Interplay of structural, electronic, and transport features in copper alloys

Frank C. Maier a, Stephen Hocker b, Siegfried Schmauder b, Maria Fyta a, *

a Institute for Computational Physics, Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany
b Institut für Materialprüfung, Werkstoffkunde und Festigkeitslehre (IMWF), Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany

ARTICLE INFO

Article history:
Received 28 May 2018
Accepted 26 October 2018
Available online 3 November 2018

Keywords:
Copper
Alloys
Impurities
Electronic structure
Electronic transport
Conductivity

ABSTRACT

Copper alloys show a structural variability leading to a range of diverse electronic, transport, and mechanical properties. Here, we investigate the influence of the type and amount of alloying on the electronic transport properties across copper alloys. Specifically, we investigate the electronic transmission along copper in its fcc crystal structure. The characteristic change when adding impurities, such as nickel, aluminum, and silicon in the structure and transport properties is assessed through density functional theory calculations together with the non-equilibrium Greens functions approach. The results are analyzed with respect to the structural characteristics, the electronic and transport properties in these alloys for different concentrations of the impurities. A clear trend in the electronic transmission, thus the conductance, along these materials was found with the addition of certain impurities and their clusters. Coherent with experimental observations, we conclude that the higher the concentration of the impurities, the lower the electronic transmission along the alloys as compared to a pure copper crystal. Furthermore, we show that the bonding environment in the impurity clusters can be associated to additional valence states and significantly influences the conductance. In the end, we discuss the relevance of our results for practical applications.

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1. Introduction

Copper-based alloys are widely used in electronic applications because they combine high electrical conductivity and high strength. The electrical conductivity of alloys with crystal defects such as vacancies, impurities, precipitates, dislocations or grain boundaries is lower than for defect free crystals [1]. Especially impurities dissolved in the matrix can significantly reduce the electrical conductivity depending on types and concentrations of alloying elements [2]. However, the strength of an alloy is improved by crystal defects which effectively impede dislocation motion. Many efforts have been made in order to develop copper-based alloys which maintain the electrical conductivity of the host, but also show an increased strength.

A very promising material system is Cu—Ni—Si because Ni and Si form precipitates, which strongly contribute to an improved strength. Furthermore, the precipitation process reduces the number of dissolved Ni and Si atoms and consequently a high electrical conductivity is obtained. Experimental studies of copper alloyed with Ni and Si revealed that coherent disk-shaped δ-Ni2Si precipitates formed during thermal aging on [110] planes of copper [3,4]. The δ-Ni2Si precipitates possessing an orthorhombic structure are most important for precipitation strengthening in these alloys. Other precipitates such as β-Ni3Si (L12 structure) were also found depending on the thermal treatment and the concentrations of alloying elements [5,6]. Additional alloying elements such as Al, Mg, Cr or Zr can have a significant influence on the precipitate structures as well as electrical and mechanical properties of the alloy. For example, it was found that aluminium leads to an improvement of the mechanical properties, but lowers the electrical conductivity [7]. On the other hand, chromium alloying increases the electrical conductivity because of additional precipitation processes [8].

As opposed to many experimental studies on the Cu—Ni—Si alloy system there were only few attempts to gain a more detailed understanding of the observations using simulations. Ab initio calculations on the work of separation for three different Cu/Ni5Si interfaces revealed strong interfacial bonding [9]. Insight into the underlying mechanisms of increased electrical conductivity in the case of Cr addition and the higher strength observed for Al addition
was obtained by atomistic kinetic Monte Carlo simulations based on \textit{ab initio} calculations. In case of Cr addition it was revealed that the formation of Cr–Ni–Si precipitates leads to a reduction of impurities dissolved in the copper matrix, whereas Al addition leads to an increased interfacial strain \cite{10}. \textit{Ab initio} calculations of electrical conductivities were performed for pure copper with regard to size effects of thin films \cite{11} and the influence of surface roughness \cite{12} or grain boundaries \cite{13}. A surprising experimental result, namely the increase of electrical conductivity with impurity doping was obtained for a silver single crystal alloyed with copper. In order to understand this effect, electronic structure \textit{ab initio} calculations were applied \cite{14}. However, to our knowledge, no calculations for the electrical conductivities of copper-based alloys depending on the types and concentrations of alloying elements have been performed. Since it is highly desirable to understand the effects of different alloying elements and the changes caused due to precipitation, this work aims to calculate electrical conductivities of a copper crystal with several impurities or small Ni–Si clusters. For this task, quantum mechanical calculations are performed on a number of copper alloys. This work is organized as follows: we first outline the methodology used here, then analyze and discuss the results on the structural, electronic, and transport properties of the alloys, and conclude in the end.

2. Methodology

Simulations based on the density functional theory (DFT) \cite{15,16} as implemented in the code SIESTA \cite{17} were carried out. We have used the generalized gradient approximation of Perdew-Burke-Ernzerh of (PBE-GGA) \cite{18}, and non-relativistic norm-conserving Troullier-Martins pseudopotentials \cite{19}. For expanding the Kohn-Sham states, we have considered a single-z\textsuperscript{\text{\textperiodcentered}} with polarization basis-set (SZP) with an energy shift of 0.02 Ry and a real space sampling grid (mesh cutoff) of 450 Ry. Structural relaxations were performed until the net forces of each atomic component become smaller than 0.01 eV/Å. The Cu(111) unit cell was fully relaxed with $12 \times 12 \times 12$ kpoints using the Monkhorst-Pack scheme. With these parameters, we obtained a lattice constant of 3.702 Å, which compares well with the literature value of 3.615 Å \cite{20}, leading to an error of approximately 2%. The relaxation of the infinite copper alloys composed of a supercell made out of $12 \times 6 \times 6 = 864$ atoms was done with $3 \times 3 \times 3$ kpoints. For the electronic density of states (EDOS) a finer Monkhorst-Pack grid with $10 \times 10 \times 10$ kpoints was taken. For the transport calculations and the device we have used $3 \times 3 \times 1$ kpoints.

The electronic transport calculations were performed using DFT combined with the non-equilibrium Green’s functions (NEGF) formalism \cite{21,22}, as implemented in TranSIESTA \cite{23}. For these calculations, a scattering region and semi-infinite leads as sketched in Fig. 1 need to be considered. The zero bias Green’s function $G(E)$ of the scattering region (device) at an energy $E$ can be written as:

\[
G(E) = [ES - H - \Sigma_L(E) - \Sigma_R(E)]^{-1}
\]

where $S$ and $H$ are the overlap and Hamiltonian matrices, respectively for the scattering region. $\Sigma_L(R)(E)$ is the self energy for the left ($L$) or right ($R$) semi-infinite electrode. Accordingly, the electronic transmission $T(E)$ can be defined by

\[
T(E) = \text{Tr}[\Gamma_L(E)G(E)\Gamma_R(E)G^\dagger(E)],
\]

Fig. 1. A typical copper structure used in our simulations. The position of the electrodes and the scattering/central region is denoted by the labels. This structure represents a copper alloy with three nickel impurities. The copper and nickel atoms are shown in orange and green, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
impurity content within the crystalline matrix of copper were simulated. We modeled copper alloys including one up to 27 Ni atoms. Crystalline Ni and Cu have a small lattice mismatch, with lattice constants of 3.524 Å and 3.615 Å, respectively [20]. In addition to pure nickel impurities, we also investigated Cu–Ni–Si materials, that is copper alloys with both nickel and silicon impurities. Note, that due to computational restrictions in the electronic transport calculations, the simulated Cu system is small in comparison to standard alloys used in applications. The scattering region of our system has a width of approximately 12.8 Å, with an effective radius of 8.5 Å for including impurities. The mean radii of the precipitates in these systems are in the range of few Å corresponding to very early stages of the precipitation process. Here, we have modeled a unit cell of the face-centered cubic $\beta$-Ni$_3$Si precipitate. Additionally, six different arrangements of three nickel atoms with a single silicon atom were considered as depicted in Fig. 2. We refer to these different alloys as ‘Type 1’- ‘Type 6’ as notated in this figure.

3. Results and discussion

3.1. Structural analysis

We begin the analysis with the structural properties of the simulated structures. The results will be discussed with respect to the type and amount of alloying in the copper (111) crystal structures. In our simulations of bulk copper (111), the Cu–Cu bond-length was found to be 2.618 Å. In the case of the copper alloys with one impurity, the bond-lengths are average values over the whole fcc lattice, taking into account the twelve closest neighbors of each impurity. In the case of two and three impurities the bond-length average is calculated in the same way, taking also into account all possible permutations. All results for the bond-lengths of the copper alloys with different impurity concentration are summarized in Table 1. The data are presented as changes with respect to the bond-length in a perfect copper crystal.

These results indicate, that adding aluminum leads to a stretched average Cu–Cu bond-length around the impurity with respect to the reference Cu–Cu bond in pure copper. This is in agreement with experiments, in which the bond length of crystalline fcc aluminum was found to be 2.863 Å [20], also longer than that of 2.618 Å in crystalline fcc copper [20]. Both crystalline fcc Ni

<table>
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<tr>
<th>impurity/concentration</th>
<th>0.232 wt %</th>
<th>0.465 wt %</th>
<th>0.699 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum (Al)</td>
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<td>0.50</td>
<td>0.47</td>
</tr>
<tr>
<td>silicon (Si)</td>
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<td>−0.35</td>
<td>−0.35</td>
</tr>
<tr>
<td>nickel (Ni)</td>
<td>−0.12</td>
<td>−0.50</td>
<td>−0.49</td>
</tr>
</tbody>
</table>

Table 1
Changes in the bond lengths around an impurity site as compared to the ideal Cu(111) crystal. The results are shown for the Al, Si, and Ni impurities at different concentrations.

![Fig. 2](image-url)

Fig. 2. Different configurations (Types) of the fcc $\beta$-Ni$_3$Si copper alloy. The silicon atom is colored yellow and the three nickel atoms are colored green. The view is along the [111] direction of the copper lattice, which is the same as the transport direction used in our simulations. The axes are shown in panel (a). An extended view (including periodic images) of the unit cell is shown for all configuration types. The labeling shown for all cases is used throughout. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
and crystalline diamond Si have shorter bond lengths, 2.492 Å and 2.352 Å, respectively as inferred from experiments [20]. This trend can be qualitatively observed from our simulations in the case of two and three impurities. In order to estimate the influence of precipitates on the electrical conductivity calculations containing impurity clusters were performed. We note that the main precipitate phase namely orthorhombic $\delta$-Ni$_2$Si is not stable for very small clusters of few atoms. In our calculations it was observed that the atomic positions in such clusters relax to the sites of the fcc matrix. Accordingly, we focus on coherent clusters on the fcc lattice and consider another precipitate phase, that of $\beta$-Ni$_3$Si, as well as pure Ni clusters.

In all simulations for the Ni clusters in the copper crystalline matrix, the nickel atoms remain in the fcc positions and do not destroy the symmetry of the lattice. This is expected as the fcc lattice is also a stable configuration for Ni and the lattice mismatch between Ni and Cu is small. In this way, no large distortions are observed. As the lattice constant for fcc Ni is 0.09 Å shorter than that for fcc Cu, increasing the impurity content of Ni will lead to shortening of the bond lengths of the closest neighbors. In order to quantify this behavior, we calculated the radius of gyration of all the 27 copper atoms step-wise replaced with nickel atoms by $R_{\text{gyr}} = \sqrt{\sum_{i=1}^{27} (r_i - r_{\text{CM}})^2}/27$, where $r_i$ is the position of the $i$th atom and $r_{\text{CM}}$ is the center of mass of all 27 copper atoms. The results are given in Fig. 3 and include clusters with one up to 27 nickel impurities. These data clearly indicate, that as more Cu atoms are exchanged with Ni atoms, the radius of gyration of the 27 selected atoms decreases leading to a more compact and dense clustering. During structural relaxation of the fcc $\beta$-Ni$_3$Si copper alloys in Fig. 2, the impurities got aligned along the fcc lattice of Cu, even if the $\beta$-Ni$_3$Si cluster was off lattice before relaxation. We also created two larger clusters of $\beta$-Ni$_3$Si with a double and a triple size of that of the single cluster. In order to analyze the structural properties we calculated the radius of gyration of the affected 12 atoms, shown in Fig. 3. Similar to the case of pure nickel atoms in the copper device, the change of the atoms causes a more dense region.

### 3.2. Electronic properties

Having investigated the changes in the bonding environment in the copper alloys, we move on with the specific characteristics of their electronic properties. In the following, we will present results on the total eDOS, as well as on the projected DOS (PDOS) underlying the contributions from different components of the alloys. This gives a quantitative measure of the available electronic states and indicates the conducting nature of the material. The eDOS data for the pure copper crystal are shifted so that the Fermi level is at 0 eV. In order to promote comparison, all other data for the alloys are also shifted with respect to the Fermi level of the pure Cu crystal. Due to the periodic boundary conditions, the three different permutations of the two impurities show a negligible difference in the DOS and are not considered in the following. The results for the copper alloys with the Si, Ni, and Al impurities for the three concentrations are summarized in Fig. 4. It is clear from this figure, that all structures remain metallic for a small amount of impurities.

Copper alloys with aluminum or silicon impurities show a similar behavior. The eDOS is shifted towards lower energies near the Fermi level and a reduction of available states near the Fermi level is visible. A comparison of the aluminum and the silicon impurity reveals that the former exposes a larger impact in the conduction band compared to silicon. On the other hand, nickel impurities show a slightly different behavior. The respective eDOS show a shift towards higher energies near the Fermi level. We can observe that the introduction of nickel atoms into the copper matrix results in an increase of the density of states in the valence band around $-0.8$ eV. Comparison of the three impurities in Fig. 4 reveals that the trends in the eDOS moving from a lower to a higher impurity concentration are not uniform. Below the Fermi level, the larger Ni concentration corresponds to a higher eDOS, which is not exactly the case for the Al and Si impurities. Above the Fermi level, though all impurities show a similar trend, with the higher impurity concentration corresponding to a higher eDOS. However, this variation is stronger for Al and Si, rather than for Ni impurities.

In regard of the electrical conductivity at room temperature, we consider the range from $-0.2$ to $+0.2$ eV as previously suggested [14]. The eDOS results predict the highest conductivity for the alloy with the Ni impurity whereas alloying with Al or Si leads to much lower conductivities. The same trend is found in the projected DOS shown in Fig. 5 for the Cu alloys with the highest impurity concentration. A clear deviation is mapped in Fig. 5 for the case of Ni compared to Al and Si. A clear peak below the Fermi level is observed for Ni, denoting that this impurity enhances the valence band of the alloy. This is exactly not the case for Al and Si, which show a smooth behavior below and above the Fermi level and non-varying metallic features. This observation denotes, that

![Fig. 3. a) The radius of gyration with respect to the cluster size of Ni in a copper alloy. The results are given with respect to the number of nickel atoms in the crystalline copper matrix. b) The radius of gyration with respect to the copper alloys consisting of three different sizes of the $\beta$-Ni$_3$Si cluster.](image-url)
embedding the Ni atom into the Cu alloy enhances its metallic character, introducing additional states below the Fermi level, which can be populated with electrons eventually used to accommodate electronic current across such an alloy, i.e. enhance its conductivity. This trends observed here agree with conductivities determined experimentally \[2\]. However, the experimental value for Si is much lower than for Al. A reason for this discrepancy is that the electrical conductivities do not only depend on the number of states around the Fermi level, but also on the carrier mobilities that cannot be obtained from the DOS calculations. In order to take mobilities into account we perform the transmission calculations discussed in the next section. Nevertheless, the DOS calculations are helpful to understand the contributions to the reduced conductivities of alloys in comparison to pure copper. For Ni alloying that leads to a smaller decrease in the conductivity than in the case of Al alloying, we conclude that a large contribution is the increased number of states around the Fermi level.

Moving to the copper alloys including nickel clusters of varying sizes, the total eDOS again shows a decreasing trend with the cluster concentration below the Fermi level (data not shown). However, due to the periodicity of the computational cell, there’s neither a difference between the different \(\beta\)-Ni\(_3\)Si clusters shown in Fig. 2 nor between the four tested systems in which the alloy atoms are spread across the supercell. Thus, only one representative is shown. We could also not find significant variations in the eDOS of the different types of the fcc \(\beta\)-Ni\(_3\)Si copper alloys in Fig. 2. In order to elucidate differences in the electronic features such as the conductivities in these alloys, we focus on their PDOS. As a representative case of the alloys with clustered impurities, we take the \(\beta\)-Ni\(_3\)Si structures with three clusters of different sizes. The results are summarized in Fig. 6. Again the enhanced valence band below the Fermi level for the case of the nickel clusters is evident. Comparing the enhancement of the valence band of the alloy as the impurity clusters become larger shows the same trend for both Ni and Si: a larger cluster leads to additional metallic states in the alloy. For Ni, again the increase denoted by the peaks in the PDOS is very strong. As a final remark on these results, we can associate the increasing peak in the PDOS for Ni with the decreasing radius of gyration.

Fig. 4. Electronic density of states (eDOS) of aluminum, nickel, and silicon impurities in copper. In the region of the Fermi level \((E_F = 0 \text{ eV})\) the addition of the impurities cause a shift towards lower energies and consequently a reduction of available states.

Fig. 5. Projected density of states (PDOS) of aluminum, nickel and silicon in the bulk copper device with three alloy atoms each.

Fig. 6. The projected density of states (PDOS) show the contribution of nickel (solid lines) and silicon (dotted lines) to the total electronic density of states in the three different sized \(\beta\)-Ni\(_3\)Si clusters.
shown in Fig. 3(a), that is the shortening of the bonds within the Ni clusters.

3.3. Electronic transmission

We further analyze the trends observed in the electronic density of states by means of the electronic transport properties in the copper alloys studied here. From our simulations, we can obtain the electronic transmission across an alloy. As a measure for the electrical conductivity, we use the conductance that corresponds to the electronic transmission at the Fermi level. The results for the copper alloys with different concentrations of distributed Al, Si or Ni impurities are summarized in Fig. 7. In the case of the three different impurities - aluminum, silicon and nickel - an increasing impurity concentration causes a reduction in the electronic transmission. As shown by the lower panel in this figure, silicon impurities impose the largest impact around the Fermi level, followed by nickel and then aluminum. Interestingly, for the nickel case, a significant drop shown as a valley in the electronic transmission around $-0.8$ eV is evident. This decrease corresponds to the increase of the density of states at the same energy level in Fig. 4. This drop in the electronic transmission denotes that at this certain energy range, the nickel atoms provide much less electronic states, that is pathways for the electrons to move through the material.

Comparing the conductance (i.e. electronic transmission at the Fermi level) (lowest panel in Fig. 7) leads to a decrease with increasing impurity content, which can be attributed to the fact that the additional impurity states decrease the metallic character of the alloy. It can be clearly observed that the conductance is lowest for the alloys with Si impurities, followed by the Al and Ni impurities. However, the alloys with a high concentration of Si and Ni show an almost identical conductance. The fact that Si impurities lower the conductance, agrees with experimental results [2], which show that the electrical conductivity is also much lower for copper alloys with Si than those with Ni or Al. The decrease of conductivity with increasing impurity content is much more pronounced in the case of Si impurities [2]. This is confirmed by our calculations revealing conductance values for the Si alloyed crystal that vary with the impurity concentration twice as much as in the case of the alloys with Ni or Al (see Fermi level trends in Fig. 7). Below the Fermi level, a drop in the electronic transmission is observed when increasing the Ni content. This drop is observed at the energy range of a significant peak coming from the Ni impurity in Fig. 5. Accordingly, nickel provides additional electronic states deeper in the valence band. These are filled with electrons decreasing their mobility and leading to the observed lower transmission. In contrast to the experimental results, we found a conductance for Al that is close to the one obtained for Ni impurities. Consequently, there is a contribution to the lower electrical conductivity of the alloy with Al, which is not considered in our calculations. We note that our crystals are defect-free besides the considered impurities, whereas the experimental conductivity measurements were performed on copper alloys possibly containing vacancies, dislocations, and/or grain boundaries. All these crystal defects can influence the impurity distribution and as a consequence the electrical conductivity as well.

The electronic transmission obtained for small Ni and $\beta$-Ni$_3$Si clusters are depicted in Fig. 8 and reveal a very interesting result regarding the conductance. Increasing the cluster size leads to a reduced electronic transmission capability of the copper alloy. In panel (b) the electronic transmission for copper alloys with different $\beta$-Ni$_3$Si clusters are summarized. The configurations 1 and 2 (Fig. 2), in which the nickel atoms are in the same plane perpendicular to the transport direction, show an identical transmission spectrum. The same with configurations 3 till 6, wherein two nickel and one silicon atom are placed in the same plane perpendicular to the transport direction. The comparison of the transmission values at the Fermi level with the systems with...
distributed atoms are clearly higher even for small clusters. For example, the decrease of the conductance of the cluster containing 3 Ni and 1 Si atoms in comparison to pure copper is only around $\frac{1}{3}$ of the value obtained for the distributed system. We conclude that already small clusters of few atoms have a strong influence on the electrical conductivities. We have observed that the conductance decreases with increasing cluster size. Nevertheless, even for the largest cluster containing 9 Ni atoms and 3 Si atoms the conductance is on the same level as in the case of 3 distributed Si atoms (Fig. 7). Finally, for the different $\beta$-Ni$_3$Si clusters, the electronic transmission shows clear trends with the larger clusters decreasing the conductivity of the alloys (data now shown). We have found a drop of about 12% in the conductance for the alloys with the larger clusters compared to the ideal copper crystal.

4. Conclusions

In this work, we have performed electronic structure and quantum transport calculations of copper alloys including silicon, aluminum, and nickel impurities in various concentrations. Clusters of different impurities were also considered. We have provided a deep insight into the electronic and conductance properties of these alloys. A clear trend with respect to impurity type and concentration was evident. The conductance is lowest for Si alloyed copper and highest for the alloy with Ni impurities. It decreases with increasing concentration for all types of alloying elements. This decrease is most pronounced in the case of Si. In comparison with experimentally determined electrical conductivities of Si, Al or Ni alloyed copper our calculations reveal the same trends. Our investigation of the influence of impurity clusters reveal a strong effect on the conductance. Even in the case of very small clusters containing only 4 atoms a significantly higher conductance is obtained. Consequently, the electrical conductivity of solid solution hardened alloys can be improved by doping with elements which favor the formation of small clusters.

The good agreement between the trends in our calculations and those experimentally observed, allowed us to provide a deeper understanding on the structural properties and the electronic characteristics of various copper alloys. We were able to associate the larger radius of gyration of the $\beta$-Ni$_3$Si clusters to their electronic features: a lower radius of gyration, that is shortening of the bond-lengths within the cluster lead to a more pronounced peak in the electronic density of states below the Fermi level, that is more available states in the valence band denoting lower conductivity. This is indeed what we have observed. For increasing the Ni impurities a decreasing transmission below the Fermi level could again be associated with an increasing eDOS at the energy range associated with the Ni impurity. This denotes, that the impurity offers additional electronic states within the valence band, which the electrons can fill becoming less mobile leading to the lowest conductivity. Overall, the interplay between the type of impurity, as well as structural and electronic characteristics is of high importance for the transport features of the alloys. The results presented in this study can provide a pathway in designing copper alloys for practical applications. Depending on the desired conductance, the alloys can be doped with the respective type of element. The concentration and distribution of this element within the alloy can also be controlled during synthesis which allows to selectively produce materials with desired properties.

Acknowledgements

The authors acknowledge support from the German Funding Agency (Deutsche Forschungsgemeinschaft-DFG) as a part of the collaborative research center SFB 716 “Dynamic simulations of systems with large particle numbers”. This research was supported in part by the bwHPC initiative and the bwHPC-CS project provided through associated compute services of the JUSTUS HPC facility at the University of Ulm and the computational resources ForHLR Phase II. The bwHPC and bwHPC-CS (http://www.bwhpc-cs.de) are funded by the Ministry of Science, Research and the Arts Baden-Württemberg (MWK) and the German Research Foundation (DFG).

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