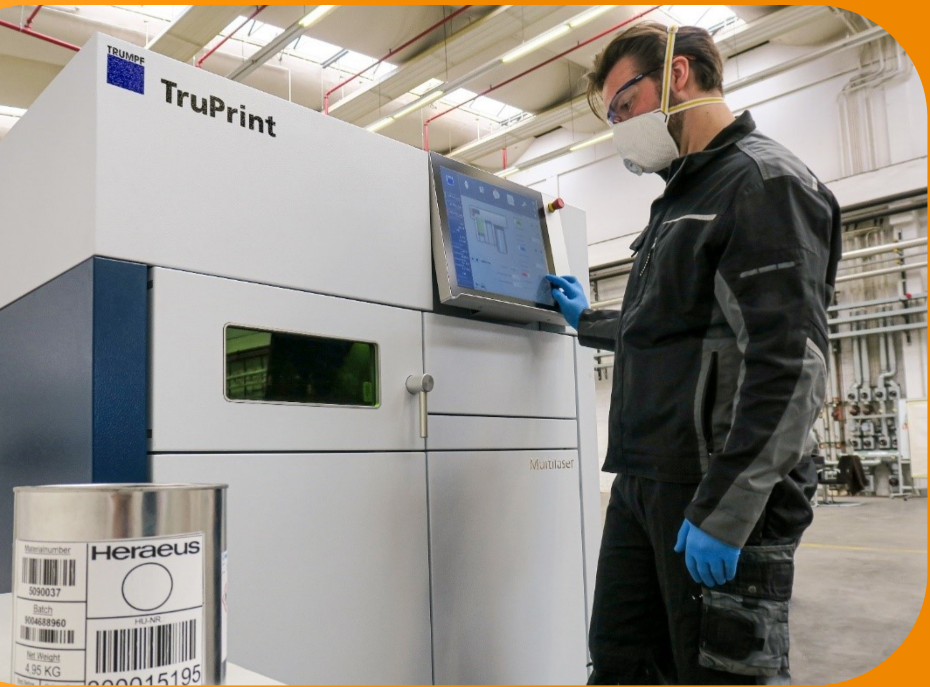
WHITEPAPER



Production of amorphous components via additive manufacturing on the way to commercialization

AMLOY
Amorphous Alloy Technologies

TRUMPF

TECHNOLOGICAL ADVANTAGE THROUGH EFFICIENT PARTNERSHIP.

In recent years, considerable progress has been made in the field of amorphous metals, also known as metallic glasses. Here, new insights were gained into the composition of alloys in order to achieve a better glass forming ability and thus enable larger components.
While the first amorphous alloys usually consisted of two elements, the currently most promising amorphous alloys often consist of four to five elements. Occasionally zirconium-based alloys show the best glass-forming ability, with which the largest component dimensions can be realized.
The first industrial process successfully used for amorphous metals was the melt spinning process. In this process, amorphous strips which are a few micrometers thick are produced by stripping the melt onto rotating copper wheels. In suction casting, the newly developed zirconium-based alloys can be used to produce solid plates up to 3 mm thick, rods or simple component geometries with a diameter of up to 6 mm.

"Newer promising technologies are injection molding as well as additive manufacturing, which enable the production of complex and larger component geometries on an industrial scale."

In injection molding, it is possible to produce near-net-shape components with very good surface quality within approx. 90 seconds. This technology can be used to produce component geometries and sizes that are of industrial relevance and can be manufactured in an automated process with tight tolerances. Depending on the component size, one or more components can be produced in one injection cycle. Often the removal of the sprue is the only post-processing step.

The additive manufacturing of amorphous components offers new possibilities. Due to the targeted melting by laser, a small melt pool is obtained, which allows rapid cooling, thus ensuring amorphous solidification of the melt. Therefore, the size of the component is only limited by the size of the installation space of the equipment. As it is generally the case in additive manufacturing, complex geometries can be realized here as well, which cannot be produced in other manufacturing processes or only at great expense.

Due to the high strength of amorphous metals, wall thicknesses can be reduced, or bionic structures can be used in the component design, thus reducing component weight and production times without negatively affecting the mechanical values.

Heraeus AMLOY and TRUMPF have formed a partnership to further develop 3D printing of amorphous components. The aim of this partnership is to improve the surface quality of printed components while increasing the efficiency of the printing process. Heraeus AMLOY is optimizing the alloy composition and developing the printing parameters, while TRUMPF is optimizing the system according to the requirements in order to enable a market for amorphous additive-manufactured components.

Figure 1: Cooperation between Heraeus AMLOY and TRUMPF in the additive manufacturing of amorphous components

In addition to optimizing the printing process itself, the company is also working on the realization of components made of other amorphous solidifying alloys.
Due to their material properties, a wide range of applications is offered, so that a large number of industries, such as medical technology, aerospace, lifestyle or industrial applications are working on the development and use of amorphous components.

AMORPHOUS ALLOYS.

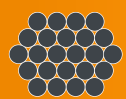
Amorphous metals are subcooled frozen melts. This means that the phase transformation from liquid to solid is suppressed and the molten state is frozen. Due to the missing phase transformation, a **low shrinkage of <0.5 %** results. Furthermore, no grain and phase boundaries are formed which serve as accumulation of impurities and promote corrosion. As the only material amorphous metals combine physical properties that are normally mutually exclusive. Thus, the material has a **high hardness and strength combined with high elasticity**. This results in completely new areas of application.

As already mentioned, the high strength of the components makes it possible to design thinner, material-saving and thus lighter components. This is of great importance in **miniaturization** in robotics or medical technology but is also highly relevant in aerospace and e-mobility in order to save weight.
The high yield strength combined with an **elastic elongation of almost 2%**, which is significantly higher than that of crystalline materials, offers advantages for components that experience spring properties, damping or high loads, such as implants, sensors, hinges or spring elements. The material shows a flexural fatigue strength at a frequency of 25 Hz of about 400 N/mm^2 at a number of cycles of more than one billion cycles. To achieve these values, amorphous metals require a **good surface quality**. It is therefore advisable to polish the heavily loaded areas to counteract crack initiation.
Amorphous metals are **low-temperature ductile**, so they are well suited for extremely low temperature applications. This is one of the reasons why this class of materials is so important for the aerospace industry.
At temperatures above 400 degrees Celsius, the material begins to flow similar to polymers, that means it can be molded thermoplastic.

Another advantage of amorphous metals is their **isotropic behavior**. Consequently, components have the same material properties in all spatial directions. Advantages arise, for example, in additive manufacturing, since the installation space can be optimally used in conjunction with the orientation of the component.

AMLOY-ZR01.

AMLOY-ZR01 is a beryllium-free zirconium-based alloy with good glass forming properties. During most alloys are compatible with good glass forming properties from five elements AMLOY-ZR01 comes with four elements. The material is composed as follows: 70 % zirconium, 24 % copper, 4% Aluminum and 2 % niobium (data in weight %). The density of the material is 6.7 g/cm^3. In combination with the high bending strength of 2,300 MPa and a tensile strength of 1,600 MPa for cast components, material can be saved by changing the design. Thus, components with a 20% lower weight , compared to titanium components, can be produced. Due to its biocompatibility, the material is also suitable for medical technology or medical implants. The material has passed the cytotox test according to DIN ISO 10993-5 several times. Furthermore, the alloy has a relatively low modulus of elasticity (87 GPa), so that it is close to the value of human bone (modulus of elasticity 40 GPa) in comparison to other materials, e.g. titanium, and can therefore be used well for implants for splinting and bone fusion, especially in places where a certain flexibility and freedom of movement is desired. AMLOY-ZR01 has been optimized for additive manufacturing, so it can be processed in 3D printing. Together with the laser technology company TRUMPF, Heraeus AMLOY has developed a concept for optimizing the 3D printer to enable amorphous components on an industrial scale. The basis for this was the TruPrint 1000 from TRUMPF, with which Heraeus AMLOY carried out various development activities and customer sampling in order to achieve better component density, as well as surface quality and shorter construction job times.



Crystalline material

Amorphous Material

TruPrint 1000.

Within the scope of the cooperation project, the TruPrint 1000, a compact and robust LMF machine for generative manufacturing of small industrial individual parts and series, was used. The 3D printer from TRUMPF GmbH + Co. was introduced to the market in 2015 and has been continuously developed to meet new challenges. Today, the TruPrint 1000 is one of the best-selling small-format metal 3D printers.

To ensure the industrial processing of amorphous metals, the following requirements for the system must be met:

- Ensuring the necessary cooling speeds
- High surface quality of the generated applications
- High purity adjustable and detectable process atmospheres
- Increase in productivity

The technical data and the optional machine configurations which are available can be taken from the following figure 2:

TruPrint 1000		
Construction volume (cylinder)	mm x mm	Ø 100 x 100 Optional: Reduced installation space
Processable materials [1]		Weldable metals in powder form, such as: Stainless steels, tool steels, aluminum [2], nickel-based, cobalt-chromium, copper, titanium [2] or precious metal alloys [2], amorphous metals
Build-up rate [3]	cm^3 /h	2-18
Layer thickness [4]	µm	10-50
Max. laser power at the workpiece (TRUMPF fiber laser)	W	200 Optional Multilaser: 2 x 200
Beam diameter	µm	55 Optional: 30
O_2 concentration	ppm	Up to 3,000 (0.3%) Optional: up to 100 (0.01%)
Inert gas		Nitrogen, argon
Power supply	V / A / Hz	230 – 7 – 50/60
Dimensions	mm	1445 x 730 x 1680
Weight	kg	650

Figure 2: Technical specifications of the TruPrint 1000
[1] Current material and parameter availability on request [2] Available with option packages [3] Actual build-up rate consisting of exposure and coating. Depending on system configuration, process parameters, material and filling level [4] Individually adjustable (subject to change without notice. The specifications in the quotation and order confirmation are authoritative).

The amorphous alloys require a very fast cooling rate so that the melt is supercooled and can solidify in the amorphous structure. Only with the amorphous atomic structure the material can unfold its potential of its unique properties. Additive manufacturing technology can master this challenge, so the TruPrint 1000 meets the best requirements.

The extra small beam diameters of 30 µm or 55 µm create a small melt pool, which enables the heat to be dissipated from the melt as quickly as possible, thus maintaining the critical cooling rate.

Furthermore, the small beam diameters allow highest surface qualities, which simplifies and almost eliminates the need for post-treatment of the applications. For this purpose, the fine focus diameter of up to 55 µm allows the energy to be precisely applied to the powder bed, thus reducing the adhesion of powder particles.

Like titanium, amorphous metals are generally susceptible to elemental contamination by oxygen and require therefore a high-purity process atmosphere. Oxygen indirectly influences the mechanical properties of the material by reducing its ability to form glass, preventing the formation of the amorphous structure and making the material brittle. To counteract this and to monitor the process optimally, the TruPrint 1000 was equipped with a high-resolution oxygen sensor that delivers reliable values in the measuring range from 100 ppm and can also be conveniently analyzed using the integrated condition monitoring.

Increasing productivity is also a very important point if you are thinking in the direction of series production. To this end, the TruPrint 1000 comes with the optionally selectable variation of the multi-laser principle for the small-format sector. With this system, the two 200 W TRUMPF fiber lasers can work parallel and thus drastically reduce construction time, which can result in an increase in productivity of up to 80% compared to the standard machine.

Both the hardware and the implemented software solutions of the TruPrint 1000 systems allow processing amorphous metals on an industrial scale.

TRUMPF

The high-tech company TRUMPF offers manufacturing solutions in the fields of machine tools, laser technology and electronics. TRUMPF drives the digital networking of the manufacturing industry by providing consulting, platforms and software. The company is the technology and market leader in machine tools for flexible sheet metal processing and industrial lasers.

In 2018/19, the TRUMPF Group generated sales of 3.78 billion Euros with approximately 14,490 employees. The R&D quota of currently 10.5 percent as well as the long-term orientation of an independent family-owned company make TRUMPF a guarantor for continuous innovative strength.

Machine tools for flexible sheet metal and tube processing form the core business. The product range includes machines for bending, punching, for combined punch-laser processes and for laser cutting and laser welding applications. Diverse automation solutions and a broad range of software round off the portfolio.

In the Laser Technology Business Field, TRUMPF offers high-power CO2 lasers, disk and fiber lasers, direct diode lasers, ultra-short pulse lasers, as well as marking lasers and systems. Like Additive Manufacturing, laser systems for cutting, welding and surface processing of three-dimensional parts are also part of the product range.

The products of the Electronics Business Field include direct current, high and medium frequency generators for inductive material heating, for surface coating and processing using plasma technology, and for laser excitation.

The headquarters of the family business is in Ditzingen near Stuttgart. With over 70 subsidiaries, the TRUMPF Group is represented in all important markets worldwide. Production sites are located in Germany, France, Great Britain, Italy, Austria, Switzerland, Poland and the Czech Republic, in the USA, Mexico, China and Japan.

PATHBREAKING PROJECT RESULTS.

The creation of an amorphous structure of the printed components is fundamental to ensure the material properties. This can be verified, for example, by X-ray diffraction and thermal analysis. Figure 3 shows the X-ray diffractogram of an amorphous sample produced with the TruPrint 1000. It shows the measured scattered intensity as a function of the angle of diffraction. The absence of sharp reflections (Bragg peaks), which is typical for crystalline materials, allows the (X-ray) amorphous structure of the components to be confirmed. Additional insights can be gained by means of thermal analysis methods such as dynamic differential calorimetry (DSC).

The printed, amorphous solidified alloy is heated and the heat flow to increase the temperature of the sample is determined and compared to a reference sample. In the case of endothermic processes within the sample, more energy must be applied compared to the reference, in exothermic reactions less. If an amorphous sample is heated, the same heat flow is required as for a crystalline sample (see Figure 4). Consequently, the difference in heat flow is very small. The reason for this is that the heat capacity of amorphous and crystalline substances of the same chemical composition is approximately the same. When the glass transition temperature at approx. 400°C is reached, the atomic dynamics thaw out: the frozen melt (glass) now behaves again like a highly viscous liquid and can be deformed thermoplastic, similar to plastics.

Due to the higher heat capacity of the liquid compared to the solid, there is an increase in the measured heat flow (see Figure 4). By further heating the atomic dynamics, in the (strongly supercooled) liquid, increases continuously. When a critical temperature is reached, the atoms rearrange themselves and the material assumes its thermodynamic state of equilibrium (crystal). As a result, thermal energy is released, which is reflected in the thermal analysis data as exothermic signatures. Within the measurement curve in figure 4 this is characterized by the appearance of exothermic peaks (negative heat flow). The enclosed area corresponds to the energy released during the conversion and allows a determination of the amorphous part.

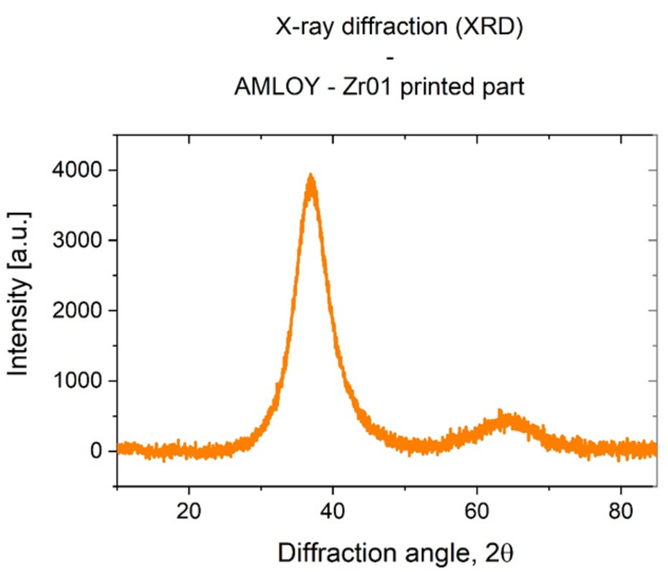


Figure 3: X-ray diffractogram of a component produced with the TruPrint 1000.

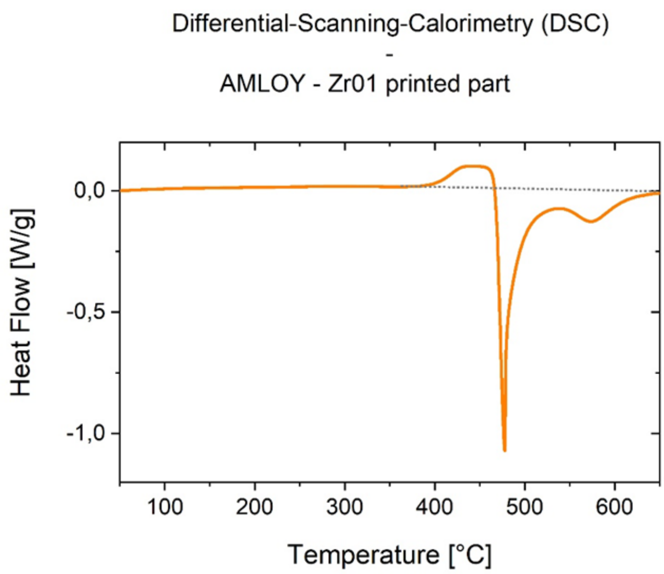


Figure 4: Dynamic differential calorimetric measurement of a printed amorphous sample.

PRINTED ACCURATELY.

Measurements on printed surfaces also show a high surface quality for 3D printing. Printed surfaces have roughness values of Rz = 17.13 ± 0.16, Ra = 2.63 ± 0.18 (see Table 1).

The surface qualities can also be further improved by simple finishing processes such as blasting or brushing. Better roughness requires reworking with classical, chip-removing processes, mechanical or electrochemical surface finishing processes.

Figure 5: Finest geometries combined with reproducible surface accuracy

Roughness AMLOY-ZR01 *	Rz [µm]	Ra [µm]
As-printed	17,13 ± 0,16	2,63 ± 0,18
Brushed	12,78 ± 2,43	2,40 ± 0,61
Glass bead-blasted	8,65 ± 0,94	1,46 ± 0,02
Corundum blasted	13,64 ± 1,14	2,14 ± 0,33

Table 1: Measured roughness values for different post-processed surfaces.

*measured on Sideskin according to DIN EN ISO 4287:2010, following DIN EN ISO 4288:1998

Material properties AMLOY-ZR01 (printed)	
Relative density [%]	> 99,9%
Young's modulus	87 GPa or 87,000 N/mm²
Compressive strength [N/mm²].	1500 - 1700
Flexural strength [N/mm²]	1700 - 2000
Yield strengths: tension, compression, bending [N/mm²].	> 1300
Elastic elongation [%]: tension, compression, bending	> 1,5 %
Hardness	480 HV

Table 2: Mechanical properties of printed amorphous metals

By using suitable process parameters and exposure strategies, amorphous components with relative densities of > 99.9% can be manufactured (see figure 6).

Due to the residual porosity, the mechanical properties of cast specimens are generally still below the mechanical properties of cast specimens, but printed specimens already exhibit impressively high strength and hardness without the components having to undergo subsequent heat treatment. An overview of the mechanical properties of printed components made of AMLOY-ZR01 is shown in Table 2 and Figure 7.

Figure 6: Ground section of an amorphous sample for determination of relative density and residual porosity

EXCELLENT MATERIAL CHARACTERISTICS.

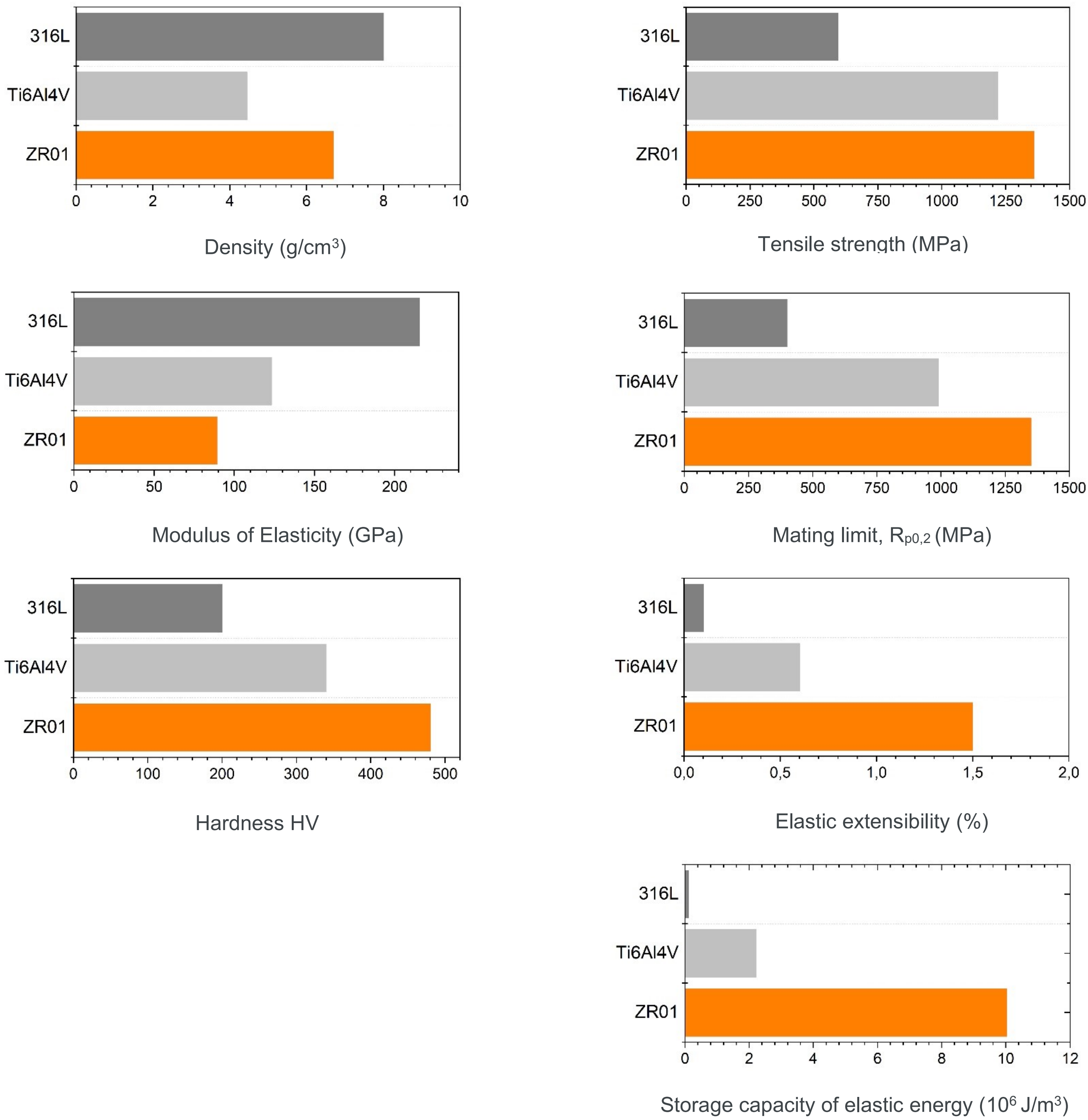


Figure 7: Comparison of mechanical properties of amorphous metals with conventional materials

CONTINUATION TO MAKE SUCCESSFUL PROGRESS.

The generated project results show the successful processability of the alloy AMLOY-ZR01 with a TruPrint 1000, but with this combination of powder and machine only a small range of the application variety of amorphous metals can be produced.

Further fields of application and a wider variety of amorphous metals are to be detected and developed with the TruPrint 2000, which also enables larger applications with a construction volume (cylinder) of 200 mm diameter and a height of 200 mm.

Figure 8: The perfectly coordinated, inert machine concept of the TruPrint 2000 with powder preparation station offers a high-quality print result with economical production. Metal serial components can be assembled highly productively using a multi-laser and unpacked inside the machine. The production process of the TruPrint 2000 is based on a closed powder circuit under inert gas. This enables simple, practical handling and the highest powder quality.

In addition to the use of larger packaging volumes to produce larger components with increased productivity, the main focus of further investigations is also the use of integrated packaging heating so that alloys that are more susceptible to cracking can be reliably processed. Furthermore, the new function "Melt Pool Monitoring" allows the thermal history of the components during the construction process to be recorded in-situ, which reduces or avoids performance-damaging local overheating in the material.

Likewise, parameters and exposure patterns in critical areas can be specifically modified to avoid local overheating and reduce thermally induced stresses. As a result, cheaper copper- and titanium-based alloys with lower glass-forming capabilities and thermal stability can also be processed industrially.

In addition, it will be investigated to what extent alloys with higher degrees of impurity can be made "printable" in order to reduce material and component costs and to open up further fields of application.

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