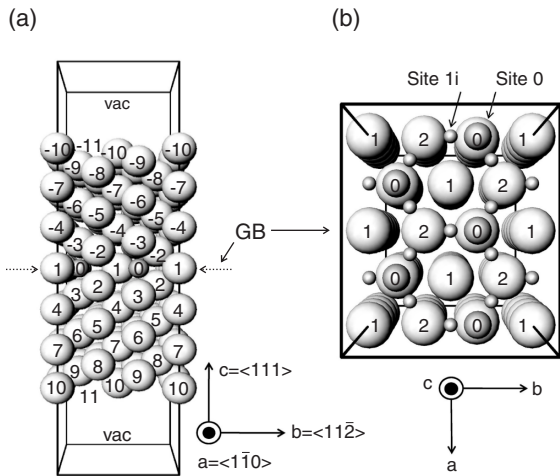# 12-1 Elucidation of Embrittlement of Iron by Sulfur and Phosphorous
─The Mechanism of Grain Boundary Embrittlement Elucidated by First-Principle Calculations─
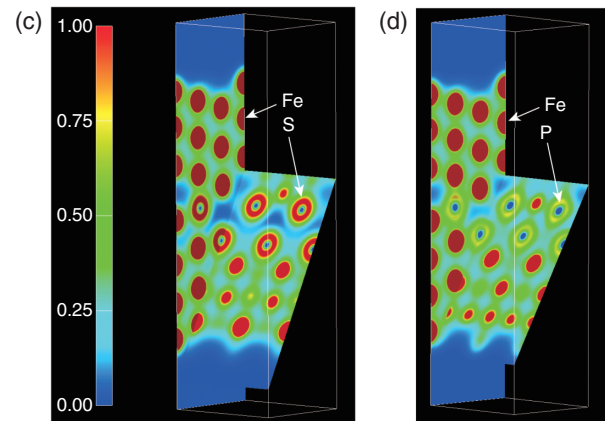

**Fig.12-2 Unit cell including grain boundary (GB)**
Iron slab is placed in vacuum region (vac). The largest sphere is an iron atom. The positions of atoms are labeled by numbers. (a) Side view. (b) Top view of the cross section at the grain boundary (GB) plane. Site 0 is a hole. Site 1i is an interstitial site.

Fig.12-3 Electron distribution map at the grain boundary when sulfur (S) or phosphorus (P) atoms are segregated (c) S. (d) P.

Fig.12-4
The correlation between relative change in temperature of ductile-to-brittle transition due to segregation of boron (B), carbon (C), phosphorous (P), or sulfur (S) at grain boundaries (ΔDBTT) and the segregation-caused change in the calculated cohesive energy between atoms at the grain boundary ($\Delta 2\gamma_{int}$).
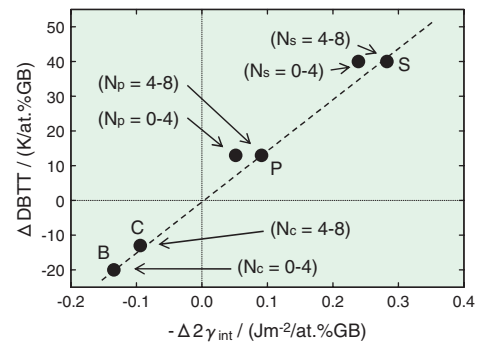
Metallic materials are usually polycrystalline, consisting of crystal grains the size of which is about several ten micrometers. The boundaries between the grains are called "grain boundaries". The impurity or alloying atoms which are included in metals can move and be trapped at grain boundaries when the temperature of metals is high. This trapping is called "grain boundary segregation". Grain boundary segregation is known to bring about a large change in the mechanical properties of metals. A famous example is tempering embrittlement of low alloy steels, which is caused by phosphorous segregation. It is well known that sulfur has a much stronger embrittlement effect than phosphorous, and that boron and carbon have a strengthening effect on the grain boundary.

It is already known that grain boundary segregation occurs only in the first few atom layers, as verified by Auger electron spectroscopy. Thus, grain boundary embrittlement is considered to be caused by the change in the cohesion of metal atoms at the grain boundary caused by the segregated atoms. However, why and how the cohesion of metal atoms is changed has been a mystery for many years.

We performed first-principle calculations to simulate this phenomenon on the supercomputer in JAEA. First-principle calculation investigates the properties of materials by solving the relevant Schröinger equations numerically on computer. We made great efforts to reduce the computational time, because this calculation is very time-consuming, and so were able to perform calculations simulating the grain boundary segregation (Figs.12-2 and 12-3).

From our calculations, we found that the cohesive energy of the grain boundary is reduced by the phosphorous and sulfur segregation, and that the energy is increased by the boron and carbon segregation. These results are consistent with the experimental results. Moreover, we found an excellent correlation between the calculated cohesive energy and the experimental ductile-to-brittle transition temperature (Fig.12-4). This demonstrated that the cohesion of the atoms at grain boundaries can be understood from first-principle calculations.

Reference
Yamaguchi, M. et al., Decohesion of Iron Grain Boundaries by Sulfur or Phosphorous Segregation: First-Principles Calculations, Physical Review B, vol.76, no.3, 2007, p.035418-1-035418-5.