Comment on “Grain Boundary Decohesion by Impurity Segregation in a Nickel-Sulfur System”

Yamaguchi et al. (1) examined the embrittlement of nickel (Ni) by progressively adding sulfur (S) atoms to a grain boundary (GB). From first-principles calculations, they concluded that S atoms tend to aggregate at the GB and that the repulsive S-S interactions induce boundary expansion, thus weakening Ni-Ni binding across the boundary. The agreement between their calculated critical S concentration in the bulk and the temperature as parameters reported in (1). Our calculations demonstrate that although the GBn (n = 3, 4, 5, 6) site is still less stable than the GB0 site, the binding energy difference is greatly reduced when GB0 is occupied by S. For example, a GB0-GB3 pair is 0.05 eV less stable than a GB0-GB2 pair; in an isolated 1/4 monolayer, S at the GB3 site is 1.16 eV less stable than at the GB2 site (1). Interestingly, we find that although the binding energy of the GB1 site in an isolated monolayer is only 3.25 eV, it increases considerably to 4.29 eV when all GB2 sites are occupied by S. The binding energy of other sites, on the other hand, increases to lesser extents, and the occupation probability under the experimental conditions remains low. Moreover, we calculated the binding energy of a 1/4 monolayer GB1 progressively added, to a GB2 4/4 monolayer. The binding energies are 4.15, 4.23, 4.26, and 4.55 in sequence. Our first-principles calculations thus suggest the formation of GB2-GB1 S combinations at a high concentration.

Using the same technique as in (1), we evaluated the tensile strength of six cases of S segregation, namely, (i) clean GB; (ii) GB2 4/4; (iii) GB2 4/4, GB1 1/4; (iv) GB2 4/4, GB1 2/4; (v) GB2 4/4, GB1 3/4; and (vi) GB2 4/4, GB1 4/4. The tensile strengths are 26, 16, 14, 11, 7.2, and 3.9 GPa, respectively. The calculated tensile strength for the clean GB (26 GPa) is the same as that reported by Yamaguchi et al. The decrease in tensile strength is proportional to the increase of the GB2-GB1 S-S pair concentration, and in the range of S occupations from (GB2 4/4, GB1 2/4) to (GB2 4/4, GB1 4/4), strong GB decohesion occurs. The GB displacement (with respect to the clean GB) caused by (GB2 4/4, GB1 4/4) is about 0.6 Å, much smaller than that caused by (GB2 4/4, GB0 4/4) (1.2 Å), which has been shown here to be unstable. Further detailed analysis will clarify whether GB expansion or directional change of chemical bonding is the key to the strong decohesion caused by S segregation.

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