NASA Technical Memorandum 107168

Cu-Au Alloys Using Monte Carlo Simulations and the BFS Method for Alloys

Guillermo Bozzolo
Analex Corporation
Brook Park, Ohio

Brian Good and John Ferrante
Lewis Research Center
Cleveland, Ohio

March 1996

National Aeronautics and
Space Administration

Cu-Au ALLOYS USING MONTE CARLO SIMULATIONS AND THE BFS METHOD FOR ALLOYS

GUILLERMO BOZZOLO*, BRIAN GOOD** AND JOHN FERRANTE**
* Analex Corporation, 3001 Aerospace Parkway, Brook Park, OH, 44142-1003
**National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135.

ABSTRACT

Semi empirical methods have shown considerable promise in aiding in the calculation of many properties of materials [1,2]. Materials used in engineering applications have defects that occur for various reasons including processing [3]. In this work we present the first application of the BFS (Bozzolo, Ferrante and Smith) method for alloys [1] to describe some aspects of microstructure due to processing for the Cu-Au system (Cu-Au, $CuAu_3$, and Cu_3Au). We use finite temperature Monte Carlo calculations, in order to show the influence of 'heat treatment' in the low-temperature phase of the alloy. Although relatively simple, it has enough features that could be used as a first test of the reliability of the technique. The main questions to be answered in this work relate to the existence of low temperature ordered structures for specific concentrations, for example, the ability to distinguish between rather similar phases for equiatomic alloys (CuAu I and CuAu II, the latter characterized by an antiphase boundary separating two identical phases).

Engineering materials of necessity have various defects that result from annealing and processing procedures. In general, the ideal thermodynamic equilibrium is rarely achieved in the laboratory process of making the actual alloy, particularly in the case of large scale structures. It is of interest, therefore, if these procedures can be simulated. In this paper we have used Monte Carlo methods [4] to simulate this processing using the BFS method [1] for system energetics. We accomplish this end by starting from a random distribution at high temperature, then examining the structure by freezing the solid at various temperatures, and examining the micro-structure. The organization of the paper is as follows: first we discuss the Monte Carlo procedure, then give a brief description of the BFS method and finally examine the defects appearing as a result of "quenching" the solid.

The Monte Carlo procedure employed is a variant of that used to simulate the Ising system. The computational cell used in all simulations consists of 1008 atoms arranged on a face-centered cubic lattice. Boundary effects are minimized through the use of periodic boundary conditions. Each lattice site is characterized by the species of the atom (i.e. Cu or Au) occupying the site. The initial state of the computational cell is a random alloy having a specified composition. The cell's lattice constant is assumed to depend only on composition and its variation with temperature is ignored. The lattice constant is determined from static zero-temperature BFS calculations (to be discussed below).

A sequence of temperatures (the "cascade") is chosen, in all cases, where, the system is allowed to equilibrate sequentially at each of the temperatures (simulating the "slow cooling" of the actual alloy starting from a disordered solid solution) via a procedure where pairs of atoms of opposite species are chosen randomly, and the atomic species of each of the two atoms is reversed. The reversal is accepted or rejected using the standard Metropolis criterion. Because the lattice constant and all other properties are assumed to be independent of temperature, the temperature enters into the simulation only through the Metropolis criterion [4]. After the system has achieved equilibrium

(based on the total energy), the simulation is allowed to proceed further while various properties of the system are computed and averaged. These include the average energy of the cell, the specific heat, and bond correlations.

While these simulations do not attempt to mimic the detailed dynamics of the equilibration process, they do offer a qualitative view of the effects of rapid versus slow cooling of the system. The temperature treatment (that is, the sizes of the steps between the various temperatures in the cascade) is of critical importance in determining the final state of the system. Slow cooling results in a highly-ordered low-temperature state, while rapid cooling results in an alloy with grain structure, in which each grain has essentially the ordering of the thermodynamic ground state.

The current simulation procedure does not allow for relaxation of neighbors of atoms whose species have been reversed. In cases where the lattice constants of the two species are substantially different (which is the case in the Cu-Au system), neglecting such relaxation may result in a significant error in the system energetics, with the result that quantities such as phase transition temperatures may not be accurately predicted. In order to eliminate this limitation and to more accurately predict transition temperatures, we have begun follow-up work on the Cu-Au system in which the lattice is relaxed via a molecular dynamics process, while the system is ordered concurrently using the Monte Carlo procedure described above. Because this new work is computationally more intensive than that described in this paper, we are developing our computer code for a 16-processor SP2 parallel processing computer using the PVM environment.

The phase diagram of Cu-Au is shown in Fig. 1 [5]. A solid solution exists for the whole range of concentration, with a rather well defined order-disorder transition, that leads to simple $L1_2$ (for $CuAu_3$ and Cu_3Au) and $L1_0$ (for CuAu) fcc ordered structures. Of special interest is the ordering found for equiatomic alloys. For a narrow range of temperatures, there is a long-period superlattice (CuAu II) where an antiphase boundary (APB) arises. While antiphase boundaries introduced by plastic deformation belong to the microstructure of the alloy, the former belongs to the phase. On either side of the APB, the alloy has the $L1_0$ structure, which for even lower temperatures becomes the only phase found for the Cu-Au alloy (CuAu I). The purpose of this work is to determine the ordered structures of Cu-Au as a function of composition by means of Monte Carlo simulations and to examine the influence of the temperature (heat) treatment in the simulation in relation to the type of ordering found. The energetics of the system are calculated with the BFS method for alloys, which has been successfully applied to the study of other properties of the Cu-Au system. In what follows we provide a brief description of the BFS method and some comments on the Monte Carlo calculations performed, followed by a discussion on the main features of the Cu-Au phase diagram obtained in this work.

The BFS method is based on the idea that the energy of formation of an alloy is the superposition of individual contributions ε_i of non-equivalent atoms in the alloy [1]:

$$\varepsilon_i = \varepsilon_i^S + g_i(\varepsilon_i^C - \varepsilon_i^{C_0}). \tag{1}$$

ε_i has two components: a *strain* energy ε^S, computed with equivalent crystal theory (ECT) [6], that accounts for the actual geometrical distribution of the atoms surrounding atom i, computed as if all its neighbors were of the same atomic species, and a *chemical* energy $\varepsilon^C - \varepsilon^{C_0}$, which takes into account the fact that some of the neighbors of atom i may be of a different chemical species. For ε_i^C we interpret the chemical composition as a defect of an otherwise pure crystal. We represent this defect by 'perturbing' the electronic density in the overlap region between dissimilar atoms and locating them at equilibrium lattice sites of atom i. The ideas of ECT [6] are used to develop a procedure for the evaluation of the energy associated with this 'defect'. To free the chemical energy of structural defect energy which should only be included in the strain energy, we reference ε_i^C to a similar contribution where no such perturbation is included ($\varepsilon_i^{C_0}$). The coupling function g_i, which ensures the correct asymptotic behavior of the chemical energy, is defined as $g_i = e^{-a_i^S}$, where a_i^S is a solution of $\varepsilon_i^S = -E_C^i \left[1 - (1 + a_i^S) exp(-a_i^S)\right]$ (see ref. [7]), and where E_C^i is the cohesive energy

for atom i. In the context of BFS, the terms 'strain' and 'chemical' represent quite different effects than the usually assigned meanings. For a clear understanding of this paper, we direct the reader to Ref. 1 where a detailed description of the calculation of the strain and chemical energy contributions is provided. Except for two parameters determined by fitting to experimental or theoretical alloy properties, the method relies on pure element properties. The BFS parameters used in this work, as well as the ECT parameters are listed in refs. 1 and 6, respectively. The parameters used in this work have been previously used, with a great degree of success, in previous BFS applications to the Cu-Au system, including surface segregation as well as multilayer surface relaxation studies [1].

There are some general observations regarding the results of the current study. Most simulations were performed following a 'cascade' process: starting with a random configuration at very high temperature, the cell was stabilized for successive temperature steps, which could be loosely related to a slow cooling of the actual alloy starting from a disordered solid solution. The temperature treatment of the sample is essential in determining the final state. Slow cascade processes always resulted in highly ordered compounds at low temperatures, with very few antisite defects, whereas sudden cooling of the sample results in an alloy with grain structure, where each grain has basically the ordering pattern to be expected for the thermodynamic ground state. This process can be understood as if the quenching of the sample 'freezes' ordered domains within the cell, whose seed is already present in the initial disordered state.

Fig. 2 indicates the final states of 'cascade' calculations for three specific concentrations: 25, 50 and 75 at. % Au. As expected, at low temperatures these structures follow the $L1_2$ (Cu_3Au and $CuAu_3$), Fig. 2(a) and the $L1_0$ (CuAu I) ordering Fig. 2(b). The coordination parameter σ, which indicates the probability that a Cu atom has a Au atom as a nearest-neighbor, should attain the values 0.3333 (Cu_3Au), 0.6667 (CuAu I) and 1.0000 ($CuAu_3$) if perfect order was achieved. In our calculations these values are 0.3327, 0.6630 and 0.9940, respectively. The final temperature for each one of these three alloys is T=100K.Slow cooling of certain disordered alloys to temperatures in the 400 K range result in the CuAu II structure, with a clearly defined APB, as seen in Fig. 2(c).

Finally, as mentioned above, sudden cooling of a disordered alloy results in partially ordered alloys, as shown in Fig. 3. Close examination of the final cells shows the possibility of identifying domains within the computational cell which essentially follow the $L1_0$ ABAB stacking for the equiatomic case (Fig.3(b)) and the $L1_2$ ordering for alloys with 25 and 75 at. % Cu. To guide the eye, Fig. 3 shows a deformed computational cell for each concentration, where different (Fig.3(a),(c)) regions showing $L1_2$ ordering can be seen. The $L1_0$ ordering can be seen in more than one direction. In order to highlight this fact, Fig. 4 shows a front view of the quenched CuAu alloy, where some domains are indicated as well as their orientation relative to each other.

In spite of the microstructure of the alloys shown in Fig. 3 there is a high degree of ordering as measured by the probability of an atom A having a nearest-neighbor of species B. If A denotes a Cu atom, this quantities should have the values 1.0, 0.6667 and 0.3333 for $CuAu_3$, CuAu, and Cu_3Au, respectively. As mentioned above, a slow cooling process yields the values 0.9940, 0.6630 and 0.3327. The corresponding probabilities for the samples shown in Fig. 3 are 0.9735, 0.6524 and 0.3208, respectively, thus indicating that the domains of $L1_0$ and $L1_2$ ordering locate themselves so as to optimize the expected coordination. The degree of order and the size and abundance of these domains is clearly a manifestation of the short range ordered that could exist in the high temperature alloy.

Restrictions were imposed in these calculations although none of them, if lifted, are expected to lead to qualitatively different outcome. In all cases, the initial state for the Monte Carlo simulation was a random state at a very high temperature (5000 K), which is obviously well beyond the melting temperature. However, the atoms were constrained to locate themselves in equilibrium lattice sites. Moreover, no local atomic relaxations were allowed, therefore eliminating the possibility of detecting a tetragonal distortion. The computational cell was restricted to retain a constant volume throughout the calculation. The main effect of such a restriction could be the degree of

ordering achieved at each given temperature, but given the nature of the results presented here, it might be safe to assume that this limitation will not alter the essential nature of the final state, i.e. the type of ordering found.

In conclusion, we have proposed the use of Monte Carlo techniques with the BFS method for energetics in order to simulate certain aspects of alloy processing for Cu-Au, namely, slow cooling and rapid quenching. This approach appears to reproduce some of the features of processing. Slow cooling to 100 K produces a single crystal for each alloy examined. Slow cooling to 400 K produces the CuAu II structure with antiphase boundaries as observed in the phase diagrams. Rapid cooling gives a granular micro-structure with grains having the equilibrium ground state structure of each alloy studied. This Monte Carlo procedure could then be a possible non-dynamic method for studying the effects of alloy processing.

REFERENCES

1.. G. Bozzolo, J. Ferrante and J. R. Smith, Phys. Rev. B **45**, 493 (1992); G. Bozzolo and J. Ferrante, Scr. Met. Mater. **26**, 1275 (1992); Phys. Rev. B **45**, 12191 (1992); Phys. Rev. B **46**, 8600 (1992); Ultramicroscopy **42-44**, 55 (1992); G. Bozzolo, B. Good and J. Ferrante, Surf. Sci. **289**, 169 (1993); B. Good, G. Bozzolo and J. Ferrante, Phys. Rev. B **48**, 18284 (1993); R. Kobistek, G. Bozzolo, J. Ferrante and H. Schlosser, Surf. Sci. **307-309**, 390 (1994).

2. M.S. Daw, S.M. Foiles and M.I. Baskes, Mat. Sci. Reports **9**, 251(1993).

3. P. Haasen, **Physical Metallurgy**, (Cambridge University Press, Cambridge, New York, Melbourne, 1978).

4. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, J. Chem. Phys. **6**, 1087 (1953).

5. M. Hansen and K. Anderko, **Constitution of Binary Alloys**, p.198, (McGraw Hill Book Co. Inc. 2nd ed., New Yourk, Toronto, London 1958).

6. J. R. Smith, T. Perry, A. Banerjea, J. Ferrante and G. Bozzolo, Phys. Rev. B **44**, 6444 (1991)

7. J. H. Rose, J. R. Smith and J. Ferrante, Phys. Rev. B **28**, 1835 (1983); J. H. Rose, J. R. Smith, F. Guinea and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).

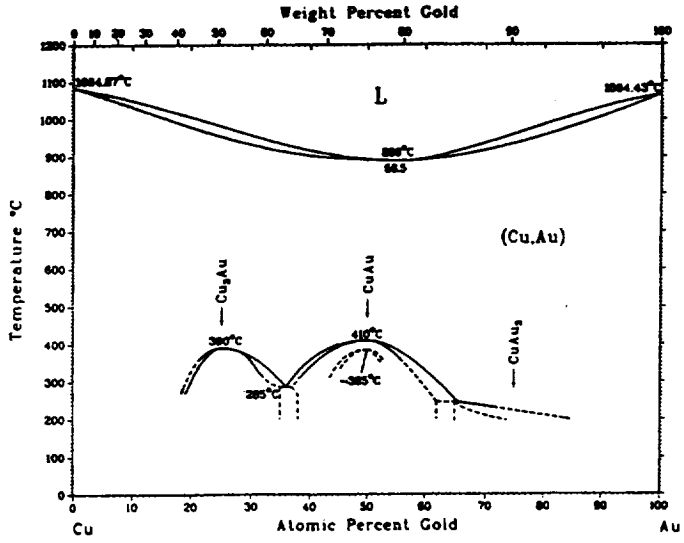
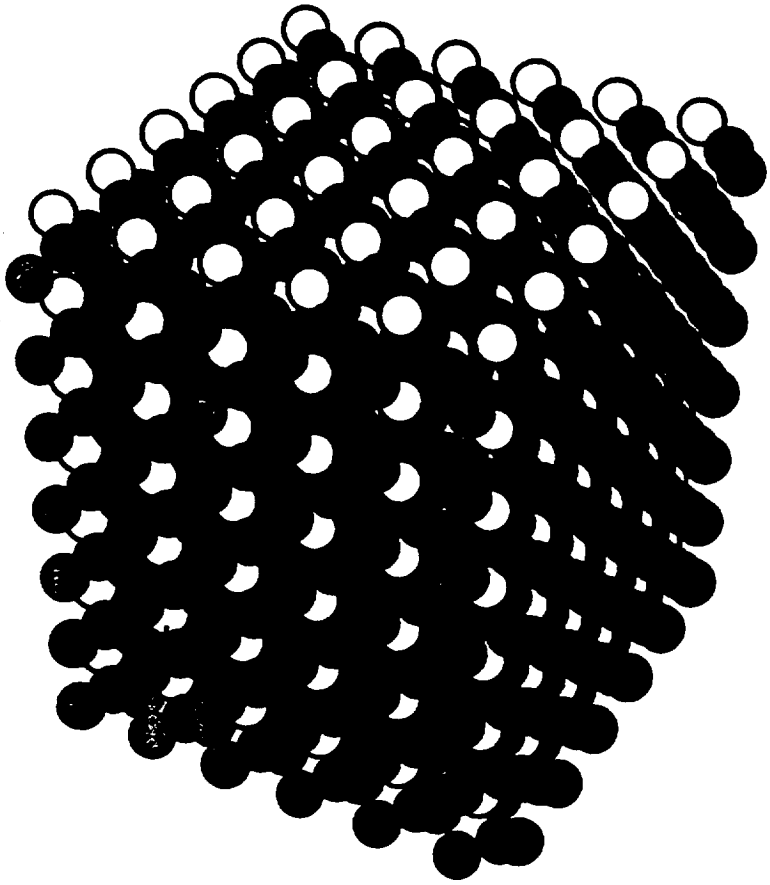
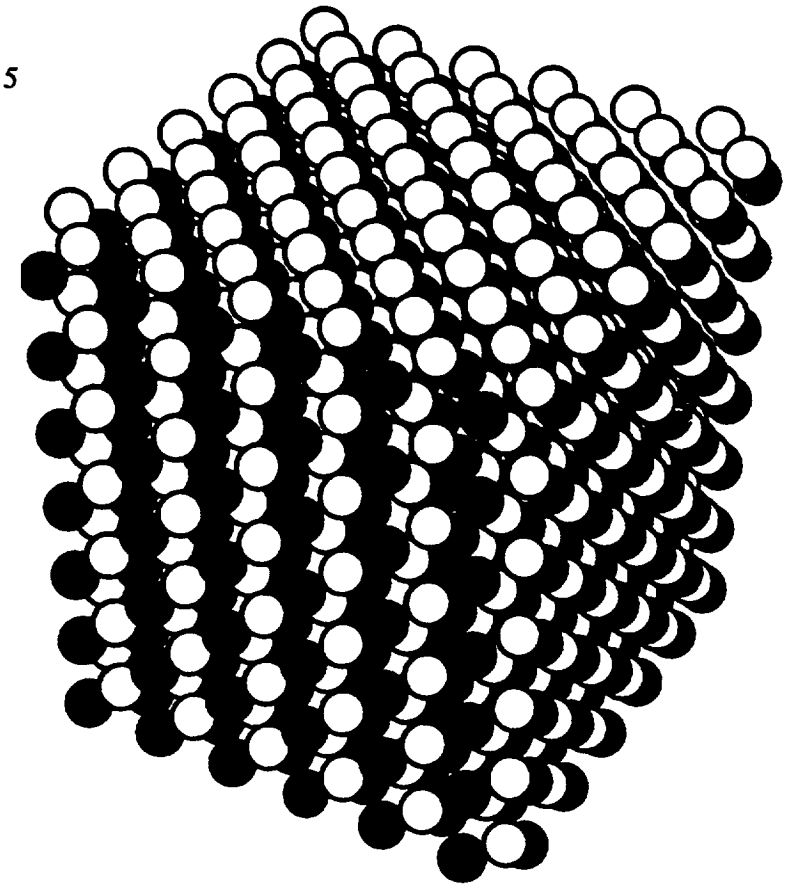


Fig. 1: Phase diagram for the Cu-Au system [5].





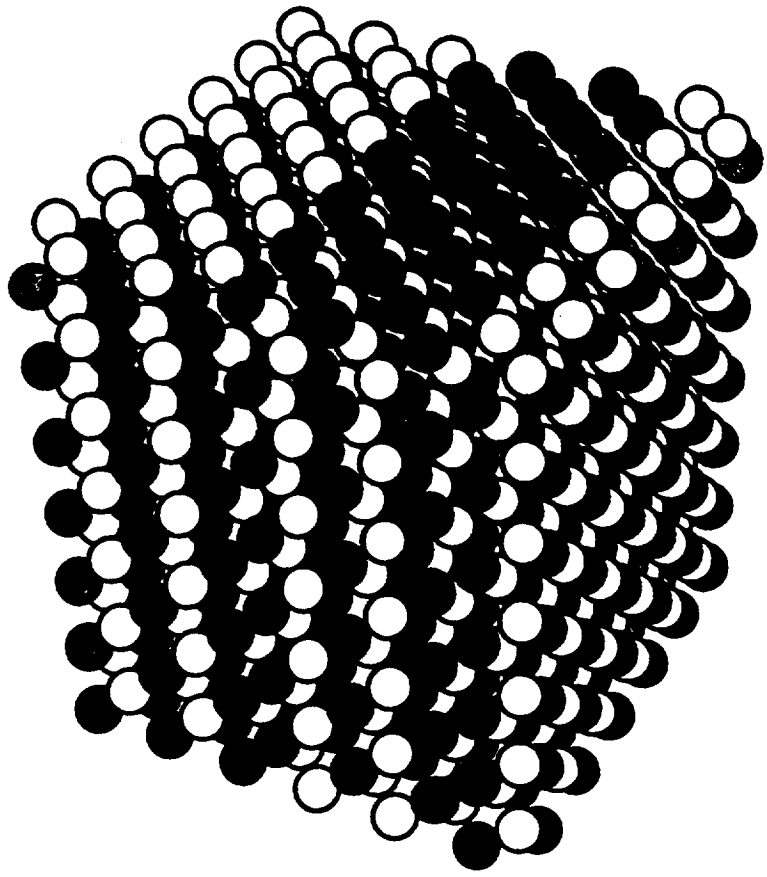


Fig. 2 Final geometries for slow cooling to 100 K giving the correct ground state structures of (a) $CuAu_3$ ($L1_2$) (or Cu_3Au) (b) CuAu I ($L1_0$) and (c) CuAu II. Solid spheres denote Cu atoms.

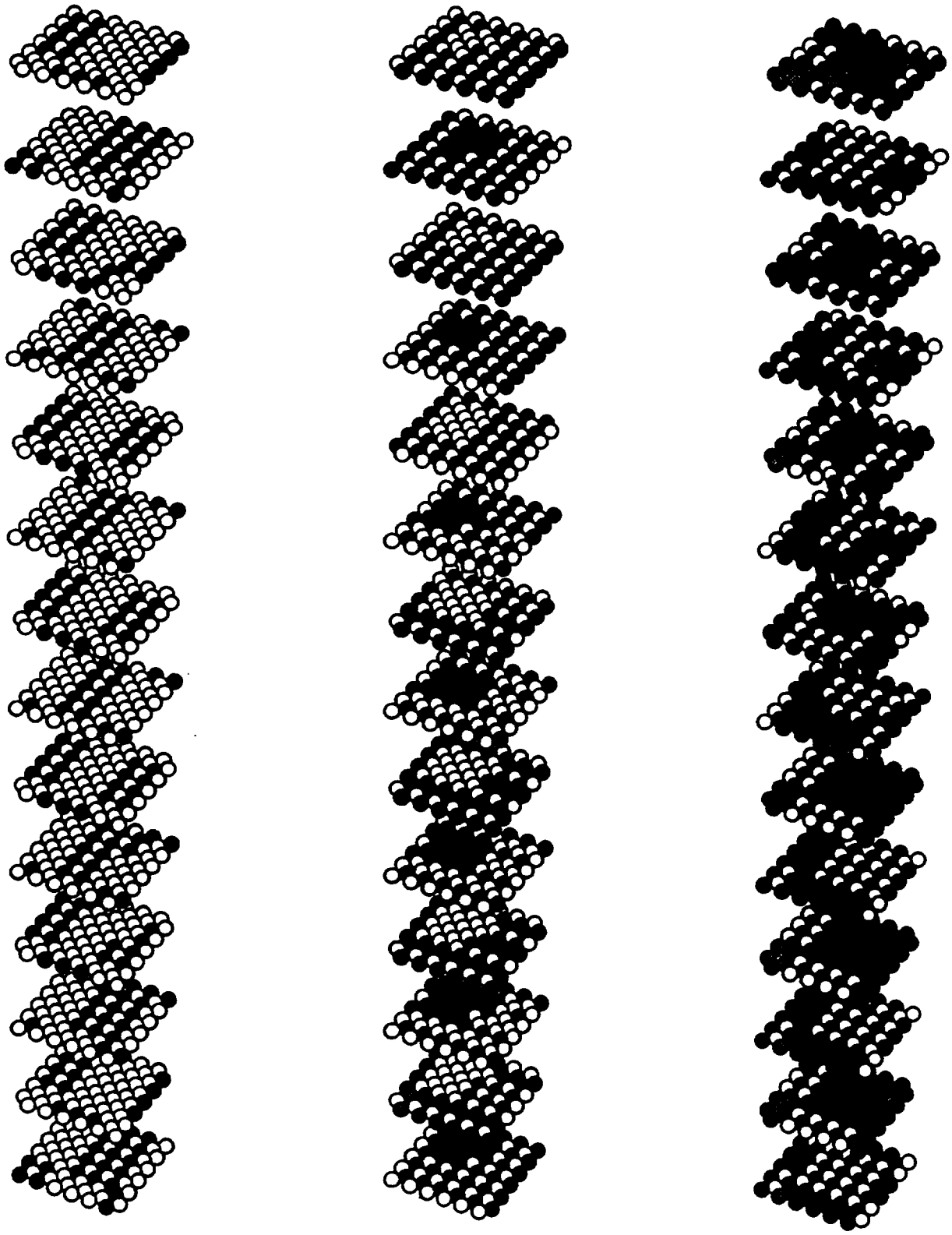


Fig. 3 Expanded cells for quench cooling to 400K: (a) $CuAu_3$, (b) CuAu, and (c) Cu_3Au showing resulting grain structure. Solid spheres denote Cu atoms.

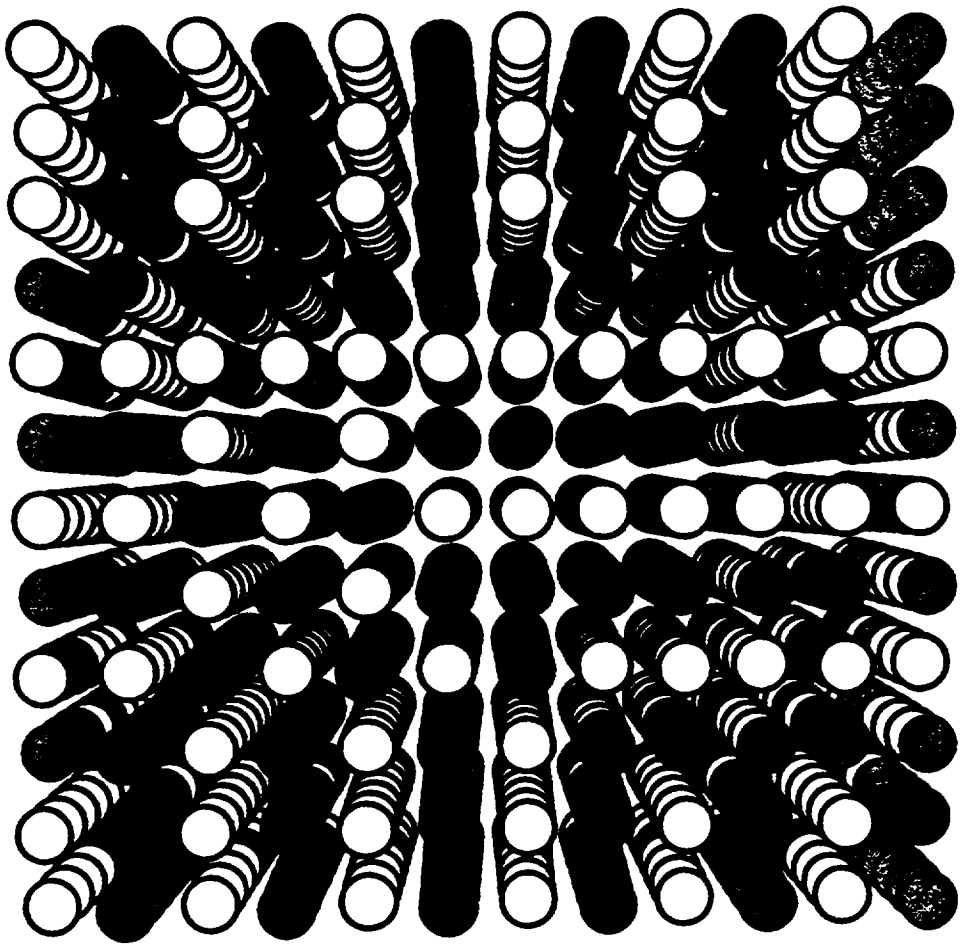


Fig. 4 End view of Fig. 3(b) showing domains with ABAB structures in each direction following quench cooling to 400K. Solid spheres denote Cu atoms.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	March 1996	Technical Memorandum

4. TITLE AND SUBTITLE

Cu-Au Alloys Using Monte Carlo Simulations and the BFS Method for Alloys

5. FUNDING NUMBERS

WU-505-90-53

6. AUTHOR(S)

Guillermo Bozzolo, Brian Good, and John Ferrante

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E-10120

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM-107168

11. SUPPLEMENTARY NOTES

Guillermo Bozzolo, Analex Corporation, 3001 Aerospace Parkway, Brook Park, Ohio 44142 (work funded by NASA Contract NAS3-25776); Brian Good and John Ferrante, NASA Lewis Research Center. Responsible person, John Ferrante, organization code 0130, (216) 433-6069.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Categories 26 and 76

This publication is available from the NASA Center for Aerospace Information, (301) 621-0390.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Semi empirical methods have shown considerable promise in aiding in the calculation of many properties of materials. Materials used in engineering applications have defects that occur for various reasons including processing. In this work we present the first application of the BFS (Bozzolo, Ferrante, and Smith) method for alloys to describe some aspects of microstructure due to processing for the Cu-Au system (Cu-Au, $CuAu_3$, and Cu_3Au). We use finite temperature Monte Carlo calculations, in order to show the influence of 'heat treatment' in the low-temperature phase of the alloy. Although relatively simple, it has enough features that could be used as a first test of the reliability of the technique. The main questions to be answered in this work relate to the existence of low temperature ordered structures for specific concentrations, for example, the ability to distinguish between rather similar phases for equiatomic alloys (CuAu I and CuAu II, the latter characterized by an antiphase boundary separating two identical phases).

IN-26
9243

14. SUBJECT TERMS	15. NUMBER OF PAGES
Alloys; Microstructure; Semi-empirical methods	9
	16. PRICE CODE: A02

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

National Aeronautics and
Space Administration

Lewis Research Center
21000 Brookpark Rd.
Cleveland, OH 44135-3191