ENTROPY OF MELTING AND STRUCTURAL CONDITION OF A MELT

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SUMMARY

Some reasons of calculation of an item making entropy of melting are submitted. The entropy of melting is represented by the sum of components of change of a condition of atoms and free electrons regularity. Influence of a structural condition of a melt on an entropy is analyzed.

Key words: metal alloys, melting entropy

It is known that melting crystallization phase transition is accompanied by spasmodic change of volume and entropy. At this, the change of specific volume reflects only quantitative processes of change of an aggregative state. The entropy of melting for concrete substances changes not only quantitatively, but also in its structure - it contains the information on both change as the state conditions of a nuclear structure and an energy spectrum of electrons of conductivity (conduction electrons). The entropy depends also on the conditions of realization of phase transition. The peculiarity of melting is that contrary to other types of phase transitions the level of the disorder changes not only statically, but also dynamically sense.

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For simple melts (including eutectic ones) the entropy of melting (EM) can be presented as a sum of oscillation ($\Delta S_{\text{oscill}}$), electronic ($\Delta S_{\text{el}}$) and position ($\Delta S_{\text{pos}}$) components:

$$\Delta S = \Delta S_{\text{oscill}} + \Delta S_{\text{el}} + \Delta S_{\text{pos}}.$$  

Here the first component is responsible for the loss of the far ordering and, according to the theory of structural diffusion, it contains the information about the change in the spectrum of parameters of atom oscillations around equilibrium centers. Within the approximation, according to which melting is accompanied only by the change of the oscillation spectrum of harmonic oscillators, with the close ordering being the same, Mott got for this component:  

$$\Delta S_{\text{oscill}} = \frac{1}{80} \ln \left( \frac{\rho_L}{\rho_S} \right),$$  

where $\rho_L$, $\rho_S$ — are specific electric resistances of liquid and solid phases near the phase transition ($P_T\tau$).

The second EM component ($\Delta S_{\text{el}}$) is the change of current carriers transition entropy and, in accordance with irreversible processes thermodynamics, it is determined by the change in absolute thermal electromotive force (Zeebeck coefficient) during melting.

The third component ($\Delta S_{\text{pos}}$) of melting entropy is the most important as it is this very component that is responsible for both quantitative and qualitative change of the atomic dynamics. $\Delta S_{\text{pos}}$ must reflect the critical changes in the short-range ordering, including transformation of structural melt elements – clusters – caused by intensive atomic dynamics of translational motion with the account of cooperative processes. For complete change of entropy during melting there is used an expression in which the above mentioned components are assigned.

$$\Delta S = \frac{1}{80} \ln \frac{\rho_L}{\rho_S} + F \Delta \alpha + \Delta S \left( \frac{Z_L - Z_S}{Z_S} \right),$$  

where:

- $\Delta \alpha$ - is a change in absolute thermal electromotive force;
- $F$ - is a Faraday constant;
- $Z_L$ & $Z_S$ - are coordination numbers.

The entropy calculated by (1) reflects the experimental values quite well for both normal metals (Cu, Ag, Zn, In, Pb) and semimetals (Ga, Bi). In normal metals $\sim 90\%$ of the calculated value is taken by the first component and in semimetals $\sim \frac{1}{2} \Delta S$ is composed by electron and especially position components.

The position component of entropy is particularly essential in conditions of especially principal change in the level of ordering, in particular in eutectic melts based on Bi and Cd. Yet, the proposed empirical and speculative representation of the position component of entropy (1) does not contain obvious information about rather complicated processes of structural transformations taking place during the change of aggregate state.
First of all, it is necessary to note that the degree of atom ordering is substantially 
violated yet in a crystalline state with the approach to the melting temperature. On the 
other hand, the melt in a pre-melting state cannot be considered as an absolutely 
disordered melt. The parameter of the disordering level can be presented via relative 
root-mean-square function of the inter-atomic distance \( \{a\} \)
: \( \varepsilon = \frac{1}{a} \sqrt{\langle (\Delta a)^2 \rangle} \). The 
evaluations of the level of disordering have shown that in a crystal close to melting 
\( 0.11 \leq \varepsilon_L \leq 0.16 \). At the same time the analysis of the results of X-ray imaging of metal melts close to crystallization shows that \( \varepsilon_S \geq 0.25 \). The change of \( \varepsilon \)-parameter in these 
limits corresponds to the jump of entropy during melting. This shows the necessity for a 
more detailed analysis of the melt’s structural state and its effect on the formation of \( \Delta S_{\text{POS}} \).

First of all, it should be emphasized that the expression \( \Delta S = \frac{Q_{\text{rot}}}{T_{\text{rot}}} \) is valid only 
in cases when thermodynamic parameters \( (T, p, c) \) conform to the conditions of 
equilibrium. It is in this case that transmutation of phases can be considered as a 
reversible process. In real conditions the process reversibility is only a desirable 
idealization that we should try to achieve, but one should be aware of the processes and 
phenomena that hinder this as well as one should be aware of how (using what 
constructional and technological techniques) these obstacles can be avoided or, more 
precisely, minimized.

As far as the eutectic melts considered here are concerned, the most essential 
obstacles on the way to establishing the conditions of the melting – crystallization 
process reversibility will be the following: \( \ast \) incomplete transition from the crystalline 
structure to the homogeneous liquid structure (the microheterogeneous state of the 
melt); \( \ast \) overcooling of the melt to the temperature that is lower than the equilibrium 
crystallization temperature; \( \ast \) deviation from the eutectic concentration.

Let us analyze the first group of processes as the most important one for the melting 
entropy structure formation.
Let us consider the system consisting of \( N_{AB} = N_A + N_B \) atoms of A and B types that are chaotically mixed in space. \( N_{AB} \) = an Avogadro constant. In this case, in accordance with Boltzman equation, the entropy position component can be expressed through the probability of the corresponding states (elementary cells occupied by atoms A or B):

\[
\Delta S_{\text{POS}} = k_B \ln \left( \frac{N_{AN}!}{(N_A ! \times N_B !)} \right),
\]

or using the notions of atomic particles (in the Stirling approximation): \( x_A = N_A/(N_A + N_B) \); \( x_B = N_B/(N_A + N_B) \), we get: \( \Delta S_{\text{POS}} = -R \left( x_A \ln x_A + x_B \ln x_B \right) \) that in this case is the entropy of mixing of arbitrary-oriented-in-space structural units.

However, as the results of the diffraction experiments (both X-ray and neutronography) have shown, in the certain temperature interval after melting, eutectic compounds are not characterized by the statistic (as to the atoms’ type) atomic distribution. This interval ranges from 30 to 150K above the eutectic melting temperature and within this interval the specific quasi-eutectic structure is preserved. In this structure, but for the elementary A and B cells, there also exist larger structural units in the form of clusters or fractals which are mostly composed of the atoms of the same type. It is assumed that such structural units have short life, however, instead of them there emerge others and the clusters inclusion volume fracture \( \phi \) is statistically constant for every particular temperature. Thus, in a certain temperature interval after melting the structure of eutectic melts is microheterogeneous.

It is obvious that physical properties of microheterogeneous melts can be substantially different from those of genuine physical melts. In particular, viscosity of colloidal melts according to Einstein model can be described by the expression:

\[
\nu = \nu' (1 + 2.5 \phi + 7.5 \phi^2),
\]

where:

\( \nu \) and \( \nu' \) are a really determined (measured) kinematic viscosity of a melt and the viscosity of an “ideal” homogeneous melt.

This expression can certainly be used for evaluation of fracture \( \phi \) of clusters in the case considered.

So, the position component of entropy will be determined by the thermodynamical probability of the presence \( N_A(1-\phi) \) of the type “A” atoms that are not combined in clusters and \( N_B(1-\phi) \) of type “B”.

198
Other atoms of both types are bound into clusters and fractals of mostly the same type, which, close to crystallization, become precursors of the emerging crystalline phases of $\alpha$- and $\beta$- solid solutions. At this, the expression (2) becomes, to some extent, more complicated:

$$\Delta S_{\text{mot}} = k_b \ln \left( \frac{[N_A (1-\varphi) + N_B (1-\varphi)]!}{[N_A (1-\varphi)]! \times [N_B (1-\varphi)]!} \right)$$

After corresponding transformations in Stirling approximation we get:

$$S_{\text{mot}} = -R (1-\varphi) \left( x_A \ln \left( \frac{x_A}{x_A + x_B} \right) + x_B \ln \left( \frac{x_B}{x_A + x_B} \right) \right)$$

(4)

It is easy to see that when $\varphi=0$, this expression will look like (2) and when $\varphi=1$, the position component will be zero – the atoms of both types form solid solutions $\alpha$ and $\beta$ and are blocked in a crystalline structure of eutectics.

Thus, the position component of the melting-crystallization entropy can substantially change and this, in its turn, will cause some uncertainty in the temperature of phase transition. The reason may be micro-heterogeneous of the working melt or the presence of internal stresses in a material before melting. It is obvious that uncertainty of temperature must not be allowed. So, the use of these (eutectic) melts as functional material for temperature points leads to the necessity of developing additional preliminary technological treatment of the functional material and the necessity of controlling the melt’s thermodynamic state.

In the scopes of the accepted model the share of $\varphi$ clusters in an alloy structure can be determined experimentally using methods of radiographic analysis and viscometry. We have performed calculation on the basis of the measurements of viscosity of eutectic alloys of Li-Pb, Li-Sn and In-Ga system. Near to temperature of melting the experimental values of viscosity are much higher than the values calculated using an additive model.

On this basis may it is possible to believe that except for the atoms pure a components in an alloy more complex structural units - clusters cal also be found. Therefore, it is possible to apply the formula (3) to evaluate of their share. Believing that at high temperatures clusters degrade to a condition of a homogeneous solution, - we extrapolate high-temperature dependence v(T) up to the temperature of crystallization. Various methods of extrapolation give the $\varphi$ value in a range from 0.10 up to 0.05.

Presence in an alloy of up to 10% of the associated complexes results in essential difference of an entropy of melting and crystallization and also may cause significant overcooling of an alloy.
ENTROPIA TOPNIENIA I STAN STRUKTURALNY CIECZY

Entropia topnienia podaje się przez sumę składowych zmian stanu uporządkowania atomów oraz elektronów swobodnych. Analizuje się wpływ stanu strukturalnego cieczy na entropię.

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