G. BOCZKAL*#

MELTING POINT OF METALS IN RELATION IO ELECTRON CHARGE DENSITY

TEMPERATURA TOPNIENIA METALI W ODNIESIENU DO PRZESTRZENNEJ GĘSTOŚCI ŁADUNKU ELEKTRONÓW W ATOMIE

The concept of spatial criterion of the electron charge concentration is applied to determine the metal melting point. Based on the model proposed for bcc metals, a model for hcp metals and general form for others has been developed. To calculate the melting point, only structural data and atomic number are required. The obtained results show good consistency with the experimental data for metals with atomic number $Z < 70$.

Keywords: Melting point; Thermal analysis; Structure analysis; Metals

Praca stanowi rozwinięcie koncepcji kryterium przestrzennej koncentracji ładunku elektronowego jako miary temperatury topnienia metalu. Na bazie modelu zaproponowanego dla metali o sieci *bcc* został opracowany model dla metali o sieci *hcp*. Do obliczenia temperatury topnienia wymagane są jedynie dane strukturalne i liczba atomowa. Uzyskane wyniki wykazują dobrą zgodność z danymi eksperymentalnymi dla metali o liczbie atomowej $Z < 70$.

1. Introduction

In [1] the theoretical possibility of determining the melting point of *bcc metals* was mentioned. The method used basic crystal lattice parameters and the atomic number of metal. In this study, an attempt was made to further develop the aforementioned method and calculate the melting point of *hcp metals*. *Bcc* and *hcp structures* exhibit certain similarities in their crystallography, i.e. both have two atoms per unit cell. Other parameters are, however, different [2,3]:

– coordination number of *hcp structure* = 12 and of *bcc* = 8,
– angular symmetry – *hcp cell base* is of a rhombic shape, and *bcc cell base* is of a square shape,
– dimensional symmetry – *hcp unit cell* is described with two different constants, i.e. *a* and *c*,
– the coordination number of *hcp metals* with *c/a* other than 1.633 divides the group into two 6 + 6 subgroups with different length of the lattice constants,
– the atomic packing factor is 68% for *bcc* and 74% for *hcp*,
– *bcc phase* is usually the last high-temperature phase in a metal structure, while *hcp phase* is mostly transient (only 10 metals and metallic hydrogen can keep *hcp structure* within the whole range of existence of the solid phase),
– interatomic bonding in metals with *hcp structure* is of a mixed type with a significant share of covalent part.

Because of these differences, slightly different approach to the problem of the melting point calculation has been adopted for hcp metals than for bcc metals [1]. Theoretical calculation method were applied for analysis of solidification process and phase transformation [4,5].

2. Methods & calculations

Symbols used in the text and their meaning:
$\rho_{el.}$ [nm^{-3}] – spatial concentration of the electron charge, Z – atomic number, a [nm] – length of an edge in a basis of a unit cell, c [nm] – height of the hexagonal prism, b [nm] – the smallest *bcc lattice constant* (corresponding to the constant a in *hcp lattice*), x [nm] – lattice constant in the coordination

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS METALS, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

Correspomding author: gboczkal@agh.edu.pl

subgroup for hcp lattice with c/a ratio different from the ideal one (for $c/a = 1.633$; x corresponds to a), V_{at} [nm^3] – volume belonging to a single atom, T_{hcp} [K] – melting point of *hcp metals*, T_{bcc} [K] – melting point of *bcc metals*.

For the purpose of this analysis, the spatial criterion of the electron charge concentration ρ_{el}, discussed in previous article [1], has been used:

$$\rho_{el} = \frac{Z}{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3} \qquad (1)$$

The electron charge concentration was calculated for a simplified model of structure based on the spheroidal symmetry. The atomic radius was assumed to be ½ interatomic distance along the <11-20> direction. It is the direction parallel to the edge a of the hexagonal unit cell. As in the case of *bcc structures* [1], also now it has been observed that the melting point of *hcp metals* is proportional to the ratio:

$$T_{hcp} \approx \rho_{el} \approx \frac{Z}{V_{at}} \qquad (2)$$

In the next step, the space occupied by a single atom was estimated. In most hcp metals, the c/a ratio differs from the ideal value of 1.633. The result is the existence of two coordination subgroups (6 + 6) [6]. Therefore it was decided to introduce an ellipsoid for the description of the space occupied by a single atom. Arms of this ellipsoid define the lattice constants a and x for both coordination sub-groups. The quantity x has been defined as:

$$x = \sqrt{\left(\frac{a}{2\sin 60^{\circ}}\right)^2 + \left(\frac{c}{2}\right)^2} \qquad (3)$$

The volume V_{at} has been described as an ellipsoid:

$$V_{at} = \frac{4}{3}\pi\left(\frac{a}{2}\right)^2\frac{x}{2} \qquad (4)$$

The preliminary rough calculations were based on equation given in [1] with the V_{at} parameter of the space volume occupied by a single atom adapted to hcp structure:

$$T_{hcp} \simeq \frac{2Z}{\frac{4}{3}\pi\left(\frac{a}{2}\right)^2\frac{x}{2}} = \frac{12Z}{\pi a^2 x} \qquad (5)$$

The structural data of metals necessary to perform the calculations are compared in Table 1. The analysis covers the elements for which the *hcp phase* remains stable within the entire range of existence of the *solid phase*.

Careful analysis of the results obtained with equation (5) showed significant discrepancies due to the differences in c/a parameters of individual metals. To correct these discrepancies, an additional term allowing for a change in the c/a ratio was introduced:

$$T_{hcp} = \frac{12Z}{\pi a^2 x} / N \qquad (6)$$

TABLE 1

Data of *hcp metals* arranged according to the increasing c/a ratio [2,3,7,8]

Element	Atomic number	a [nm]	c [nm]	c/a	Melting point
	Z	at 300 K			[K]
Er	68	0.3559	0.5587	1.569	1802
Tm	69	0.3538	0.5555	1.570	1818
Ho	67	0.3577	0.5616	1.570	1747
Os	76	0.2735	0.4319	1.5791	3306
Ru	44	0.2706	0.4281	1.582	2607
Lu	71	0.3503	0.5551	1.584	1936
Re	75	0.2761	0.4458	1.6146	3459
Mg	12	0.3209	0.5210	1.6235	923
Metallic H	1	0.3776	0.6162	1.631	14
Zn	30	0.2664	0.4947	1.857	693
Cd	48	0.2979	0.5619	1.886	594

where

$$N = \left(\frac{c}{a}\right)^3 \qquad (6a)$$

The adjustment was of purely phenomenological nature and enabled obtaining good consistency between the experimental results and theoretical calculations for the whole range of the c/a values reported. Detailed analysis of changes in the values of a-x has showed, that within the whole range of its occurrence the difference was always less than 2%, meaning that the value of a/x was close to 1. Appropriate simplifications gave equation (7). For comparison equation (8) obtained for *bcc metals* was presented [1].

$$T_{hcp} = \frac{12Z}{\pi a^2 x}\left(\frac{a}{c}\right)^3 \qquad (7)$$

$$T_{bcc} = \frac{2Z}{a^3} \qquad (8)$$

3. Results and conclusions

The aim of equation (8) was to compare the melting point of *bcc metals* [1]. To make this comparison easier, both equations, i.e. (7) and (8), were converted to the form using the smallest lattice constant as a measure of the side of a cube in the space occupied by one atom. By transformation of equation (7) assuming that $a = c/1.633$ and equation (8) assuming that the smallest *bcc lattice* constant is $b = 0.866a$, the following equations were obtained:

$$T_{hcp} = \frac{0.866Z}{a^3} \qquad (9)$$

$$T_{bcc} = \frac{1.299Z}{b^3} \qquad (10)$$

The ratio of $1.299/0.866 = 1.50$, which is exactly an equivalent of inverse proportion of coordination numbers $(8_{bcc}/12_{hcp})^{-1}$. The coordination number is equal to a hypothetical number of equally-important directions of bond formation for a single atom
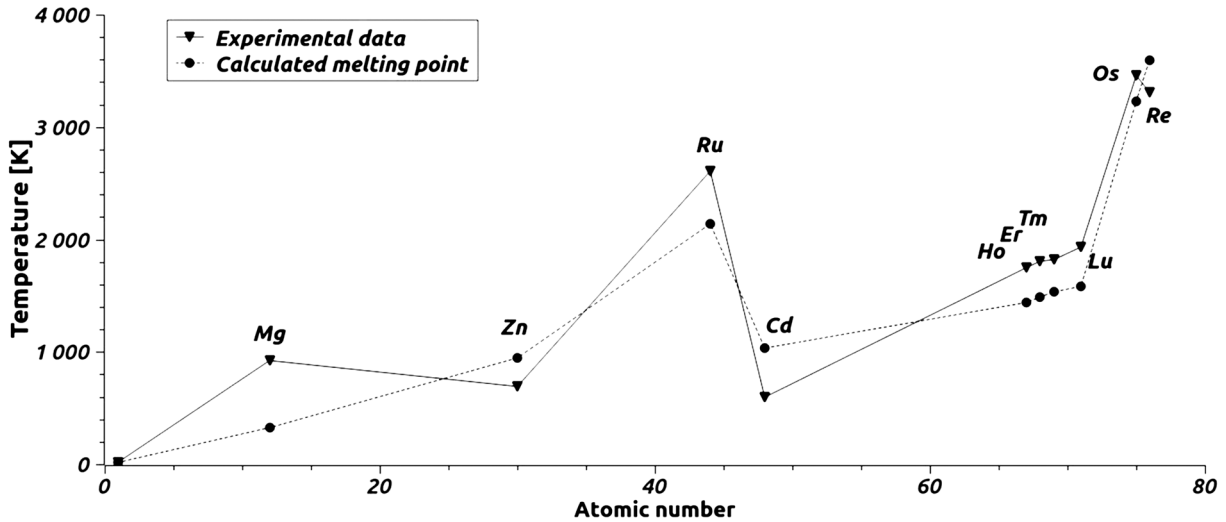
Fig. 1. The results of calculations based on equation (7) compared with the experimental data. Melting points are shown as a function of the atomic number Z

in a crystal lattice. The real number of possible bond directions is equal to 12 only in respect of metals with c/a ratio close to ideal one 1.633. In case of other metals it can assume intermediate values from the range of 6 to 12. The lowest values may be reached for zinc and cadmium with the largest deviation from 1.633. The large variation of c/a ratio from the ideal value causes significant discrepancies in distances between the central atom and its coordination atoms laying in basal plane and in parallel planes. As a result, a decreased number of the closest neighbors of the atom to the level of 6 occurs and, as a consequence, a change of interatomic bond structure takes place. The described changes adequate to the coordination number and c/a ratio can be correlated obtaining equation (11):

$$T_{hcp} \approx \frac{-0.6\ln\left|1.633-\dfrac{c}{a}\right|Z}{0.866a^2 c} \approx \frac{X_{hcp}}{V_{hcp\ unit\ cell}}Z \qquad (11)$$

$$T_{bcc} \approx \frac{X_{bcc}}{V_{bcc\ unit\ cell}}Z \qquad (12)$$

where X is a structural factor including symmetry and distribution of interatomic bonds in metal structure. X_{hcp} for *hcp metals* gets values from the range 0.82 (Cd) to 2.79 (Mg). For comparison, the X_{bcc} value for bcc metals (equations 8 and 12) is equal to 2 [1]. The equation (11) includes moreover restriction for ideal *hcp structure* ($c/a = 1.633$), not existing in nature. The argument of natural logarithm function must be greater than zero. The value closest to zero is observed for metallic hydrogen, the phase that exists at ultra high pressure.

The final results received by application of equation 11 are presented in Figure 2.

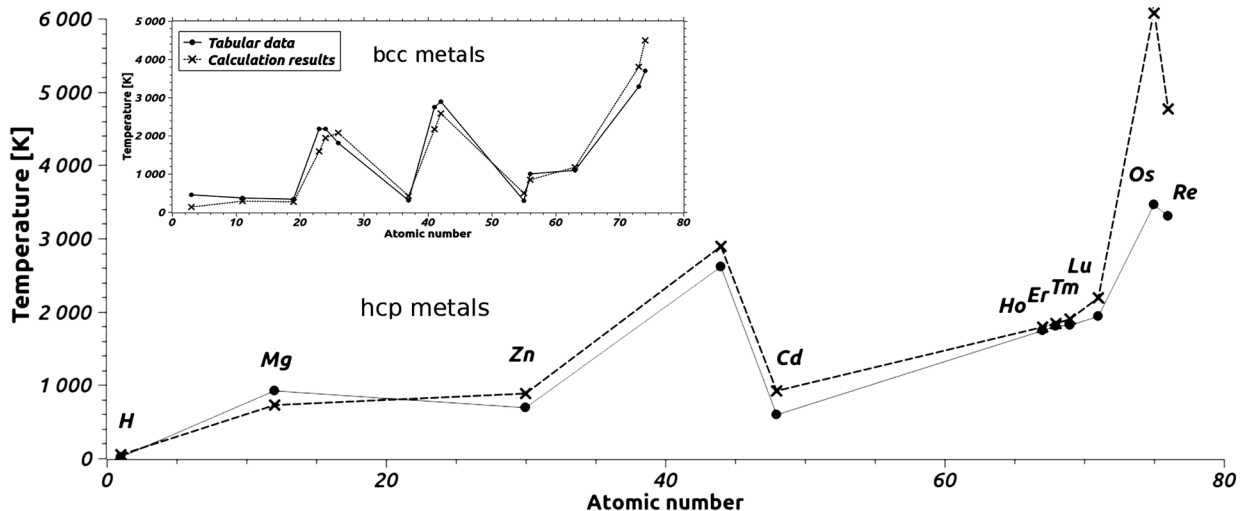For comparison, the results obtained for *bcc metals* [1] are inserted.

Fig. 2. The results of calculations based on equation (11) compared with the experimental data. Melting points are shown as a function of the atomic number Z

4. Summary

Based on the previous considerations, a general equation could be proposed:

$$T_{melting\ point} \approx X\left(symmetry, bonds\ model\right)\frac{Z_{metal}}{V_{metal\ unit\ cell}} \quad (13)$$

where: X – is a structural factor including symmetry and distribution of interatomic bonds in metal structure, V – volume of metal unit cell, Z – atomic number of metal.

Melting points calculated according to equation (7) show some deviations from the experimental data. The largest error occurs in the case of Mg, Zn and Cd. Taking into account changes in interatomic distances in first coordination zone caused by deviation from ideal value of c/a ratio, what was done in equation 11, allowed to attain a good consistence of results for all hcp metals up to the atomic number of 71 (Lu). The variations occur only for elements with big atomic number (Os and Re), characterized also by high melting temperatures and large density up to 20g/cm^3.

REFERENCES

[1] G. Boczkal, Electrons charge concentration and melting point of bcc metals, Materials Letters **134,** 162-164 (2014).

[2] E.R. Schulze, Gustav, Metallphysik, Akademie-Verlag, Berlin (1974).

[3] H. Ibach, H. Luth, Solid-State Physics, Springer-Verlag (1991).

[4] W. Wolczynski, J. Janczak-Rusch, J. Kloch, T. Rutti, T. Okane, A model for solidification intermetallic of phases from Ni-Al system and its application to diffusion soldering, Archives of Metallurgy and Materials **50,** 4, 1041-1054 (2005).

[5] J. Trzaska, Empirical Formulae for the Calculation of Austenite Supercooled Transformation Temperatures **60,** 1, 181-185 (2015).

[6] O.H. Wyatt, D. Dew-Hughes, Metals, Ceramics & Polymers: An introduction to the structure and properties of engineering materials, Cambridge University Press (1974).

[7] ASM Alloy Phase Diagrams Center, P. Villars, editor-in-chief; H. Okamoto and K. Cenzual, section editors; www.asminternational.org/AsmEnterprise/APD, ASM International, Materials Park, OH, USA 2007.

[8] P. Eckerlin, H. Kandler, A. Stegherr, Structure data of elements and intermetallic phases, Landolt-Bornstein, New Series Vol.III/6, Springer, Berlin, Heidelberg (1971).