THE THERMAL AND TRANSPORT PROPERTIES OF MOLTEN METALS & ALLOYS

Valentim Nunes[1,2]*, Maria José Lourenço[2], Fernando Santos[2], Carlos Nieto de Castro[2]

[1] Centro de Investigação em Cidades Inteligentes, Instituto Politécnico de Tomar, Campus da Quinta do Contador, 2300-313, Tomar, Portugal
[2] Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016, Lisboa, Portugal
* Corresponding Author (valentim@ipt.pt, ORCID No: 0000-0002-1525-5829)

Abstract

Metals and alloys are key functional materials since ancient civilizations. We coined one of our prehistoric periods as the age of metals (cooper, bronze, and iron) between *circa* 3300 to 1000 BC, when man developed casting techniques and started metallurgy. But even if we are aware of the importance of metals and alloys in our daily lives, sometimes we forgot that for the processing of these materials we need to have them in the liquid state. In fact, these liquids are very important in many industrial processes, such as steelmaking, nonferrous metallurgy, aluminium smelting, foundries, glass manufacturing, and others, including cooling and refrigeration at high temperatures. To model and optimize these processes the thermal and transport properties are decisive. Despite this fact, industry still needs new data for several pure metals and alloys, as the available data frequently show large discrepancies, and the effect of "impurities" is difficult to model.

In this paper we will perform an overview of the relevant properties of molten metals and alloys, exemplifying with a few examples, including the utilization of liquid metals and alloys in refrigeration at high temperatures, electronic cooling or casting of metal alloys for engine blocks.

Key Words: *Metals, Alloys, Thermal and Transport Properties, Metallurgy, Cooling*

1. Introduction

Metals and alloys are present in civilizations since ancient times. The bronze and iron ages, during approximately from 3300 BC to 1000 BC, depending on the regions of the globe, assisted to the developing of casting techniques and the emerging of metallurgical processes. Included are techniques for melting of cooper and tin, ferrous metallurgy, manufacturing of tools, molding, and everything else that helped to push civilization to the Ancient History [1]. Almost all civilizations raised their economic power based on the production and use of metals and alloys. For instance, just to mention an example, the Ottoman Empire expanded from almost five centuries by promoting the silver and steel production (essential for the manufacturing of weapons) assuring expansion and economic growth [2].

To see how relevant the processing of metals and alloys is, just consider that the European Union (UE) can be traced back to the European Coal and Steel Community what demonstrates the huge importance of metal processing and its impact in social welfare.

Metals are abundant in nature, and it should be highlighted that metals constitute 77% of the elements in the periodic table, as shown in figure 1.

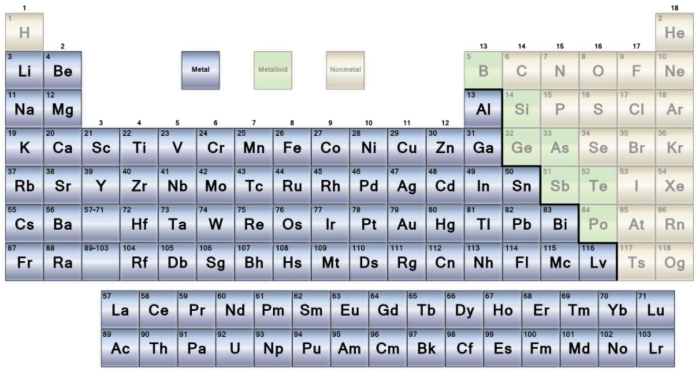

Figure 1. The Periodic Table of the Elements (metals highlighted)

Iron is by far the less expensive metal, with many applications, and accounts for almost 90 % of the worlds production of metal. But other metal and alloys are also of decisive importance. A classical textbook on engineering alloys [3] makes mention to iron carbon alloys, alloy steels, aluminum alloys, cooper and cooper alloys, stainless steels, cast irons, titanium and titanium alloys, nickel and cobalt alloys, magnesium, and zinc alloys, but many other can be added to this list.

But even if we are aware of the importance of metals and alloys in our daily lives, to process or use these materials we need to have them in the liquid state, which is sometimes forgotten. Liquid metals were identified in the past as crucial high temperature fluids [4], not only for conventional technologies, like aluminum foundry, but also new and important processes like cooling, phase change and others. In all this processes, steelmaking, aluminum foundry, die casting processes, the knowing of the thermal and transport properties assume a fundamental role [5-6]. The recognition of this is the effort done by the International Union for Pure and Applied Chemistry (IUPAC) in establishing reference data for the thermophysical properties of molten metals [7-9]. But even with this precious data, industry still needs new data for several pure metals and alloys, as the available data frequently show large discrepancies, and the effect of “impurities” is difficult to model [10]

In the next sections we will briefly review the relevant thermal and transport properties for molten metals and alloys applications, using a few examples, like the utilization of sodium for cooling at high temperatures, light metal alloys for electronic cooling or the use of special alloys for block motor engines.

2. Physical Properties of metals and alloys

Within the physicochemical properties that are relevant for many applications, we consider the following as the most important:

- Vapor pressure
- Surface tension
- Density
- Heat capacity
- Viscosity
- Thermal conductivity

2.1. Vapor pressure

The vapor pressure is an indication of vaporization rate and can be defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature. The equilibrium vapor pressure of molten metals can be assessed in several ways, including manometry, the measuring of dew points or by using the Knudsen effusion effect. Values usually are very low in the range between 10^{-15} to 10^{-3} atm. [11]. They can be given by a classical expression of Clapeyron type:

$$log(p/\text{atm}) = A + \frac{B}{T(\text{K})} \tag{1}$$

For instance, for sodium A = 4.704 and B = -5377 K and for iron A = 6.347 and B = -19574 K [11]. Some aluminum-based alloys can exhibit anomalous higher values near melting (or glass transition) temperatures [12], due to structural effects but, compared with other liquids, their vapor pressures are generally low.

2.2. Surface tension

Surface tension, γ, is crucial in industrial processes such as casting or welding and can be defined as the energy required to change the surface area of a material. It can be measured by several methods including capillary rise, drop weight method, maximum bubble, and pendent drop. Surface tension is closely related with the ability to wet a surface. In fact, the contact angle, θ, is related with the surface tension. Figure 2 shows a drop of liquid metal on a solid surface, that is incompletely wetted.

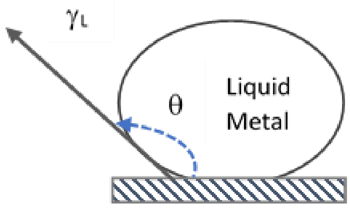

Figure 2. Drop of a liquid metal on a solid surface

Usually, the surface tension of liquid metals and alloys changes negatively with temperature, and can be expressed by a simple equation:

$$\gamma(\text{mN} \cdot \text{m}^{-1}) = A - B \times T(\text{K}) \tag{2}$$

As examples, for cooper A = 1585 $\text{mN} \cdot \text{m}^{-1}$ and B = 0.21 $\text{mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and for tin A = 580 $\text{mN} \cdot \text{m}^{-1}$ and B = 0.065 $\text{mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [13]. As it can be seen, by the examples given, the surface tensions of liquid metals are very high, compared with other liquids. Pure liquid iron can reach as high as 1.87 N.m^{-1} [14] and gallium-based alloys have values of the order of 700 mN.m^{-1} [15] (for comparison, this value is 72 mN.m^{-1} for water at room temperature).

2.3. Density

Density, ρ, is, obviously, a key property, as it represents the mass of material per unit volume (in SI units kg.m^{-3}). The density of metals is generally higher than nonmetals (with some exceptions). It can be obtained with different techniques, including Archimedean method, maximum bubble pressure, pycnometric techniques and electromagnetic levitation. Density of alloys also decrease with temperature, showing a linear dependence (as for surface tension) and sometimes a non-linear term is also necessary [16], and a generic quadratic type of equation can be used.

$$\rho = \rho_m + \frac{\partial \rho}{\partial T}(T - T_m) + \frac{\partial^2 \rho}{\partial T^2}(T - T_m)^2 \tag{3}$$

The subscript m refers to the melting point. The first derivative is always negative. Typical values at melting point are 2.38×10^3 $\text{kg} \cdot \text{m}^{-3}$ for Al and 6.58×10^3 $\text{kg} \cdot \text{m}^{-3}$ for Zn [17]. The density of alloys can be fairly estimated knowing the alloy composition. For example, for a Zn/Al based alloys we could calculate the density of alloys using the following equation [18]:

$$\frac{1}{\rho} = \frac{x_{Zn}}{\rho_{Zn}} + \frac{x_{Al}}{\rho_{Al}} + \sum_{j=3}^{N} \frac{x_j}{\rho_j} \tag{4}$$

In this equation x are molar fractions and the summation accounts for minor components existing in the alloy.

2.4. Heat Capacity

When we think about heat transfer characteristics of materials, heat capacity is clearly a fundamental property. It defines the amount of energy (heat) required to rise the temperature of a given amount of substance, and in SI units it will be expressed either in $J \cdot kg^{-1} K^{-1}$ or $J.mol^{-1}K^{-1}$. It can be assessed by several methods, including differential scanning calorimetry, pulse heating or drop calorimetry. This property is especially important in cooling and casting processes. It can be expressed as a polynomial function of the temperature:

$$C_p = a + b \times T(\mathrm{K}) + c \times (T(\mathrm{K}))^2 \tag{5}$$

For instance, for sodium a = 37.51 $J \cdot mol^{-1} \cdot K^{-1}$, b = -1.9221·10^{-2} $J \cdot mol^{-1} \cdot K^{-2}$ and c = 1.0636×10^{-5} $J \cdot mol^{-1} \cdot K^{-3}$ [5]. By comparison the heat capacity of water is approximately 75.2 $J \cdot mol^{-1} \cdot K^{-1}$, but the equation for sodium is valid from 371 K to 1150 K, a large range of temperature in the liquid state as usually found for other metals.

2.5. Viscosity

The viscosity of a fluid measures its tendence to dissipate energy when it is perturbed from equilibrium by the imposition of a velocity gradient. It represents the resistance of fluid to flow. The existence of the viscosity can be easily understood by looking at two parallel layers of fluid (see figure 3). If we apply a given force F in one layer the other will also move. In steady-state conditions there will be a gradient of velocities along the intermediate layers. The shear stress F/A will be given by the Newton law:

$$\frac{F}{A} = -\eta \frac{\mathrm{d}v}{\mathrm{d}y} \tag{6}$$

in which η is the viscosity coefficient, or simply viscosity. The units are Pa·s in the SI.

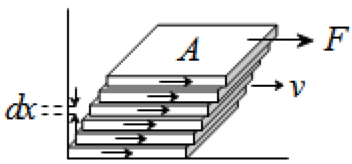

Figure 3. Newton law of viscosity

The viscosity of molten metals and alloys depend on temperature and often obeys to the Arrhenius equation [19]:

$$\eta(T) = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \tag{7}$$

where E_η is the activation energy of viscous flow, η_0 a preexponential factor and R the gas constant. There are several methods to measure the viscosity of liquids, but for liquid metals due to the low viscosities of metals, the order of magnitude is ~ 1 mPa, the chemical reactivity and generally high melting points, the most suitable are the capillary, oscillating cup, oscillating plate, and rotational methods. As typical values, the viscosity at melting point is 0.68 mPa·s for sodium, 5.5 mPa·s for iron and 1.3 mPa·s for aluminum [19], which compares reasonably with the viscosity of water at room temperature. Recently reference data for several metals were proposed[1] [7-9]. But, for molten alloys, and when several elements are present, the viscosity is difficult to predict, including in some cases non-Arrhenius behavior [10].

2.6. Thermal conductivity

The thermal conductivity is a measure of the ability of a material to conduct heat. Considering a given direction, the thermal conductivity, λ, relates the heat flux, Q, with the temperature gradient, according with the Fourier´s law:

$$Q = -\lambda \frac{\mathrm{d}T}{\mathrm{d}x} \tag{8}$$

and the units are W·m^{-1}· K^{-1} in the SI. Thermal conductivity is a very important property, especially for the proper design of cooling devices. Although we may think that this is important at very high temperatures, in fact, for instance in electronic cooling, low melting point metals and alloys can be used like gallium or gallium alloys. Contrarily to other properties the variation with T is a matter of debate as experimentally the slope dλ/dT can be either positive or negative, or shown a non-dependence on T. Figure shows as an example the thermal conductivity of liquid Indium [20]:

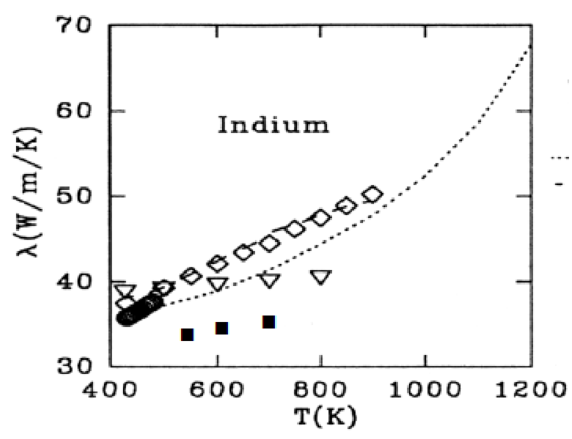

Figure 4. Thermal conductivity of molten Indium. ◇– Yurchak and Smirnov, 1969; ····· Touloukian *et al.*, 1970; ∇ - Duggin, 1972; - - - Ho *et al.*, 1974; ○ - Goldratt and Greenfield, 1980; ■ - Peralta-Martinez and Wakeham, 2001. Details of the works in reference [20]

The measuring of thermal conductivity is a challenging task. In principle, there are three different classes of measurement methods: Steady state methods, non-steady state methods and transient methods [21]. First one is especially hard to apply for metals with high melting points. The thermal conductivity of liquid aluminum, to use an example, changes from 89.3 W·m^{-1}·K^{-1} at melting point to 105.1 W·m^{-1}·K^{-1} at 1500 K [22]. The thermal conductivity of gallium and EGalinstan at room temperature are 29.4 W·m^{-1}·K^{-1} and 16.5 W·m^{-1}·K^{-1}, which are approximately 49 and 28 times higher than water, respectively [23].

[1] The authors are currently measuring the viscosity of EGalinstan (a eutectic mixture of Gallium, Indium and Tin) suitable for electronic cooling, and anticipate the report of new data for this system in a short time.

3. Some applications

As could be inferred from previous section, the applications of molten metals and alloys are very diverse, from casting, welding, cooling, to mention a few, exploring the unique properties of this class of materials. To illustrate this we will, in this section, describe some examples of those applications.

3.1. Sodium for cooling

Alkali metals, and in particular sodium, have excellent thermophysical properties, such as low density, low melting point, high heat capacity and high thermal conductivity when compared to other metal groups [24]. Additionally, liquid sodium exhibits a lower chemical reactivity in comparison with the other alkali metals. The low melting point (98 °C) and the high boiling point (883 ºC) makes sodium very attractive as coolant for fast breed reactors. Figure 5 shows a scheme of this type of reactors [25].

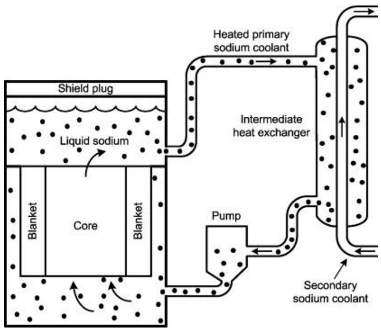

Figure 5. Liquid sodium as a coolant for the core of a nuclear reactor

At 450 ºC the relevant properties are [26]: ρ = 845 kg·m^{-3}, γ = 163 mN·m^{-1}, C_p = 1.269 kJ·kg^{-1}·K^{-1}, λ = 68.8 W·m^{-1}·K^{-1} and the viscosity is approximately η = 0.3 mPa.s (0.68 mPa.s at melting point as mentioned before) and the vapor pressure is extremely low.

3.2. Gallium based alloys for electronics cooling

A few metals are liquid at room temperature (or near). Among them we can list mercury (Hg), gallium (Ga), rubidium (Rb), cesium (Cs) and francium (Fr). Aspects related with reactivity and toxicity (in the case of mercury) leaves Gallium and its alloys as a viable option for low temperatures applications [27]. Galinstan an eutectic mixture with the composition of 68.5% Ga, 21.5% In, and 10.0% Sn (by weight) has been used in electronic devices cooling due to its excellent properties [28]. It is liquid at room temperature, the melting point is around 13.2 ºC [29], although this, surprisingly, is still a matter of debate. It has an excellent fluidity although a moderate surface tension. Some of its properties at room temperature are [28], ρ = 6440 kg·m^{-3} and η = 2.4 mPa·s. The thermal conductivity is 16.5 W·m^{-1}·K^{-1} as mentioned before and the surface tension is relatively high, γ = 718 mN·m^{-1}. Figure 6 shows a drop of Galinstan on a solid surface [30].

Figure 6. Drop of Galinstan evidencing the high surface tension

3.3. Zinc aluminum alloys for casting engine blocks

Aluminum and zinc alloys are some of the most common metallic alloys used in manufacturing die-cast products. [31]. One of the more important property is the viscosity. Figure 7 shows the viscosity of quasi eutectic alloys with the incorporation of minor quantities of lead (500 ppm and 1000 ppm respectively) measured in our laboratories [18]. The addition of Pb decreases the viscosity. This could be an important effect in enhancing the castability of the alloys, for instance, optimizing mold-filling aspects and reducing the porosity, improving in this way the quality of alloys for instance to produce new engine blocks.

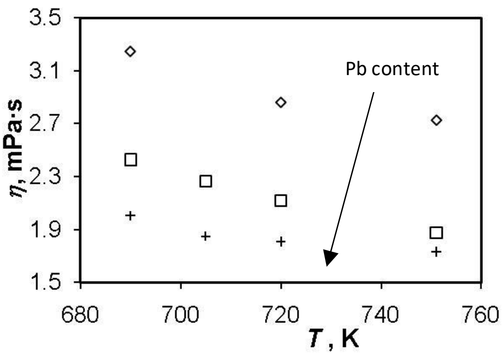

Figure 7. Effect of lead addition on the viscosity of molten alloys I, II and VII, based on Zn/Al, with Mg, Si, Fe and Pb as minor components. Details in reference [18].

4. Conclusion

In this brief article, we describe some of the important physicochemical properties of molten metals and alloys. These materials possess unique properties, allowing them to be used in a variety of applications crucial to the economy and well-being of nations. The importance was exemplified with a few examples. demonstrating that the large variety of metals and alloys allow us to choose the right fluids that meet our needs. Therefore, the use of metals comes from the birth of civilizations, and they will certainly be used for times to come.

References

[1] S. Srinivasan, S. Ranganatham, A. Giumlia-Mair, Metals and Civilizations, Proceedings of the Seventh International Conference of the Use of Metals and Alloys, National Institute of Advanced Studies, Bangalore, 2015

[2] N. Nerantzis, Pillars of Power: Silver and Steel of the Ottoman Empire, Mediterranean Archaeology and Archaeometry, 9(2), 71-85, 2009

[3] W. F. Smith, Structure and properties of Engineering Alloys, 2nd ed., McGraw-Hill, New York, 1993

[4] A. Nagashima, Thermophysical Properties Research on Fluids at the Technology Frontier, Status of Current Research, Appl. Mech. Rev, 41(3), 113-128, 1988

[5] T. Iida, R.I.L. Guthrie, The Physical Properties of Liquid Metals, Claredon Press, Oxford,,1988

[6] Y. Sato, Viscosity and Density Measurements of High Temperature Melts, High Temperature Measurements of Materials, ed. H Fukuyama, Y. Waseda, Springer, Berlin, 2009

[7] M.J. Assael, I.J. Armyra, J. Brillo, S.V. Stankus, J. Wu, W.A. Wakeham, Reference Data for the Density and Viscosity of Liquid Cadmium, Cobalt, Gallium, Indium, Mercury, Silicon, Thalium, and Zinc, J. Phys. Chem., Ref. Data, 41(3), 033105, 1-16, 2012

[8]. M.J. Assael, A.E. Klyva, K.D. Antoniadis, R.M. Banish, I. Egry, J. Wu, E. Kaschnitz, W.A. Wakeham, Reference Data for the Density and Viscosity of Liquid Cooper and Liquid Tin, J. Phys. Chem., Ref. Data, 39(3),

033105-1-8, 2010
[9] M.J. Assael, K. Kakosimos, R.M. Banish, J. Brillo, I. Egry, R. Brooks, P.N. Quested, K.C. Mills, A. Nagashima, Y. Sato, W.A. Wakeham, Reference Data for the Density and Viscosity of Liquid Aluminum and Liquid Iron, J. Phys. Chem., Ref. Data, 35(1), 285-300, 2006
[10] V.M.B. Nunes, C.S.G.P. Queirós, M.J.V. Lourenço, F.J.V. Santos, C.A. Nieto de Castro, Viscosity of Industrially Important Zn-Al Alloys Part II: Alloys with Higher Contents of Al and Si, Int. J. Thermophys., 39, 68, 2018
[11] C.B. Alcock, V.P. Itkin,, M.K. Horrigan, Vapour Pressure Equations for the Metallic Elements: 298–2500K, Canadian Metallurgical Quartely, 23, 309-313, 1984
[12] J.I. Jeong, S.H. Lee, J. Jeon, S.J. Kim, Excessively High Vapor Pressure of Al-Based Amorphous Alloys, Metals, 5, 1878-1886, 2015
[13] J. Lee, W. Shimoda, T. Tanaka, Surface Tension and its Temperature Coefficient of Liquid Sn-X (X=Ag, Cu) Alloys, Materials Transactions, 45(9), 2864-2870, 2004
[14] I. Egry, E. Ricci, R. Novakovic, S. Ozawa, Surface tension of liquid metals and alloys — Recent developments, Advances in Colloid and Interface Science, 198-212 (2010)
[15] X. Zhao, S. Xu, J. Liu, Surface tension of liquid metal: role, mechanism and application, Front. Energy, 11(4), 535–567, 2017
[16] Y.J. Lv, M. Chen, Thermophysical Properties of Undercooled Alloys: An Overview of the Molecular Simulation Approaches, Int. J. Mol. Sci, 12, 278-316, 2011
[17] D.J. Steinberg, A Simple Relationship Between the Temperature Dependence of the Density of Liquid Metals and Their Boiling Temperatures, Metallurgical Transactions, 5, 1341-1343, 1974
[18] V.M.B. Nunes, M.J.V. Lourenço, F.J.V. Santos, C.A. Nieto de Castro, Viscosity of Industrially Important Al-Zn alloys. I Quasi eutectic Alloys, Int J Thermophys. 31, 2348-2360, 2010
[19] L. Battezzati, A.L. Greer, The viscosity of liquid metals and alloys, Acta Metall., 37, 1791-1802, 1989
[20] C.A. Nieto de Castro, Thermal Conductivity of Molten Materials. Is Experiment Necessary? Proceedings of TEMPMEKO 2004, 9th International Symposium on Temperature and Thermal Measurements in Industry and Science, ed. D. Zvizdic, Volume 1, 49-58, (2005), ISBN number 953-6313-72-3.
[21] P. Pichler, G. Pottlacher, Thermal conductivity of liquid metals, Impact of Thermal Conductivity on Energy Technologies, InTech-Open Access Publisher, 81-86, 2018
[22] M. Leitner, T. Leitner, A. Schmon, K. Aziz, G. Pottlacher, Thermophysical Properties of Liquid Aluminum, Metallurgical and Materials Transaction A, 48A, 3036–3045, 2017
[23] T. Hao, H. Ma, X. Ma, Experimental Investigation of Oscillating Heat Pipe with Hybrid Fluids of Liquid Metal and Water, Journal of Heat Transfer, 141, 071802-1071802-6, 2019
[24] G. Mohan, M. B. Venkataraman, J. Coventry, Sensible energy storage options for concentrating solar power plants operating above 600 °C, Renewable and Sustainable Energy Reviews, 107, 319–337, 2019
[25] R. L. Murray, K. E. Holbert, Chapter 25 - Breeder reactors, Nuclear Energy (Seventh Edition), 459-475, 2015
[26] Liquid metal coolants for fast reactors cooled by sodium, lead, and lead-bismuth Eutectic, IAEA NUCLEAR ENERGY SERIES No. NP-T-1.6, International Atomic Energy Agency, 2012
[27] K. Kalantar-Zadeh, M. A. Rahim, J. Tang, Low melting temperature liquid metals and their impacts on physical chemistry, Accounts of Materials Research, 2, 8, 577-580, 2021
[28] S. Cheng, Z. Wu, Microfluidic electronics, Lab Chip, 12, 2782–2791, 2012
[29] S. Chen, H. Z. Wang, R. Q. Zhao, W. Rao, J. Liu, Liquid Metal Composites, Matter 2, 1446–1480, 2020
[30] Y. Chen, J. L. Wagner, P. A. Farias, E.P. DeMauro, D.R. Guildenbecher, Galinstan liquid metal breakup and droplet formation in a shock-induced cross-flow, International Journal of Multiphase Flow, 106, 147–163, 2018
[31] Y.H. Liu, Density and viscosity of molten Zn-Al alloys, Metall. Mater. Trans. A 37, 2767-2771, 2006