

**SIMULATIONS OF DEFECT AND DIFFUSION PROPERTIES IN  
THE INTERSTITIAL CU-C SOLID SOLUTIONS**

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**ABSTRACT**

HRSEM analyses of copper/graphite interfaces are presented, showing a narrow solid solution zone. Atomistic simulations in the framework of the Generalized Simulated Annealing approach lead to very reasonable relaxed geometries around carbon interstitials and vacancy complexes of a Cu host, and for a Cu/graphite interface. Embedded Cluster Density Functional results indicate a charge transfer of  $\sim 1 e$  to carbon, mostly from the first neighbor shell, in all relaxed environments studied.

## INTRODUCTION

In metallic conductors like copper, small particle precipitates are found to improve hardness and wear resistance of contacts. For high temperature applications, matrix-embedded carbon fibers have also been considered to provide stiffness and prevent ductile failure, and may be useful to reduce sliding friction [1]. An understanding of C diffusion in Cu, and its behavior at the Cu/C interface is fundamental to developing successful strategies for improving fiber-matrix composite performance. In this paper we report combined theoretical and experimental analyses of the Cu-C interaction, using atomistic simulations, density functional methodology, and high-resolution scanning electron microscopy (HRSEM). Wettability-enhancing efforts [2] based upon alloying elements benefit by connection between the fundamentals of the wetting of solids by liquid metals and the practice of the preparation of metal-matrix composites (MMC)[3]. In [4-6] it was shown that the interfacial energy in a metal-carbon fiber system is modified by the interfacial adsorption of the alloying elements which are added to the metal matrix.

Our HRSEM study shows the existence of a ~50nm solid solution zone at the copper-carbon interface, after annealing. After heat treatment of one hour at 1000C the interface faded and we can see the copper-carbon solid solution region of width ~ 50 nm. Formation of a very dilute Cu-C interstitial solid solution at the interface may be diffusion-controlled. To predict the diffusion behavior of carbon atoms we have to study the structure and interatomic interactions in such alloys. Phenomenological studies of these phenomena[7] have now been augmented by quasi-continuum models [8] which reflect some aspects of the underlying electronic structure. We here extend the analysis to the atomic scale, using a combination of atomistic simulations and first-principles density functional embedded cluster schemes.

## EXPERIMENTAL STUDY OF Cu-C INTERFACE

Contact pairs of copper-carbon were prepared from copper powder of 99.5 purity, typically 10 microns average size or less, produced by CERAC Ltd. The purity indicated is based on 100% minus spectrographic analysis of trace metallic contents. Spectrographically pure carbon rods of 6.15 mm diameter and 300 mm long, produced by AGAR Ltd were used. The total content of impurities was less than 20 ppm. The rod was cut in chemically pure petroleum ether to obtain compact cylindrical discs of 6.1 mm diameter and 1 mm height with polished bases, which were embedded into the copper powder matrix. The samples were consolidated by cold pressing at 1950 MPa pressure with a hydropress BAUSTOFF PRUF (TONI TECHNIK) to full density (97 % for type 1 samples and 100 % for type 2 samples). Heat treatment was performed at 1000 C for 1 hour in a vacuum of  $10^{-6}$  -  $10^{-7}$  Torr. As received and annealed specimens were cut in the chemically pure petroleum ether and polished to prepare cross-sectioned samples for a study by secondary electron microscope (SEM) and high resolution SEM (HR SEM). SEM study was carried out with a JSM 840 (JEOL)

Scanning Electron Microscope equipped with an Energy Dispersive Spectrometer (EDS) LINK ISIS (Oxford Instruments). EDS allows to determine all elements starting from Be. The limit of detection for the majority elements was not worse than 0.1 wt. %. High resolution (HR) SEM study was carried out with GSM 982 electron microscope under 2 & 10 KeV accelerating voltage. Typical working distance was 2 mm. In-lens detector of secondary electrons was used for capture of secondary electron images. HR SEM images of the interphase region for the as received and annealed samples show the fading of the sharp interface of the as received composite after annealing. We estimate the region of this fading about 50 nm.

## THEORETICAL STUDY

### Atomistic Simulations

The Generalized Simulated Annealing approach (GSA) is based on the correlation between the minimization of a cost function (conformational energy) and the geometry randomly obtained through a slow cooling to sample and explore basins of stability. The artificial temperature acts as a convenient stochastic source for eventual detraining from local minima, with the endpoint of the process falling within the attractive basin of the global minimum. The challenge is to cool the system as fast as possible and still have the guarantee that the no irreversible trapping at any local minimum has occurred. The procedure used to search the minima (global and local) or to map the energy hypersurface consists in comparing the conformational energy for two consecutive random geometries  $x_{t+1}$  and  $x_t$  obtained from the GSA routine.  $x_t$  is a N-dimensional vector that contains all atomic coordinates (N) to be optimized. The geometries, for two consecutive steps, are related by  $x_{t+1} = x_t + \Delta x_t$  where  $\Delta x_t$  is a random perturbation on the atomic positions. To generate the random vector  $\Delta x_t$  the present GSA approach [9,10] uses a numerical integration of the visiting probability distribution.

We consider here the energy of the system in the simple form:

$$E(r) = \frac{1}{2} \sum_{i,j} K_{ij} (r_{ij} - R_{0ij})^2 + \sum_{i<j} \left[ \frac{C_{12}(i,j)}{r_{ij}^{12}} - \frac{C_6(i,j)}{r_{ij}^6} \right] + E_0 \quad (1)$$

Our MD simulations are deliberately constrained to small displacements of the Cu host atoms, for which the framework of elastic Hook-law Cu-Cu interactions are quite adequate ;As follows from simple pseudopotential calculations (see a paper of Dorfman and Fuks from Ref.[2]) the Cu-C interaction is repulsive at least to several coordination shells surrounding the carbon atom. The repulsive part of interaction may be fitted by any functional form, and we have chosen Lennard-Jones (LJ) parameters to reproduce the experimentally measured properties. Unfortunately, experimental data on dilute Cu-C solid solutions are absent. To estimate the parameters of, for example, LJ-type of potential we use the results of previously mentioned pseudopotential studies. The last term,  $E_0$ , represents the volume-dependent part of the energy and includes the information about electronic density redistribution, which is gathered from the

embedded cluster density functional scheme, or may be obtained from other electronic structure calculations. The parameter values are:  $R_0=2.475 \text{ \AA}$ ,  $K=6.920 \text{ eV/\AA}^2$ ,  $E_0=-0.875 \text{ eV}$ ,  $C_6=41.548 \text{ eV/\AA}^6$ ,  $C_{12}=2989.105 \text{ eV/\AA}^{12}$

## Embedded Cluster Density Functional Scheme

Density Functional (DF) theory is a first-principles self-consistent approach to electronic structure, which has wide applications to molecules and solids [11]. Our own development of the Embedded Cluster scheme permits a spatially localized expansion of electronic wavefunctions, densities, and derived properties by treating fragments of the extended system [12]. This approach gives a feasible methodology for self-consistently treating large systems with low symmetry, and is thus particularly well suited for problems of impurities, surfaces, and interfaces [13,14].

Very briefly put, the system electronic charge and spin densities are decomposed into overlapping cluster sums:

$$\mathbf{r}(\vec{r}) = \sum_i w_i(\vec{r}) \mathbf{r}_i(\vec{r} - \vec{R}_i) \quad (2)$$

and the individual cluster densities are expressed in terms of the single-particle DF wavefunctions and their Fermi-Dirac occupation numbers:

$$\mathbf{r}_i = \sum_j n_{i,j} |\mathbf{y}_{i,j}(\vec{r})|^2 \quad (3)$$

Extraction of the interior 'seed' volume of each cluster, and alignment of equivalent partial densities of states (equivalent Fermi energies) completes the self-consistent fragment matching procedure. The DF wavefunctions for each embedded cluster are obtained by the well developed Discrete Variational (DV) method [12-15], using the DF potential derived from the total density  $\mathbf{r}$ .

## RESULTS

### Atomistic Simulation Results

Initial calculations were made on a pure copper 'sample' of 48 atoms confined to a box of experimentally correct dimension, showing that the parametrization reproduced the bulk structure adequately. A single C interstitial, surface, or vacancy atom was next added and allowed to migrate freely. We find that at the octahedral O site, relaxation is accompanied by outward expansion of nearest neighbors (NN) by slight inward contraction of second neighbors (NNN), as predicted in the continuum model, and a small disorder or distortion as measured by standard deviation  $\sigma$ . The simulation results are seen to be about 1/2 the size ( $\sim 0.12 \text{ \AA}$ ) of the continuum model predictions for nearest neighbor (NN) and  $\sim 1/5$  ( $\sim 0.01 \text{ \AA}$ ) for the NNN. About 0.5 eV is gained by relaxation around O. At the crowded tetrahedral T site, an initial energy penalty of 8 eV is largely relieved by outward relaxation of the NN shell, accompanied by a slight inward motion and distortion of the NNN shell. The final T site energy is 0.7

eV above that of the O site, in accordance with qualitative expectations. The O-O transition state is of considerable interest, due to its critical role in determining the barrier for carbon diffusion. We find that the TS presents a barrier of 1.2 eV relative to the relaxed O site, and is characterized by a rather strong axial distortion of the pseudo-octahedral local geometry.

A second series of simulations was made to study defect clustering and carbon agglomeration in Cu. A typical GSA 'sample' with C concentration of ~6%, perhaps characteristic of the graphite:copper interface region is shown in Fig. 1. Bulk solubility is <0.02%. All atoms were relaxed to search for different equilibrium conformations.

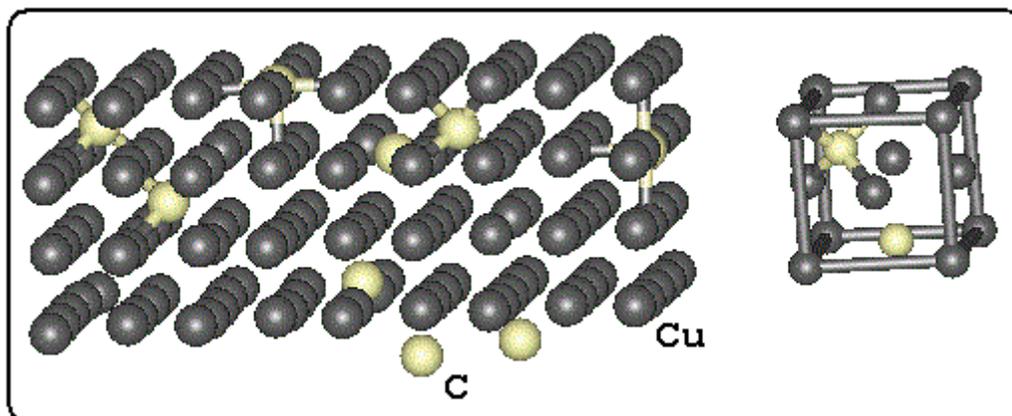


Fig.1 Schematic of high-C concentration simulation volume, showing vacancy, O- and T-site carbon, shown as light colored atoms.

We observe that the O- and T- sites are relatively stable, as in the isolated impurity case. In addition to the monomers previously studied, some carbon atoms migrate to the surface and others are attracted to form C-C dimers. For the most stable  $C_2$  configuration one carbon is localized in a T-site while the second occupies a neighboring Cu vacancy. This configuration achieves low energy by simultaneously reducing the Cu-C repulsion and taking advantage of C-C attraction. It marks the onset of particle growth as a precipitate in Cu. In case of migration of C atoms to the surface, we observe that some are localized in 5-fold quasi-O sites, while others are repelled from the Cu surface. Thus it appears that surface defects facilitate the adsorption and eventual penetration of Cu by C.

In a third series, the consolidation of the interface of a metal-matrix composite has been investigated. For this purpose, the relaxation and rearrangement of a copper(001) /graphite(0001) interface was determined using GSA. All atoms close to the surface have been relaxed, and a pattern of atomic disorder is observed in the first few atomic layers on either side of the interface, generally consistent with our experimental observations. Preliminary studies of influence of vacancies on the diffusion of carbon have been made, and will be reported elsewhere. Emphasis will next be given to the influence of impurities in the carbon diffusion process. The addition of chromium to copper has been shown to increase the level of matrix bonding to graphite fibers, as evidenced by observations of fractured tensile specimens. Auger electron spectroscopy analyses indicate that a chromium carbide phase present at the

interface is responsible for the improved bonding, so it should be interesting to see the predictions of Cu:Cr:C mixtures simulations.

### Embedded Cluster Results

We have previously reported a series of embedded cluster DF calculations with isolated carbon interstitials placed at S, O, T, and TS sites[15]. The resulting data base provides a consistent picture of C as an acceptor in copper, with charge largely drawn from the NN environment. A kind of “polarization wave” expected on general principles for charged impurities is seen, in that second neighbors often show net charge accumulation. Despite its low solubility and supposed repulsive interaction with Cu, bond order analysis shows the formation of Cu-C bonds in all but the most crowded environments. This is not too surprising, as it is the relative energy of surface states to interstitial states which determines solubility. We find that relaxation tends to increase charge transfer onto C, with a typical value of Mulliken charge of  $\sim -1e$ . The C volume charge, which integrates a local region and minimizes diffuse overlapping and C-Cu hybridization contributions, gives smaller values as expected, with the same trends. Cu-C bond orders of  $\sim 0.3$  e/atom are seen to be typical for NN interactions in relaxed environments, and as expected, are very sensitive to interatomic distances. The NNN bond orders are seen to be much smaller, indicating the rather short range of chemical interaction between C and Cu.

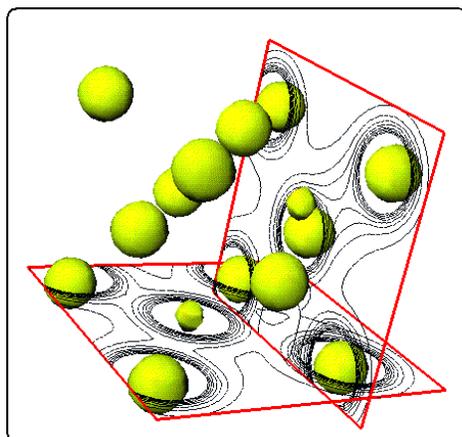


Fig. 2. A low-energy vacancy-tetrahedral interstitial  $C_2$  complex in copper: electron density isosurface and contour projection.

The NNN charges are often negative, indicative of a polarization wave. Contour maps show no accumulation of localized covalent charge, so the bonding is of a diffuse character. Space limitations prevent a detailed analysis of the electron densities found in defect-complex, dimer, and surface environments. We hope that the structural and density maps of Fig. 2 will give the reader an idea of the main features. An analysis of cluster energetics will be presented elsewhere.

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