Rheological Characterization of Metal Melts

Relevant for: Newtonian, Oxidation, Slip, Surface Tension, Apparent Shear-thinning, Vortices, High-temperature Viscosity

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The rheological characterization of metal melts poses several challenges due to their following characteristic properties: very low viscosities in the one-digit mPas range, strong oxidation tendency, high surface tension, and high density. An air-bearing rheometer with high sensitivity, a reducing purging gas to avoid oxidation, and a profiled measuring geometry with a narrow measuring gap to avoid slip and turbulent vortices are required.

A comprehensive rheological characterization of liquid and semi-solid metal melts is presented, considering shear rate and temperature as major influencers on viscosity. Further, density characterization of the metal alloys and dynamic mechanical analysis of the solid sample are presented.

1 Characteristic Properties of Metal and Metal Alloy Melts

The flow behavior of metal melts is important to understand numerous industrial processes, such as pumping, welding, galvanization, coating, kinetics of reactions, casting and rheo-casting processes, where the metal is processed in its semi-solid state [1-3].

Different methods can be used to measure the viscosity of metal melts. Examples are capillary, oscillating vessel, draining vessel, oscillating plate and rotational bob or crucible [4]. All mentioned methods except for rotational bob and crucible yield a single viscosity value without directly giving information about the applied shear. Partially the applied shear rate is not even constant. Therefore, those methods are only appropriate for the viscosity measurement of Newtonian fluids.

The flow behavior of metal melts above liquidus temperature is considered Newtonian. However, recent literature also shows results with shear-thinning behavior [2]. Such behavior is controversial and in the majority of studies experimental conditions and setup, namely surface oxidation and tension, are at least partly responsible for the deviation from Newtonian behavior [5].

Semi-solid metals actually show shear-thinning and thixotropic behavior [6]. Thus, for the holistic rheological investigation of liquid and semi-solid metals, rotational rheometry has been often used in recent literature [2].

In this article the characterization of metal melts using high-temperature rheometers from Anton Paar, which apply the rotating bob method, are presented.

2 Materials & Methods

The measurements were performed either on the Furnace Rheometer System (FRS) or a Modular Compact Rheometer (MCR) from Anton Paar equipped with a convection temperature device (CTD). Those devices enable quick and accurate temperature control in a wide temperature range. The air bearing of the rheometer allows the measurement of very low viscosities (1 mPas and below). In addition, those devices enable oscillatory rheometry and density measurements [7]. Measuring geometries used were profiled concentric cylinder geometries made of carbon (liquid sample) or a three-point-bending geometry made of Inconel (solid sample).

3 Results

3.1 Rheological Characterization of Metal Melts and Its Challenges

Typical rheological behavior of a metal melt as function of temperature is shown for a titanium alloy in figure 1. Above liquidus temperature, the viscosity is found in the lower mPas-range and shows a moderate increase with decreasing temperature. Once crystallization starts, viscosity increases sharply.

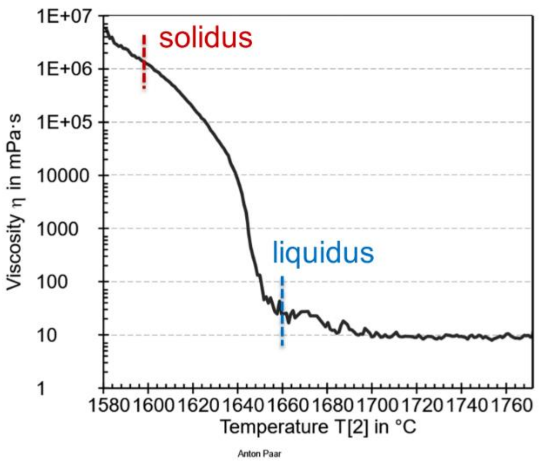

Figure 1: Temperature sweep in rotation of a titanium alloy. The sample was cooled down (-2 °C per minute) and a shear rate of 2 s^{-1} was applied. Liquidus and solidus temperatures of the alloy were taken from literature [8].

In order to generate such rheological data for metal melts, the major challenges are low viscosities, chemical interaction and inefficient wetting of the measuring geometry as well as oxidation of the sample.

3.1.1 Chemical Interaction with - and Wetting of the Measuring Geometry

At high temperatures resistance and solubilities can vary widely even with similar materials. If there are doubts about the interaction between crucible and sample material, it is recommended to test the corrosion behavior of the sample material with the measuring geometry material in a standard laboratory furnace.

The higher the temperature, the more reactive materials are. At elevated temperatures, at which metal melts are characterized, metal melts are reactive with various materials. Here, chemical resistance and solubilities can vary widely even among metals. Thus, it is crucial to choose a suitable measuring geometry material in order to avoid misleading effects on the rheological measurement.

Carbon and Al_2O_3 are stable materials up to very high temperatures and especially carbon is known to show little interaction with metal (alloy) melts. In addition, carbon counteracts unwanted oxidation processes.

However, unoxidized metals often do not wet materials such as carbon. Therefore, profiled measuring geometries are recommended to compensate for bad wetting. The grooves facilitate a better contact and help to avoid sample slip. An example for a profiled measuring geometry made of carbon is shown in figure 2.

Figure 2: Carbon measuring geometry with a profiled cylinder

3.1.2 Viscosities as low as 1 mPas

Above liquidus temperature, metal melts show viscosities in the lower one-digit mPas range. Thus, a device with high torque sensitivity is required. The rheometers from Anton Paar including the MCR-series and the DSR 502 rheometer head use an air-bearing-supported synchronous EC motor. This deploys a frictionless synchronous movement of the rotor inside which enables the most sensitive and therefore most precise movements for the largest range of viscosities and shear rates.

Pure silicon, an example of such a low viscous metal melt is shown in figure 3. The viscosity at 25 s^{-1} at increasing temperatures was measured.

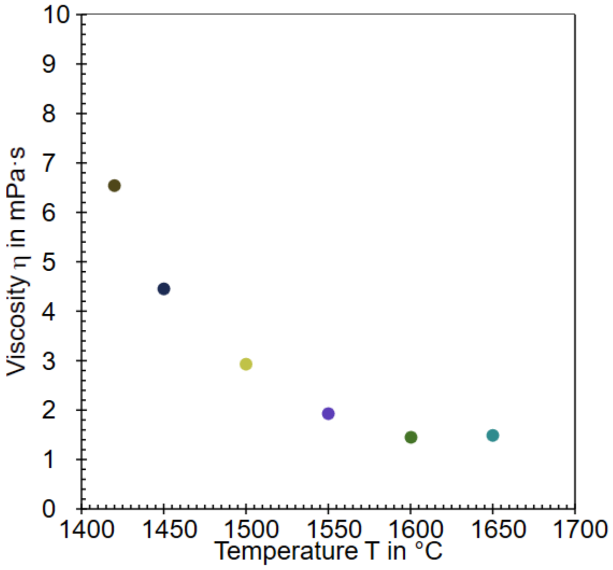

Figure 3: Viscosity measurement of pure silicon at different temperatures with a constant shear rate of 25 s^{-1}

At temperatures of 1600 °C and above, the viscosity of the silicon melt is 1.5 mPas. Further, figure 3 depicts, that the temperature dependence of the viscosity is high around the melting point/liquidus temperature, but decreases at significantly higher temperatures.

3.1.3 Metal Oxidation

Interfacial oxidation of metals is a major issue due to the high process/measuring temperatures and the high reactivity of metals. Even small impurities may enhance oxidation and thus can have a big influence on measurement results [9]. Thus, appropriate measuring methods, environmental conditions and data interpretation are crucial.

The FRS gas-tight from Anton Paar provides a gas-sealed measuring chamber enabling oxygen-free characterization of melts up to 1800 °C furnace temperature.

An exemplary measurement of a metal (copper) in the gas-tight chamber in syngas atmosphere is shown in figure 4.

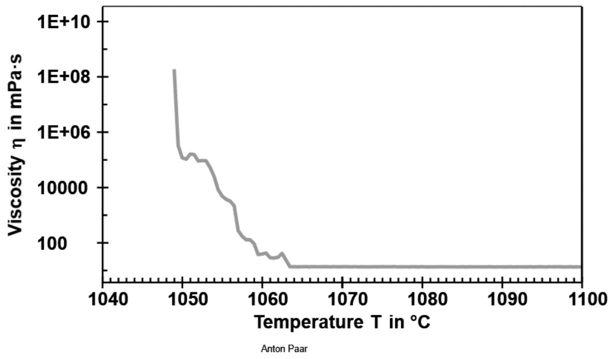

Figure 4: Temperature sweep of copper

After the measurement, visual inspection of the copper sample shows no signs of oxidation and relatively large crystalline domains are observed (figure 5).

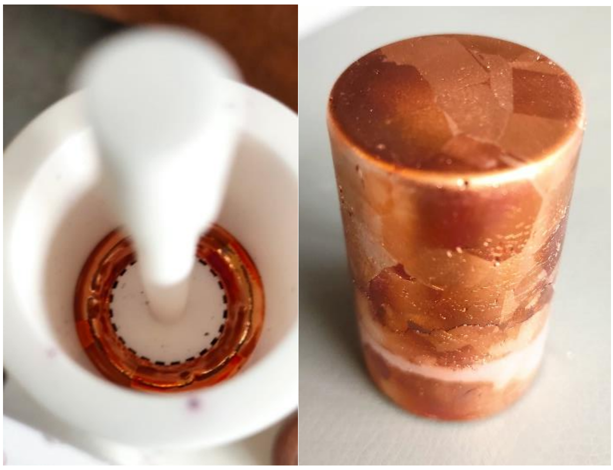

Figure 5: The copper sample after measurement

3.1.4 Shear Rate Dependent Behavior of Metal Melts and the Influence of Vortices

For the measurement of viscosity in a rotational bob rheometer, laminar flow conditions in the measuring gap are a requirement. For the metal melt characterization by means of concentric cylinder geometry, there is a critical value at which the liquid flow starts to be instable due to internal and centrifugal forces leading to turbulences which cause increasing flow resistance. This critical value depends on the rotational speed, measuring geometry diameter, measuring gap, density and viscosity of the sample [10].

In the flow curve conducted for a gold alloy which is depicted in figure 6, the influence of turbulences can already be observed at shear rates higher than 7 s^{-1}. The measurements were done using a profiled bob with a diameter of 25 mm in a 30 mm crucible. Thus, the measuring gap was 2.5 mm. Due to bad wetting caused by the high surface tension of the alloy melt, a bigger bob could not be used without pushing the sample out of the measuring gap.

Below the shear rate of 7 s^{-1} the expected Newtonian behavior of metal melts was observed. Lower viscosities, at which shear-thinning behavior might occur, were not investigated.

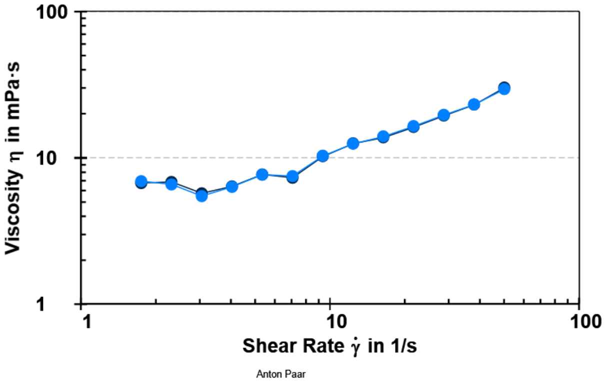

Figure 6: Viscosity curve of a gold alloy at 1000 °C

Apparent shear-thinning behavior can often be observed as an artefact of an oxide layer on the surface of the melt. If it is not possible to fully remove this oxide layer, its influence can be overcome by applying high shear rates to the sample. Figure 7 shows a zinc melt where apparent shear-thinning behavior occurs at shear rates lower than 20 s^{-1}, which in reality is an artefact of the oxide layer. At shear rates higher than 20 s^{-1} a viscosity plateau is reached before turbulences at even higher shear rates occur. Assuming a Newtonian behavior and neglecting possible shear-thinning effects at very low shear rates, the viscosity at the plateau can be used as viscosity of this melt at measuring temperature.

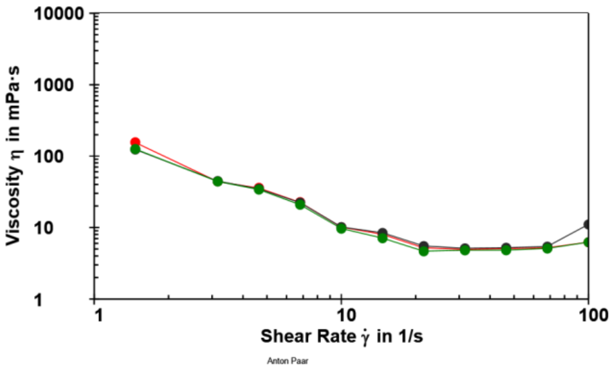

Figure 7: Viscosity curve of a zinc melt at 500 °C

Highly shear-thinning behavior and thus dependence of the melt viscosity on the shear rate can be observed for the semi-solid metal and thus at measurements below liquidus temperature. This is shown for an aluminum alloy by cooling under applied shear from above to below liquidus. Above liquidus the viscosity is independent of the shear rate. The further the temperature goes below liquidus temperature, the more shear rate dependent the viscosity is (figure 8).

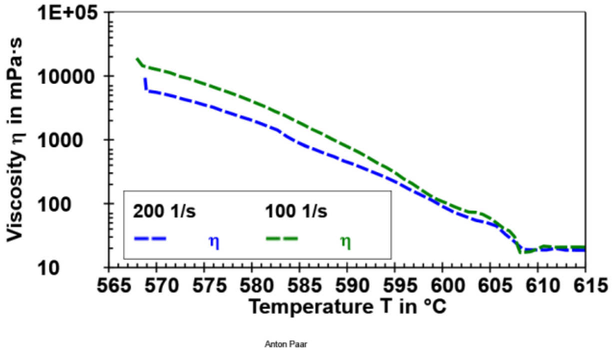

Figure 8: Temperature ramp of aluminum A356 at two different shear rates.

3.2 Additional Methods for Metal Characterization Using a Rheometer

Apart from rheological characterization, the normal force sensor of Anton Paar rheometers enables density determination of liquid metal (alloys). Further, not only liquid and semi-solid metals can be characterized, but also solid metals applying dynamic mechanical analysis (DMA).

3.2.1 Determination of Metal (Alloy) Melt Density

In addition to characterization of softening/melting, normal force can be used to determine the liquid sample density. This approach is based on the Archimedean principle utilizing the normal force that originates from the bouyancy of the cylinder immersed in the sample. The measurement mimics an inverted Archimedean balance [11] by using equation 1.

$$\rho_{sample} = \frac{F_N}{g * V_C^T} - \rho_{air} \qquad \text{(Eq. 1)}$$

F_N is the normal force (due to bouyancy), g is the gravity constant, V_C^T is the volume of the cylindrical bob at measurement temperature, and ρ_{air} is the density of air.

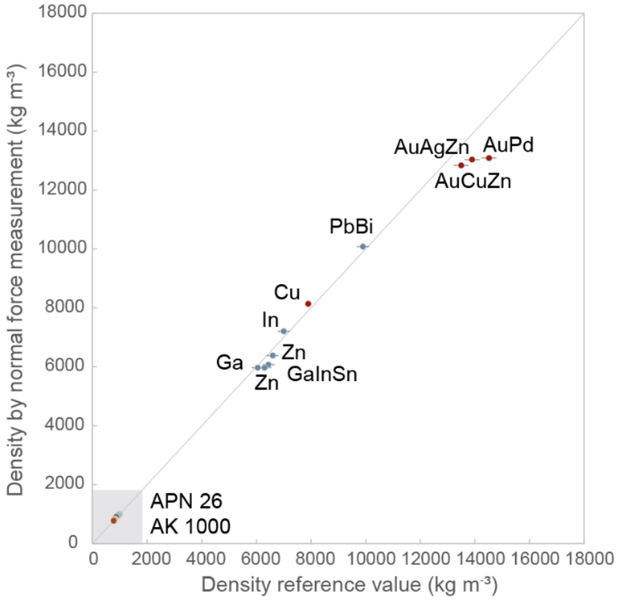

Figure 9: Comparison of density values based on normal force measurements and reference density values for metal melts and metal alloy melts. Blue data points were measured with an MCR combined with a CTD, red data points were measured with an FRS [12].

Simultaneous measurement of density and viscosity has several advantages in terms of data comparability: identical setup, identical sample, identical temperature, and less sample material. Furthermore, it allows direct determination of the kinematic viscosity, which is defined as the ratio between viscosity and density and is commonly used for process design.

3.2.2 Dynamic Mechanical Analysis: Characterizing the Solid Sample at Elevated Temperatures

A modular setup based on a Modular Compact Rheometer (MCR) from Anton Paar, a linear measuring drive, and a convection temperature device (CTD) which enables the characterization of materials at temperatures up to 950 °C was used (figure 10). Measurements in rotation, torsion, tension, bending, and compression are possible – depending on the used measuring geometry.

Figure 10: The CTD 1000 with three-point-bending (TPB) geometry

The material properties of steel depend, among others, on composition or heat treatment. In this example, two components of a lamellar damascene steel (with a carbon content of ~0.9 % in the case of steel 1 and 0.45 % in the case of steel 2), provided by Balbachdamast GmbH & Co. KG, were investigated over a wide temperature range using a three-point-bending geometry. For these tests, samples with a width of 3 mm and a thickness of 1 mm where used.

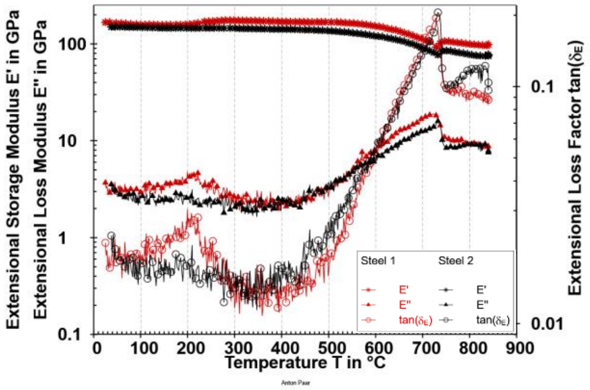

Figure 11: Storage and loss modulus, as well as damping factor of the two steel samples over temperature.

The curves of the moduli as well as the loss factor in figure 11 show slight differences between the two components, steel 1 and steel 2. The significant change in the curves in the range between 720 °C and 740 °C occurs for both steels and is most likely attributable to solid state phase transitions.

4 Summary

The rheological characterization of metal melts is challenging due to very low viscosities in the one-digit mPas range, strong oxidation tendency, high surface tension and high density. Using the high temperature rotating bob rheometers from Anton Paar enables to face those challenges and determine the rheological behavior of metal melts considering influences of shear rate and temperature.

Going beyond viscosity, the density of the liquid melt can be determined in parallel to rheological characterizations. Further, the solid metal can be analyzed using dynamic mechanical analysis which was exemplarily shown on two steel samples using three-point bending.

5 References

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