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THEORETICAL STUDIES OF NI_3AL AND NIAL WITH IMPURITIES

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INTRODUCTION

Intermetallic compound has been extensively studied because of their superior properties in strength, low creep rate, and high melting point [1,2]. But most of the systems have room tempertaure ductility problems, like $L1_2$ and B2 compounds. Both $L1_2$ Ni_3Al [3,4] and B2 NiAl [5,6] exhibit intergranular fracture mode. Understanding grain boundaries in these materials is of particular importance since intergranular fracture limits the applicability of these otherwise promising material. In an effort trying to understand the fracture mechanism, we have used embedded atom potentials [7] to study the properties of Ni_3Al [8,9,10] and NiAl [11]. We also consider the effect of boron, sulfur, and nickel segregation on the strength of grain boundaries in Ni_3Al and NiAl.

COMPUTATIONAL METHOD

The simulation results presented here were obtained by first generating ideal symmetric tilt [001] grain boundaries. The resulting cluster of atoms was then allowed to relax via a steepest descent, energy-minimization algorithm. In the present work, the embedded atom approach has been applied to Ni, Al, B [12] and S [13]. In order to obtain boron-metal (or sulfur-metal) potentials, the embedded atom potentials were fitted to data obtained from linearized muffin tin orbital (LMTO) calculations [12] on the hypothetical structures fcc B, B2 NiB, B2 AlB, $L1_2$ Al_3B and $L1_2$ Ni_3B (similarily for S [13]). Therefore, the interactions of boron (sulfur) with Ni and Al are derived entirely from the electronic calculations. To study the effect of B and S on the grain boundary strength, we have computed the grain boundary (and bulk) cohesive properties in two different ways: frozen and slow straining. In the frozen method, the GB structure is first optimized, and then the two grains are pulled apart while keeping all the atomic positions in each grain frozen. The quantity we focus on is σ_{max}, the maximum stress required to separate the GB. This approach has the advantage that one can choose where to cleave the system. One result is that values for σ_{max} can occur that are greater than the σ_{max} for the surrounding matrix. The disadvantage is that the atoms near the cleavage plane are not allowed to respond. In the slow straining method, the optimized GB was pulled apart with clamps at four lattice constants away on either side, allowing the system to relax to the lowest possible energy at increments of 2% in the successively increasing strain. The slow straining approach allows the system to respond to the strain and, in principle, the break occurs at the weakest point, possibly away from the boundary.

RESULTS OF $L1_2$ NI_3AL

grain boundary compositions (when the two grains are perfect crystals). The grain boundary composition can be described by the Ni percentage of the first layer on each side of the grain boundary, namely: 100/100 GB, 100/50 GB, and 50/50 GB. The 100/100 grain boundary is Ni-rich, the 100/50 grain boundary has the bulk stoichiometry, and the 50/50 boundary is Al-rich. By studying grain boundaries with different compositions in otherwise perfect Ni_3Al crystals, we hope to understand the experimentally observed sensitivity of the ductility of boron doped boundaries to small variations in composition [3,4]. The Al-rich grain boundaries are always higher in energy than the stoichiometric and Ni-rich boundaries [8,9,14]. The Al-rich grain boundaries show larger net expansions than do the Ni-rich boundaries with the same grain misorientation. Similar to the GB energy, we find the same trend in the grain boundary cohesive energy (the sum of the two surface energies minus the grain boundary energy), i.e., the Al-rich boundaries are the weakest. This cohesive energy, although small compared to the total work for fracture, has been suggested by McMahon and Vitek [15] to control the plastic work associated with fracture.

The structural units of the alloy grain boundary are generally very similar to those in the pure metals, though in some instances the structural unit in the ordered alloy is twice the size of that for the pure metal [9,16,17]. Further, in some cases, the type of unit [B or B', in the nomenclature of Vitek and co-workers [16,17]] may vary with grain boundary stoichiometry and misorientation angle [9].

Figure 1 shows the results of the frozen method for cleavage of Ni_3Al boundaries with and without boron. We find that perfect planes in the bulk exhibit larger values of σ_{max} than those of the GB without boron for all three GB stoichiometries. The GB/bulk ratio is about 80%, which is the same as for pure Ni.

The substitution of boron for Ni atoms at the boundary only slightly increases σ_{max}. Insertion of a boron atom into a low density grain boundary site, on the other hand, has a much more pronounced effect on σ_{max}, and the beneficial effect of adding boron (i.e., raising σ_{max}) increases with increasing Ni concentration at the boundary. In the case of the Ni-rich boundary, adding boron to certain sites or certain combinations of sites raises σ_{max} for the boundary above that for certain perfect crystal planes [10]. This implies that boron segregation can effectively make the Ni_3Al grain boundaries stronger than the bulk (within this frozen grain approximation).

Figure 2 shows stress-strain curves computed using the slow straining method for the (210) GB's. Examination of various GB's for Ni_3Al show that w is 40% - 55% of w for bulk planes. The GB doped with one monolayer of boron breaks away from the boundary with a work ratio of ~58% (up from 46%). With one monolayer of extra Ni, the break occurs away from the boundary with a work ratio of 98%, and with five monolayers of extra Ni the break is also away from the boundary with a ratio of 97%. If both B and one or five monolayers of Ni are present, the break is again away from the GB with a ratio of ~95%.

For the (310) plane, we find that in slow straining, the GB break occurs at the GB and the GB/bulk work ratio is only ~50%. Adding one monolayer of boron at the center of the

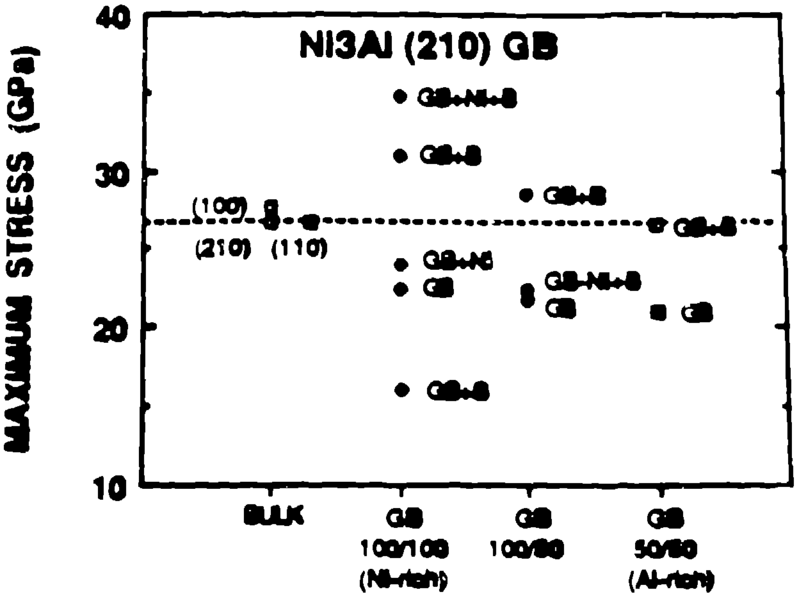

Figure 1: The maximum stress (calculated by frozen method) needed to separate perfect (100), (111), and (210) crystal planes and the (210) GB with boron (GB+B), extra Ni (GB+Ni), extra Ni and boron (GB+Ni+B), boron replacing Ni (GB-Ni+B), and sulfur (GB+S). (All segregation levels of Ni, B and S are one monolayer).

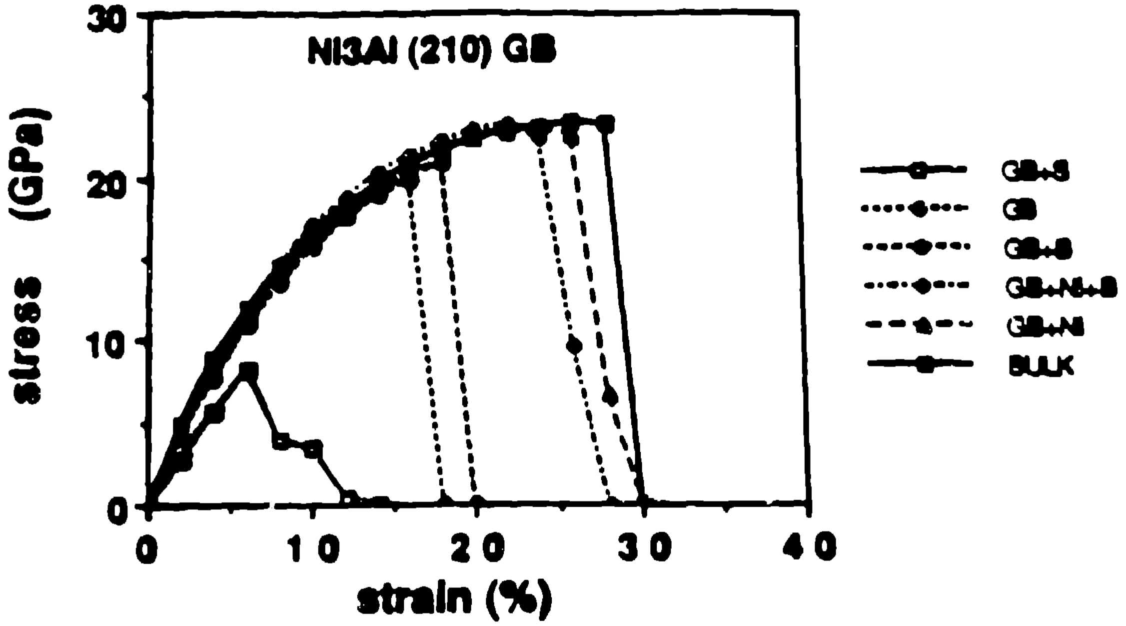

Figure 2: Slow straining method stress-strain curves for (210) planes in Ni_3Al with and without extra Ni, segregated B, and segregated S.

in a structure that is quite distorted [10,12], but the work ratio is not improved. Replacing one and a half monolayer of aluminum atoms at the boundary with nickel atoms (two per GB unit cell), without any boron, leads to a work ratio of ~90% but still breaks at the GB. If both boron and extra nickel are present, the GB is so strong that the slow straining causes a break not at the GB but in the bulk matrix.

In the (310) and (210) GB's, very good cohesive properties occur when both extra Ni and B are present at the boundary. However, for the (210) GB, extra Ni alone appears to be sufficient to significantly enhance the GB strength. The importance of B at the (210) GB may be that it stabilizes excess Ni. In a Ni-rich enviroment, as exists experimentally, extra Ni atoms exist as antisite defects. Moving a Ni atom from an antisite defect to the (210) GB is favorable by 0.14eV, ignoring entropy effects, while moving a boron from an octahedral interstitial site to the (210) GB is favorable by 1.9eV. However, cosegregation of both Ni and B is favorable by an additional 0.46eV [18]. Extra Ni brought to the boundary by the B also has another effect. By disrupting the $L1_2$ order in the GB region, the dislocation mobility should be enhanced, thereby further reducing the propensity for intergranular fracture [19]. Thus, the B may play more than one role in ductilizing Ni_3Al: it enhances the GB strength, it brings in extra Ni which also strengthens the GB, and the extra Ni increases the local plasticity.

We find that the energetically favored site for sulfur is substitution for Al at the free surface. The next most favored site is substitution for Ni at the surface, followed by substitution of Al in every period at the (210) GB , followed by substitution of Ni in every period at the (210) GB. Relaxation of a structure in which S is placed in a GB interstitial site that is favored for B leads to a geometrical rearrangement to yield substitutional sulfur. We would therefore not expect B and S to compete for sites. The slow-straining stress-strain curve for Ni_3Al with 2 sulfur atoms per (210) GB period is shown in Fig. 2. The work ratio is dramatically reduced (~ 25%), as is σ_{max}, and the strain before fracture. The fracture path runs through where the S resides [10,13].

RESULTS OF B2 NIAL

Point defects and planar defcts in the system are studied [11,6]. We found that the stoichiometric sample of NiAl will not have energy favorable point defects except for the thermally activated vacancies and antisites. The Ni-rich sample will have large concentration of Ni-antisite in the bulk and Al vacancies at the GB. Al-rich sample will have Ni vacancy at the GB wedge [11], vacancy at the GB pointer [11] and then the Ni vancancy in the bulk. These results are consistent with experimental findings [6]. The vacancy at the GB makes the GB weaker at the GB for Al-rich sample and likely for Ni-rich sample. The stoichiometric sample is the least likely to develop problems with defects. Some of the results on the surface are presented earlier [20], here we only list some of the results about surface and GB. For (310) GB, the GB structure of B2 NiAl (bcc based system) is almost the same as

GB has energy of 823 mJ/m^2, so the Griffith cohesive energy of GB is 2823 compared with 3646 of the (310) surface with a ratio of 77%. For the relaxed method, the GB has a highest stress of 16 GPa and work ratio 1.00. Ni replacing Al atoms in GB were found to be -0.42 eV which is less than the Ni antisite energy, -0.89eV. The boron energy at 4Ni 2Al octahedral site is -3.03 eV and 2 Ni and 4 Al site is -1.91 eV. Fcc boron cohesive energy is -5.33 eV. The boron in the GB with 6 Ni 3 Al site is -6.95 eV, 3 Ni 6 Al site is -5.06 eV. There is an energy advantage of when boron and Ni are at the GB simultaneously, but the energy is -0.88 and -0.87 for every Ni which is slightly less favorable than the Ni-antisite energy in the bulk (-0.89 eV). Therefore we expect that boron will segregate to the GB but the extra Ni in a Ni-rich sample will not segregate to the GB on its own. Also it is not likely to segregate to the GB even with the help of boron. Boron was found to increase the frozen maximum stress, but the relaxed highest stress and work ratio are actually down to 15 GPa and 0.77 compared to pure GB. We conclude that boron is not likely to strengthen (probably hurt) the GB in NiAl even when the sample is Ni-rich. Although the extra Ni are not expected to happen at the GB, we calculated the cohesive properties anyway. The frozen maximum stress with 5 Ni per period is 16 GPa for relaxed stress and work ratio of 1.07. If with boron and Ni at the GB simultaneously is 19 GPa for relaxed and 1.55 for work ratio and the strain before fracture is much higher than pure GB. Similar trend were found for the (210) GB [11].

CONCLUSIONS

We have performed a series of simulations Ni_3Al and NiAl (with and without boron or sulfur) using embedded atom potentials. The interactions for boron and sulfur were derived

purely from electronic band structure calculations. Using the derived interaction potential, boron is found to segregate more strongly to grain boundaries than to free surfaces, which is consistent with Auger experiments [21]. Adding boron to grain boundaries in Ni and Ni_3Al increases their cohesive strength. This effect is much more dramatic for Ni-enriched boundaries. Boron and Ni are found to co-segregate to the GB and increase the maximum stress and local plasticity at the GB. In this manner, we conclude that the boron and stoichiometric effect of Ni in ductilizing the polycrystalline Ni_3Al are largely understood. Sulfur segregation behavior shows exactly the opposite trend, which is also consistent with experiment [21]. Sulfur is found to occupy the Al lattice sites at the free surface and at the GB. Segregated sulfur is bad for the GB mechanical strength [10,22]. In B2 NiAl, the GB with boron is not likely to help to strengthen the GB even in Ni-rich sample (contrary to the Ni_3Al case). Although there is some co-segregation of Ni and B but not strong enough to bring extra Ni into the GB. If extra Ni can be brought to GB by other method (or doping with elemet like Fe) then there is good chance to strengthen GB with boron.

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REFERENCES

1. High temperature Ordered Intermetallic Alloys, ed. by C. C. Koch, C. T. Liu, and N. S. Stoloff, Mat. Res. Soc. Proc. vol. 39, Materials Research Society, Pittsburgh, PA (1985).
2. High temperature Ordered Intermetallic Alloys II, ed. by N. S. Stoloff, C. C. Koch, C. T. Liu, and O. Izumi , Mat. Res. Soc. Proc. vol. 81, Materials Research Society, Pittsburgh, PA (1987).
3. K. Aoki and O. Izumi, J. Japan Inst. Metals, 43, 1190 (1979).
4. C. T. Liu, C. L. White, and J. A. Horton, Acta Metall. 33, 213 (1985).
5. A. G. Rozner and R. J. Wasilewski, Journal of Institute of Metals, 94, 169 (1966).
6. K. H. Hahn and K. Vedula, preprint 1988; K. Vedula and J. R. Stephens, p. 381 in Ref. 2.
7. A. F. Voter and S. P. Chen, Mat. Res. Soc. Proc., 82, 175 (1987).
8. S. P. Chen, A. F. Voter, and D. J. Srolovitz, Scripta Metall. 20, 1389 (1986).
9. S. P. Chen, A. F. Voter, and D. J. Srolovitz, J. Mat. Res.
10. S. P. Chen, A. F. Voter, R. C. Albers, A. M. Boring, and P. J. Hay, Scripta Metall. February, (1989).
11. S. P. Chen and A. F. Voter, submitted to Scripta Metall.
12. S. P. Chen, A. F. Voter, R. C. Albers, A. M. Boring, and P. J. Hay, submitted to J. Mat. Res. (1989).
13. S. P. Chen, A. F. Voter, A. M. Boring and R. C. Albers, to be published.
14. S. P. Chen, A. F. Voter, and D. J. Srolovitz, Mat. Res. Soc. Proc. vol. 81, 45 (1987).
15. C. J. McMahon, Jr. and V. Vitek, Acta Metall. 27, 507 (1979); J. E. Hack, D. J. Srolovitz, and S. P. Chen, Scripta Metall. 20, 1699 (1986); J. E. Hack, S. P. Chen, and D. J. Srolovitz, Acta Metall., in press.
16. A. P. Sutton and V. Vitek, Phil. Trans. Roy. Soc. (Lond.) A309, 1 (1983).
17. G. J. Wang, A. P. Sutton, and V. Vitek, Acta Metall. 32, 1093 (1984).
18. D. D. Sieloff, S. S. Brenner, and M. G. Burke, Mat. Res. Soc. Proc. vol. 81, p. 87 (1987).
19. V. Vitek, S. P. Chen, A. F. Voter, J. J. Kruisman, and J. Th. M. DeHosson, in "Grain Boundary Chemistry and Intergranular Fracture," ed. by G. S. Was, Trans. Tech. Publications (1989).
20. S. P. Chen, A. F. Voter, and D. J. Srolovitz, Phys. Rev. Lett. 57, 1308 (1986); Mat. Res. Soc. Proc., 82, 515 (1987).
21. C. L. White, R. A. Padgett, C. T. Liu, and S. M. Yalisov, Scripta Metall., 18, 1417 (1985).
22. C. L. White and D. F. Stein, Metall. Trans. A, 9A, 13 (1978).