Computer simulations of the influence of atomic structure disorder on the hardness of Cu–Ag and Au–Ag alloys

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Abstract. In this paper, computer simulations of the hardness of ordered and disordered alloys of Cu–Ag and Au–Ag were performed using the Sutton-Chen potential and the GULP software package within several models. In addition, Poisson ratios were estimated. When simulating a chemical disorder, a super-cell containing 108 atoms was built. Numerical experiments have shown that chemical disorder in the studied alloys leads to hardness degradation.

1. Introduction
Structural materials are often exposed to various influences, such as extreme temperatures, strong radiations, particle bombardment with high kinetic energy, and so on. Often under such circumstances the atomic structure of a poly-atomic substance is destroyed, that is, the arrangement of atoms in space changes. For example, a crystalline object as a result of such influences loses its regular atomic structure and disorder occurs in the arrangement of atoms. Mostly, systems with either chemical or structural disorder are considered. It is possible to have a combination of these two types of disorders. In this paper, the goal is to investigate the influence of a chemical disorder on some mechanical properties of metallic alloys in particular, hardness and Poisson’s ratio.

Despite the obvious interest in such research, it has not yet been possible to perform it within the framework of traditional mechanics of deformable solids for obvious reasons. However, with the emergency of nanomechanical approaches [1], computer simulation methods enabled us to study the influence of atomic structure disorder and various defects at nanoscale level. In this paper, we use a combination of empirical methods for determining hardness and other characteristics in the frame of nanomechanics.

It should be emphasized that in fact we calculate the so-called intrinsic hardness, which naturally differs from the real hardness, since we do not take into account the formation of dislocations under the influence of the load and other factors. However, there is an undoubted correlation between the behavior of intrinsic and real hardness.

2. About the hardness of materials
Hardness is one of the most important mechanical properties of metals and alloys, which characterizes its resistance to deformation under the influence of external forces. It determines
surface resistance to wear and is an indicator of the strength of a materials [2]. Ultimately, hardness is determined at atomic level [3].

Hardness is currently measured by Vicker’s or Brinell’s methods. The Vicker’s method is a frequent choice due to it’s ability in measuring the hardness of materials ranging from brittle to extremely hard materials and is one of the main methods for studying the physical properties of materials [4]. The Vickers hardness ($H_V$) is defined as the the ratio of the applied load to the area of the depression and is evaluated using the equation given by [5]:

$$H_V = \frac{2F \sin(\frac{\theta}{2})}{d^2},$$  \hspace{1cm} (1)

where $F$ is the applied force (in kgf), $\theta$ is the angle between the opposite faces of the square based pyramid indenter ($\theta = 136^\circ$), and $d$ is the mean length of the diagonals (in mm).

For many years, bulk and shear modules have been used as predictors of material hardness [6, 7]. It has been shown in [8] that there is a correlation between hardness and ductility of the material. The hardness of materials is closely related to their Young’s module [9]. Jiang et al. [10] established a formula that relates hardness with Young’s modulus which is given in Eq. (2) by fitting data into a linear relationship with a mean error of 12.6 %:

$$H_E^V = 0.0608E.$$  \hspace{1cm} (2)

Teter [3] in 1998 noted that the shear modulus is a better predictor of hardness than the bulk modulus, and further indicated that there is a linear relationship between these characteristics. Using the definition of Vickers hardness (1), Chen et al. [11] proposed a formula for estimating hardness as a linear function of the shear modulus which was later confirmed by Zhou et. al [12]:

$$H_G^V = 0.151G.$$  \hspace{1cm} (3)

However, some authors [13] believe that hardness does not depend linearly on the shear modulus. Pugh [14] suggested that the coefficient

$$K = \frac{B}{G},$$  \hspace{1cm} (4)

which is used to classify whether a material is brittle or not. Material will be brittle if $K < 1.75$ [15]. Using Pugh’s ratio and data from Teter [3] and Gilman [16], Chen et.al [11] obtained another empirical formula for estimating hardness:

$$H_{VC} = 2(k^2G)^{0.585} - 3,$$  \hspace{1cm} (5)

where $k = K^{-1}$. For metals with small hardness values, the calculated results using Eq.(5) would give negative values. To eliminate this shortcoming, Tian [17] proposed a modification of this formula:

$$H_{VT} = 0.92k^{1.137}G^{0.708}.$$  \hspace{1cm} (6)

Further, an empirical formula is also used to estimate the hardness of metals [18, 19]:

$$H_{VS} = \frac{(1 - 2\sigma)E}{6(1 + 2\sigma)},$$  \hspace{1cm} (7)

in which hardness is a function of bulk and shear moduli.
Table 1. Parameters of Sutton-Chan potential for metals Cu, Au and Ag [22].

| Metal | ν | µ  | ε (eV)     | c    | a (Å) |
|-------|---|----|------------|------|-------|
| Cu    | 6 | 9  | 1.2382 × 10^{-2} | 39.432 | 3.6100 |
| Au    | 8 | 10 | 1.2793 × 10^{-2} | 34.408 | 4.0800 |
| Ag    | 6 | 12 | 2.5415 × 10^{-3} | 144.41 | 4.0900 |

3. Methodology of calculating the elastic moduli required to calculate hardness

The equilibrium crystal structure and elastic moduli of the crystals were calculated using the GULP software package code 5.1 [20] where it is available free of cost for academic works (http://gulp.curtin.edu.au/gulp/). To describe inter-atomic interactions in metals and their alloys, the Sutton-Chen mathematical model was used [21]. The total potential energy of a system of \( n \) interacting atoms in the framework of this model is written as follows [21]:

\[
U = U(r_1, r_2, \ldots, r_n) = \sum_i U_i = \sum_i \epsilon \left[ \frac{1}{2} \sum_{j \neq i} V(r_{ij}) - c \rho_i \right]^{1/2},
\]

where

\[
V(r_{ij}) = \left( \frac{a}{r_{ij}} \right)^\nu,
\]

\[
\rho_i = \sum_{j \neq i} \left( \frac{a}{r_{ij}} \right)^\mu,
\]

\[
r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}.
\]

Here \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( c \) is a positive dimensionless parameter, \( \epsilon \) is a parameter with an energy dimension, \( a \) – the length parameter, \( \mu \) and \( \nu \) are positive integers.

The Sutton-Chen potential parameters for the metals Cu, Au and Ag are given in table 1.

When considering two-component alloys, the formula (8) takes of the form:

\[
U_{tot} = \sum_i U_i = \sum_i \left[ \frac{1}{2} \sum_{j \neq i} \epsilon_{ij} \left( \frac{a_{ij}}{r_{ij}} \right)^\nu_{ij} - c_i \epsilon_{ii} \left( \sum_{j \neq i} \left( \frac{a_{ij}}{r_{ij}} \right)^\mu_{ij} \right)^{1/2} \right].
\]

Parameters for \( Cu - Ag \) and \( Au - Ag \) binary alloys can be estimated by mixing rules [23]. In fact, the values of the parameters built into the GULP program were used. The calculations were performed at 0\(^\circ\)K. To find the equilibrium crystal structure at absolute zero temperature, the total potential energy was minimized by the Newton-Raphson method. Spatial configurations in the zeroth approximation were constructed using data on the crystal structure of metals \( Cu \), \( Au \) and \( Ag \), which under normal conditions have a face-centered cubic lattice [23].

To simulate the effect of chemical disorder in the atomic structure on the mechanical properties of alloys, both ordered and disordered configurations were considered. The ordered alloys \( AgCu_3, CuAg_3, AgAu_3 \) and \( AuAg_3 \) have the crystal structure \( L1_2 \) [23]. For example, the unit cell of the ordered alloy \( AgCu_3 \) has the following basis vectors:

1) \( Ag \): \( a(0.0, 0.0, 0.0) \);
2) \( Cu \): \( a(0.5, 0.5, 0.0) \);
3) \( Cu \): \( a(0.0, 0.5, 0.5) \);
4) \( Cu \): \( a(0.5, 0.0, 0.5) \).
Here \( a \) is the edge of an elementary cube. To simulate chemical disorder, a supercell was constructed by translating the unit cell in three directions to create a cube of 27 unit cells \((3 \times 3 \times 3 = 27)\), which is now more appropriate to call the basic units primary cells. Thus, from the primary cells a supercell that contains 108 atoms was obtained. Periodic boundary conditions were used. This allows us to consider the systems under study macroscopically homogeneous. For all studied alloys, primary and supercells were constructed in the same way. The simulation of chemical disorder in the alloy was carried out using a random number generator. The atoms were located in the nodes randomly, without violating stoichiometric ratio in the disordered alloy. For example, in the ordered alloy of \( \text{AgCu}_3 \), each unit cell contains one silver atom and three copper atoms. After simulating chemical disorder, each primary cell also contains one silver atom and three copper atoms. It is clear that, generally speaking, the primary cells in the disordered alloys that make up the supercell are not equivalent to each other due to the random arrangement of atoms in the nodes of the primary cubes.

4. Details of calculations, results and discussions
Using the GULP program, the values of bulk \( B \) and shear \( G \) moduli of metals and their alloys were calculated. Then, Young’s modulus \( E \) and Poisson’s ratio \( \sigma \) were calculated using the

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**Figure 1.** Comparison of the hardness \( H_{VS} \) of ordered and disordered alloys: a) \( \text{Cu} – \text{Ag} \); b) \( \text{Au} – \text{Ag} \).

**Table 2.** Ordered \( \text{Au} – \text{Ag} \) alloys and their crystalline components. \( B, G, E, H_{VS}, H_{VT}, H_V^G \) and \( H_V^E \) in GPa; \( K \) and \( \sigma \) are dimensionless quantities.

| Metal   | \( B \)    | \( G \)  | \( E \)  | \( \sigma \) | \( K \)  | \( H_{VS} \) | \( H_{VT} \) | \( H_V^G \) | \( H_V^E \) |
|---------|------------|----------|----------|-------------|---------|-------------|-------------|-------------|-------------|
| \( \text{Au} \) | 158.48360  | 28.61083 | 80.9606  | 0.41        | 5.5393  | 1.2558      | 1.4116      | 4.3202      | 4.9224      |
| \( \text{AgAu}_3 \) | 153.70141  | 33.87514 | 94.6704  | 0.40        | 4.5373  | 1.8051      | 1.9960      | 5.1151      | 5.7560      |
| \( \text{AuAg}_3 \) | 114.47574  | 36.23646 | 98.3338  | 0.36        | 3.1591  | 2.7384      | 3.1598      | 5.4717      | 5.9787      |
| \( \text{Ag} \) | 84.17421   | 30.31093 | 81.1876  | 0.34        | 2.7770  | 2.5918      | 3.2241      | 4.5770      | 4.9362      |
Table 3. Ordered Cu – Ag alloys and their crystalline components. $B$, $G$, $E$, $H_{VS}$, $H_{VT}$, $H^G_V$ and $H^E_V$ in GPa; $K$ and $\sigma$ are dimensionless quantities.

| Metal    | $B$   | $G$   | $E$   | $\sigma$ | $K$   | $H_{VS}$ | $H_{VT}$ | $H^G_V$ | $H^E_V$ |
|----------|-------|-------|-------|----------|-------|----------|----------|----------|----------|
| Cu       | 142.52 | 37.67 | 103.86 | 0.38     | 3.78  | 2.39     | 2.65     | 5.69     | 6.31     |
| Ag$_3$Cu | 127.38 | 41.07 | 111.26 | 0.35     | 3.10  | 3.16     | 3.53     | 6.20     | 6.76     |
| Cu$_3$Ag | 95.79  | 33.94 | 91.06  | 0.34     | 2.82  | 2.86     | 3.43     | 5.12     | 5.53     |
| Ag       | 84.17  | 30.31 | 81.19  | 0.34     | 2.78  | 2.78     | 3.23     | 4.58     | 4.94     |

Figure 2. Comparison of the hardness $H_{VT}$ of ordered and disordered alloys: a) Cu – Ag; b) Au – Ag.

Figure 3. Comparison of the hardness $H^G_V$ of ordered and disordered alloys: a) Cu – Ag; b) Au – Ag.
Figure 4. Comparison of the hardness $H_{EV}$ of ordered and disordered alloys: a) Cu – Ag; b) Au – Ag.

Figure 5. Comparison of $H_{VS}$, $H_{VT}$, $H_{V}^G$ and $H_{V}^E$ of ordered alloys: a) Cu – Ag; b) Au – Ag.

Table 4. Disordered Cu – Ag alloys. $B$, $G$, $E$, $H_{VS}$, $H_{VT}$, $H_{V}^G$ and $H_{V}^E$ in GPa; $K$ and $σ$ are dimensionless quantities.

| Metal   | $B$   | $G$       | $E$       | $σ$   | $K$   | $H_{VS}$ | $H_{VT}$ | $H_{V}^G$ | $H_{V}^E$ |
|---------|-------|-----------|-----------|-------|-------|----------|----------|-----------|----------|
| AgCu$_3$| 119.10613 | 14.83030  | 42.7179  | 0.44  | 8.0313 | 0.4526   | 0.5811   | 2.2394    | 2.5972   |
| CuAg$_3$| 90.97134  | 21.02665  | 58.5676  | 0.39  | 4.3265 | 1.1733   | 1.5032   | 3.1750    | 3.5609   |
formulas given below [15]:

\[ E = \frac{9BG}{3B+G}, \]  
\[ \sigma = \frac{3B-2G}{2(3B+G)}. \]  

Next, hardness was calculated using the formulas (2), (3), (6) and (7). The calculation results are shown in tables 3 – 5 and figures 1 – 6.

From the results of the calculations, it follows that the hardness values \( H_{VS}, H_{VT} \) are close to each other, the quantities \( H_{V}^G \) and \( H_{V}^E \) behave in a similarly manner. It is worth noting that the hardness values calculated by different formulas may differ by 2 or more times. Nevertheless, the obtained results allow us to draw some qualitative conclusions. The hardness of the ordered alloy \( AgX_3 \) is greater than the hardness of crystalline \( X \), where \( X = Cu, Au \). Further, the chemical disorder in the atomic structure of \( AgCu_3 \) and \( AuAg_3 \) leads to a sharp decrease in hardness. In the disordered alloys \( CuAg_3 \) and \( AgAu_3 \), hardness also decreases. The coefficient \( K \) in disordered alloys also increases.

5. Conclusions

The present work shows that there exist physical and mathematical approaches that are capable of assessing the intrinsic hardness of metals and alloys qualitatively at nanoscale level. Computer
modeling resources has the capacity to reveal the tendency of change in these characteristics when a chemical disorder occurs in the atomic structure of the objects under study.

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