History and Modern State of Grain Boundary Segregation Problem

and Related Phenomena

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Atomic segregation at grain boundaries (GB) as a result of solute interaction with GB has a prolonged history. The viewpoint that grain boundary segregation (GBS) tends to reduce grain boundary diffusion flux of the solute atoms is now generally recognized. The physical mechanism of such effect still remains unclear.

The simplest model of GBS effect on grain boundary diffusion (GBD) was the proposal of the linear dependence between GB and bulk concentration. After, the following effects were analysed: limited number of segregation sites in GB, nonideality of GB solution, GB inhomogeneity, “poison” effect etc. All these attempts are based on the thermodynamic method. The main results of these attempts are the following: the segregation effects decrease the diffusion rate (even if the mobility of the atom is the same); the concentration profile becomes curved at high concentrations and remains linear at small concentrations (large penetration depth).

At the recent years some efforts have been made to connect the effect with the atomic interaction on the micro level. For this purpose the concept of complexes or complexions has been introduced. The complex can be treated as thermodynamically stable state. Its electronic structure and chemical bonds resemble these in a nearest bulk phase according to phase diagram. Thermodynamic study of the complexes formation in GBs, based on the model of ideal associated solutions, showed that it leads to the change of GBS isotherms. In assumption, that complexes mobility is significantly less comparing with free atoms, complexes formation decreases GBD flux and the mean-layer concentration of diffusant.

Recently, it was also shown by the molecular dynamics simulation with the use of semi empirical potential designed for Cu that the complexes formation leads to decrease of mean-square displacements and effective GBD coefficient in Cu-based system.

Meanwhile, it was shown in a number of recent studies that segregation of Zr at GBs in nanocrystalline Cu, in combination with annealing at elevated temperatures, can lead to formation
of amorphous intergranular films. Usually, formation of such amorphous state in the bulk tends to increase diffusion rate, in other words, leads to effect opposite the above mentioned.