

## Alloyed pleasures: Multimetallic cocktails

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The English language insists on unalloyed pleasures, thereby implying that the sensation of pleasure must be pure and not admixed with other emotions. Exactly the opposite rules in metallurgy, where pure metals have few uses and can always be improved upon by alloying. It is true that the civilizational journey of mankind began with the discovery of native metals such as gold and copper as pure metals. In fact this love at first sight of gold several millennia ago has persisted till this day and has its most exuberant expression in India. The Indian women buy pure gold in such quantities every year that it is the only metal that India consumes in relation to its population. In all other metals per capita consumption by India lags behind that of developed nations.

Alloying was an accidental discovery. In the primitive fires in the caves, ores of copper got mixed with ores of arsenic, zinc and tin. Thus the alloying of tin with copper gave birth to the Bronze Age, as bronze was superior in its mechanical properties and made better swords. But the master of them all was steel – an alloy of iron with carbon. Again this accidental discovery led to the production of wootz steel in India. This has been rightly celebrated as the most advanced material of the ancient world, as this steel was used to fashion the Damascus swords. Indian metallurgists also used *panchaloha* and *asta dhatu* (alloys of five and eight metals) for making idols of unmatched precision by mastering the lost wax process.

The 20th century saw the slow transformation of the art of alloying into the science of alloying. The microscope allowed the metallurgist to see a whole world in a grain of metal<sup>1</sup>. Soon it was established that there is a strong correlation between microstructure and properties. Metallurgists could then develop various alloys required for demanding applications in aerospace, nuclear and defence industries. This golden age of alloy development began in the sixties of the previous century and lasted for three decades.

Metallurgists confined themselves to systems where the number of alloying

elements was limited in any one phase. This was partly because as alloys are made with an increasing number of component metals, the database necessary in terms of phase diagram information increases sharply. If the processing variables are superimposed leading to metastable phases and altered microstructures, the possibilities become astronomical. In fact one German scientist estimated the possibilities to exceed the number of atoms in the entire universe! In the presence of such cornucopia metallurgists retreated to produce alloys with a few components and assume that incremental improvement is the only possible route. Binary alloys still produce surprises as witness the recent discoveries of quasicrystals and superconductors<sup>2</sup>. However by and large, metallurgists were reconciled to watch the more dazzling feats in materials science, nanotechnology, nanobiotechnology and bionanotechnology and their mutants.

This impasse has now been broken with three startling discoveries of recent vintage. Metals are mixed in a multi-metallic cocktail to make bulk metallic glasses, multi-functional, superelastic and superplastic alloys and nanostructured high entropy alloys. These discoveries were made in Asia – the first two in Japan and the third in Taiwan. These as-

tonishing developments breathe new life into metallurgy.

The discovery of a metallic glass in 1960 by Pol Duwez was serendipitous, as he quenched liquid melts of gold–silicon alloys at a rapid cooling rate of over one million degrees per second. The liquid froze as glass. The high cooling rates limited the product dimensions to microns. It was only in 1988 that Akihisa Inoue at the Tohoku University, Japan made a path-breaking discovery that by mixing many metals of different sizes together, it is possible to freeze the melt as glass at slow cooling rates of one degree per second. The specimen dimensions reached centimeters. One of the celebrated alloys has zirconium as the main element with addition of titanium, copper, nickel, aluminium and beryllium. Figure 1 displays some possible combinations<sup>3</sup>. These glasses contained a minimum of three metals and occasionally reached giddy proportions of more<sup>4</sup>. An example of the latter is Fe–Al, Ga–P, B, Si.

In addition to the intrinsic interest of metallic glasses being produced at slow rates of cooling comparable to those of the millennia-old inorganic silicate glasses, these possess some unique properties. Figure 2 shows this<sup>5</sup>. Their elasticity is comparable to that of polymers and higher than that of crystalline coun-

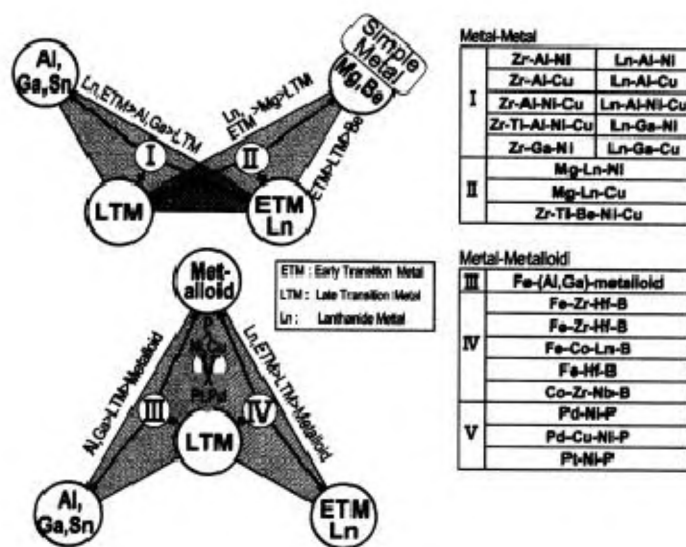


Figure 1. Multicomponents in bulk metallic glasses (ref. 3).

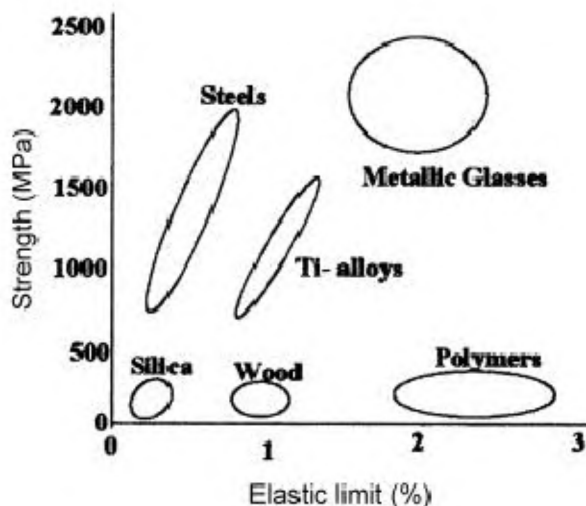


Figure 2. Strength vs elastic limit for bulk metallic glasses compared with conventional alloys (ref. 5).

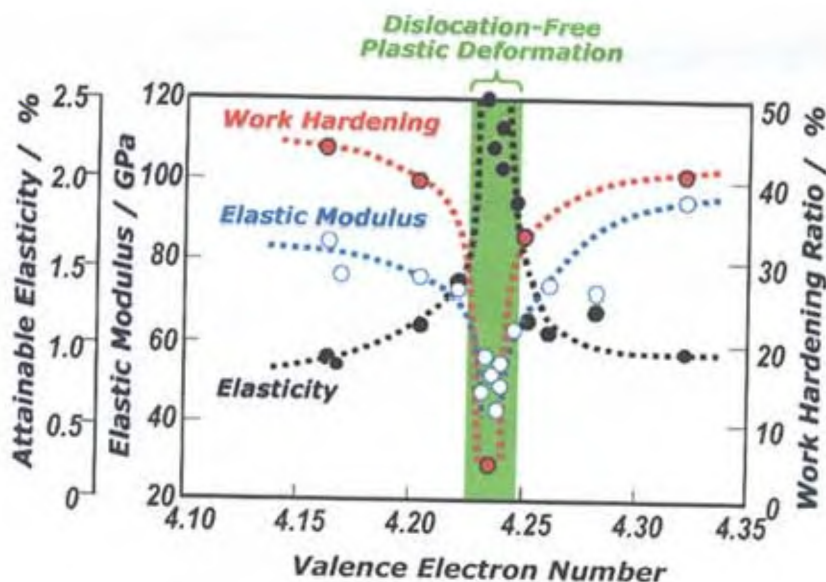


Figure 3. Anomaly in properties of Ti-Nb-Ta-Zr-O alloys (ref. 6).

terparts. Thus metallic glasses have found unusual applications as golf heads and cell phone shells.

The Japanese automobile companies are justly famous for the sleek design and durability of their products. They are a familiar sight on the Indian roads nowadays. No one would have imagined that a car company would come up with a radically new innovation in alloys. The Toyota Central Research and Development Laboratories Incorporated is the Corporate R&D Centre for all the Toyota group companies. In the April 2003 issue of *Science*, Takashi Saito and coworkers<sup>6</sup> from this R&D Centre announced the

discovery of a multifunctional alloy with compositions such as Ti-23Nb-0.7Ta-2Zr-1.2O alloy. The alloy had almost as many components as the authors of this multi-author paper! This paper created sufficient excitement to attract commentators in *Science*, *Nature* and *Scientific American*.

This new group of alloys exhibits a striking combination of 'super' properties. They show an unusual combination of ultra-low elastic modulus and ultra-high strength. This leads to both super elasticity and superplasticity. As a result, these alloys have been christened as 'gum metal' – a somewhat irreverent

way to indicate the rubber-like properties. What is more, they also show Elinvar and Invar behaviour. The term Elinvar indicates the stability of the elastic modulus over a temperature range while Invar indicates the stability of length over a temperature range. It is well known that the coefficient of thermal expansion CTE of alloy is inversely proportional to its melting temperature. This empirical rule suggests that thermal expansion is one of the intrinsic properties of a material which is very difficult to control. Invar alloys were discovered in Fe-Ni system in 1896. It earned C. Guillaume the Nobel Prize for Physics in 1920. However gum metal outperforms these earlier alloys as its properties are invariant over a much wider temperature excursion. The gum metal displays Invar and Elinvar characteristics over a much wider temperature excursion than previously known examples.

The gum metal is not an accidental discovery but based on sound alloy design principles. The Japanese scientists used a combination of Group IV and V transition elements and controlled three 'magic' numbers. They ensured that the electron/atom ( $e/a$ ) ratio was 4.23 to 4.24. The bonding strength with a bond order number of 2.87 and the electronegativity was kept at a certain value with a  $d$ -electron level of 2.45 eV. In addition, a small amount of oxygen was incorporated. Figure 3 shows the anomaly of properties achieved as a function of  $e/a$  ratio. The elastic modulus as well as the work hardening dip to a low value at the magic number of 4.24. The behaviour is illustrated in Figure 4. The superelastic and superplastic behaviour is clearly seen. These unusual properties are explained by Saito and colleagues by invoking new mechanisms for deformation. In most metallic materials, deformation is mediated by dislocations. In the cold worked state the gum metal deforms like clay, without any dislocations along the maximum shear stress plane. The elastic strain is accumulated hierarchically in the alloy. This novel explanation needs further study.

Figure 5 compares various alloys. Again it is clear that the gum metal occupies a niche. This has already attracted commercial applications as spectacle frames and precision screws. Further applications in automotive parts, medical equipment, sporting goods as well as the aerospace industry are anticipated.

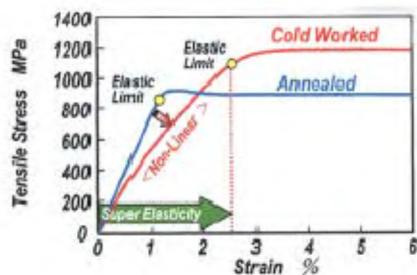


Figure 4. Stress-strain curve of gum metal (ref. 6).

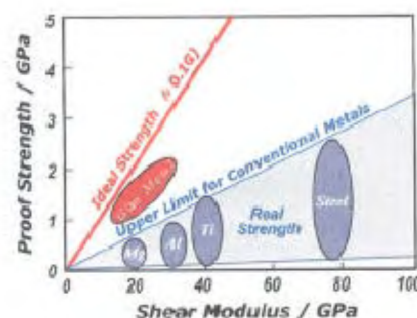


Figure 5. Shear modulus vs proof strength of gum metal (ref. 6).

A completely different route has been followed by Jien-Wei Yeh of Tsing-Hua University in Taiwan. Under a project sanctioned by The National Science Council, Yeh decided to produce high entropy alloys consisting of several metals in equal proportions so that it can no longer be classified as an alloy based on a particular metal<sup>7</sup>. Gibbs phase rule permits the number of phases in equilibrium to increase with the number of components. Thus one might expect a

multicomponent alloy to consist of many phases. In a similar vein one may also expect multinary intermetallics. However it is already known that the number of intermetallics as a function of components increases at first but drops off after four components. Alan Mackay<sup>8</sup> has discussed this problem in complexity. Thus at most one might expect several phases with a few components in each of them. Our ability to deal with this question is hampered by the fact that multinary phase diagrams need to be mapped in many dimensions. Thus even a quaternary diagram cannot be visualized in three dimensions and we need to resort to projections. In this situation Yeh used the argument that entropy of mixing will be a dominant factor and may lead to single phase multicomponent solid solutions in equimolar multicomponent alloys. While this idea needs to be thoroughly tested about its range of applicability, Yeh has synthesized several alloys with 5 to 13 components. Some examples are CuTiVFeNiZr and AlTiVFeNiZrCoCrPd-3at%B. They are forming solid solutions with simple bcc and fcc structures. The alloys exhibit very high hardness that varies widely depending on the number, contents, and species of the component elements. After full annealing at 1000°C for 12 h, the alloys retain their high hardness levels. This work has led to several patents and is submitted for publication.

The multicomponent alloys represent a new frontier in metallurgy. They require hyperdimensions to visualize. If we use a coarse mesh of 10 at% for mapping a bi-

nary system, the effort involved in experimental determination of phase diagrams rises steeply. Thus the effort of experimental determination of a seven component system will be  $10^5$  times that of a binary diagram and will alone need as much effort as has been spent over the last hundred years in establishing ~4000 binary and ~8000 ternary diagrams. While the computation of phase diagrams from first principles has made impressive progress in the last decade, the prospect of calculation of higher order systems is a daunting task. In this scenario we have explorers like A. Inoue, T. Saito and J. Yeh pointing to exciting new alloys with applications. Many of these involve transition metals. There is more waiting to be conquered.

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