

# Gold and Gold Alloy foams

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## Abstract

**The possibilities to manufacture gold-based foams are explored. Gold powder and various powdered alloying elements are mixed with a small volume fraction of a gas-releasing blowing agent. The blend is compacted to a dense precursor, which is then melted in a further step in order to trigger foam formation. We find that gold-silicon alloys containing 2–3 wt.% of silicon or around 8 wt.% of germanium can be foamed using  $\text{TiH}_2$  or  $\text{ZrH}_2$  as a blowing agent. Foams with about 85% porosity are obtained.**

## Introduction

Metals can be foamed applying a variety of processing methods. 'Foaming' means dispersing gas bubbles in a melt and allowing them to arrange into a state of transient equilibrium. A solid metal foam is obtained by solidifying a liquid foam at a given instant, usually near maximum volume expansion [1]. As liquid foams contain gas bubbles completely surrounded by the liquid phase, solid foams are materials with closed porosity. Such materials, especially those based on aluminium alloys, have good mass-specific properties, such as a high elastic stiffness and are therefore being considered useful materials for light-weight construction. Due to their strongly non-linear crush behaviour metallic foams are also good mechanical energy absorbers [2,3]. Currently there is a small market for aluminium foams and a few companies producing aluminium alloy foams. Applications range from parts for mobile lifting systems, an 'Ariane V' rocket adaptor and crash absorbers for a light city railway car [4].

Besides foaming, there are a number of other ways to process metals into porous, spongy or other cellular states: By applying powder metallurgy, investment casting, electroplating or electrodeposition [3,5], just to name the most common ones. As an example, macroporous gold has been produced by filling the interstices of polymer sphere packings with gold powder, pressing the mix, removing the polymer and sintering. The skeletal plates of marine echinoids were used as templates that were then gold-coated chemically to create microporous gold with pore sizes around 15  $\mu\text{m}$  [6]. Even nanoporous gold can be manufactured by selective de-alloying of Ag-Au alloys [7] or by using colloidal crystal templates from stacked latex microspheres and filling the interstices with colloidal gold particles [8]. Alternatively, micro-templates can be coated by electrochemical plating to manufacture pure porous gold with up to 77% porosity [9].

In the following, we will discuss the possibilities to foam gold alloys in the narrow sense described above, i.e. by generating gas bubbles in a liquid gold alloy. Gas bubbles injected into a liquid will float to the surface and burst there unless the melt contains stabilising particles that adhere to the bubble surfaces and prevent the bubbles from merging with each other. Aluminium alloy foams are stable because they contain oxide particles or other non-metallic particles such as silicon carbide [10]. Other metals such as zinc [11], lead [12] or steel [13] can be foamed following the same principles. One particularly successful method comprises mixing aluminium or zinc powder with the gas-releasing blowing agent titanium hydride ( $\text{TiH}_2$ ), compacting this mixture and melting it thereafter. During melting the blowing agent releases gas and creates bubbles [14]. The oxides present in the melt stem from the oxide films present on and inside the former powder particles and remain in the compacted powder and in the final foam [10,15,16].

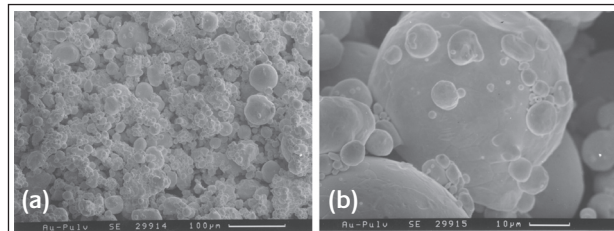
When trying to transfer this foaming method to gold alloys, one encounters two problems. First of all, the melting

point of gold – 1064°C – is much higher than the decomposition range of TiH<sub>2</sub> – about 350 to 800°C [17] – and therefore it can be anticipated that TiH<sub>2</sub> is not suitable for foaming pure gold. Second, gold does not contain oxides which could stabilise the gas bubbles. Although it is known that the blowing agent particles themselves can act as stabilisers [18], their volume content is usually low and it is expected that additional measures for stabilising gold foams are necessary.

The strategy followed in this work is to alloy gold with a selection of elements in order to both lower the melting point so much that TiH<sub>2</sub> can be used as a blowing agent, and to allow the alloying elements to act as stabilisers, either directly or via the generation of non-metallic constituents. In addition to TiH<sub>2</sub>, two further hydrides were tested, ZrH<sub>2</sub> and MgH<sub>2</sub>.

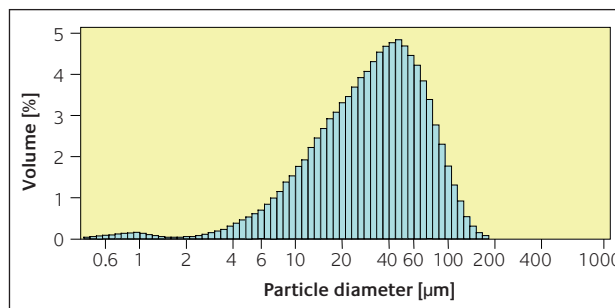
## Experimental

Gold powder was provided by C. Hafner (Pforzheim, Germany) who used the Plasma Rotating Electrode Process (PREP) to atomise rods of pure gold. The powders were examined by scanning electron microscopy and characterised in a laser particle size analyser. Figure 1 shows two images at different magnifications, illustrating the wide range of particle sizes and the near-spherical shape of most of the particles. This shape is typical for such PREP powders. The particle size distribution in Figure 2 yields a mean value of ≈40 μm ( $d_{50}$  = 34 μm) and shows that there is a significant fraction of smaller particles residing on the larger ones as



**Figure 1**

SEM images of gold powder used. (a) low magnification, (b) higher magnification



**Figure 2**

Particle size distribution of the gold powder as obtained by laser particle analysis

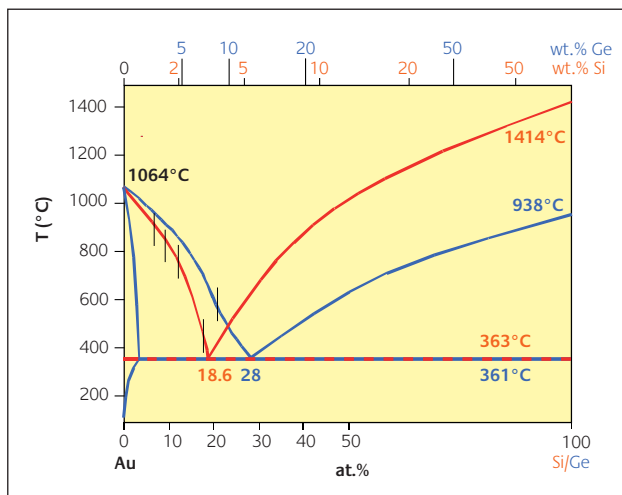
satellite particles, see Figure 1b. In addition, some very large particles and flakes were detected. From the experience with aluminium foams it can be expected that these powders should be compactable without encountering major problems.

The alloys were selected by screening the available phase diagrams and searching for systems in which a small addition of an alloying element reduces the melting point considerably

**Table 1**

Alloys and blowing agents used for foaming. Extrusion conditions and resulting precursor densities are given.  $T_{pre}$  = temperature of pre-heating;  $p_{peak}$  peak pressure occurring at beginning of pressing;  $\rho_{calc}$  and  $\rho_{expt}$ : calculated and measured experimental density; relative density =  $\rho_{expt}/\rho_{calc}$ ; n.d.: no determination of density because extruded material was too rough. Asterisk in 1st column: expansion data for these materials given in Figure 4

no.	alloy [wt.%]	blowing agent [wt.%]	$T_{pre}$ [°C]	$p_{peak}$ [MPa]	$\rho_{calc}$ [g/cm <sup>3</sup> ]	absolute $\rho_{expt}$ [g/cm <sup>3</sup> ]	relative [%]
1	Au	none	600	300	19.30	19.17 ± 0.02	99.3
2	Au	1% TiH	500	525	18.63	18.37 ± 0.04	98.6
5*	AuSi1	1% TiH	350	600	17.40	17.02 ± 0.07	97.8
8*	AuSi1.5	1% TiH	350	1125	16.85	16.40 ± 0.06	97.3
13*	AuSi1.5	1% TiH	350	675	16.85	16.50 ± 0.41	97.9
14*	AuSi2	1% TiH	350	810	16.33	15.79 ± 0.06	96.7
16	AuSi2	1% TiH	350	1020	16.33	n.d.	n.d.
6*	AuSi2	1% TiH	350	1035	16.33	15.87 ± 0.05	97.2
9*	AuSi2	1% ZrH	300	930	16.56	15.88 ± 0.1	95.9
11*	AuSi2	1% MgH	300	1005	15.53	14.74 ± 0.06	95
3*	AuSi3	1% TiH	450	1050	15.38	n.d.	n.d.
12*	AuSi2Cu4.5	1% TiH	350	1050	15.61	14.62 ± 0.07	93.7
4	AuAl2	1% TiH	600	187	16.65	16.84 ± 0.04	100.0
7	AuAl2	1% TiH	350	675	16.65	16.45	98.8
10	AuSn5	1% TiH	225	885	17.31	17.07 ± 0.14	98.6
15	AuGe8	1% TiH	350	630	15.46	14.14 ± 0.09	91.



**Figure 3**  
Phase diagram of Au-Si and Al-Ge alloy systems (redrawn from Ref. 20).  
Short vertical dashes indicate the compositions used

and yields an extended semi-solid range. Figure 3 shows the phase diagram of the system Au-Si which eventually led to the best results. Small additions in terms of mass lead to the formation of a very deep eutectic that solidifies at 363°C. At such temperatures and above, the hydrides that are commonly used as blowing agent for aluminium alloys release sufficient amounts of hydrogen. Si is practically insoluble in gold. No stable intermetallic phases are observed, but the existence of metastable phases is known [19].

Other alloy systems selected were Al-Ge, Au-Al, Au-Sn, and the ternary alloy Au-Si-Cu. Al-Ge is very similar to Al-Si with the difference that more Ge is required to lower the melting point of gold and that Ge is soluble in Au at small concentrations, see Figure 3. Both Al and Sn lower the melting temperature of gold, form intermetallic phases with gold and are soluble. The corresponding phase diagrams can be found in Ref. 20.

The blowing agent  $TiH_2$  was purchased from Chemetal (Frankfurt, Germany),  $ZrH_2$  from Chempur (Karlsruhe, Germany),  $MgH_2$  from Goldschmidt (Essen, Germany). All these powders have a size distribution with  $d_{50}$  in the range of 13 to 20  $\mu m$ .

Powders were mixed in a tumbling mixer for 30 minutes in the fractions given in Table 1. In some cases, mixing was not uniform and some of the lighter powder was found on top of the mixture. In such cases, manual stirring was applied until the powder blend appeared to be visually uniform.

Powder compaction was done by extrusion. For this, 100 g of powder mixture were first pre-compacted at room temperature and 250 kN pressure to tablets of 29 mm diameter in a cylindrical die. Two (three for experiment no. 16) such tablets were loaded into the extrusion die followed by a graphite disk of the same size. The die was pre-heated for about 2 hours at the temperature  $T_{pre}$  given in Table 1, after which the material was extruded to wires of 9.5 mm diameter. This corresponds to an extrusion ratio of 9.3. The extrusion peak pressure  $p_{peak}$  ranged between about 200 and 1100 MPa. After extrusion, the density was determined by

buoyancy measurement, see Table 1.

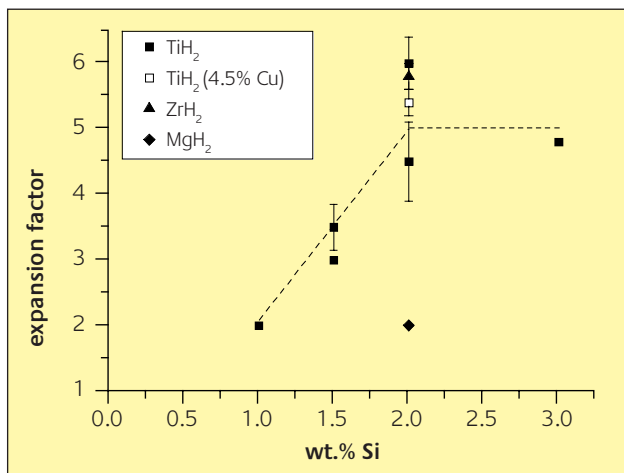
For foaming, a furnace was pre-heated to a temperature 50 K above the liquidus temperature of the respective alloy and was left there for some time for temperature equilibration. After this, a piece of the pressed material, about 1 cm long, was put into the furnace and was left there for heating and foaming. The sample was exposed to air all the time. The foaming process was followed by visual observation. In some cases the pressed material started to foam. The foaming process appeared similar to the foaming of other metals: after an initial expansion stage, a maximum volume was reached. Then, foam collapse was observed which eventually destroyed the foam. After a picture of the overall foaming course had been obtained, the foaming process was interrupted in further experiments at or near maximum expansion by taking the samples out of the furnace and cooling them in a stream of cool air. Foams which could be preserved in a state near maximum expansion were used for further analysis. After measuring the density (or porosity), the foam was sectioned and the cell structure observed.

## Results

Extrusion led to a good consolidation of the powder to wires in most cases. The peak pressure needed to initiate flow shows considerable scatter. Lower pre-heating temperatures required higher pressures in most cases. Except for experiments 3 and 16 the surface of the wires was smooth and the wires all showed some bending ductility. The density values given in Table 1 indicate that densification was best in pure gold, followed by Au-Al and Au-Sn. The powder mixtures alloyed with Si and Ge showed the highest level of porosity.

In the foaming experiments the different alloys behaved differently. No notable or just a small volume expansion was observed for pure Au, Au-Al and Au-Sn alloys. After cutting, these specimens showed some pores of different sizes distributed all over the sample, but the total pore volume was small and pore distribution was irregular. It was obvious that these alloys in the current composition are unsuitable for foaming.

In contrast, Al-Si and Al-Ge yielded much better results. In all cases, the extruded powder mixtures started to expand after some time in the furnace. Foaming took place in a smooth and continuous way as it is known from aluminium alloys. The resulting foams at near-maximum expansion had expanded to 2 to 6 times the original precursor volume. The volume expansion factor defined as the ratio of foam volume to original precursor volume depended on the silicon content in the sample, see Figure 4. Below a silicon content of 2% expansion factors up to 3.5 are reached, whereas for 2% Si an expansion factor of more than 6 was found. For more than 2% Si the expansion factor appears to remain at this level. Replacing  $TiH_2$  by  $ZrH_2$  did not change the foaming behaviour and produced very similar foams, whereas  $MgH_2$  did not yield satisfactory results at all. Addition of 4.5% Cu did not have a



**Figure 4**

Volume expansion factors for various Au-Si foams and a AuSi<sub>2</sub>Cu<sub>4.5</sub> alloy foam produced with different blowing agents. Each point represents foaming experiments based on one of the extruded alloys marked by an asterisk in Table 1. Error bars specify a range whenever more than one experiment was carried out on the same batch of extruded material. The dotted line is just a guide line

pronounced effect on foaming. The sample containing 8 wt.% Ge expanded to 3.5 times the original volume.

The best foam obtained is shown in Figure 5a. This structure which has expanded to about 6 times the original volume – and therefore contains about 84% porosity or, equivalently, has a mean density around 2.5 g/cm<sup>3</sup> – shows a diversity of pore sizes. The largest visible pore is about 4 mm in diameter.

The foam did not appear shiny since both the outer surface and the interior cell walls were rough. Immediately after foaming and cooling the foams had a silvery colour. After a few hours at room temperature the colour changed to what can be described best as light ochre. The micrograph in Figure 6 reveals that the cell walls are rather jagged. The high volume fraction of silicon (2 wt.% corresponding to about 14 vol.%) is reflected by the dark silicon phase in the light gold matrix.

Au-Ge foams assumed a clear bluish hue after foaming which could be polished off. The copper containing AuSi<sub>2</sub>Cu<sub>4.5</sub> alloy had turned into a silvery colour.

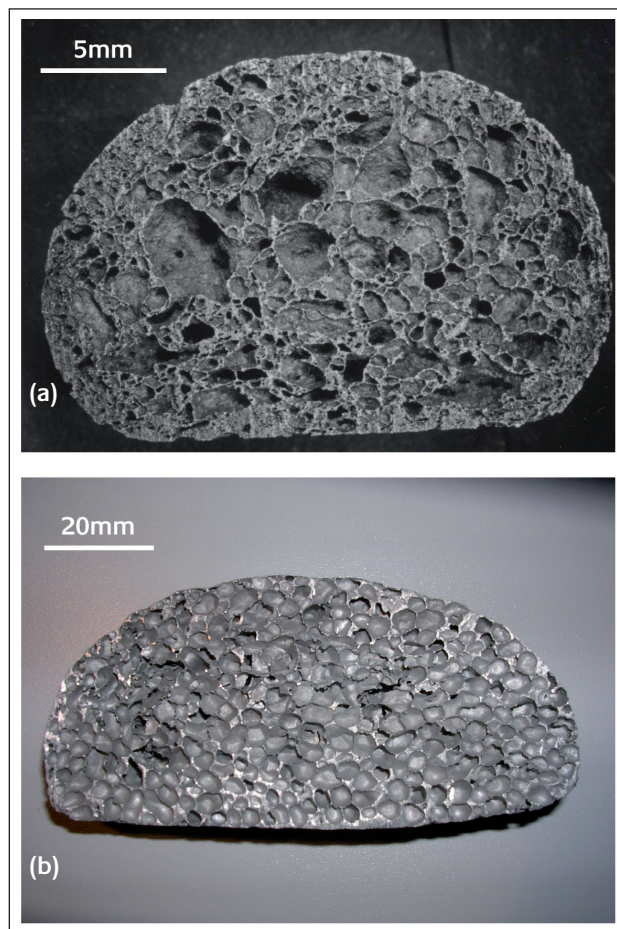
## Discussion

The study showed that Au-Si alloys can be foamed by using a procedure very similar to that used to foam aluminium or zinc alloys. Both TiH<sub>2</sub> and ZrH<sub>2</sub> are well adapted to the low melting point of the deep eutectic of this alloy. Addition of silicon leads to a pronounced stability of the foam. It could not be clarified how silicon acts as stabiliser. As the silicon powder contains 0.6 wt.% of oxygen – as measured by hot gas extraction – one could assume that silicon oxide acts in a way similar as aluminium oxide in aluminium foams. The same applies to the Au-Ge alloy since Au-Si and Au-Ge have very similar phase diagrams and the germanium powder

most likely also contained oxygen picked up during powder manufacture.

Applying standards of state-of-the-art aluminium foams, the pore structure is inhomogeneous and the quality of the foam is not optimal as one sees when one compares Figure 5a with Figure 5b that shows an aluminium-based foam. However, it is an indication of good foaming behaviour that the entire cross section of the foam appears to have foamed in the same way and that there is no pronounced zone of drainage at the bottom of the foam, although the density of the metal is so high. From the foaming behaviour of other metals it is known that inferior foaming caused by insufficient compaction of the powders or an unsuitable choice of powders often leads to irregular pores and heavy drainage, see e.g. Ref. 10. This is obviously not the case here.

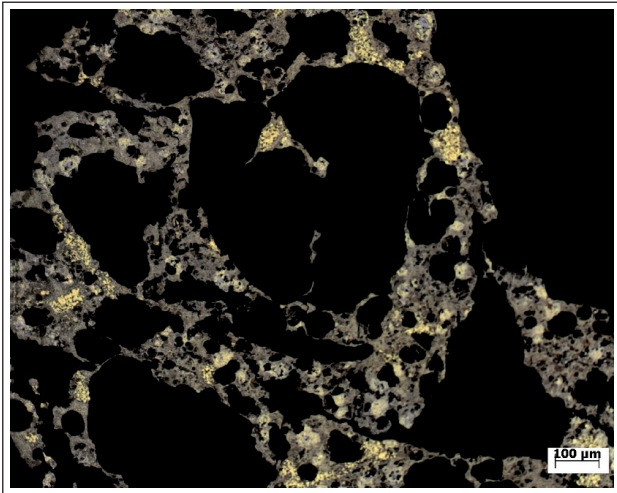
The presence of silicon together with the roughness of the surface can be held responsible for the colour of the Au-Si foam. The colour change of Au-Si during room temperature storage has also been confirmed for non-porous ingots prepared under argon [21]. It was found that only the surface changes its colour, whereas deeper lying layers remain silvery and that the effect is reversible when the alloy is heated again. Most likely, the solidified alloy contains non-equilibrium



**Figure 5**

(a) AuSi<sub>2</sub> foam expanded to 6 times the volume of the extruded precursor. Maximum width of foam is 22.5 mm. Precursor no. 6 in Table 1 was used. (b) AuSi<sub>6</sub>Cu<sub>4</sub> foam expanded to 8 times the volume of the extruded precursor





**Figure 6**

Microstructure of AuSi<sub>2</sub> foam shown in Figure 5. Sample ion-polished and imaged by light microscopy

intermetallic phases that have a silvery colour and diffusion-controlled processes cause the decomposition of these phases into the gold/silicon eutectic at the surface. Similar colour changes have been described for rapidly solidified Au-Ge-Si-based solders, however, not at room temperature but at 285°C [22].

The colours of all the alloys investigated in the current study deviated from those of the usual commercial alloys, see Ref. 23, since our alloys have been selected to optimise foaming behaviour. Moreover, the surfaces are rough and partially oxidised. As not only the occurrence of intermetallics but also that of oxides or other patinas can produce a wide range of colours [24], there are many possible reasons for the observed colours in the foams investigated. Even the blowing agents could lead to further colour shifts, since after decomposition the elements Ti or Zr remain in the metallic matrix.

For two reasons it can be assumed that the quality of the gold alloy foams could be improved by further optimising the process parameters. First, the parameters applied in this study merely represent a first guess based on some theoretical considerations and the experience with other metals. Second, experience also shows that the powder selection and compaction process contains many hidden parameters which have to be fine-tuned. The blowing agent used in this study was untreated hydride powder. Pre-treatment of these powders could lead to a better coordination of gas release and alloy melting, which in turn could further improve the foaming behaviour as it is known for aluminium alloys, see e.g. Ref. 25.

## Conclusions

Low-melting Au-Si and Au-Ge alloys can be foamed to about 6 times the volume of the starting material using TiH<sub>2</sub> or ZrH<sub>2</sub> as a blowing agent. Pore sizes are comparable to those of aluminium foams, while the less uniform pore structure

reflects a more provisional status of development. It was shown that foaming a pure metal such as gold without stabilising particles is not possible and therefore alloying other metals to gold is a necessary pre-condition.

It came as a disappointment that it was not possible to foam gold without strongly interfering with its visual appearance. All additives changed the colour of gold more than was hoped initially. It was not possible to reduce the amount of additives to below a level that would affect the appearance of the metal in such a marginal way that it could be used for jewellery or design objects as originally planned. However, there might be some use for such foams for other industrial sectors: Electrical connectors with unique functionalities, medical implants or materials helping to heat plasmas by laser radiation are just some examples that have been suggested in discussions.

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## About the author



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