Brazes for jewelry, silverware, and objets d’art merit separate consideration from industrial brazing alloys because, in addition to providing joints that are mechanically durable (in terms of their strength, ductility, and wear resistance), they must satisfy two additional and fundamentally different criteria specific to this usage: They must match the caratage and the color of the components. The surface texture of the solidified filler metal and its resistance to corrosion also must not differ greatly from that of the joined parts, so that any joints remain essentially invisible to the naked eye (Fig. 1).

Some jewelry manufacture is highly automated, like much other industrial assembly. A good example is silver and gold chain production, in which the links are formed, brazed, and finished on fully automatic machines at many tens of links per second.

In earlier times, chain was handcrafted, and premium-quality items are still made this way. Chain represents the oldest form of jewelry, and foxtail-style chain dating from 2500 B.C. has been excavated from the city of Ur. It remains one of the most popular styles, although well over 200 other varieties of chain are currently available.

In mass-produced chain making, the links are fashioned from stock wire or tape. This may be a homogeneous precious alloy or cored with base metal. If the latter, during the chain-forming process, the core is dissolved out, prior to brazing, thereby reducing weight. The links are formed into chain by machines and removed as cut lengths. The brazing operation is by a powder method, which involves tumbling the chain in a non-gold, silver-base braze powder. It is then re-tumbled in talc to remove braze powder adhering to exposed surfaces, leaving it only in the gaps of the links. The chain is then brazed by passing the prepared chain through a belt furnace in an inert atmosphere.

Brazes for gold jewelry

Most readers will be familiar with the term carat. It is a unit for measuring the purity of gold and, quite separately, as the mass of precious stones. On the scale of gold purity, 24 carat (karat in the United States and Germany) represents pure gold. Thus, an 18 carat gold alloy contains 18/24 (i.e., 75%) weight fraction of the precious metal. Quality items of jewelry are made with yellow gold of 18 or higher caratage. The word carat actually derives from the Arabic word quirrat, meaning seed, and the weight of a semiprecious carob seed was taken as one carat. Nowadays, by definition, a one carat gemstone has a mass of 0.2 gm (0.00705 oz).

Brazes for carat gold jewelry must meet or exceed the fineness/caratage of the component piece parts of the assembly for it to meet the national fineness/caratage standards and marking or hall-marking regulations for jewelry.

New 22-carat gold solders

The term “solder” in jewelry manufacture is equivalent to the term “braze” in metallurgy. Gold solders of 22 carat composition based on the ternary combination of gold, silicon, and germanium take advantage of the deep eutectic valley that extends through the ternary phase diagram. This eutectic, which intercepts the 22 carat fineness, is illustrated in Fig. 2. In common with the industry standard gold solders in the electronics industry, foil can be manufactured by hot rolling and wire by hot extrusion. Strip casting is another possibility, but strip cast foils of carat gold-germanium-silicon alloys are brittle, because the hard metastable intermetallic Au3(Si,Ge) forms when the cooling rate exceeds 5°C/s.

Ductility can be restored by heat treating the foil at 285°C (545°F), which is 0.9T solidus, for 20 minutes or more (Fig. 3). No satisfactory flux has been identified for gold-silicon-germanium alloys or, indeed, for the industry-standard gold-
silicon and gold-germanium eutectics. Silicon and germanium react with oxygen when heated to form stable refractory oxides on the free surfaces, which impede wetting by these alloys. Rosin fluxes have been found to be ineffective in either dissolving or disrupting these oxides, and stronger acids or halogens corrode the alloys, owing to the large electrochemical potential difference between gold on the one hand and germanium and silicon on the other.

Flux mixtures
Fluxes based on mixtures of salts and hydroxides of the alkali metals show some promise and have the merit that the residues are soluble in water. The fluxing mechanism, in this case, is believed to involve a combination of oxygen exclusion and chemical attack of the refractory oxides. Both the jewelry and the electronics packaging industries would benefit from more research in this area.

The binary gold-silicon and gold-germanium alloys can be successful as solders if the joining operations are carried out in a nitrogen atmosphere with low oxygen and water vapor content (~5 ppm in total). These and the ternary gold-germanium-silicon alloys can be made more tolerant to the joining environment by protecting the solder foil or wire with a coating of gold that is impervious to oxygen.

An alternative approach that is widely practiced in the electronics industry with the constituent binary solders is to dip preforms of the filler metal in hydrofluoric acid (then rinse and dry) immediately prior to use. This treatment strips both the oxide and the near-surface nonmetal, and hence significant reoxidation does not occur until more of the nonmetal has had an opportunity to diffuse through and oxidize at the surface. The shelf life of solder so prepared is short, typically 30 minutes at room temperature, but is adequate for handcrafting of jewelry.

Solder foil
A 22 carat solder foil has been successfully developed for yellow gold jewelry alloys. It comprises a core that is slightly deficient in gold and also the light element silicon, with respect to the eutectic valley linking the Au-3Si and Au-12.5Ge binary eutectics. It is coated with a gold plating to inhibit formation of dross and thereby facilitate wetting and spreading of the solder.

The thinness of the plating means that preforms have a finite shelf life, although it is several months. The core alloy is of composition 90Au-8Ge-2Si, which has a melting range of 362 to 382°C (684 to 720°F). The application of the gold coating of sufficient thickness raises the overall caratage to 22, and reduces the melting range to 362 to 370°C (684 to 698°F). In jewelry terminology, the two-metal structure of the preforms is referred to as a “double” or “onlay.”

The requisite protective atmosphere conditions for this solder (~5 ppm combined oxygen and water vapor) can be made by drawing nitrogen gas off a liquid nitrogen tank. The inlet needs to be made leak-tight, but the outlet beyond the mouth of the furnace can be left open, provided the nitrogen flow rate exceeds 0.5 m/s. This gas velocity is faster than back diffusion, and hence the flowing nitrogen maintains low oxygen and water vapor levels in the furnace. Because of good heat transfer from the heating elements via the nitrogen at near-atmospheric pressure, the soldering cycle on jewelry items can be completed rapidly.

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**Gold-base eutectic solders**

<table>
<thead>
<tr>
<th>Eutectic composition</th>
<th>Actual caratage</th>
<th>Color</th>
<th>Melting point, °C (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-3.2Si</td>
<td>23.2</td>
<td>Light yellow</td>
<td>363 (685)</td>
</tr>
<tr>
<td>Au-12.5Ge</td>
<td>21.0</td>
<td>Pale yellow</td>
<td>361 (682)</td>
</tr>
<tr>
<td>Au-20.0Sn</td>
<td>19.2</td>
<td>White</td>
<td>278 (532)</td>
</tr>
<tr>
<td>Au-24.0In</td>
<td>18.2</td>
<td>Gray</td>
<td>458 (856)</td>
</tr>
<tr>
<td>Au-25.4Sb</td>
<td>17.9</td>
<td>White</td>
<td>360 (680)</td>
</tr>
</tbody>
</table>

*Some of these are used for engineering applications, and are possible candidates as filler metals for jewelry.*
Although the furnacing requirements are modest, they are more sophisticated and expensive in terms of capital expenditure than a simple set of torches, which means that the main area of application would be for jewelry manufacture offering sufficient profit margins.

The joint quality resulting from this plated solder foil at a process temperature of 425°C (800°F) is excellent, as demonstrated by the T-joint shown in Fig. 4. The spread and filleting of the solder are comparable to that possible with conventional high-temperature 22 carat braze with flux, but the low-temperature solder offers the advantages of not requiring post-process cleaning to remove flux residues, and of not noticeably softening the gold jewelry items. As made, the joints appear whitish with respect to the 22 carat yellow gold jewelry, but the color match is readily restored by a modest temperature heat treatment, at 285°C (545°F), maintained for at least 120 minutes in a shroud of nitrogen.

**Joint microstructure**

The yellowing effect of the heat treatment correlates well with the joint microstructure. On heating, the morphology of the germanium-silicon precipitates throughout the solder, changing from dendritic to spheroidal, so that the same proportion of this phase accounts for a smaller proportion of the area of the free surface of the alloy than it does prior to the heat treatment. In consequence, the yellow-gold matrix becomes dominant, and the overall color of the alloy favorably alters accordingly.

The mechanical integrity of joints made to 22 carat gold substrates has been assessed in lap shear and peel resistance tests, with joint areas in the waisted region of 2 mm x 2 mm. Joints always failed in the 22 carat gold substrate rather than through or adjacent to the joint. For the reasons explained in Chapter 4, section 4.3.3, this result should not be taken as evidence that the joint is stronger than the parent materials.

Such a presumption neglects the role of stress concentration in this style of joint. The important metric is that joint shear strengths typically exceed 210 MPa (30 ksi), with good peel resistance and fracture toughness, and are therefore adequate for jewelry applications. Likewise, corrosion tests, designed to assess the susceptibility of joints to degradation from skin acids and household chemicals, did not reveal any deficiencies in the joints.

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Visit www.asminternational.org to view a sample chapter or to order a copy of *Principles of Brazing*.