Inverse Kirkendall mixing in collision cascades

K. Nordlund* and R. S. Averback

Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 29 July 1998)

We study ion-beam mixing of metallic bilayer interfaces using classical molecular-dynamics simulations of 5 keV collision cascades in the vicinity of Co/Cu and Ni/Cu (111) interfaces. We find that the production of vacancies and interface roughening is asymmetrical. On average, more Cu is introduced into the Co or Ni parts than vice versa, and more vacancies are produced in the Cu, indicative of an inverse Kirkendall effect in collision cascades. The effect is explained by the difference in melting points leading to different recrystallization rates of the two materials. [S0163-1829(99)11601-1]

The forced mixing of atoms across interfaces is of both technological and scientific interest for ion implantation in layered structures, precipitation dissolution in reactor materials, and processing of materials by high strain conditions. Theoretical approaches to treating materials under such driving conditions has recently been reviewed by Martin and Bellon.[1] An as yet unknown element in these formulations, however, is an atomistic description of the mixing events at the interface. Such a description, specifying the configuration of mixed atoms and any defects that are created, is important as these details strongly influence the resulting microstructures. The kinetic roughening of interfaces is for instance expected to be sensitive to the average number of atoms forced to cross the interface as a result of a single cascade.[1] The present work considers the mixing across Co/Cu and Ni/Cu interfaces during energetic particle irradiation.

Copper-cobalt alloys have been extensively studied as a model system of immiscible alloys and because of their possible use for magnetoresistance applications.[2–5] Both metals are close-packed and have almost the same mass and nearest-neighbor spacing, so lattice mismatch effects are not overly significant. For the same reasons they can be expected to behave quite similarly from a ballistic point of view. Their melting points, on the other hand, are quite different, about 1360 K for Cu and 1780 K for Co. Also, Co is elastically far stiffer than Cu. Therefore comparing ion beam effects close to a Co/Cu interface can be instructive for deducing how thermodynamic effects affect the development of collision cascades. We also study mixing close to an interface of Ni and Cu to provide a contrast to the Co/Cu system. Since Ni has nearly the same mass and melting point as Co, but has a much smaller heat of mixing with Cu, comparison of cascade mixing in Ni/Cu with that in Co/Cu distinguishes the effects of melting temperature from effects of immiscibility.

Effects of the heat of mixing and melting point on ion beam mixing have been explored previously by Gades and Urbassek using MD simulations.[6] Their work, however, was limited to energies below 1 keV. In this low energy regime heat spike effects are often not overly significant in relation to ballistic events. In the present simulations, we study 5 keV collision cascades at Co/Cu and Ni/Cu (111) interfaces and show that the lower melting temperature of Cu than of Ni and Co leads to vacancy fluxes across the interface in these systems and thus also to non-equal solute fluxes. Thus the

behavior is analogous to the inverse Kirkendall effect,[7] in which a vacancy flux drives a net solute flux in the opposite direction.

Classical molecular dynamic (MD) simulations have proved appropriate for studying mixing effects.[6,8–10] The simulations in this work were carried out similarly to those described in Ref. 10. The atoms were arranged in cubic simulation cells with periodic boundary conditions containing about 88 000 atoms. The temperature of the cell was initialized to 0 K and scaled down towards zero at the outermost two atomic layers using the Berendsen temperature control algorithm[11] with a time constant of 70 fs. This value was found to provide optimal damping of the pressure wave emanating from the cascade. A variable time step,[12] linkcell method[13] and two-dimensional spatial decomposition of the simulation cell for message-passing parallel computers were employed to speed up the simulations.

To describe the atomic interactions in Co we used the embedded-atom-method (EAM) interatomic potential of Pasianot and Savino,[14] which is fitted to all elastic constants of Co and the vacancy formation energy. To find whether the potential is appropriate for the present study we tested a few additional properties of the potential. Using the method of a liquid and solid in equilibrium,[15] the melting point of the potential was found to be 1620 ± 20 K, in reasonable agreement with experiment. The potential was further fitted to the Ziegler-Biersack-Littmark universal repulsive potential[16] for small atomic separations to realistically describe strong collisions. The fit was calibrated to exactly reproduce the experimental threshold displacement energy of 22 eV. For Cu and Ni we used the EAM interatomic potential by Foiles, Baskes, and Daw[17] fitted to a repulsive potential. Details of the collision-cascade related properties of the Cu and Ni interatomic potentials can be found in Ref. 18.

To describe the interaction between Co and Cu we constructed a cross pair potential term which gave the correct heat of mixing for Co impurities in Cu for low Co concentrations, and the correct lattice parameter change.[4] With this potential a random $Cu_{70}Co_{30}$ alloy was stable up to about 1100 K, at which temperature it spontaneously decomposed into Cu and Co precipitates over a few tens of picoseconds. This is in good agreement with experiment, where decomposition is observed around 800–1000 K on much longer time scales.[3,4] For the Ni-Cu interactions we used the cross term

TABLE I. Average defect results of the 5 keV collision cascades close to a Co/Cu or Co/Ni interface. $Cu_{Co/Ni}$ denotes Cu impurities in Co or Ni, Co/Ni_{Cu} Co or Ni impurities in Cu, $I_{Co/Ni}$ interstitials in Co or Ni, and $V_{Co/Ni}$ vacancies in Co or Ni.

	$Cu_{Co/Ni}$	Co/Ni_{Cu}	I_{Cu}	I_{other}	V_{Cu}	$V_{Co/Ni}$
Co/Cu	17.3 ± 1.9	13.6 ± 1.6	5.7 ± 1.1	6.9 ± 1.0	9.3 ± 1.0	3.3 ± 0.7
Co/Ni	29 ± 5	23 ± 4	9.5 ± 1.9	6.5 ± 1.6	14.7 ± 1.4	1.3 ± 0.5

as described in Ref. 17. The heat of mixing for a random 50% alloy was found to be 0.44 eV/atom for Co/Cu and 0.08 eV/atom for Ni/Cu, to be compared with the experimental values of roughly 0.2 eV/atom and 0.03 eV/atom, respectively.[3,5] Thus the heats of mixing predicted for the two alloys are clearly too high, but their ratio is still reasonable. We feel that while the simulation model does not correspond exactly to the real systems, it still should give a reasonable description of cascades in immiscible alloys, with the Co/Cu alloy representing a highly immiscible system and the Ni/Cu alloy representing an almost miscible one.

We constructed a perfect (111) interface by dividing a cubic simulation cell into two parts along a (111) plane going through the origin, in the middle between two (111) atom planes. The entire cell had the face-centered cubic (fcc) crystal structure. Although this is not the equilibrium structure for Co at low temperatures, the energy difference between the fcc and equilibrium hexagonal phase is quite small. To make the different cases easily comparable the same cell size, 100.12 Å, was used in all the simulations. While this put the elemental cells under slight slight strain, comparison with previous results[18] indicated that the small level of strain did not affect the results significantly.

Collision cascades were initiated by giving an atom a kinetic energy of 5 keV in a randomly chosen direction, choosing its initial position so that the initial movement was directed towards the interface. To avoid the initial direction biasing the results, half of the recoils were started from the Co or Ni side and half from the Cu side of the cell. The initial position and velocity of the atoms were selected so that the resulting cascade was roughly centered on the Co/Cu interface. The SRIM96 electronic stopping power[19] was used to describe energy loss to electrons for all atoms with a kinetic energy higher than 10 eV. Lattice defects were analyzed using the Wigner-Seitz method,[18] comparing to a perfect fcc lattice. Furthermore, Co atoms on the Cu side of the original interface, and vice versa, were counted as ‘‘impurities.’’ We denote Co impurities in Cu with Co_{Cu}, Cu impurities in Co Cu_{Co}, and similarly for Ni. Vacancies in Cu are denoted by V_{Cu} and interstitials I_{Cu}, and similarly for Co and Ni.

The impurity and defect results are summarized in Table I, which lists the averages of all events. We describe first the results in the Co/Cu system and then discuss how the Ni/Cu results relate to these. The results in the table show that on average more Cu impurities seem to be in Co than vice versa. Inspection of each cascade showed that in almost all events more Cu impurities had entered the Co than vice versa, regardless of where the recoil was started. This may at first seem surprising, as the number of atoms must of course be conserved in a simulation with no atom sources or sinks. A similar effect was reported by Gades and Urbassek, but

they attributed it to the presence of a surface in their simulations.[6]

The defect behavior offers an explanation to this apparent paradox. An energetic collision cascade is well known to produce vacancies close to its center, and interstitials outside the cascade core.[20,21] In this case the final position of almost all the vacancies is in the Cu part (on average, about 9 vacancies are in Cu but only 3 in Co), and analysis of the defect positions showed that most of the Cu_{Co} impurities are right at the interface and close to the center of the cascade and to the vacancies. Thus, the impurity flux is balanced by a vacancy flux of opposite direction, that is, the results can be understood in terms of inverse Kirkendall-like behavior. Previously the effect has been described under conditions closer to thermal equilibrium.[7] In the present case the conditions under which the flow occurs are obviously different, but due to the analogous flow behavior we think it can be termed inverse Kirkendall mixing in collision cascades. The driving force for the vacancy flux is described next.

It is known from other simulation studies that when the liquid zone produced by a collision cascade cools down, the vacancies are dragged by the advancing solidification front towards the center of the cascade.[8,18,22] Furthermore, the solidification time of the cascade has been found to depend on the melting point of the material.[18] In the present case, the Co part of the liquid zone is expected to cool and recrystallize much faster due to its higher melting point (1620 K for Co vs 1230 K for Cu for the present model potentials). Hence the recrystallization of the Co part will push most of the vacancies into the Cu part, thereby establishing both vacancy and solute fluxes across the interface.

The interstitials are on average distributed evenly in the two elements (cf. Table I). Since equal number of interstitials and vacancies are produced, the difference between the impurity concentrations, ~ 4, is comparable to the number of interstitials in each of the components, ~ 6. Analysis of the final locations of the vacancies in Cu showed that 44% of them where in the layer closest to the interface, and 83% were in the three closest layers. This shows that while there is a driving force pushing vacancies from the Co towards the Cu, once they are there they do not move much more.

We analyzed the sizes of the impurity clusters with the method described in Ref. 18, using 3.0 Å as the cutoff for defining defects as belonging to the same cluster. The results are illustrated in Fig. 1. On average about 65% of both the Cu and Co impurities are clustered, and these clusters consist almost always of only Cu or Co impurities: only 9 out of 83 clusters are ‘‘mixed.’’ Since most impurities are clustered and surrounded by atoms of their own species, this essentially shows that the ion irradiation will produce a roughening of the interface. About 90% of the impurities were in the atom layer closest to the interface. A typical distribution of
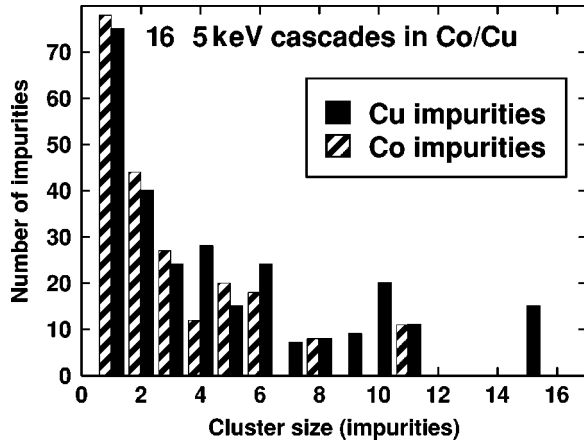
FIG. 1. Statistics of the distribution of impurities in clusters as a function of the cluster size for the 16 cascades close to the Co/Cu interface.

the impurities and vacancies is shown in Fig. 2. The Co part of the cell is to the left and below the solid line. The vacancies are almost all in the Cu part of the cell, and the impurities are clustered on both sides of the interface.

To understand whether the presence of an interface has other effects on the cascade development, we compare the results of the present simulations with cascades in pure fcc Cu and Co in Table II. The table lists the the average number of interstitials remaining after the cascade N_{int}, the ion beam mixing Q, the number of atoms displaced by more than half the nearest neighbor distance N_{displ}, and the number of atoms displaced over the interface N_{ifmix}. For the interface cascades N_{ifmix} is simply the sum of the number of impurities. For the elemental cascades this quantity is evaluated for an imagined interface at the same position as the interface for the Co/Cu system. It is noteworthy that N_{ifmix} is smaller across the Co/Cu interface than the imaginary interfaces in pure Cu or Co. This illustrates the influence of the positive heat of mixing, as well established previously both by experiment[23] and simulation.[6]

The simulations of cascades in Ni/Cu served as a test on whether the ideas described for the Co/Cu system indeed can be understood on the basis of the melting point difference and heat of mixing (rather than being due to some more subtle interface effect, for instance). Since both Ni and Co have a higher melting point than Cu, the vacancy flux effect should be present for Ni/Cu as well. But since the heat of mixing of Ni and Cu is much less than that of Co and Cu, the

TABLE II. Average values for the results of 5 keV cascades in Co, Ni, and Cu and close to the Co/Cu and Ni/Cu interfaces. n gives the number of events simulated in each case; the other quantities are defined in the text.

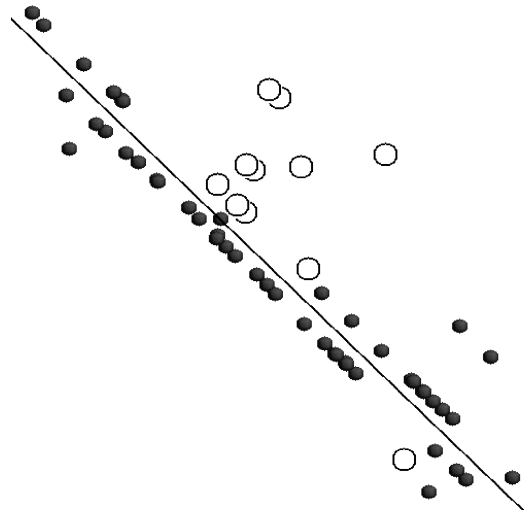| Material	n	N_{int}	Q (Å^5/eV)	N_{displ}	N_{ifmix}
Cu	6	8.2±1.3	6.4±0.6	1000±50	50±10
Co/Cu	16	12.6±0.8	6.0±0.3	960±50	31± 3
Co	6	11.8±0.8	5.0±0.5	800±90	60±20
Ni/Cu	6	16.0±1.2	4.4±0.3	950±30	51± 9
Ni	6	12.8±1.0	3.4±0.2	710±30	35± 5

FIG. 2. Distribution of impurities and vacancies after one 5 keV event close to a Co/Cu interface. The line shows the position of the (111) interface, the filled circles the positions of impurities, and the open circles the positions of vacancies. The Co part of the crystal is in the lower left part of the figure; thus all filled circles in this part are Cu impurities.

mixing over the interface should not be much different from the pure elements. These expectations are confirmed by the results in Tables I and II. Almost all the vacancies are in the Cu part, and there are more Cu_{Ni} than Ni_{Cu} impurities. The difference in impurity numbers is again comparable to the number of interstitials in each part of the mixed system. The number of mixing occurring over the interface N_{ifmix} is about the same as that in the pure elements, as expected.

The results in Table II also show that the presence of an interface does not dramatically affect the overall development of the collision cascade. The total damage production is rather similar in all cases, in agreement with our previous observation that defect production in dense metals is not strongly affected by the elastic or melting properties.[18] The differences in mixing can be understood in terms of the different melting points.[10] Atom mixing over the interface, N_{ifmix}, is clearly suppressed in the Co/Cu system due to the large positive heat of mixing, but since this number is in any case only a small fraction of the total atom displacement N_{displ}, this does not affect the total mixing in the system.

Lastly we note the experimental work of Auner *et al.* who reported asymmetric mixing in a number of bilayer systems where one element had a significantly larger cohesive energy (and melting point) than the other.[24] In apparent contrast to the present results, they observed the impurity distribution extending deeper into the metal of lower cohesive energy. The experimental resolution in ion beam mixing experiments is ~10 nm, however, so their observations refer to mixing for high ion doses at times when no sharp interface was present. Since mixing increases with decreasing melting temperature of the metal, their results were expected. The present asymmetry of mixing derives strictly from the sharp interface. At elevated temperatures, mixing at such interfaces is important since radiation-enhanced diffusion tends to restore the sharp interfaces in precipitating systems.[1]

By simulating high-energy collision cascades close to the interface of immiscible metals, Co and Cu or Ni and Cu, we

have shown that an interface between two materials can introduce a large asymmetry in the vacancy production and in the mixing of atom species over the interface. When there is a large difference in the melting points, the quenching phase of the collision cascade tends to push the vacancies into the material with the lower melting point. This will also introduce an imbalance in the impurities; more atoms of the material with a lower melting point are introduced into the material with a higher one. Furthermore, we found that about 80–90% of the impurity atoms produced are in the atom layer closest to the interface, and demonstrated that except for the peculiar vacancy production and impurity introduc-

tion properties, the cascades close to the interface behave much like cascades in elemental metals.

---

*Present address: Accelerator Laboratory, P.O. Box 43, FIN-00014 University of Helsinki, Finland. Electronic address: kai.nordlund@helsinki.fi

[1] G. Martin and P. Bellon, in *Solid State Physics*, edited by H. Ehrenfest and F. Spaepen (Academic Press, New York, 1997), Vol. 50, p. 189.

[2] D. J. Kubinski and H. Holloway, J. Magn. Magn. Mater. **165**, 104 (1997).

[3] C. Gente, M. Oehring, and R. Bormann, Phys. Rev. B **48**, 13 244 (1993).

[4] P. P. Macrí, S. Enzo, N. Cowlam, R. Frattini, G. Principi, and W. X. Hu, Philos. Mag. B **71**, 249 (1995).

[5] J. C. Gachon, J. P. Hilger, M. Notin, and J. Hertz, J. Less-Common Met. **72**, 167 (1980).

[6] H. Gades and H. M. Urbassek, Phys. Rev. B **51**, 14 559 (1995).

[7] A. D. Marwick, J. Phys. F **8**, 1849 (1978).

[8] T. Diaz de la Rubia, R. S. Averback, R. Benedek, and W. E. King, Phys. Rev. Lett. **59**, 1930 (1987).

[9] K. Nordlund, L. Wei, Y. Zhong, and R. S. Averback, Phys. Rev. B **57**, 13 965 (1998).

[10] K. Nordlund, M. Ghaly, and R. S. Averback, J. Appl. Phys. **83**, 1238 (1998).

[11] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, J. Chem. Phys. **81**, 3684 (1984).

[12] K. Nordlund, Comput. Mater. Sci. **3**, 448 (1995).

[13] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, England, 1989).

[14] R. Pasianot and E. J. Savino, Phys. Rev. B **45**, 12 704 (1992).

[15] J. R. Morris, C. Z. Wang, K. M. Ho, and C. T. Chan, Phys. Rev. B **49**, 3109 (1994).

[16] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Matter* (Pergamon, New York, 1985).

[17] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[18] K. Nordlund, M. Ghaly, R. S. Averback, M. Caturla, T. Diaz de la Rubia, and J. Tarus, Phys. Rev. B **57**, 7556 (1998).

[19] J. F. Ziegler, 1996, SRIM-96 computer code (private communication).

[20] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1956), Vol. 2, p. 307.

[21] R. S. Averback and T. Diaz de la Rubia, in *Solid State Physics*, edited by H. Ehrenfest and F. Spaepen (Academic Press, New York, 1998), Vol. 51, p. 281.

[22] K. Nordlund and R. S. Averback, Phys. Rev. B **56**, 2421 (1997).

[23] Y. T. Cheng, M. V. Rossum, M.-A. Nicolet, and W. L. Johnson, Appl. Phys. Lett. **45**, 185 (1984).

[24] G. W. Auner, Y.-T. Cheng, M. H. Alkaisi, M. M. Karmarkar, and K. R. Padmanabhan, Nucl. Instrum. Methods Phys. Res. B **59/60**, 504 (1991).