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ENERGETICS AND CONFIGURATIONS OF LATTICE DEFECTS IN CuTi.

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ABSTRACT

The energies and configurations of interstitials and vacancies in the ordered compound CuTi were calculated using atomistic simulation. Vacancies created by the removal of either a Cu or Ti atom resulted in a vacant Cu site, with an antisite defect in the latter case. The vacancy at the Cu site was found to be very mobile within two adjacent (001) Cu planes, resulting in two dimensional migration. Interstitials created by inserting either a Cu or Ti atom had complicated configurations containing one or more antisite defects.

INTRODUCTION

Irradiation-induced amorphization of alloys has been experimentally investigated for many years. One of the key questions has been why some alloys but not others can be amorphized during irradiation, and various theories of amorphization have been proposed based on volume expansion, chemical disorder and/or point defects [1,2,3]. A recent computer simulation study of the amorphization of CuTi indicated that point defects were a critical factor in amorphization, although volume expansion and chemical disorder could also play a role [4,5]. The importance of point defects suggests that defect properties of alloys must be different than those of pure metals, since pure metals cannot be amorphized under irradiation. The purpose of the present work is to investigate point defects in the alloy CuTi.

METHOD

The computational methods employed in the present work were molecular statics and molecular dynamics, using a modified version of the code DYNAMO [6]. The simulations used rectangular volumes containing $N = 1024$ atoms and whose edge lengths were free to vary with external pressures. The interatomic potential functions for CuTi are the same as in the previous study of amorphization [5]. Local energy minimization was performed using the Fletcher-Powell method, adapted for a large number of independent variables [7]. The search for global minima was carried out using a variation of simulated annealing [8]. The systems were initially heated to 750K for a few hundred time steps, then minimized using the Fletcher-Powell method. This two-step process was repeated at 650K, 550K, etc., down to 250K. Migration energies were calculated by minimizing the system energy with the jumping atom constrained at various points along the jump path [7].

These minimization techniques allow one to determine the minimum energy configuration of each defect. In pure metals, given the energy of the perfect lattice and of the lattice with the defect, it is then straightforward to calculate the formation

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energies. In alloys, the formation energies of a Frenkel pair and an antisite pair can be calculated in a similar way. The calculation of the formation energy of a isolated vacancy or interstitial is not so simple, however, because the perfect lattice and the system with the defect have different chemical compositions [9,10]. Because of this, we report here only the total system energies for vacancies and interstitials instead of formation energies. The migration energy, on the other hand, is well defined since it is calculated from energy differences between configurations of the same system, and these energies will be reported.

RESULTS AND DISCUSSION

For reference, the CuTi structure is depicted in Figure 1. It is essentially a bcc structure, with alternating pairs of planes of Cu and of Ti. The total energy of the perfect lattice containing 1024 atoms is -4404.4207 eV. The general results of the calculations are summarized in Table 1.

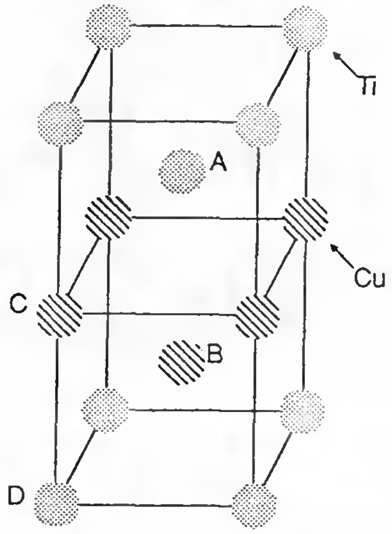

Fig. 1. Structure of CuTi. The labelled atoms are referenced in the text.

Table 1. Summary of Stable Configurations.

System	Number of Atoms	Energy [eV]	Configuration
Perfect Crystal	1024	-4404.4207	
Antisite Defect	1024	-4404.0397	
Cu Vacancy	1023	-4399.6440	Slight relaxation around vacant Cu site
Ti Vacancy	1023	-4398.4100	Antisite defect and vacant Cu site
Cu Interstitial	1025	-4406.2327	Complex with antisite defect(s)
Ti Interstitial	1025	-4407.1013	" "

The simplest defect in a substitutional alloy is an antisite defect, where an atom is on a lattice site but is of the wrong type. In the present work, the formation energy of an antisite pair was calculated to be $E_{\mathrm{anti}} = 0.381$ eV. Although no experimental value of E_{anti} is available for CuTi, it is known that CuTi does not become chemically disordered upon heating. This implies that E_{anti} must be significantly larger than kT_{m}, where k is Boltzmann's constant and T_{m} is the melting temperature of the alloy. For CuTi, where $T_{\mathrm{m}} = 1275K$, we have $kT_{\mathrm{m}} \approx 0.1$ eV, and thus the calculated value of E_{anti} is in good agreement with experimental observations.

A Cu vacancy was created by removing a Cu atom from the system (Site C in Fig. 1). Subsequent minimization resulted in a system energy of -4399.6440 eV, and no large atom displacements were observed. No lower energy configurations were found in subsequent attempts to locate other minima by simulated annealing. The migration energy of the Cu vacancy was calculated for two cases: 1) migration confined to two Cu (001) planes, and 2) migration across the Ti planes. Migration within the Cu planes is accomplished by the jump of a nearest-neighbor Cu atom into the vacancy (Site B to Site C). The migration energy calculated for this jump was 0.189 eV, a surprisingly low value compared to typical vacancy migration energies in pure metals [11]. The migration of the vacancy across the Ti planes was calculated as a sequence of vacancy jumps, such that the final configuration did not contain an antisite defect. This migration occurs through a sequence of ring mechanisms, since a Cu atom must migrate through the Ti planes to prevent the formation of an antisite defect. The migration energy for the complete sequence was 1.324 eV.

The initial relaxation of the lattice after the removal of a Ti atom (Site A) was similar to what was observed with the Cu vacancy; the atoms around the vacancy were displaced slightly, moving toward the vacant site. Simulated annealing revealed that this was not the lowest energy configuration, however. The Ti vacancy at Site A was replaced by a Cu atom, resulting in an antisite defect at Site A and a vacant Cu site at Site B. This configuration corresponded to a system energy of -4398.4100 eV and was considerably more stable than the initial configuration since its energy was 0.402 eV lower. The migration energy barrier from the initial configuration to the stable configuration was only 0.151 eV, showing that the vacancy could easily move to the Cu site. The results of the migration energy calculations for the minimum energy configuration were similar to the results for the Cu vacancy. The energy for the movement of a Ti atom (Site D) into the vacant Cu site (Site B) was 0.556 eV. The resulting configuration was weakly metastable, since the migration barrier for the reverse process was calculated to be about 0.05 eV. Migration within the Cu planes was similar to the migration of the Cu vacancy discussed above, with the added complication that the vacancy was bound to the Ti antisite defect with a binding energy of 0.17 eV.

The results for vacancies are interesting because the behavior they predict is considerably different from what is observed in pure metals. At room temperature, the migration energy must be about 0.7 eV or less for migration to occur. Clearly, the vacancies in this case will be confined to the Cu planes, in which they can diffuse in two dimensions below room temperature. The Ti vacancy convert to a Cu vacancy and an antisite defect, and the Cu vacancy will be free to migrate within the Cu planes.

The minimum energy of a Cu interstitial was found by inserting a Cu atom into the perfect lattice and using simulated annealing. The system energy of the lowest energy configuration was -4406.2327 eV. The energy of the configuration with the next lowest energy was 0.1 eV higher than the minimum. The most stable configuration of the Cu interstitial is complex. Although the Cu atom was initially placed between two Cu planes, the final configuration had a Cu atom between Cu and Ti (001) planes. This atom lies approximately midway between two Cu atoms, one atom in the Cu plane, and the other-an antisite defect-in the Ti plane. These two Cu atoms were displaced away from the interstitial in the [111] direction, and resulted in the displacement of other atoms along this line. The Ti atom that was located at the Cu antisite defect formed an antisite defect in a Cu plane.

The minimum-energy configuration of a Ti interstitial was found using the same procedure as was used for the Cu interstitial. The system energy of the most stable configuration was -4407.1013 eV, which was 0.211 eV lower than the energy of the next most stable configuration. The configuration of the Ti interstitial was the most complicated of the defects studied. Five antisite defects were created, and a Cu-Ti dumbbell was formed that was approximately parallel to the [111] direction.

The most stable configurations of the interstitials are considerably different from what is typically found in pure metals. Interstitials are in <100> and <110> dumbbell configurations fcc and bcc metals, respectively, and are highly mobile. In CuTi, the interstitial configurations are highly disordered and include the formation of one or more antisite defects. Although the migration energy was not calculated here (it is not obvious that the static methods used for the vacancy calculations will be applicable to these complicated configurations), it seems likely that the interstitial migration energy will be relatively large.

CONCLUSIONS

The complicated configurations of the interstitials in the alloy suggests that interstitials are significantly less mobile than vacancies. The theory of radiation-induced amorphization by Pedraza [3] proposes that amorphization is caused by the buildup of stable interstitial-vacancy complexes. Our results suggest, however, that the crystalline-to-amorphous transition can be driven by stable, highly-disordered atom clusters (formed by the production of interstitials), whose accumulation is favored by fast two-dimensional diffusion of vacancies resulting in reduced interstitial-vacancy recombination.

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