Crossref
UDC 669.432.669.046.42
DOI: 10.31643/2021/6445.08

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IRSTI 53.37.91

Explanation of the cluster structures melting mechanism and their influence on the molten state's physical and chemical nature

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Received: *30 January 2021*
Peer reviewed: *25 February 2021*
Accepted: *05 March 2021*

ABSTRACT

There are results of the melts of semimetals and semiconductors of various structural groups research in the article. On the example of simplified regular Bethe lattice one can model destruction and aggregation of structures in clusters and on it's basis to substantiate the metal melts properties in the form of nanolayers. The variety of compressibility polytherms forms in electronic melts requires typing, since their analysis makes it possible to explain the mechanism of the aggregation and dissolution processes of extended objects in melts. The article contains formulas that allow explaining the mechanism of the dissolution of cluster structures and their influence on the physicochemical nature of the molten state. There is considered the process of cluster fragmentation. Larger fragments of clusters are formed in the process of crushing, and this fact leads to the compressibility that decreases more rapidly, only after passing through the extremum it begins to increase due to the thermal loosening. The study of the function's compressibility for an extremum in the compressibility's temperature dependence also indicates the changing process of the clusters decomposition mechanisms in melts with an increase in temperature and vice versa to aggregation with a decrease in the melt temperature to the melting temperature.

Keywords: pair potentials, radial distribution of atoms, semiconductor, structural factor atoms, molecular dynamics, density function, cluster structure.

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Introduction

The article is devoted to an important problem in the development of the theory of the liquid state, which allows to create new technological processes of metal production and improve existing processes. In a cluster solution, the forces of interaction between monomers and clusters are assumed to be pure van der Waals forces. Simultaneously obtained the ratios required for the calculation of the wave function and the radial distribution function of the electron, the knowledge of which allows to calculate the free energy.

Model formulas of interatomic potentials can be used to calculate the physical properties of liquid metals: energy, pressure, equation of state, surface tension, viscosity and other parameters.

The presence of clusters not only near the crystallization temperature, but also at very high temperatures, in alloys of semi-metals and semiconductors is due to the presence of two types of chemical bonds - covalent and metallic [1-12].

The type of covalent bond that exists and predominates in a crystal, it cannot disappear immediately after melting or further heating when it is in a liquid state. These bonds are embedded in the nature of the atoms that make up semi-metals and semiconductors, in the outer electron shell of atoms, and cannot be lost in any aggregate state of matter. The problem is only in the degree of their clarity. If these bonds are accompanied by bonds that differ greatly in energy, then they are significantly defined, for example, molecular liquids. If these bonds are not immersed in the matrix of other types of bonds that do not differ much in energy from them, then their individuality is close in energy, but differs in the nature of bonds, for example, metal bonds are leveled on a leveling background. Thus, the cluster model of a two-structure melt (model of a mixture of cluster and atomic components), which is different in

nature, but close in strength (energy), characterizes the possibility of equilibrium of two types of chemical bonds (covalent and metallic), ie thermodynamic aspect and two mechanisms of thermal decomposition of clusters (kinetic aspect), semi-metals and semiconductors in alloys allow to qualitatively correctly explain the main types of experimental and theoretical polytherms of compressibility.

The diversity of types of compressible polytherms in electronic alloys requires typification, otherwise their analysis allows to explain the mechanism of dissolution and aggregation of elongated objects in alloys.

Experimental research

From the point of view of the basic principles of thermodynamics we consider the modulus of isothermal elasticity [1, 6, 7]:

$$k = \frac{1}{\beta} = -V\left(\frac{\partial P}{\partial V}\right)_T . \quad (1)$$

Consider the following:

$$dQ = dU + PdV, \quad (2)$$

When $dQ = 0$, also:

$$\frac{dP}{dV} = -\frac{d^2U}{dV^2},$$

We get the following:

$$k = V\frac{d^2U}{dV^2} .$$

By volume, the energy product can be converted to the following type:

$$\frac{dU}{dV} = \frac{dU}{dR}\cdot\frac{dR}{dV} .$$

Then:

$$\left(\frac{d^2U}{dV^2}\right)_{V=V_0} = \frac{d^2U}{dR^2}\left(\frac{dR}{dV}\right)^2 .$$

Let $V = \gamma R^3$ be, then,

$$\frac{dR}{dV} = \frac{1}{3\gamma R^2},$$

where γ is the coefficient of proportionality.

Let the pair potential be interpolated with the following function:

$$U(R) = E\cdot f\left[\left(\frac{R_0}{R}\right)^m - \left(\frac{R_0}{R}\right)^n\right]. \quad (3)$$

Differentiating this function by R and putting it in formula (1), we obtain the following ratio for the modulus of elasticity k:

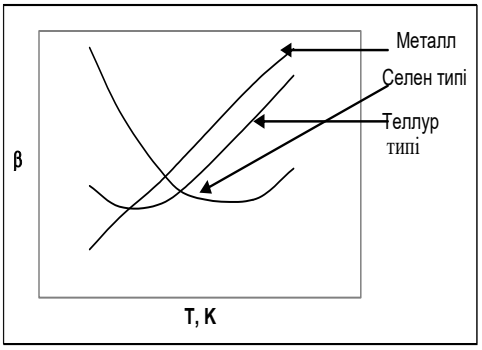
$$k = \frac{a}{R_0^3}|E|,$$

where a is some constant.

So for compression β_S we can write:

$$\beta = \frac{R_0^3}{a}\left|\frac{1}{E}\right| \quad (4)$$

Equation (4) allows to explain the mechanism of the dissolution process of cluster structures and their effect on the physical and chemical nature of the molten state. Computer modeling of the order β in T-dependence according to the formula (4) leads to the types of adiabatic compression polyters, shown in Figure 1 (where $E \sim T$ is taken into account).



Metal

Selenium type

Tellurium type

Figure 1 - Compressive polytherms

On the other hand, the matrix-cluster fluid is mentally divided into a separate matrix, ie a homogeneous atomic metallic fluid and a cluster, ie a liquid consisting only of clusters, as shown in Figure 1.

Such a division is possible only mentally, because the clusters can only be in the medium of the matrix fluid, and any attempt to separate them precisely can lead to the cessation of clusters. But mentally divide and pour into separate containers: for the first matrix liquid; for the second cluster fluid. Suppose that the compressibility of the matrix fluid in the first vessel is equal to β_1, the compressibility of the cluster liquid in the second vessel is equal to β_2. Further, assume that all clusters in the second disk are the same size and each has N atom. If N = 1, then we cannot distinguish between the contents of the second and first vessels, and $\beta_2 = \beta_1$. This is the first extreme case.

Thus, it is possible to type β_S polytherms according to the type of structural changes in the melt.

In the absence of structural changes during the heating of the condensed body, the interatomic distances increase with temperature. Therefore, the value of β_S increases with temperature, hence, the compressive polymer for liquid metals increases with temperature from thermal loosening. Such polymers are classified as polymers by type of metal.

Typification of compression polytherms of semi-metals and semiconductors in alloys requires the identification of the underlying sign. Such a sign may be the nature of the structural changes of clusters - the mechanism of their thermal decomposition. Suppose that only the clusters dissolve during heating in the "solution". Then, according to the analysis of equation (4), the compression polymer is characterized by a minimum temperature β_S, a curve that decreases uniformly with temperature.

This is especially true of tellurium alloys. Therefore, compressive polytherms are called tellurium-type polytherms. During the process of crushing clusters, the compressibility decreases sharply and begins to increase after extremum, which is characteristic of selenium. Such polytherms can be called selenium-type polytherms. The presence of extremums in the temperature dependence of compressibility also indicates a change in the mechanisms of melting processes [4, 5, 6].

Research results and discussion

Clusters can exist as individual particles only up to a certain size. As the dimensions increase, their individuality begins to "wash out". If N is very large, in order, then it makes no sense to talk about clusters N_A it is better to say that the whole container is filled with one "supercluster", ie there will be crystallization. And in this case, the contents of the dishes will not be separated again. In fact, the clusters are poured into a homogeneous mass not when N ~10^{23}, but when the values of N are much smaller. In fact, as clusters increase in size, each atom in them will be surrounded by a larger number of neighboring atoms, and the packing of atoms will become more dense. As a result, the hardness of covalent bonds begins to decrease and will often break with the release of electrons. It can be assumed that there is a finite number of atoms N_w, when the clusters cease to exist and merge into a homogeneous atomic matrix. This is the second extreme case. So, if N = $N\check{r}$ then the liquids in the first and second vessels are in equilibrium, and again $\beta_2 = \beta_1$.

$$\beta = \beta_1 \ \varphi_1 + \beta_1 \varphi_2 \quad (5)$$

Parts φ_1 and φ_2 of vapor-moving and liquid-moving particles were studied by Professor V. P. Malyshev's theory of disordered states [1, 2, 4]:

$$\varphi_1 = P_{vm} = \exp\left(-\frac{T_b}{T}\right) \quad (6)$$

$$\varphi_2 = P_{lqm} = \exp\left(-\frac{T_m}{T}\right) - \exp\left(-\frac{T_b}{T}\right) \quad (7)$$

Here P_{vm} - is the proportion of vapor-moving particles, P_{lqm} is the proportion of liquid-moving particles. Given (6) and (7), the formula for compressibility can be written as follows:

$$\beta = \beta_1 \exp\left(-\frac{T_b}{T}\right) + \beta_2 \left[\exp\left(-\frac{T_m}{T}\right) - \exp\left(-\frac{T_b}{T}\right)\right]$$

(8)

The temperature dependence β_1 is shown in Figure 1. A general description of the order of this function is given in Figure 1. As the temperature of the metal melts, the interatomic distances increase with temperature, ie heat is released. This leads to an increase in adiabatic compressibility with temperature *β.* The melt is very compressible. Formula (8) can show changes in the nature of structural changes in clusters in alloys and explain the mechanism of their thermal decomposition or aggregation. Assume that the clusters dissolve as the temperature in the cluster solution rises. In this case, according to the analysis of equation (8), the adiabatic compression polymer is characterized by a minimum temperature *β* and a decreasing curve in temperature. This process is typical of molten tellurium.

Now let's look at the process of cluster fragmentation. When crushed, large clusters of clusters are formed, which leads to a very rapid decrease in compressibility and begins to increase due to the release of heat only after the extremum. The melt is microhomogenized, the same order of compression polymers is observed for molten selenium. The study of the extremum in the temperature dependence of the function (8) shows the mechanisms of decomposition of clusters in the melt with increasing temperature and, conversely, the transition to aggregation when the melting temperature decreases to $T_{bal.}$

Conclusion

Thus, concluding that the forces of interaction between monomers and clusters in a cluster solution are pure van der Waals, it can been seen that the energy of their interaction is much less than the energy of formation of clusters themselves. This is because the main part of the deviation from the ideal order of solutions in the cluster solution is explained by the interaction that leads to the formation of clusters. The study of extremum in the temperature dependence of compressibility shows the mechanisms of decomposition of clusters in melts when the temperature rises and, conversely, the transition to aggregation when the temperature melts.

Conflicts of interest. The author states that there is no conflict of interest.

Cite this article as: Shaikhova.G. S. Explanation of the Cluster Structures Melting Mechanism and Their Influence on the Molten State's Physical and Chemical Nature. *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources = Mineraldik Shikisattardy Keshendi Paidalanu.* 2021. №1(316), pp. 62-68.
https://doi.org/10.31643/2021/6445.08

Кластерлік құрылымдарды еріту механизмін түсіндіру және балқытылған күйдің физика-химиялық табиғатына әсер етуі

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Мақала келді: *30 қаңтар 2021*
Рецензенттен өтті: *25 ақпан 2021*
Қабылданды: *05 наурыз 2021*

ТҮЙІНДЕМЕ

Кластерлік құрылымдардың еру механизмі және олардың балқытылған күйдің физика-химиялық табиғатына әсер етуін қолдану арқылы металл балқытпалардың құрылымын және геометриялық параметрлерін зерделеу негізінде олардың табиғатын нақтылау зерттеулердің негізгі мақсаты болып табылады. Мақалада әртүрлі құрылымдық топтардың жартылай металл балқытпалары мен жартылай өткізгіштерін зерттеу нәтижелері келтірілген. Бете торының мысалында кластерлердегі құрылымдардың бұзылуы модельденген және оның негізінде наноқабаттары түріндегі металл балқытпаларының қасиеттері негізделген. Атомдардың орналасуы әр түрлі атомдардың өзара әсерлесу потенциалы арқылы сипатталады, және де тордағы атомдардың тек аз саны ғана қарастырылады. Берілген тұжырымдаманы пайдаланып, квазитор энергиясының орташа мәні есептелген. Электрондық балқытпалардағы сығылғыштық политермалары түрлерінің алуан түрлілігі типтендіруді талап етеді, әтпесе

оларды талдау балқытпалардағы созылған объектілердің еру және агрегация процестерінің механизмін түсіндіруге мүмкіндік береді. Мақалада кластерлік құрылымдарды еріту процесінің механизмін және олардың балқытылған күйдің физика-химиялық сипатына әсерін түсіндіруге мүмкіндік беретін формулалар келтірілген. Кластерлерді ұсақтау процесі қарастырылады. Ұсақтау кезінде кластерлердің аса ірі жарқыншақтары түзіледі де, бұл сығылғыштықтың аса жылдам төмендеуіне әкеледі және экстремумнан өткеннен соң ғана жылумен босатылатындықтан ұлғая бастайды. Сығылғыштықтың температуралық тәуелділігінде экстремумға зерттеу температура жоғарылағанда балқытпалардағы кластерлердің ыдырау механизмдерінің және керісінше балқу температурасына дейін төмендегенде агрегацияға ауысу процесін көрсетеді. Жұмыстың практикалық маңыздылығы түсті және қара металлургияда қолданылатын технологияларды әзірлеу үшін ғылыми негізделген алғышарттарды құру, термодинамикалық модельді жасауға және балқытылған күйдің химиялық активтілігін болжауды дамытуға көмектесу болып табылады.

Түйін сөздер: жұптық потенциалдар, атомдардың үлестірім функциясы, жартылай өткізгіштік, функционал тығыздығы, атомдар, молекулалық динамика, кластерлік құрылым.

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Разъяснение механизма растворения кластерных структур и влияние их на физико-химическую природу расплавленного состояния

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Статья поступила: *30 января 2021*
Рецензирование: *25 января 2021*
Принята в печать: *05 марта 2021*

АННОТАЦИЯ

Основной целью исследовании является уточнение природы на основе изучения структуры и геометрических параметров металлических расплавов с использованием механизма плавления кластерных структур и их влияния на физико-химическую природу расплавленного состояния. В статье приводятся результаты исследовании расплавов полуметаллов и полупроводников различных структурных групп. На примере упрощенной регулярной решетки Бете можно моделировать разрушение и агрегацию структур в кластерах и на ее основе обосновать свойства расплавов металлов в виде нанослоев. Расположение атомов описывается через потенциал взаимодействия различных атомов, причем рассматривается лишь малое число атомов в решетке. Используя данную концепцию вычисляем среднее значение энергии квазитора. Разнообразие форм политерм сжимаемости в электронных расплавах требует типизации, так как их анализ позволяет разъяснить механизм процессов агрегации и растворения протяженных объектов в расплавах. В статье приведены формулы, которые позволяют разъяснить механизм процесса растворения кластерных структур и влияние их на физико-химическую природу расплавленного состояния. Рассматривается процесс дробления кластеров. При дроблении образуются более крупные осколки кластеров и это приводит к тому, что сжимаемость падает более быстро и только после прохождения экстремума начинает возрастать из - за тепловые разрыхления. Исследование функции сжимаемости на экстремум в температурной зависимости сжимаемости указывает также на процесс смены механизмов распада кластеров в расплавах при возрастании температуры и наоборот к агрегации при понижении температуры плавления. Практическая значимость работы заключается в создании научно обоснованных предпосылок для разработки технологии в цветной и черной металлургии, содействии разработке термодинамической модели и развитию прогнозирования химической активности расплавленного состояния.

Ключевые слова: парные потенциалы, радиальные распределения атомов, полупроводник, функционал плотности, структурный фактор, атомы, молекулярная динамика, кластерная структура.

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