Specific heat capacity of aluminium and aluminium alloys

by **Dan Dragulin, Marcus Rüther**

Material and product designing in the field of aluminium and aluminium alloys is a permanent challenge. The present paper embraces an important thermodynamical aspect, the specific heat, of a metal having an extreme large representation in the industry: aluminium. The various applications (from heat treatment to ablative materials and nuclear fuel) analyzed within the framework of the present paper reveal the utmost representativity of the topic (Preamble by Oleg Hoffmann – BAGR Berliner Aluminiumwerk GmbH).

Specific heat capacity (as intensive property) or heat capacity (as extensive property) is a fundamental concept of thermodynamics having a seminal importance for practical applications.

The specific heat capacity builds the very basis of every theoretical and practical heat transfer calculation. The present work will delineate the above mentioned practical importance of the specific heat capacity in the case of aluminium using various methods of calculation. The differences resulted from the application of different methods could appear, at the first glance, to be not significant, but for large industrial applications (such as heat treatment of aluminium), lead to significant technical and economical consequences.

Principally the perception of the specific heat capacity has not changed since 1760 (the year of the first documented approach of "specific heat") till today ("The heat capacity is a constant that tells how much heat is added per unit temperature rise. The value of the constant is different for different materials." [1]) What is changing is the accuracy of estimation.

Table 1 shows an outline of the historical development.

Table 1: Historical development [2]

Name	Year	Person
	1760	Joseph Black (1728-1799) Scottish physicist and chemist
Absolute heat	1770s	William Irvine (1743-1787) Irish chemist and physician
Specific fire	c.1777	Richard Kirwan (1733-1812) Irish chemist
Capacity of bodies for receiving the matter of heat	c.1777	Richard Kirwan
Absolute heat of bodies	1779	Adair Crawford (1748-1795) Irish chemist
Specific heat	1780	Joao Magellan (1722-1790) Portuguese physicist
Specific heat	1782	Johann Wilcke (1732-96) Swedish chemist
Capacities [of substances] for heat	1807	Thomas Young (1773-1829) English polymath
Caloric specific	1824	Anon, Dictionary of Chemistry
Capacity for heat / Specific heat	1846	Karl Friedrich Peschel
Heat-capacity	1848	Leopold Gmelin (1788-1853) German chemist
Specific heat | Capacity of bodies for heat	1860	John Johnston
Specific heat (capacity for heat referred to a given weight)	1861	Leopold Gmelin
Specific heat [Capacity for heat]	1865	Rudolf Clausius (1822-1888) German physicist
Real specific heat [Real capacity for heat]	1865	Rudolf Clausius
Specific heat capacity	1869	Anon, Nature, Vol. 290
Specific heat-capacity	1880	James Hamblin Smith, An Introduction to the Study of Heat
Heat capacity	1894	Wilhelm Ostwald

Table 2: Heat capacity for aluminium – approximate expressions

C_p	Source
$C_{p,m} = a + bT + c / (T^2)$	[3]
$C_p = a + bT - c / (T^2)$	[5]
$C_p = a + bT + c(T^2) + d(T^3) + e / (T^2)$	[6]
$C_p = aT + b(T^3) + c / (T^2)$	[7] → [8]
$C_p = a(T^b)(e^{cT})(e^{d/T})$	[8]
$C_p = a + bT + c / (T^2)$	[9] → [8]
$(C_p^0(T)) / R = a_1 + a_2T + a_3(T^2) + a_4(T^3) + a_5(T^4)$ R = universal gas constant	[10]

The following calculations are based on data and methods published after 1900.

BASIC NOTIONS

The following definitions are from Atkins [3].

Heat capacity at constant volume – extensive property:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad (1)$$

where: U: internal energy; T: temperature [Kelvin].

Molar[1] heat capacity at constant volume – intensive property:

$$C_{V,m} = \frac{C_V}{n} \ [\mathrm{J\,K^{-1}\,mol^{-1}}] \quad (2)$$

Analogue to the heat capacity at constant volume:

Heat capacity at constant pressure – extensive property:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p, \quad (3)$$

where: H: enthalpy; T: temperature.

The molar heat capacity at constant pressure $C_{p,m}$ is an intensive property.[2]

DATA AND CALCULATION METHODS

The variation of heat capacity with temperature can sometimes be ignored if the temperature range is small; this approximation is highly accurate for a monoatomic perfect gas (Atkins [3]). This statement is very often, in practice, completely ignored: calculations performed using a single value for a large temperature interval (the case of aluminium heat treatment processes) are a common practice with negative economic consequences.

Formulae such as (4) & (5) [4] should be avoided in the practice of heat treatment. Later in this article other approaches will be presented:

$$q = m \cdot C \cdot \Delta T \quad (4)$$

$$q = m \cdot C \cdot (T_f - T_i) \quad (5)$$

q = amount of heat energy gained or lost by substance
m = mass of sample
C = heat capacity (J °C^{-1} g^{-1} or J K^{-1} g^{-1})
T_f = final temperature
T_i = initial temperature

In the case of a heat treatment process[3] the temperature variation is the core of the process and therefore has to be taken into account. **Table 2** presents several approximation expressions delineating the dependency of the heat capacity of the temperature; the values[4] of the equation parameters (e. g. a, b, c …) are to be found in the respective literature source and are valid only for the specified temperature interval. For practical applications the energy required to heat a product can be calculated using the formula (6).

$$Q = m \cdot \int_{T_i}^{T_f} C_p \, dt \quad (6)$$

Fig. 1 provides a graphic depiction of literature data showing, for some temperature intervals, significant differences. For the intervals where these differences, at the first glance, are not significant one has to take into account the global quantity of material submitted to an industrial heat treatment process.

Fig. 2 shows results of recent research works [8]; the inherent differences are clearly depicted.

Pure aluminium is for the practice of heat treatment not relevant. Aluminium alloys are the object of industrial heat treatment processes. The best way to get credible information about their heat capacity is to measure it; a very recent publication [11] provides valuable data concerning the AlSi7Mg0.3 alloy. These data are, together with the calculation (after [5]) for pure Al, presented in **Fig. 3**. Between the two sorts of AlSi7Mg0.3 alloys there are no significant differences, but between pure Al and the alloy the differences are significant. Therefore, the transfer of data from pure Al to Al-alloys has to take into account the inherent significant differences.

In the case of alloy one can use Kopp´s law: "The molecular heat capacity of a solid compound is the sum of the atomic heat capacities of the elements composing it; the elements having atomic heat capacities lower than those required by the Dulong-Petit law retain these lower values in their compounds." [Wikipedia]

$$C = \sum_{i=1}^{n} (C_i \cdot x_i) \quad (7)$$

1 $C_{V,s} = C_V/m$ – specific heat capacity: the heat capacity of the sample divided by the mass, usually in grams; analogue for $C_{p,m}$

2 In the case of quoted material all notations, spelling and measuring units correspond to the original

3 A heat treatment process is a heat transfer process; the present paper refers to solid state heat transfer processes.

4 (Of course) are different from author to author

C_i, x_i are the specific heat respectively the mass fraction of the "i" element

The specific heat of an alloy can be approximated, near ambient temperature, by a linear combination of the specific heats of the constituent elements [12 → 13]. This seems to be refuted, at least by the some of the data presented [14]; the explanation is: "A disordered distribution of the solute atoms leading to a defect structure may be considered to be responsible for the observed trend in the heat capacity of Al-Cu and Al-Zn alloys."

SPECIAL APPLICATIONS

Aluminium, both as base material and alloying element is used in a very large variety of so called special application. One has to emphasize that aluminium has also a very important strategic property: it is present in very large quantities and it is, compared with other metals, easier to process (especially under exceptional circumstances) and at lower costs.

CRYOGENIC APPLICATIONS

The very actual environment discussions and legislation development will rapidly bring alloys for cryogenic applications in the automotive daily business. **Fig. 4** presents a comparison between alloys used for such applications.

ALUMINIUM AS FUEL

Aluminium can be used as alloying element for the fabrication of nuclear fuels. Its heat capacity is a seminal property dictating the characteristics of the respective fuel (**Fig. 5**)

Aluminium is also an important component of RAM-JET fuel. The jet thrust directly depends on the ratio of specific heats.

$$F_j = p \cdot \gamma \cdot A \cdot M^2 \qquad (8)\ [16]$$

F_j = jet thrust
p = atmospheric pressure
γ = ratio of specific heats
A = nozzle-exit area
M = flight Mach number

ALUMINIUM AS DECOY MATERIAL

The heat capacity is one of the most important property in designing decoy materials

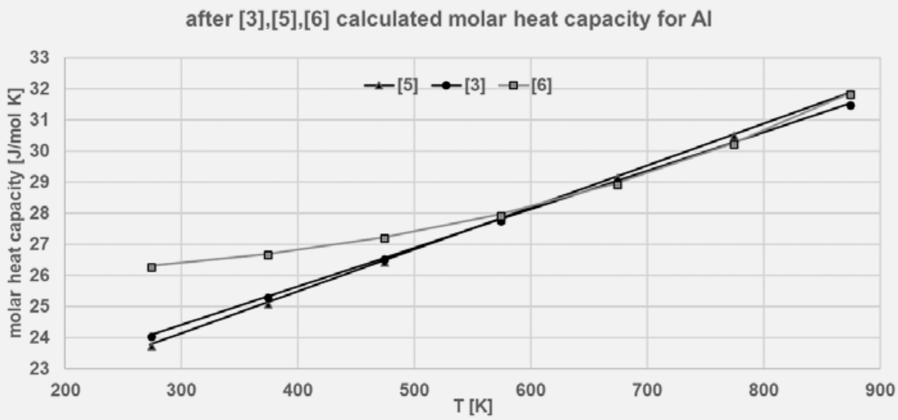

Fig. 1: Calculated molar heat capacity using different methods

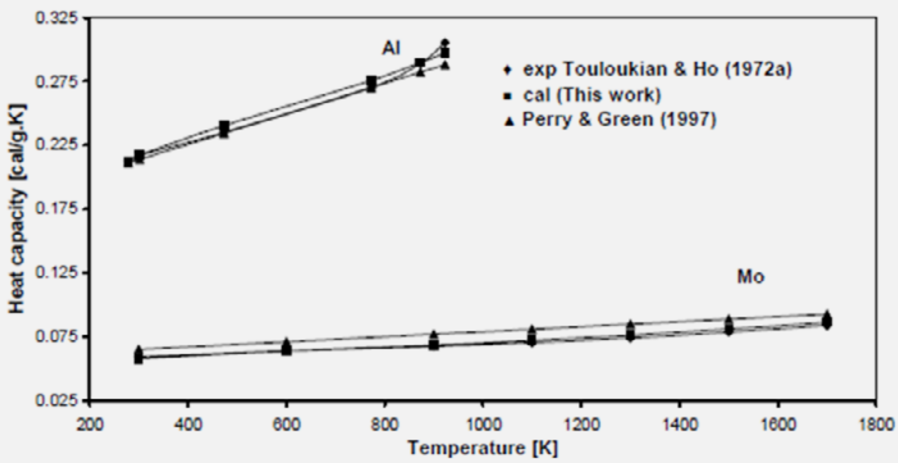

Fig. 2: Calculated specific heat vs. temperature for Al and Mo [8] (cal [8] / Touloukian [7] → [8] / Perry [9] → [8])

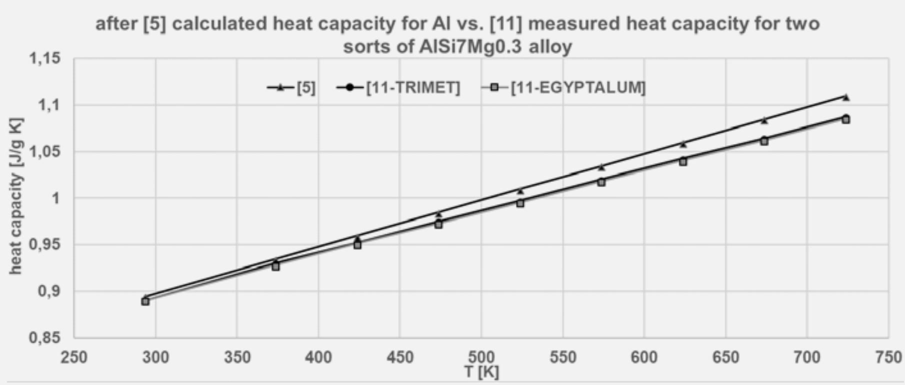

Fig. 3: Calculated heat capacity of Al vs. measured heat capacity of AlSi7Mg0.3

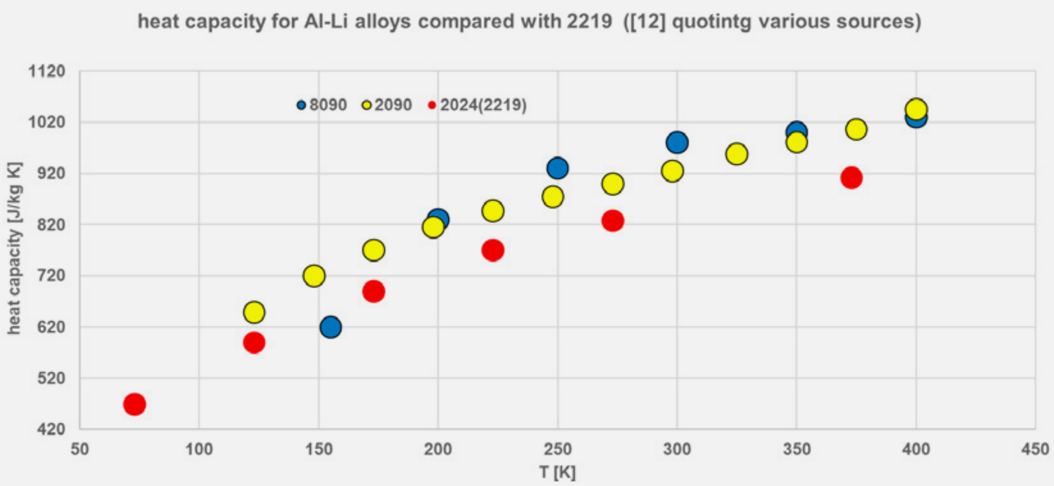

Fig. 4: Heat capacity for alloys used for cryogenic applications (after [12])

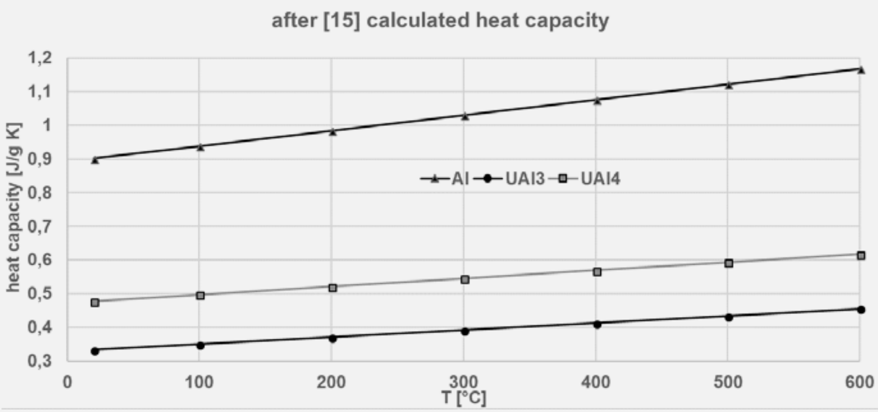

Fig. 5: Heat capacity for alloys (Al-U) used for nuclear applications (after [15])

for space working objects. "The rate of temperature change may also reveal information about the heat capacity of the target or of its outer layer. For example, a light balloon decoy (with a low heat capacity) would be expected to change temperature much more rapidly than a heavy warhead." [17]

ALUMINIUM AS ABLATIVE MATERIAL

In the case of re-entry vehicles, the designing of the heat shields using ablative materials has to take into account not only the density and the melting point of the respective material, but also thermodynamic properties such as the specific heat. Due to these mixtures of properties aluminium is one of the most important ingredients for ablative materials (along with other materials such as: Be, Cu, Graphite, Fe, Mo, Ni, Ag, Au, W); for further information see [18].

In the case of specific heat transfer ablative, multilayer materials or coatings the relationship between heat capacity and the elasticity modulus is very important. **Table 3** will present a comparison between aluminium, silver and gold. As these data show, the competitiveness of aluminium is indisputable (do not forget the other strategic properties of aluminium exposed above).

Conclusion The present paper presents various results regarding the implication of the accuracy (without making a mathematical excursus trying to define the difference between accuracy vs. precision) of a large variety of methods and algorithms to calculate or to estimate the value of the specific heat capacity. The choice of the estimation/calculation method has to take into account the very specific temperature interval and the very specific material.

In the case of industrial heat treatment/transfer processes of Al-alloys, the production specialist has very little data at

Table 3: E-Modulus and heat capacity at room temperature for Al, Ag, Au

[19] / [20]	C at 25°C [J/g°C]	E [kp/mm²]
Al	0.9	6,750
Ag	0.24	8,160
Au	0.129	7,900

his disposal. Therefore, further research work is needed.

Although the scientific study of "heat capacity" is more than 200 years old, the actuality of this topic is stringent and of seminal importance (fact underpinned by very numerous publications) not only for aluminium or solid-state applications, but for every material irrespective of the state of aggregation.

LITERATURE

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AUTHORS

Dr. **Dan Dragulin**
Director Research & Development
ATC ALUVATION Technology Center
Paderborn GmbH

Marcus Rüther
Director Marketing & PR
ATC ALUVATION Technology Center
Paderborn GmbH