

# AMORPHOUS METAL ALLOYS FORM LIKE PLASTICS

*The lack of long-range periodicity and related grain boundaries in amorphous metals gives rise to many novel properties, including ultrahigh strength, improved corrosion resistance, and attractive magnetic properties.*

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**M**etallic glasses, also known as amorphous metals, are basically frozen liquids with amorphous atomic structure formed through bypassing crystallization during solidification. These unique and interesting alloys can be considered as an entirely new class of materials. The amorphous atomic structure and composition results in high strength alloys that can be processed like a plastic, when handled in the appropriate manner. The combination of attractive properties and processing advantages, suggest a new paradigm for the processing and use of high strength alloys. This article gives an overview of Liquidmetal Alloy amorphous metal technology and discusses its potential.

## Amorphous metals history

More than fifty years ago, a German scientist discovered during cooling tin with a rate of roughly a trillion Kelvins per second that the atoms did not have time to find their energetically favorable crystalline positions, and consequently formed an amorphous structure.

In the early nineteen sixties, Paul Duwez at the California Institute of Technology cooled liquid  $Au_{75}Si_{25}$  faster than about a million Kelvins per second, which also resulted in avoiding crystallization during solidification. To establish such high cooling rates, heat has to be rapidly extracted, which restricted the material's geometry in one dimension to less than 50 microns.

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Fig. 1 — The frame for the upscale models of the Vertu mobile phone is made of Liquidmetal alloy because of its high strength, hardness, and scratch resistance. The random yet homogeneous arrangements of the atoms in the amorphous structure provide the unusual properties of the alloys.

The lowest rate by which crystallization can be avoided is called the critical cooling rate. This can be correlated to the largest thickness a melt can be cast in the amorphous state, and this is known as the critical casting thickness.

Prof. Duwez's discovery led to the introduction and acceptance of this new class of materials into the academic community. However, it was not until the early nineteen nineties that bulk amorphous alloys were produced and began to attract tremendous academic and commercial interest. This interest was triggered by the discovery of Liquidmetal amorphous alloys, multicomponent zirconium-based alloys that can be solidified in the amorphous state with cooling rates as low as one Kelvin per second, which results in a critical casting thickness of several centimeters.

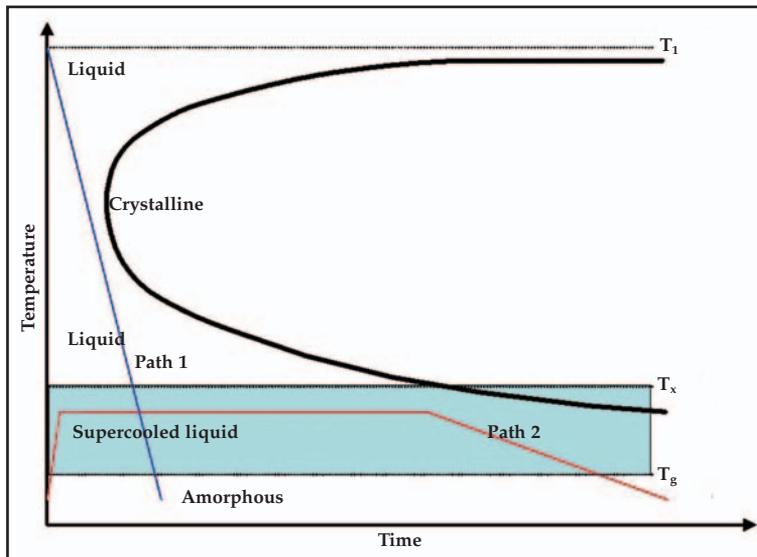


Fig. 2 — Schematic time-temperature-transformation diagram. During any processing, the crystallization nose has to be avoided. Direct casting is carried out by means of Path 1, where the liquid is cooled fast enough to avoid the crystallization nose. On the other hand, material is superplastically formed (SPF) by reheating amorphous “feedstock” material into the supercooled liquid region. During this two-step process, fast cooling and forming can be decoupled.

Today, Liquidmetal alloys that solidify into an amorphous structure with low critical cooling rates contain zirconium, nickel, copper, iron, titanium, palladium, platinum, and gold.

### Glass forming ability

The intrinsic basis for the formation of amorphous atomic structure with low critical cooling rates is their chemistry. Crystallization has two causes:

- **Thermodynamics:** The molten metal is thermodynamically driven to crystallize below its thermodynamic melting temperature. This can be quantified by the energy difference between the undercooled liquid (below thermodynamic melting temperature) and the competing crystal, and is defined as the driving force for crystallization.
- **Kinetics:** The other contribution is the ki-

### Properties of selected Liquidmetal alloys

Property	Zr-based	Pt-based	Au-based
$T_g$ , °C	350	230	130
$T_m$ , °C	~600	~500	~400
$\sigma_y$ , MPa	2000	1470	~1200
Hv 560	400	360	
$\epsilon_{el}$ , %	2	1.5	1.5
Y, GPa	95	95	74
$K_{1c}$ , MPa m <sup>-1/2</sup>	40	80	—
$T_{process}^{Casting}$ , °C	800	650	550
$T_{process}^{SPF}$ , °C	380 to 470	250 to 300	150 to 190

$T_g$  is the glass transition temperature, at which the amorphous phase relaxes into the liquid. It represents an upper limit for the service temperature.  $T_m$  represents the melting temperature,  $\sigma_y$  the yield strength, Hv the Vickers hardness,  $\epsilon_{el}$  the elastic strain limit, Y the Young’s modulus,  $K_{1c}$  the fracture toughness,  $T_{process}^{Casting}$  the casting processing temperature, and  $T_{process}^{SPF}$  the processing temperature region for SPF.

netics, the time required to rearrange atoms in the undercooled liquid to form a crystal.

To easily form amorphous alloys, the energy difference between liquid and crystalline phase must be small, and the time required to rearrange atoms must be long. These two requirements may be met by choosing the constituents of the alloy such that at least two substantially differ in size. This “confusion principle” destabilizes competing crystalline phases and also increases the packing efficiency in the liquid, thereby reducing mobility of atoms in the undercooled liquid state.

In addition, the composition must be close to a deep eutectic, low lying liquidus in the phase diagrams, resulting in formation of molten metals that are stable at relatively low temperatures.

### Amorphous metal properties

Even more than the chemistry of the alloy, the structural arrangement of the atoms within the amorphous structure defines the mechanical properties. The absence of grain boundaries and crystal defects such as dislocations, which are the points of weakness in crystalline metals, results in a large elastic strain limit and very high yield strength, close to the theoretical limit.

As an example, the zirconium-based Liquidmetal alloy possesses a yield strength of up to 2 GPa and an elastic strain limit of about 2%. Upon yielding, the absence of strain hardening results in formation of shear bands in which the strain is highly concentrated, which means that the alloy can fail along a single shear band.

To overcome this limited plasticity, recent efforts have been focused on creating Liquidmetal composites. Alternatively, new alloys have been designed with a high Poisson’s ratio, which results in plasticity of the monolithic material up to 20%. Despite the tendency toward localized deformation, Liquidmetal alloys can be considered to be “tough,” with  $K_{1c}$  values up to 40 to 80 MPa m<sup>-1/2</sup>.

### Processing opportunities

In contrast to most crystalline metallic alloys, Liquidmetal alloys do not require post-cast processing or heat treatment, as all properties are already achieved in the as-cast state. This, together with the absence of a phase transition and the slow crystallization kinetics, opens up an opportunity for a wide range of processing methods.

Fundamentally, they can be separated into two categories. This can be best explained on a time-temperature-transformation diagram, schematically shown in Fig 2. In order to synthesize Liquidmetal alloys, the crystallization nose has to be avoided during cooling from above the liquidus temperature. This is indicated by Path 1.

Direct casting processes can be carried out by means of this path. The advantages of Liquidmetal alloys in direct casting are obvious: Due to the absence of a phase transition, the solidification shrinkage, typically around 5% in crystalline metals, is less than 0.5%. Furthermore, a homogeneous casting down to the atomistic scale can be

achieved because no grain size, solidification pattern, or direction is present.

Because Liquidmetal alloys have composition close to deep eutectics, their melting temperature is low. Zirconium-base alloys melt at around 700°C, and platinum base alloys melt at around 500°C. This compares to about 1800°C for conventional crystalline zirconium alloys, and 2000°C for conventional crystalline platinum alloys.

The low processing temperature can provide several economic benefits, including less heating power, shorter cycle times, less sophisticated tool materials, and longer tool life. A further economic advantage is the precision of the diecasting process and the almost complete absence of solidification shrinkage, Fig. 3.

These processing advantages suggest the possibility of an economic net-shape process. Liquidmetal Technologies already provides several mass-produced net-shape components for electronic casings such as cell phone cases and frames, camera housings, and flash drive casings, Fig. 1.

### Superplastic forming

The unique crystallization behavior of Liquidmetal alloys permits an alternative net-shape processing method similar to superplastic forming. During superplastic forming (SPF) of Liquidmetal alloys, the fast heating and forming are decoupled.

- **Feedstock:** In the first step, an amorphous feedstock material is produced, typically a simple shape such as rods, bars, or pellets. This feedstock material is heated into the supercooled liquid region indicated by Path 2 in Fig. 2.

- **Supercooling:** The supercooled liquid region is the temperature region in which the amorphous phase first relaxes into a highly viscous supercooled liquid before it eventually crystallizes. The viscosity at this temperature permits substantial plastic strain under even moderate applied pressure. The method is similar to the processing of thermoplastics, in which similar forming pressures and temperatures are applied. In contrast to thermoplastics, however, the highly viscous liquid is metastable, which limits the processing window.

- **Process time:** The processing window is alloy dependent, but may include times between minutes and hours in the preferred viscosity range.

- **Process temperature:** Because the processing temperature is even lower than during direct casting, thermal cycling and solidification shrinkage are even further reduced.

- **Isothermal cooling:** During the forming process, the crystallization nose that defines the critical cooling rate during casting no longer has to be bypassed. Therefore, the SPF part may be cooled isothermally at very low rates without compromising the properties of the alloy. This basically eliminates any internal stresses. For example, the solidification shrinkage during SPF of Zr-based Liquidmetal alloys is about 0.2%.

- **Porosity:** The degree of porosity during SPF is drastically reduced, because the forming pres-

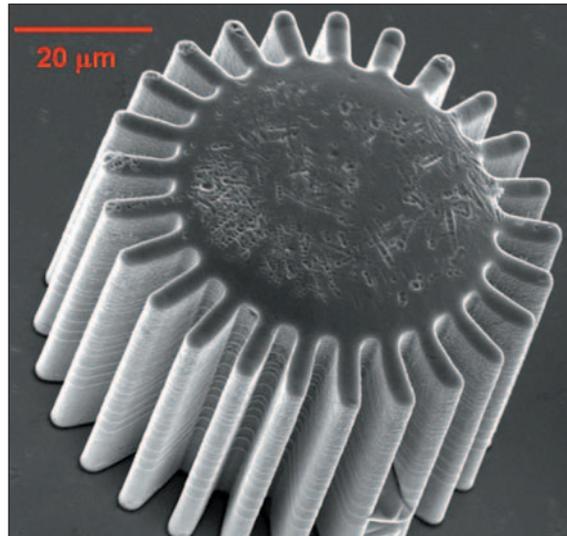


Fig. 3 — Diecasting Liquidmetal enables very high precision because solidification shrinkage is almost completely absent.

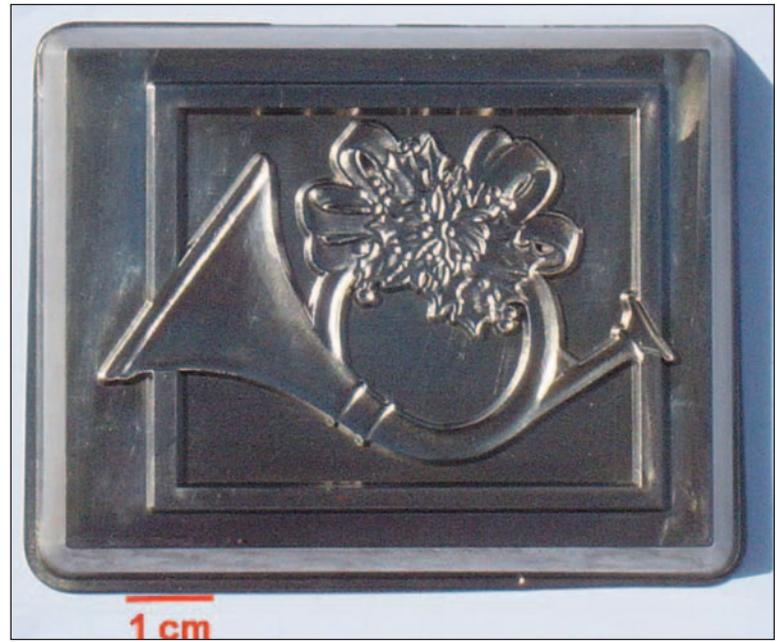


Fig. 4 — The small features in this part show the precise replication possible with Liquidmetal.

sure compresses any existing porosity in the feedstock material so that porosity levels of less than 0.005% are typical.

- **Size limit:** The size limit imposed by the critical casting thickness is also increased if pellets or powder are used.

- **Feature size:** The intrinsic feature limitation of the grain size in crystalline materials is also absent. The small molecular weight (single atoms) and access to low viscosity and a long processing window enable very precise replication of the smallest features, down to the submicron range. An example of microreplication is shown in Fig. 4. ◆

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