

Theory of diffusion creep in multicomponent solids: Application to deformed Cr-spinel

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Diffusional viscosity of crystals is explained by stress-induced movement of vacancies (i.e., point defects in the crystalline lattice), which causes the counter flow of atoms in the opposite direction. The flow law of diffusion creep was first theoretically derived by C. Herring; however, the physical meaning of chemical potential determined inside the stressed solid was not clearly explained. Because of the lack of a thermodynamic basis of diffusion under non-hydrostatic stress, theoretical models of diffusion creep were only presented for single component systems.

When diffusivities of atoms constituting solid solutions are not the same, diffusional flow derived by differential stress may lead to chemical differentiation and anisotropic zoning of initially homogeneous solids. This phenomena is called kinetic demixing and is distinguished from equilibrium segregation due to stress concentration. To derive the relation between differential stress and the compositional change due to kinetic demixing, Dimos et al. (1988) introduced a 'stress potential gradient' as a driving force of self-diffusion under stress. However, the exact form of the 'stress potential' was not presented in their theory.

The chemical potential of diffusing atoms in stressed solids was later derived by Shimizu (1997, 2001) using non-equilibrium thermodynamic approach. The theory denies the existence of a scalar potential corresponding to the 'stress potential' in a uniform stress field. Assuming an initially spherical grain, we derive the flow law of lattice diffusion creep in a binary solid solution, which is composed of a fast element A and a slow element B. The steady-state compositional gradient is determined by differential stress, temperature, initial compositions and the ratio of the diffusivities of A and B, while it is not dependent on the absolute values of self-diffusion coefficients of A and B. If diffusion of A is much faster than B, the following simple relation holds:

$$\text{differential stress} = (nRT/V) \ln (X_{max}/X_{min})$$

where n is the number of mixing sites, R is the gas constant, T is temperature, V is the molar volume, and X_{max} and X_{min} are the maximum and minimum compositions (in molar fractions) of A, respectively. If differential stress is not large and/or the concentration of A is small, the steady-state composition is attained and the rate of diffusion creep is limited by B-diffusion. On the contrary, if differential stress and the concentration of A are both large, the compositional gradient is not stabilized and diffusion creep is dominated by A-diffusion.

Anisotropic chemical zoning of minerals formed by high-temperature deformation is possibly used as an indicator of differential stress at the depth. Here we show the examples of Cr-Al spinel $(\text{Mg,Fe})(\text{Cr,Al})_2\text{O}_4$. Elongated spinel grains in deformed peridotite samples taken from the Oman ophiolite, the Miyamori ophiolitic complex, and the Horoman ultramafic complex commonly exhibit anisotropic Cr-Al zoning: Al concentrates at the extensional sites of the grains, and Cr at the compressional sites (Ozawa, 1989). Because the molar volume of Cr-spinel is larger than that of Al-spinel, the anisotropic zoning is not likely explained by the equilibrium segregation induced by stress concentration. We performed diffusion experiments on paired crystals of Cr- and Al-spinel to determine the Cr-Al inter-diffusion coefficients at 1400-1700°C and 3-7 GPa, thereby estimated the self-diffusion coefficients of Cr and Al. It was shown that Al-diffusion is more than one order of magnitude faster than Cr-diffusion. Therefore, the anisotropic zoning in spinel is considered as a result of kinetic demixing induced by differential stress.

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