

Phenomenological theory of diffusion in metal oxides and ceramics

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Diffusion in metal materials is researched thoroughly today both experimentally and theoretically. However, the issue of theoretical description of diffusion processes in ceramics, including metal oxides, remains understudied. It is crucial to note that in order to build a model to calculate parameters of bulk diffusion in ceramic materials, it is important to take into account some features of their structure and properties.

The first feature is the so-called 'loose packing' of ceramic crystalline structures as compared to metals (lower packing index). This provides additional opportunities for diffusion jumps of atoms, including jumps of lattice atoms to an interstitial space, while in close-packed metals jumps between interstices are more energetically justified for nonmetal atoms that have much smaller radius in the metal lattice as compared to metal atoms. Thus, ceramics offer an opportunity of atom diffusion both in line with the vacancy mechanism and interstitial mechanism.

The second feature is that unlike metals, the crystalline structure of ceramics consists of several kinds of atoms: in oxides it consists of oxygen ions and metal ions that have comparable activation energies. Although oxygen ions are usually smaller in size than metal ions, both oxygen and metal are equal participants in the diffusion process.

The third feature is the lack of the diffusing particles charge shielding effect typical of metals. Oppositely charged ions are generally taken into account by describing the structure of ceramics with two sublattices (oxygen and metal) and by describing jumps of ions to their vacancy: oxygen ions jump to 'oxygen vacancies', while metal ions jump to 'metal' ones.

The fourth important feature characterizing the structure of oxide ceramics crystalline lattices is that it has a strong concentration of structural vacancies and significant deviations from the ideal stoichiometry, which has a significant impact on the diffusion properties of ceramics.

Another specific feature of ceramics is an opportunity to combine two kinds of ions (oxygen and metal) and form a variety of different compounds and structures. This creates extra opportunities to carry out several bulk diffusion scenarios especially in case of violated stoichiometry.

The paper presents a phenomenological description of bulk diffusion in oxide ceramics. Ideas described in [1] are underlying the theory currently considered in this research. To describe elementary diffusion processes in metals, this paper proposes two main scenarios: 'liquid corridor' model and 'empty corridor' model. In the first model, the diffusion jump of an atom to a vacancy is described as diffusion in a fluctuatingly emerging 'melt corridor' that links the point where there is an atom with the point where there is a vacancy. In the 'empty corridor' model, diffusion occurs as a result of vacancy-free movement of an atom inside a fluctuatingly emerging cavity that links a diffusing atom with the nearest vacancy.

The paper considers vacancy and vacancy-free diffusion models. In case of vacancy models, the ion migration process is described as a fluctuation with the formation of a 'liquid corridor' along which the diffusion ion transfer in a 'melt' is performed, or as a fluctuation with the formation of an 'empty corridor' in which the ion motion proceeds without activation. The vacancy-free model considers fluctuation with the formation of a spherical liquid region the size of which corresponds to the first coordination sphere. It has been shown that both the vacancy models work well in cubic metal oxides and the vacancy-free model is effective for describing diffusion in oxides having a noncubic structure.

Detailed comparison of the proposed models with the experimental data has been performed. It has been shown that the values of the activation energies for diffusion of metal and oxygen ions agree well with the published data on bulk diffusion in stoichiometric oxide ceramics.

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References

- [1] V.N. Chvuil'deev *Non-equilibrium grain boundaries. Theory and applications*. Moscow: Fizmatlit. 2004. 304 p. (in Russian).