and partly granulated by pouring into water. The crucibles designated as 'ceramic', were carbon crucibles with a ceramic coating. Dense castings were obtained, using both ceramic and carbon crucibles, when new metal was cast. Using old metal, there was an increasingly adverse effect of the crucible material on the density of the castings. Using carbon crucibles the strength and elongation, and to a lesser extent, the density of the castings, were markedly reduced.

Fig. 7 (top) Relationship between the tensile strength and the elongation-at-rupture of castings with various degrees of gas porosity

Fig. 8 (middle) Relationship between the tensile strength and the density of castings with various degrees of gas porosity

Fig. 9 (bottom) Relationship between the density and the elongation-at-rupture of castings with various degrees of gas porosity

Table IV
Effects of Protective Gases upon the Porosity of Centrifugal Castings Produced
at a Speed of Rotation of 170 to 200 min⁻¹ and a Casting Temperature of 1 050 °C

Metal quality and type of crucible	Melt Atmosphere											
	Rm, N/mm ²	Air A, %	d, g/cm ³	Rm, N/mm ²	Argon A, %	d, g/cm ³	Rm, N/mm ²	'Forming-gas' A, %	d, g/cm ³	Rm, N/mm ²	Argon + H ₂ O* A, %	d, g/cm ³
New material												
Carbon crucible	306	25	15.42	329	36	15.43	337	36	15.46	312	28	15.43
Ceramic crucible	292	30	15.49	314	29	15.33	336	41	15.42	358	36	15.46
'Old' material (granulated)												
Carbon crucible	267	15	15.44	275	18	15.44	171	7	14.38	—	—	—
Ceramic crucible	354	41	15.27	322	35	15.44	317	28	15.42	—	—	—

Rm = Tensile Strength, A = Elongation, d = Density

* Argon saturated with water vapour at about 40 °C

Table II
Effects Upon Three Properties, Which are Affected by Gas Porosity, of the Degree of Purity of Metal Cast by the Centrifugal Method, at a Maximum Speed of Rotation of 170 to 200 min⁻¹, at 1 050 °C and after Melting in a Carbon Crucible

Material quality	Tensile strength (Rm), N/mm ²	Elongation (A), %	Density (d), g/cm ³
New	330	36	15.46
'Old' (granulated)	172	6	14.38
'Old' (pieces)	153	8	14.24
New plus added investment	149	6	14.16
'Old' plus investment	182	9	14.40
New melted under strong oxidizing conditions	342	37	15.44

Table III
Influence Upon Three Properties, Which are Affected by Gas Porosity, of the Melting and Casting Temperatures During Centrifugal Casting at a Maximum Speed of Rotation of 170 to 200 min⁻¹

Material and type of crucible	Maximum temperature 1 080 °C Casting temperature 1 050 °C			Maximum temperature 1 150 °C Casting temperature 1 080 °C			Maximum temperature 1 180 °C Casting temperature 1 150 °C		
	Tensile strength (Rm), N/mm ²	Elongation (A), %	Density (d), g/cm ³	Tensile strength (Rm), N/mm ²	Elongation (A), %	Density (d), g/cm ³	Tensile strength (Rm), N/mm ²	Elongation (A), %	Density (d), g/cm ³
'Old' material									
Carbon crucibles	171	6	14.38	244	16	15.21	—	—	—
Ceramic crucible	354	42	15.27	286	32	15.30	—	—	—
'Old' material plus 1 g of investment									
Carbon crucible	182	9	14.40	—	—	—	278	35	15.15

The assumption, sometimes encountered, that the reducing action of a carbon crucible during the melting of old oxidized material has a favourable effect on its subsequent casting cannot therefore be confirmed from these studies. In addition, the results (Table II) of casting trials with materials of varying quality, to which fired investment material had been added as an impurity, show no clear cut trend. New material, as in previous experiments, gave values for the tensile strength, elongation and density of castings, which reflected no adverse effects on their quality.

In all instances in which recovered metal, which had been melted with investment material in this way, was used for casting, the products were characterized by high porosity.

The influence of casting temperature on the gas porosity of castings can be seen from Table III. The melt was first heated to a maximum temperature (T_m) 30 to 50 K above the casting temperature (T_g) and poured. It is to be noted that a casting temperature of 1050 °C is normally used when casting the 18-carat alloy chosen for the experiments. The results demonstrate that, overheating of the melt when using old material in a carbon crucible reduces porosity. If a ceramic coated crucible is used the casting temperature has no significant effect. Good results were obtained (Table IV) using both new and old alloy which had previously been subjected to an oxidizing melt without any protective gas cover. The worst results were always obtained using carbon crucibles and old materials. Of the protective gases, 'forming-gas' (nitrogen plus hydrogen) gave the worst results.

Studies made using static casting equipment in a melting and casting chamber, revealed that gas porosity occurred only if casting was carried out in air. It did not occur if the whole melting and casting process was carried out in an inert atmosphere.

The occurrence of gas potosity in cast gold jewellery provides a typical example of the complex interplay of factors which can give rise to defects in castings which are often not reproducible.

Let us first briefly review some relevant facts in regard to the possibilities of pores being formed in cast carat gold alloys as a result

1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024, 2025, 2026, 2027, 2028, 2029, 2030, 2031, 2032, 2033, 2034, 2035, 2036, 2037, 2038, 2039, 2040, 2041, 2042, 2043, 2044, 2045, 2046, 2047, 2048, 2049, 2050, 2051, 2052, 2053, 2054, 2055, 2056, 2057, 2058, 2059, 2060, 2061, 2062, 2063, 2064, 2065, 2066, 2067, 2068, 2069, 2070, 2071, 2072, 2073, 2074, 2075, 2076, 2077, 2078, 2079, 2080, 2081, 2082, 2083, 2084, 2085, 2086, 2087, 2088, 2089, 2090, 2091, 2092, 2093, 2094, 2095, 2096, 2097, 2098, 2099, 2100, 2101, 2102, 2103, 2104, 2105, 2106, 2107, 2108, 2109, 2110, 2111, 2112, 2113, 2114, 2115, 2116, 2117, 2118, 2119, 2120, 2121, 2122, 2123, 2124, 2125, 2126, 2127, 2128, 2129, 2130, 2131, 2132, 2133, 2134, 2135, 2136, 2137, 2138, 2139, 2140, 2141, 2142, 2143, 2144, 2145, 2146, 2147, 2148, 2149, 2150, 2151, 2152, 2153, 2154, 2155, 2156, 2157, 2158, 2159, 2160, 2161, 2162, 2163, 2164, 2165, 2166, 2167, 2168, 2169, 2170, 2171, 2172, 2173, 2174, 2175, 2176, 2177, 2178, 2179, 2180, 2181, 2182, 2183, 2184, 2185, 2186, 2187, 2188, 2189, 2190, 2191, 2192, 2193, 2194, 2195, 2196, 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205, 2206, 2207, 2208, 2209, 2210, 2211, 2212, 2213, 2214, 2215, 2216, 2217, 2218, 2219, 2220, 2221, 2222, 2223, 2224, 2225, 2226, 2227, 2228, 2229, 2230, 2231, 2232, 2233, 2234, 2235, 2236, 2237, 2238, 2239, 2240, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2255, 2256, 2257, 2258, 2259, 2260, 2261, 2262, 2263, 2264, 2265, 2266, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278, 2279, 2280, 2281, 2282, 2283, 2284, 2285, 2286, 2287, 2288, 2289, 2290, 2291, 2292, 2293, 2294, 2295, 2296, 2297, 2298, 2299, 2300, 2301, 2302, 2303, 2304, 2305, 2306, 2307, 2308, 2309, 2310, 2311, 2312, 2313, 2314, 2315, 2316, 2317, 2318, 2319, 2320, 2321, 2322, 2323, 2324, 2325, 2326, 2327, 2328, 2329, 2330, 2331, 2332, 2333, 2334, 2335, 2336, 2337, 2338, 2339, 2340, 2341, 2342, 2343, 2344, 2345, 2346, 2347, 2348, 2349, 2350, 2351, 2352, 2353, 2354, 2355, 2356, 2357, 2358, 2359, 2360, 2361, 2362, 2363, 2364, 2365, 2366, 2367, 2368, 2369, 2370, 2371, 2372, 2373, 2374, 2375, 2376, 2377, 2378, 2379, 2380, 2381, 2382, 2383, 2384, 2385, 2386, 2387, 2388, 2389, 2390, 2391, 2392, 2393, 2394, 2395, 2396, 2397, 2398, 2399, 2400, 2401, 2402, 2403, 2404, 2405, 2406, 2407, 2408, 2409, 2410, 2411, 2412, 2413, 2414, 2415, 2416, 2417, 2418, 2419, 2420, 2421, 2422, 2423, 2424, 2425, 2426, 2427, 2428, 2429, 2430, 2431, 2432, 2433, 2434, 2435, 2436, 2437, 2438, 2439, 2440, 2441, 2442, 2443, 2444, 2445, 2446, 2447, 2448, 2449, 2450, 2451, 2452, 2453, 2454, 2455, 2456, 2457, 2458, 2459, 2460, 2461, 2462, 2463, 2464, 2465, 2466, 2467, 2468, 2469, 2470, 2471, 2472, 2473, 2474, 2475, 2476, 2477, 2478, 2479, 2480, 2481, 2482, 2483, 2484, 2485, 2486, 2487, 2488, 2489, 2490, 2491, 2492, 2493, 2494, 2495, 2496, 2497, 2498, 2499, 2500, 2501, 2502, 2503, 2504, 2505, 2506, 2507, 2508, 2509, 2510, 2511, 2512, 2513, 2514, 2515, 2516, 2517, 2518, 2519, 2520, 2521, 2522, 2523, 2524, 2525, 2526, 2527, 2528, 2529, 2530, 2531, 2532, 2533, 2534, 2535, 2536, 2537, 2538, 2539, 2540, 2541, 2542, 2543, 2544, 2545, 2546, 2547, 2548, 2549, 2550, 2551, 2552, 2553, 2554, 2555, 2556, 2557, 2558, 2559, 2560, 2561, 2562, 2563, 2564, 2565, 2566, 2567, 2568, 2569, 2570, 2571, 2572, 2573, 2574, 2575, 2576, 2577, 2578, 2579, 2580, 2581, 2582, 2583, 2584, 2585, 2586, 2587, 2588, 2589, 2590, 2591, 2592, 2593, 2594, 2595, 2596, 2597, 2598, 2599, 2600, 2601, 2602, 2603, 2604, 2605, 2606, 2607, 2608, 2609, 2610, 2611, 2612, 2613, 2614, 2615, 2616, 2617, 2618, 2619, 2620, 2621, 2622, 2623, 2624, 2625, 2626, 2627, 2628, 2629, 2630, 2631, 2632, 2633, 2634, 2635, 2636, 2637, 2638, 2639, 2640, 2641, 2642, 2643, 2644, 2645, 2646, 2647, 2648, 2649, 2650, 2651, 2652, 2653, 2654, 2655, 2656, 2657, 2658, 2659, 2660, 2661, 2662, 2663, 2664, 2665, 2666, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677, 2678, 2679, 2680, 26

Metal quality and type of crucible	Melt Atmosphere											
	Air			Argon			'Forming-gas'			Argon + H ₂ O ^a		
	R _m , N/mm ²	A, %	d, g/cm ³	R _m , N/mm ²	A, %	d, g/cm ³	R _m , N/mm ²	A, %	d, g/cm ³	R _m , N/mm ²	A, %	d, g/cm ³
New material												
Carbon crucible	306	25	15.42	329	36	15.43	337	36	15.46	312	29	15.43
Ceramic crucible	292	30	15.45	314	29	15.39	336	41	15.42	358	36	15.46
'Old' material (granulated)												
Carbon crucible	267	15	15.44	275	18	15.44	171	7	14.98	—	—	—
Ceramic crucible	354	41	15.27	322	35	15.44	317	28	15.42	—	—	—

* Arcon saturated with water vapour at about 40 °C

of the release of gases from solution in the alloys during their cooling and crystallization. Four gases are of special importance in this connection, namely hydrogen, oxygen, water vapour and sulphur dioxide.

Hydrogen dissolves in molten copper in atomic form and is discharged in molecular form from the metal on solidification. If oxygen is also dissolved in the copper, however, reaction occurs between it and the atomic hydrogen, when they are released, with the formation of water vapour. Sulphur and oxygen dissolved in molten copper are released from solution on cooling as sulphur dioxide. Oxygen dissolves in molten copper, but the process may be complicated because of oxide formation. In general, therefore, it is possible that porosity might be caused in molten copper by any one of these gases.

None of these gases, however, shows significant solubility in molten gold and only one of them, namely oxygen, is soluble in molten silver. The high solubility of oxygen in molten silver is well known, and its discharge from the metal in cooling gives rise to the familiar 'spitting' of silver.

It might seem feasible at first sight to predict the possibilities of gas pore formation in cast gold-silver-copper alloys from a knowledge of the above facts. There are, however, complicating factors which make this impossible. Thus the relative proportions in which the various alloy components are present is of great importance. With increasing gold content, the behaviour of the alloys approaches more and more nearly that of pure gold (28). The solvent power of the alloys for the gases which give rise to pore formation becomes restricted and the possibilities for formation of gas pores decreases. Account must also be taken of the fact that the affinity of the alloy component metals for one another has a bearing on the reactions of the alloys with the gases involved in pore formation. The enthalpy of gold-copper alloys is relatively high even in the molten state, so that the reaction of the copper with oxygen is diminished by the gold and, depending on the gold content, may be completely suppressed by it. Thus, for example, copper(I) oxide reacts with gold under certain conditions to form copper-gold alloys and gaseous oxygen (29, 30). Silver, on the other hand, behaves in an opposite way. At high temperatures, the stability of copper oxide is increased by silver, with the result that the oxidation of copper is favoured when silver is present.

The tendency of carat gold alloys to release gases from solution and to form gas pores when cast cannot therefore be directly predicted from a knowledge of the behaviour in this respect of their components and the proportions in which they are present. This is relevant to the very varied behaviour of gold jewellery alloys during casting. Thus in some instances oxidizing melting conditions, in contrast to reducing melting conditions, reduce gas pore formation. Nevertheless, this is not always the case, because reaction of the alloy with oxygen depends both on the relative proportions of its component metals and on the oxygen pressure.

In our investigations attention has therefore not been focussed

on the above possibilities but rather on the possibility that gas porosity in carat gold castings might in many instances be a result of reactions taking place between the molten alloys and calcium sulphate-containing investments.

For a complete understanding of this aspect of the formation of gas pores in jewellery castings, a full treatment would be required of the reactions of alloys of the various compositions involved with calcium sulphate-bonded investment materials. Moreover, this would have to take account of the effects of different parameters in melting and casting. Within the framework of the present investigation, consideration had to be restricted to a limited number of aspects.

Calcium Sulphate-Containing Investment Materials and Gas Porosity

Studies of gas porosity in 18-carat gold alloy cast in moulds made of different investment materials proved rewarding. In these studies, two samples of the gold alloy were mixed with finely ground investment materials bonded with calcium sulphate and with phosphate respectively. The two contaminated alloys and uncontaminated alloy were then melted and cast under the same conditions and the effects of the contaminants determined using tensile tests, density measurements and optical observations of porosity. The results are presented in Table V. They show that the castings made with 'old material' contaminated with calcium sulphate-bonded investment, and especially those made from such alloy recovered from a previous casting, displayed a marked deterioration in properties and were highly porous. The castings made from the other alloys did not have significant porosity.

Determination of Sulphide-Sulphur and Sulphur Dioxide in Castings

In the light of the effects which sulphate-bonded investment materials were found to have on the porosity of castings, the sulphur contents of castings made under various conditions were determined. The method used was the long-known 'combustion' procedure in which the metal is melted at a suitably high temperature in an oxygen stream, and its total sulphur content converted to sulphur dioxide, and under certain conditions, to sulphur trioxide. If, however, the alloy is melted in a stream of high purity argon, then only sulphur, which is present in the metal as sulphur dioxide or which is formed by chemical reactions in the metal during the melting, is released and estimated, while sulphur bound to the metal in sulphide form is not.

In this manner, sulphur present in the casting as sulphur dioxide could be determined as well as the sulphur present in sulphide form.

The castings studied were made by centrifugal or vacuum-assisted static casting methods. Melting was carried out in a carbon crucible under a protective cover of 'forming-gas'. Casting was carried out in air. Comprehensive tests demonstrated that gas porosity in appropriately contaminated metal occurred most

frequently under these conditions. The flask temperature was 600 °C and the casting temperature 1050 °C.

All the tests carried out showed the presence of only very small amounts of sulphide-sulphur in the castings, the amounts found being of the same order as those found in 'blank' experiments. It may be deduced, therefore, that such sulphur as is not present in such castings as gaseous sulphur dioxide or is not present dissolved in the metal in elemental form along with oxygen, is in general so small in quantity that it is not susceptible to exact determination. In all subsequent experiments, therefore, only sulphur bound to oxygen as sulphur dioxide was determined in castings. Our recorded figures for the sulphur contents of castings therefore refer, unless specifically stated to the contrary, to sulphur found present as sulphur dioxide. In most cases the estimation of sulphur present as sulphide was not carried out.

The sulphur content found in new material was on average less than the low level (1 ppm) found in blank experiments. The contents found in re-used material ranged up to about 10 ppm, while those found in metal which had been deliberately contaminated with investment material went as high as 70 ppm. The individual values showed a wide scatter, but in general the sulphur contents were appreciably higher in the more contaminated alloys.

Effect of Sulphur-Content on the Properties of Castings

An attempt to determine the dependence of tensile strength and elongation values on the sulphur content of castings yielded, as is illustrated in Table VI for elongation-at-rupture values, no clear-cut result. The cause was almost certainly the fact that the same test pieces could not be used for the sulphur determination and the rupture tests. From numerous earlier studies it was known, however, that the gas porosities of different tensile test pieces, produced together on the same casting tree, vary considerably.

The establishment of a relationship between the density and the sulphur content of castings also proved impossible in the light of measurements made on the densities of dumb-bell and on the sulphur contents of two other specimens cast simultaneously. The only tendency to be seen in Table VII is for increasing sulphur content to be associated with lower specimen densities. It is also possible to see from Table VII, however, how greatly the sulphur contents of different test specimens made in the same casting can vary.

In one special study, the variations in density and sulphur

Table V
Effects Upon the Tensile Strength, Elongation, Density and Gas Porosity of Centrifugal Castings, of Contamination of the Metal with Different Investment Materials. (Casting was carried out using a reclining carbon crucible, angular acceleration 81 s^{-2} , a maximum speed of rotation of 200 min^{-1} , and a protective mantle of 'forming gas'; casting was in air at 1100°C and the flask temperature was 600°C .)

Material	Contamination	Tensile strength(Rm), N/mm ²	Elongation, %	Density (d), g/cm ³	Gas porosity
New	None	329	47	15.38	Very little
New	Phosphate-bonded investment	361	51	15.41	Not detectable
'Old'*	Phosphate-bonded investment	359	45	15.43	Very little
New	Calcium sulphate-bonded investment	348	46	15.33	Considerable
'Old'	Calcium sulphate-bonded investment	60	15	13.83	Very considerable

*Already used once in casting under the same conditions

content of a dumb-bell casting were determined. Figure 10 shows that in this case there was an approximately linear relationship between density and sulphur content. A relationship between porosity and sulphur content in this study was therefore established. The porosity was about 10 per cent where the sulphur content was 38 ppm, and 13 per cent where the sulphur content was 70 ppm. This corresponds to a pore volume of 49 to 60 mm³ in the tested samples. The sulphur content corresponds, however, to a volume of sulphur dioxide of 320 mm³ at normal temperature and pressure. The discrepancy between the two figures can be explained if the gas is present in the pores under pressure. This is possible, since the pores are formed only after solidification of the outside of the casting has made escape of sulphur dioxide impossible. Account must be taken, however, of the fact that under the conditions the

Table VI
Correlation Between Elongation at Rupture and Sulphur Content in the Case of an 18-Carat Gold Casting Alloy with Various Contents of Sulphur

Elongation, %	Sulphur content, ppm SO ₂
6.5	5.0...21.5
10.5	32...33
14.5	3...5
24.5	45.5...72.0
28.5	6...7
35.0	1...2.5
36.5	0.5...3.0
40.0	12.5...24
43.0	0.5...2

Table VII
Correlation Between Dumb-Bell Densities and Sulphur Contents of Tensile Test Specimens. The Materials Tested were Made by Centrifugal Casting Under the Same Conditions

Density, g/cm ³	Sulphur content, ppm SO ₂
14.20	4.5...21.5
14.30	31.5...32.5
15.00	20.5...25.6
15.04	42.5...77.0
13.36	11.0...23.5
15.45	3.0...5.0
15.46	5.0...7.0
15.50	1.0...2.0
15.6	1.0...2.5

Fig. 10 Dependence of the densities of castings upon their sulphur content

rapid solidification of the metal may not permit completion of reaction between sulphur and oxygen dissolved in the melt, which means that some of the sulphur recorded as sulphur dioxide on later analysis would be trapped in the metal along with oxygen, possibly as sulphide and oxide respectively.

A relationship between the quality of the metal cast and the porosity and sulphur contents of castings is therefore apparent. Moreover, the serious effects, upon the properties of castings, of contamination of the metal by calcium sulphate in the investment material have been demonstrated.

Separation of Sulphides in Cast Jewellery

The investigations described above have shown that gas porosity, caused by sulphur dioxide, occurs especially in castings made from metal containing sulphur. They have also shown that it is particularly bad when the metal used for casting is contaminated with sulphate and is melted under reducing conditions before being cast under oxidizing conditions. In further studies, the influence of sulphide-sulphur on the properties of various alloys was investigated. For the purpose 14- and 18-carat yellow gold alloys and a nickel-white gold alloy (see Table VIII) were used.

The starting materials were fine gold and fine silver, together with copper, nickel and zinc of a purity of over 99.9 per cent. Sulphur was introduced as silver sulphide in the yellow gold and as copper sulphide in the white gold. The components were fused together in a carbon crucible under argon. Castings were made by the centrifugal method and by static casting in a closed vessel. Additions of silver or copper sulphide to the ternary gold-silver-copper alloys resulted in the normal manner in the separation of spherical crystallites of sulphide within the cast alloys, as can be seen in Figure 11. The nickel-white gold alloys after casting, however, displayed regions over which sulphides had separated by eutectic or peritectic crystallization (Figure 12). The solidus temperatures involved are relatively low, so that marked hot brittleness results, similar to that which has already been observed in the case of palladium-containing white golds (31).

While mould filling and surface quality are hardly affected by uptake of sulphur in the case of thin-walled castings which solidify rapidly, a more vigorous reaction occurs with the investment material when larger diameter castings are made from white gold alloys. Figure 13 shows the under-side of a stepped model, cast using alloy 3 (Table VIII), and which has been badly damaged by reaction with the investment material. Gas porosity developed extensively in white gold alloys cast under argon, but was hardly detectable in yellow gold alloys. Pore formation is a consequence of reaction with the investment material, which is promoted by sulphides present in the melt. Casting in air resulted in extensive pore formation in every instance.

In Table IX the tensile strengths and elongations of the alloys under study, and when cast under different conditions, are set out. When cast under argon, the yellow gold alloys, in accord with their

Table VIII
The Compositions (Weight %) of the Sulphide-Containing Alloys Studied

	Alloy	Au	Ag	Cu	Ni	Zn	S
1	14 ct yellow	58.5	30.0	11.45	—	—	0.05
2	18 ct yellow	75.0	18.0	8.95	—	—	0.05
3	14 ct white	59.0	—	25.95	10.0	5.0	0.05
4	18 ct white	75.0	—	12.95	8.5	3.5	0.05

low porosity, show fairly normal tensile and elongation values. The white gold alloy, however, exhibits decidedly lower elongation when cast in air. There is a significant loss of elongation with all the alloys and to a certain extent also, a loss of tensile strength in the case of the yellow alloys. Whether new or old alloy was used had little effect. These results may be attributed to the oxidation of the sulphide with formation of gaseous sulphur dioxide.

Further investigations are necessary to complete a full study of the possible reactions which occur between the various alloys, the atmospheres in which they are melted and cast, and the investment material, in the production of gold jewellery by the lost wax process. The realization that reactions between the melt and calcium sulphate-containing investment materials play an important role is, however, of great significance. It is possible that it may explain, *inter alia*, why gas porosity is so often concentrated just beneath the surfaces of castings.

Summary

- (1) Much information on shrinkage porosity, which is relevant to the casting of carat gold jewellery, can be gleaned from the dental literature on the subject. This literature has been briefly surveyed.
- (2) Little information, however, is available in regard to gas porosity in either dental or jewellery gold alloy castings.
- (3) The incidence of gas porosity in cast gold jewellery is influenced

Fig. 11 (top) Precipitates of Cu_2S in an 18-carat Au-Ag-Cu alloy (Alloy 2, Table VIII)
Magnification: 500x

Fig. 12 (middle) Sulphide inclusions of eutectic structure in a 14-carat white gold alloy (Alloy 3, Table VIII)
Magnification: 500x

Fig. 13 (bottom) Surface of a 14-carat nickel white gold alloy (Alloy 3, Table VIII), badly damaged by reaction with investment material containing calcium sulphate. Low magnification.

Table IX
The Effects of Sulphide upon the Tensile Strength and Elongation of Various Gold Alloys

Alloy no. and colour (see Table VIII)	Material	Method of casting	Casting temperature, °C	Tensile strength (Rm), N/mm ² Readings		Elongation, % Readings	
				1	2	1	2
1 yellow 14 ct	new	Static under argon	1 000	392	393	35	43
2 yellow 18 ct	new	Static under argon	1 050	353	349	35	40
3 white 14 ct	new	Static under argon	1 100	404	367	27	21
4 white 18 ct	new	Static under argon	1 100	397	399	—	11
1 yellow 14 ct	old*	Static in air	1 000	354	353	20	28
2 yellow 18 ct	old*	Static in air	1 050	187	173	7	1
3 white 14 ct	old*	Static in air	1 100	376	350	19	15
4 white 18 ct	old*	Static in air	1 100	409	408	19	12
1 yellow 14 ct	new	Centrifugal in air**	1 050	234	259	1	9
2 yellow 18 ct	new	Centrifugal in air**	1 050	250	273	13	22
3 white 14 ct	new	Centrifugal in air**	1 090	380	383	24	21
4 white 18 ct	new	Centrifugal in air**	1 090	418	428	6	1

*Material already melted once

**Crucible covered with 'forming-gas'

by many factors, some of which counteract the effects of others. Our studies have explored, in a preliminary manner, the possibility that reactions between the metal being cast and calcium sulphate-containing investments might be an important cause of this type of porosity.

- (4) Such reactions, giving rise to the formation of sulphur dioxide and sulphides have indeed been found to give rise to gas porosity.
- (5) Depending upon the composition of alloy being cast and the casting conditions, it has also been found that gas pore formation by reaction with the investment may be accompanied by the formation of various low melting sulphides.
- (6) Further investigations will be necessary in order to complete a full analysis of the various reactions which are possible between molten gold jewellery alloys and investment materials during casting.

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References

- 1 W.H. Crawford, *J. Am. Dent. Assoc.*, 1940, 27, 1459-1471
- 2 G. Ryge, S.F. Kozak and C.W. Fairhurst, *J. Am. Dent. Assoc.*, 1957, 54, 746-754
- 3 W.D. Strickland and C.M. Sturdevant, *J. Am. Dent. Assoc.*, 1959, 58, 69-78

- 4 K. Asgar and F.A. Peyton, *J. Prosthet. Dent.*, 1959, 9, 448-456
- 5 K.F. Leinfelder, C.W. Fairhurst and G. Ryge, *J. Am. Dent. Assoc.*, 1963, 67, 816-821
- 6 E. Custer and R. Diemer, *J. Missouri State Dent. Assoc.*, 1967, 47, 10-15 and 15-20
- 7 G.P. Kelly, *J. Dent. Res.*, 1970, 49, 986-993
- 8 R.L. Coleman, *U.S. Bureau Stand. J. Res.*, 1928, 1, 867-938
- 9 G. Henning, *Brit. Dent. J.*, 1972, 133, 428-435
- 10 W.J. O'Brien and J.P. Nielsen, *J. Dent. Res.*, 1959, 38, 541-547
- 11 J.S. Shell, *J. Dent. Res.*, 1966, 45, 337-342
- 12 R.W. Phillips, *J. Am. Dent. Assoc.*, 1947, 35, 329-342
- 13 J.S. Shell, *J. Am. Dent. Assoc.*, 1931, 18, 2193-2194 (cf. *Internat. J. Orthodontia, Oral Surgery and Radiography*, 1932, 18, 70-73)
- 14 D.A. Keys, *J. Am. Dent. Assoc.*, 1945, 32, 25-30
- 15 A.J. Lewis, *Austral. Dent. J.*, 1976, 21, 76
- 16 T.K. Vaidyanathan, A. Schulman, J.P. Nielsen and S. Shalta, *J. Dent. Res.*, 1981, 60, 59-66
- 17 J.P. Nielsen, *Quintessence of Dent. Technol.*, 1976, (1), 1-
- 18 R.C. Brumfield, *Thermotrol Technician*, 1950, 4, 1-
- 19 A. Wennström, *Trans. Roy. School Dent.*, Stockholm and Umeå, No. 2. Public. Umeå Res. Library, 1958, Series 2.2.
- 20 E. Sahs, *Iowa Dent. J.*, 1958, 44, 258-
- 21 R. Okuda *et al.*, *Bull. Tokyo Med. Dent. Univ.*, 1969, 16, 239-249
- 22 H. Shahani, 'Solubility of Hydrogen in Metals and its Effect on Pore Formation and Embrittlement', Dept. of Casting of Metals, Royal Inst. Technol., Stockholm, 1984
- 23 F. Oktem, 'Porosities in Gold Castings and Sprue Design', Doctoral Thesis (Istanbul), 1970, 2, 195-203
- 24 M. Myers and E.A. Blythe, *Met. Technol.*, 1981, May, 165-170
- 25 H. Hering and K. Eichner, 'Leitfaden Zahnärztl. Werkstoffe und Ihre Verarbeitung', Berlin, 1967
- 26 E. Raub, *Giesserei*, 1936, 23, 111-114
- 27 E. Raub, F. Distel and U.A. Schall, *Mitt. Forsch. Inst. Edelmetalle*, (Schwäbisch Gmünd), 1937, 11, 43-52
- 28 H. Shahani and L. Wictorin, 'Solubility of Dry Hydrogen in Liquid Gold, Gold-Copper and Gold-Palladium Alloys at One Atmosphere Pressure', in ref. 22
- 29 E. Raub and M. Engel, *Mitt. Forsch. Inst. Edelmetalle* (Schwäbisch Gmünd), 1939, 13, 1-12
- 30 K. Alasafi, Ch. J. Raub and W. Plate, *Metall.*, 1982, 36, 756-762
- 31 E. Raub, B. Wullhorst and W. Plate, *Z. Metallk.*, 1954, 45, 533-