Shape memory alloy compositing using gallium-gold putty for use in medical implants

By Jeremy Lee, Supervised by Dr Jennifer Olsen

Introduction

- Shape memory alloys are materials that are able to change shape in response to an increase in heat, returning to an original memorized shape [1], having applications in soft robotics, minimally invasive surgery and implants. However, these materials are malleable when cool.
- Gallium is a metal that melts at 29 degrees Celsius [2], and has antibacterial properties [3].However due to the human body temperature being higher, the melting point of the gallium would have to be elevated to provide stiffness.

The steps of this project includes:

1. Create the Gold-gallium alloy that can increase the melting point appropriately
2. Compositing it into a putty by mixing graphite particles into the gallium [4].
3. Insert resulting putty into a Nitinol tube and tested as a unit.

The expected result would be a composite that would be hard at low temperatures, but retain the shape memory properties when heated.

Figure 1: Gallium putty formed by mixing graphene oxide and gallium., forming a putty that easily can be cut at high temperatures but solid at low temperatures. (Wang et al., 2021)

Methodology

2 attempts of the 1st section of the project were run over the summer. Detailed below is the methodology of the second attempt.

Creating the Gold-gallium alloy was the first part of the experiment. 99.9% gallium and less than 0.01% gold is the ratio to achieve the desired melting point of ~60 degrees Celsius [5].

The sources of the materials was 150mg of gold powder from Sigma Aldritch and 40 grams of 4N gallium from Magnametals.

Gold was used due to its inertness in the human body. Usually when increasing the melting point of gallium, tin will be used, however tin is toxic in the body. [6]

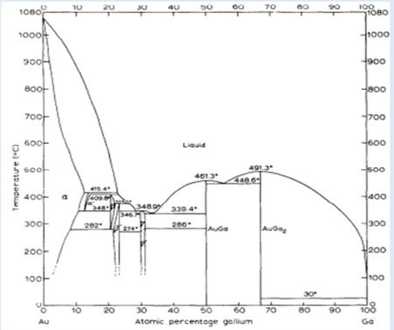

Figure 2: Phase diagram of the Gallium-gold system. Focus being on the furthest right of the graph at the gallium rich portion. [5]

Methodology (cont.) and result

Due to the reactivity of gallium to oxygen in the atmosphere and experience from a prior experiment also conducted during the summer, parts of the experiment had to be conducted in a moisture and oxygen free environment.

1. 75 milligrams of gold powder was measured outside and transferred into custom fused quartz glassware made with the support of the glassblowing workshop.
2. The apparatus was moved into a dry anaerobic glovebox, and 20 grams of gallium was transferred into the glassware.

Figure 3: Gold powder being measured (1st trial)

Figure 4: Usage of the Saffron glovebox. Many thanks for Dr Katarina Novakovic for allowing us to use her glovebox.

3. The glassware was sealed and removed from the glovebox and transferred to the glassblowing workshop.
4. Argon was connected to the sample and removed through a glass bubbler to prevent oxygen contamination during heating.
5. Heat was applied through a propane oxygen torch. The temperature of the sample was tracked with an infrared thermometer and confirmed to exceed the melting point of gold for at least 2 minutes to ensure that the gold has melted.
6. This was repeated twice.
7. Afterwards, the mixture was cooled down and the melting point of the resulting alloy was tested.

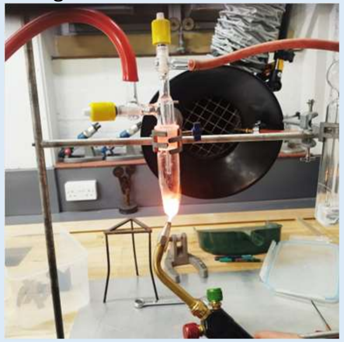

Figure 5: Gallium-gold mixure heated by propane-oxygen torch while under constant argon flow. Many thanks to Dr Robyn Hare for assisting us in making the glassware and use of the workshop for heating the sample.

Unfortunately, the gallium sample still retained the low melting point of the original sample. Some gallium wetting of the quartz glass was visualized after heating, especially around the bottom of the flask where the gold was.

Discussion

I have performed 2 experimental attempts to create a gold-gallium alloy. First round of experiments failed due to microgrooves in the Teflon centrifuge tubes trapping gallium oxide residues, as well as the exposure to oxygen causing gallium wetting surfaces when transferring the sample and also causing supercooling of the gallium, making it behave inconsistently. [2]

Therefore, for the 2nd attempt, I have designed a protocol which removes all sample transferring steps, as well as performing all steps that require handling or heating the gallium in an dry anaerobic environment. However, the oxide layer and the wetting behaviour of the gallium still occurred, especially during heating.

It is difficult to ascertain which procedure was the source of the oxygen infiltration. This problem could potentially be solved by using mechanical to break up the gallium oxide formations or using a larger amount of bulk gold and gallium instead of a powder, however I currently do not have the facilities to attempt this.

Looking forward, I wish to trial making a gallium-tin alloy. This would be much easier due to the higher percentage of tin in the alloy. [7] After which I wish to perform a trial the 2nd stage of the project, which would inform me on how the composite will perform. This mixture would still be useful for soft robotics and mechanisms in which there is no chance of contact with human tissues directly.

References

1. Popovic, M.B., Lamkin-Kennard, K.A., Beckerle, P. and Bowers, M.P. (2019). Actuators. Biomechatronics, pp.45–79. doi:https://doi.org/10.1016/b978-0-12-812939-5.00003-3.
2. Joshipura, I.D., Chung Kim Nguyen, Quinn, C., Yang, J., Morales, D.H., Santiso, E., Torben Daeneke, Vi Khanh Truong and Dickey, M.D. (2023). An atomically smooth container: Can the native oxide promote supercooling of liquid gallium? iScience, 26(4), pp.106493–106493. doi:https://doi.org/10.1016/j.isci.2023.106493.
3. Li, F., Liu, F., Huang, K. and Yang, S. (2022). Advancement of Gallium and Gallium-Based Compounds as Antimicrobial Agents. Frontiers in Bioengineering and Biotechnology, 10. doi:https://doi.org/10.3389/fbioe.2022.827960.
4. Wang, C., Gong, Y., Cunning, B.V., Lee, S., Le, Q., Joshi, S.R., Buyukcakir, O., Zhang, H., Seong, W.K., Huang, M., Wang, M., Lee, J., Kim, G.-H. and Ruoff, R.S. (2021). A general approach to composites containing nonmetallic fillers and liquid gallium. Science Advances, 7(1). doi:https://doi.org/10.1126/sciadv.abe3767.
5. Cooke, C.J. and W. Hume-Rothery (1966). The equilibrium diagram of the system gold-gallium. Journal of the Less Common Metals, 10(1), pp.42–51. doi:https://doi.org/10.1016/0022-5088(66)90044-0.
6. Kimbrough, R.D. (1976). Toxicity and health effects of selected organotin compounds: a review. Environmental Health Perspectives, 14, pp.51–56. doi:https://doi.org/10.1289/ehp.761451.
7. Anderson, T.J. and Ansara, I. (1992). The Ga-Sn (gallium-tin) system. Journal of Phase Equilibria, 13(2), pp.181–189. doi:https://doi.org/10.1007/bf02667485.