

ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the field of training 8D072 – Manufacturing and Processing Industries, Educational Program 8D07203 – Metallurgy

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THE DEVELOPMENT OF CLUSTER-ASSOCIATE THEORY OF LIQUID AS APPLIED TO THE VISCOSITY OF MELTS OF COMPLEX INORGANIC SUBSTANCES AND METAL ALLOYS

Relevance of the research topic.

The necessity of studying the properties of substances is determined both by the growing demands of modern technology and by the scientific significance of the results obtained. In this regard, the investigation of the properties of melts of inorganic compounds, which are increasingly used in modern engineering and industrial applications, is of considerable interest. The specific features of theoretical and experimental studies of such melts are determined by the physical nature of inorganic compounds. In recent years, numerous studies have been devoted to the physicochemical and thermophysical properties of inorganic melts. Along with such properties as density, thermal conductivity, heat capacity, and saturated vapor pressure, viscosity is of primary importance, as it determines the hydrodynamic and heat-transfer characteristics of a system. A comprehensive investigation of the viscosity of melts of complex inorganic compounds and metallic alloys is of both scientific and practical significance, since viscosity is a structure-sensitive characteristic of liquids that reflects the strength of interactions between particles.

At present, many researchers studying the liquid state, melts, and alloys prefer models based on the concept of a quasi-crystalline description. This approach assumes that the structure of a liquid can be modeled based on real interparticle interactions manifested in crystalline solids. Such an approach is founded on the unity of the condensed state of matter and the attractive forces acting between particles both before and after melting.

Methods for calculating the viscosity of melts are important tools for understanding and predicting their properties. These methods are based on various theoretical approaches, including diffraction studies, pseudopotential theory, Voronoi polyhedral statistical geometry, and others. Owing to these methods, a vast amount of experimental information on the structure and properties of liquid metals has been accumulated. However, despite substantial progress in this field, existing models possess inherent limitations and approximations and are usually applicable only within a limited temperature range. As a consequence, viscosity values obtained by different methods may differ significantly, sometimes by more than an order of magnitude.

Therefore, there is a need to develop alternative approaches to understanding melt viscosity and to improve the accuracy of its prediction under various conditions, enabling the effective application of new data in metallurgical processes.

The present dissertation continues the development of the concept of chaotized particles proposed and substantiated by researchers of the Zh. Abishev Chemical-Metallurgical Institute. The work is intended to substantially extend and develop this concept, since it addresses the fundamental problem of explaining the structure and properties of melts and the liquid state as a whole.

Research objective.

The objective of this study is to modify the cluster-associate model of the liquid state with respect to melts of inorganic compounds and metallic alloys in order to describe and predict the temperature dependence of their viscosity.

Research object.

Reference experimental and smoothed viscosity data for melts of inorganic compounds and metallic alloys.

Research subject.

Temperature dependence of the dynamic viscosity of melts of complex inorganic compounds and metallic alloys.

Research objectives.

In accordance with the stated objective, the following tasks were accomplished:

1. To analyze the current state of research concerning the structure and properties of melts and the liquid state in general, as well as existing viscosity-temperature relationships, identifying their approximations and sources of error.

2. To substantiate the probabilistic definition and quantitative expression of the virtual formation and existence of solid-phase clusters in liquids as the material basis of viscosity.

3. To apply the cluster-associate liquid model in combination with Frenkel's equation to describe the temperature dependence of the viscosity of melts of complex inorganic compounds containing three or more atomic species.

4. To apply the cluster-associate liquid model to describe the temperature dependence of the viscosity of metallic alloys based on their phase diagrams.

Scientific novelty.

The scientific novelty of the dissertation is determined by the following contributions:

– the use of a unified parameter (the degree of aggregation and association of clusters) for the development of a generalized semi-empirical viscosity model applicable to melts of inorganic compounds and metallic alloys;

– determination of the activation energy of viscous flow for complex inorganic compounds and metallic alloys through a modification of Frenkel's equation;

– substantiation of the existence of solid-phase clusters in liquids and quantitative characterization of the virtual formation of clusters from crystal-mobile particles as the material basis of viscosity;

– for the first time, a regular relationship has been established between the degree of cluster association and variations in the period of the periodic system of chemical elements for complex inorganic compounds, which, as a first approximation, confirms the functional nature of the proposed cluster-associate model.

The planned investigations are characterized by fundamental novelty because the liquid state has traditionally been considered only within the framework of structural approaches. The present dissertation is entirely based on revealing the nature of the liquid state through the structureless, chaotized component of matter, which had previously been regarded merely as a factor obscuring the structural organization of liquids. This new approach has made it possible, for the first time, to develop a fully consistent description of the viscous state of complex liquids throughout the entire range of their liquid-phase existence.

Practical significance of the research.

The study of viscosity in metallurgy is of great practical importance because it enables more accurate control of melting, casting, and refining processes. Knowledge of melt viscosity allows the prediction of fluidity, ensures uniform mold filling, improves casting quality, and reduces defect formation. Furthermore, controlling the viscosity of slags and metallic melts contributes to more efficient impurity removal and enhanced heat transfer within metallurgical units. These factors directly affect process stability, economic efficiency, and the quality of final products.

From a practical perspective, viscosity data are of fundamental importance for the design and optimization of metallurgical processes. In casting operations, melt viscosity determines fluidity, the ability to fill molds of complex geometry, surface layer formation, and the likelihood of defects such as shrinkage cavities and gas porosity. Insufficient consideration of viscosity characteristics may result in incomplete mold filling and deterioration of casting quality. In metallurgical furnaces (blast furnaces, open-hearth furnaces, and electric furnaces), melt viscosity influences heat and mass transfer, mixing intensity, dissolution rates of alloying elements, and refining efficiency. For example, variations in slag or metal melt viscosity significantly affect the kinetics of chemical reactions and the separation of metal–slag phases.

The practical significance of the research lies in the development of a generalized semi-empirical viscosity model for melts of complex inorganic compounds, metallic alloys, and slag systems based on the concept of chaotized particles. The proposed cluster-associate model introduces new parameters, namely the degree of cluster association and the degree of associate aggregation. The obtained results enable viscosity calculations over a wide temperature range, including temperatures approaching the boiling point, thereby substantially extending the possibilities for predicting technological properties of melts. The proposed approach may be used in the optimization of melting, casting, and refining processes, as well as in the selection of rational operating conditions for metallurgical units.

The possibility of using a limited number of experimental reference points to predict melt behavior over the entire temperature range has been established. Using alloys, including the Cu-Sn and Cu-Al systems, a quantitative relationship has been identified between the position of the liquidus line and the fraction of clusters in the melt. This relationship makes it possible to employ phase diagrams for calculating viscosity characteristics and predicting technological properties of alloys. The

developed cluster-associate model has been refined by incorporating thermodynamic parameters, including the enthalpies of mixing and melting of components, which has enabled an adequate mathematical description of viscosity based on a minimal set of input data.

Experimental validation of the proposed model using slag systems, including CaO-SiO₂-Al₂O₃-MgO-MnO, demonstrated a high degree of agreement between calculated and experimental data, confirming its applicability to the modeling of real metallurgical processes. The obtained values of the activation energy of viscous flow make it possible to apply the proposed approach for the quantitative assessment of kinetic parameters in liquid-phase processes.

The authors of the chaotized particle concept, in the work “Fusibility and Plasticity of Metals,” proposed new interpretations of metal fusibility and plasticity, substantiating the optimal plasticity range and the Bochvar-Tammann temperature. This made it possible to determine the energy efficiency of rolling mills and, on the basis of the cluster-associate viscosity model of copper, to ensure the production of high-quality copper wire rod at the Zhezkazgan Mining and Metallurgical Complex.

The results of the dissertation have been introduced into the educational process and are used in teaching the course “New Approaches to Assessing the Strength of Materials,” thereby contributing to the improvement of specialist training in the field of metallurgy.

Provisions submitted for defense.

The following provisions are submitted for defense:

- substantiation of a quantitative expression for the virtual formation and existence of solid-phase clusters in liquids as constituents of the material basis of viscosity;
- development of a theory of viscosity and fluidity of melts based on the contributions of crystal-mobile, liquid-mobile, and vapor-mobile chaotized virtual particles, applied to melts of complex inorganic compounds and metallic alloys;
- cluster-associate liquid models combined with Frenkel’s equation for describing the temperature dependence of the viscosity of melts of complex inorganic compounds containing three or more atomic species;
- substantiation of the relationship between the temperature dependence of alloy viscosity and phase equilibrium diagrams, demonstrated using the Cu-Sn system as an example;
- activation energy data for viscous flow in complex inorganic compounds and metallic alloys obtained through a modified Frenkel equation applied to dynamic viscosity.

Research environment.

The research was carried out at Abylkas Saginov Karaganda Technical University (Department of Nanomaterials and Metallurgy) and the Zh. Abishev Chemical-Metallurgical Institute.

The dissertation research is associated with the implementation of Grant Project IRN AP05130844 (2018-2020), entitled “«Development and application of a new theory of viscosity and fluidity based on the concept of randomized particles for melts of inorganic compounds and metal alloys»”. The present dissertation

represents a logical continuation of this project. The scientific results obtained within the framework of the project served as the basis for further investigations and for the development of a cluster-associate model describing the viscosity of melts of complex inorganic compounds and metallic alloys.

Author's Contribution

The author independently conducted a review of the scientific literature, processed and systematized experimental data on the viscosity of melts of complex inorganic compounds and metallic alloys, modified the cluster-associate model of the liquid state, developed calculation relationships, carried out computational studies, and performed experimental work to validate the developed model. The author conducted an experimental verification of the new model using slag systems, including the CaO-SiO₂-Al₂O₃-MgO-MnO system, which demonstrated a high level of agreement between the calculated and experimental data and confirmed the applicability of the model for simulating real metallurgical processes.

The author actively participated in the analysis and interpretation of the obtained results, the preparation of scientific papers and publications, and the presentation of the research findings at scientific conferences and seminars.

The main scientific results, statements, and conclusions presented in the dissertation were obtained personally by the author.

Approbation and implementation of the research results.

The results of the dissertation research have been implemented in the educational process of NJSC Abylkas Saginov Karaganda Technical University in teaching the course "New Approaches to the Assessment of Material Strength" within the educational program 7M07102 "Materials Science and Technology of New Materials", as confirmed by the certificate of implementation into the educational process.

The main scientific results of the dissertation have been published in 17 scientific works in national and international scientific journals, including:

- Two articles were published in international peer-reviewed scientific journals indexed in the Scopus and Web of Science databases: Non-Ferrous Metals (Russian Federation, 41st percentile in Scopus) and Heat Transfer (USA, 82nd percentile in Scopus, Q2 according to the JCR Category of the Web of Science database);

- six articles published in scientific journals included in the list of publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan (CQASHE), including Engineering Journal of Satbayev University, Bulletin of the Karaganda University, Kompleksnoe Ispolzovanie Mineralnogo Syra, Proceedings of the University, and Science and Technology of Kazakhstan;

- 1 intellectual property protection document: Copyright Certificate No. 59694;

- the research results were also presented by the author in eight reports delivered at national and international scientific and practical conferences.

Structure and Scope of the Dissertation.

The dissertation consists of an introduction, a main body comprising five chapters, a conclusion, and appendices.

The total volume of the dissertation is 166 pages of typed text and includes 29 figures, 39 tables, and a bibliography containing 292 references.