UDC 539.32 DOI: 10.34220/2311-8873-2020-3-3-4-15

THE STUDY OF THE INFLUENCE OF CHEMICAL DISORDER ON MECHANICAL PROPERTIES OF BINARY ALLOYS OF THE TYPE ANi_3 AND NiA_3 (A = Au; Ag) USING COMPUTER MODELING

Desta O. G., Timoshenko Yu. K.
Federal State Budget Educational Institution of Higher Education
«Voronezh State University»
E-mail: desta@amm.vsu.ru

Summary: In this work, computer simulations of binary alloys of nickel with gold and silver were performed using the Sutton-Chen mathematical model. The simulation was conducted using the general lattice program (GULP) software package [9]. For the alloys, a simulation of ordered and chemically disordered structures were carried out. Elastic moduli, Poisson's ratio, intrinsic hardness and ductility coefficient were estimated for both ordered and disordered structures. The influence of chemical disorder on the mechanical properties of the alloys was estimated. An attempt was made to assess the significance of the ratio of nickel in the alloys to their mechanical properties. The study found that the influence of chemical disorder on all studied mechanical properties of the metals is significant. In particular, the influence is much higher in shear modulus, on the elastic constant C_{44}, intrinsic hardness and coefficient of ductility.

Keywords: bulk modulus, shear modulus, elastic constant, intrinsic hardness, Poisson's ratio, ductility, chemical disorder.

Introduction

Historically metals have been used as construction materials due to their strength. Some metals and alloys are also used as high temperature materials in industries as gas turbines and heat exchangers. Nickel based alloys are used as gas turbine engines, space vehicles, nuclear reactors and many more [1]. Nickel is a corrosion resistant metal [2]. The Nickel based alloys are frequently used as in condensers and heat exchangers due to their resistance to corrosion and stress-corrosion cracking [3]. An attempt to enhance the specific properties has been done by alloying metals for many years. Nickel could be alloyed with different metals to increase their resistance to corrosion.

The purpose of this work is to study mechanical properties of Nickel alloys of the type ANi_3 and NiA_3 where A = Au, Ag. The alloys and metals were simulated using general utility lattice program (GULP). In this paper, Sutton-Chen (SC) formalism was used to model the energy of interaction among the atoms of the metals and their alloys. This empirical method is frequently used to model metals and alloys of face centered cubic (fcc) crystal lattice structure. This empirical method is applied for determining the mechanical properties such as elastic constants, bulk and shear moduli, poisson's ratio, intrinsic hardness and ductility coefficient.

1. Structure of Metals and Alloys

The metals Ni, Ag and Au have face centered cubic (fcc) while the alloys ANi_3 and NiA_3 may have variety of structures under different set of conditions [4]. The study focuses on the alloys having $L1_2$ crystal structures. Here the letters A represent the pure metals Ag and Au.

To conduct the simulation, an input file was prepared. An input file contains all the necessary information to conduct simulation as a single text file. The coordinates of the atoms used for simulation are constructed from the basic elementary cell known as unit cell. For example, the unit cell of the ordered alloy $AgNi_3$ has the following basis vectors: Ag: a(0:0; 0:0; 0:0); Ni: a(0:5; 0:5; 0:0); Ni: a(0:0; 0:5; 0:5); Ni: a(0:5; 0:0; 0:5) where a is the edge of the elementary cube. From the unit cell, a supercell was constructed by translating the unit cell in three directions to create a cube of 27 unit cells ($3\times3\times3=27$) with a total of 108 atoms. The same procedure was followed in constructing the supercell for all studied metals and alloys. To simulate the influence of chemical disorder atoms were arranged using python random number program designed solely constructing supercells with chemical disorder. It worth noting that the arrangement of atoms was done in such away that the stoichiometric ratio is not violated. For instance, elementary cell of $AgNi_3$ will have always three atoms of nickel and one atom of silver. It is worth noting that in the ordered structures the elementary cells are equivalent to each other. This may not be the case for the chemically disordered structures due to the random arrangement of atom in the unit cell.

2. Estimation of Elastic Moduli

Elastic constants can provide information on the stability, stiffness, brittleness, ductility, and anisotropy of a material [5, 6]. They are essential parameters that correlate the microscopic properties to macroscopic mechanical properties. Precise calculation of

the elastic constants is essential for gaining insight into the mechanical strength of solids, verifying their stability, and designing material applications [7].

For a general 3-D materials there are six components of stress and a corresponding six components of strain. Applying Hooke's law, the relation between stress and strain is expressed as [8]:

$$\sigma_i = C_{ij}, \tag{1}$$

where C is elastic constant, σ is stress and ε is strain. The equilibrium crystal structure and elastic moduli of the crystals were calculated using the GULP software package [9]. To describe interatomic interactions in metals and their alloys, the Sutton-Chen mathematical model was used [10]. The total potential energy of a system of n interacting atoms in the framework of this model can be found in the article published by Desta O. G., Bykova M. I. and Timoshenko Yu. K. [11, 12]. The Sutton-Chen potential parameters for the metals Au, Ag and Ni are given in table 1.

Table 1 – Parameters of the Sutton-Chen potential for metals Au, Ag and Ni

Metal	ν	μ	$\in (eV)$	c	a(Å)	Reference
Ni	6	9	1.5707×10^{-2}	39.432	3.52	[13]
Ag	6	12	2.5415×10^{-3}	144.41	4.0900	[14]
Au	8	10	1.2793×10^{-2}	34.408	4.0800	[14]

The calculations were performed at 0 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 Ni, Au and Ag, which under normal conditions have a face centered cubic lattice [15].

In the GULP formalism, these moduli are estimated from elastic constants. The values of these properties are approximated from semi-empirical potential that represents the interaction energy among the atoms of the metals and their alloys. The second derivative of potential energy function with respect to strain gives elastic constants [10]:

$$C_{ij} = \frac{1}{V}\frac{\partial^2 U}{\partial\varepsilon_i \partial\varepsilon_j}, \tag{2}$$

where C_{ij} is a component of the stiffness matrix C, U is the energy expression, V is the volume of the unit cell, ε_i and ε_j are strain. For fcc cubic crystals the only unique elements are the elastic constants C_{11}, C_{12} and C_{44}. In terms of the interatomic potentials, the equation used to compute the values for these independent elastic constants can be expressed as follows [16]:

$$C_{11} = \frac{1}{V}\frac{\partial^2 U}{\partial \varepsilon_{11}^2};\ C_{12} = \frac{1}{V}\frac{\partial^2 U}{\partial \varepsilon_{11}\partial \varepsilon_{12}};\quad C_{11} = \frac{1}{4V}\frac{\partial^2 U}{\partial \varepsilon_{12}^2}. \tag{3}$$

Mechanical stability (structural stiffness) of a material determines how much a material deforms under load. For the cubic crystal, the mechanical stability criteria is [6]:

$$C_{11} - C_{12} > 0;\ \ C_{11} > 0;\ C_{44} > 0;\ C_{11} + 2C_{12} > 0\ . \tag{4}$$

Bulk and shear moduli are important material properties. The bulk modulus (B) describes the elastic response to volume change. Conceptually, shear modulus it is the ratio of shear stress to shear strain. For isotropic polycrystalline materials, the bulk modulus (B) and shear modulus (G) can be estimated from elastic constants C_{ij} [7]. One of the most widely used methods to estimate the elastic characteristics of polycrystalline materials is the averaging of the single crystal elastic moduli, known as the Voigt (V), Reuss (R) and Hill (H)[7]. Hill showed that the Voigt approximation leads to overestimated values of the elastic moduli, while the Reuss approximation underestimated the values [17], and recommended to take the arithmetic mean of value of these approximations [18]. The formulas for estimation of bulk and shear moduli due to the Voigt(V) and Ruess (R) approximations are given as follows:

$$B_V = B_R = \frac{1}{3}\left(C_{11} + 2C_{12}\right);\ G_V = \frac{1}{5}\left(C_{11} - C_{12} + 3C_{44}\right);\ G_R = \frac{5C_{44}\left(C_{11} - C_{12}\right)}{4C_{44} + 3(C_{11} - C_{12})}. \tag{5}$$

Here we used the Hill(H) approximations to estimate the bulk and shear moduli of the metals and their alloys. For fcc crystal structures $B_H = B_V = B_R$ while the value for shear modulus according to the Hill's approximation is computed using the formula below:

$$G_H = \frac{G_V + G_R}{2}. \quad (6)$$

3. 1 Poisson's ratio, Intrinsic Hardness and Ductility Coefficient

Poisson's ratio σ defined as the ratio of transverse strain to the longitudinal strain is used to reflect the stability of the material against shear and provides information about the nature of the bonding forces [6]. The Poisson's ratio, σ, can be computed using the formalism given as follows from the values of bulk and shear moduli [19, 20]:

$$\sigma = \frac{3B - 2G}{2(3B + G)}. \quad (7)$$

Hardness is one of the most important mechanical properties of metals and alloys, which characterizes its own resistance to deformation under the influence of external forces. It determines the wear resistance of surfaces, is an indicator of the strength of the material [21] and, ultimately, is determined at the atomic level [22].

The ductility of metals and alloys is closely related to the hardness of the material. Ductility refers to the ability of a material to deform without breaking. Pugh [23] suggested the coefficient of ductility could be estimated taking the ratio between bulk and shear moduli as follows:

$$K = \frac{B}{G}. \quad (8)$$

K indicates ductility or fragility of the material. A large value of K indicates that the material is ductile and a small K describes it is brittle. A given substance will be brittle if K < 1.75 [7]. Otherwise the material is characterized as ductile. There are a number of different empirical formulas for estimating intrinsic hardness of metals and alloys. Here we apply one of the formalisms followed Desta and his co-authors given as [11,12]:

$$H_{VT} = 0.92k^{1.137}G^{0.708}. \quad (9)$$

4. Results and Discussion

In all our simulations, we used geometry optimization method by keeping the number of atoms (N) and pressure (P) constant. In addition periodic boundary conditions

were applied. This condition makes it possible to simulate a small system that is not terminated by a surface. This is due to the fact that the simulation cell is periodically repeated in all directions. This allows us to consider the systems under study to be macroscopically homogeneous. The simulation was conducted at 0 Kelvin and 0.00 GPa.

The Newton-Raphson optimizer with Broyden-Fletcher-Goldfarb-Shanno (BFGS) hessian matrix updater was used in the optimization process. For optimized structure the elastic constants and bulk and shear moduli were calculated. From the results of the simulations, intrinsic hardness for each material was calculated using equation (9) while the coefficient of ductility was estimated using equation (8) for both chemically ordered disordered structures. The calculation results are shown in tables 2 and 3 and in figures 2-7.

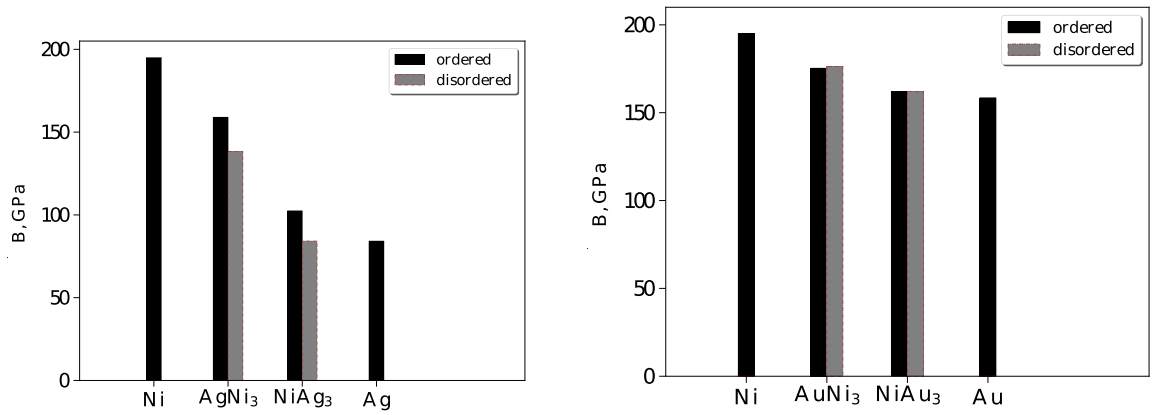


Figure 1 – Comparison of bulk moduli of the ordered and disordered alloys: a) Ni -Ag; b) Ni-Au.

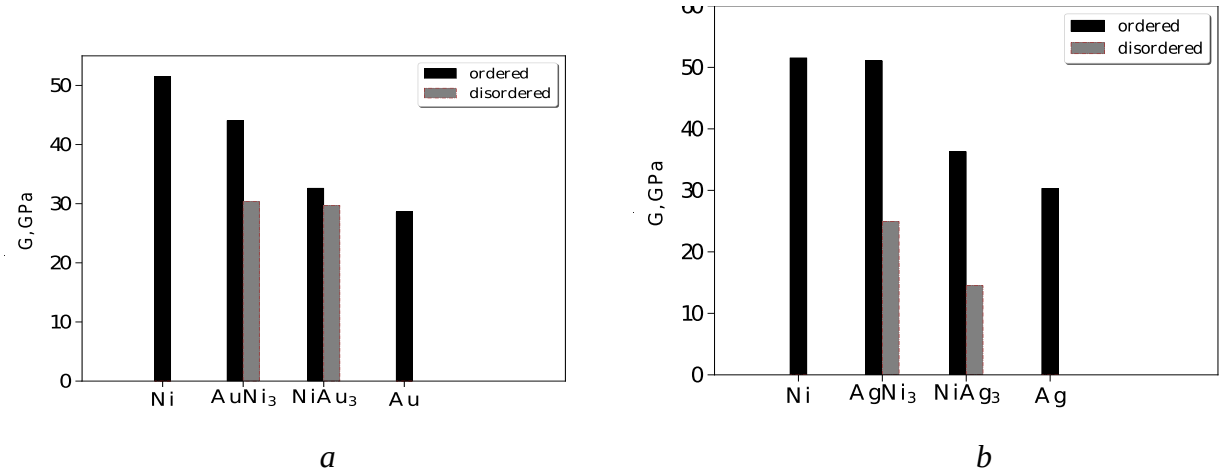
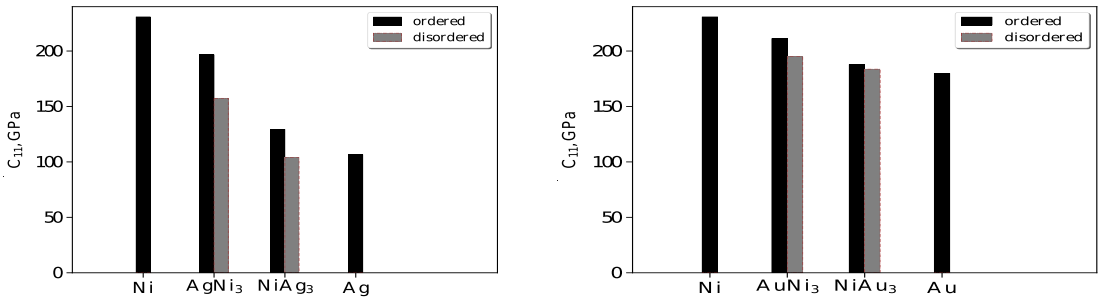


Figure 2 – Comparison of shear moduli of the ordered and disordered alloys:
a – Ni -Ag; *b* – Ni-Au.

The values of elastic constants C_{ij} were estimated using equation (3). The bulk and shear moduli were calculated using the Hill approximation. The Poisson's ratio for each metal or alloy was calculated using equation (7). The values of intrinsic hardness were calculated for all the pure metals Ni, Ag and Au and as well as for the alloys ANi_3 and NiA_3 where the letter A represent the pure metals Ag and Au. Similarly the coefficient of ductility was calculated for all the metals and their alloys under investigation. The calculations of the mechanical properties for the alloys, has been done for both chemically ordered and disordered materials to study the influence of chemical disorder on the properties.

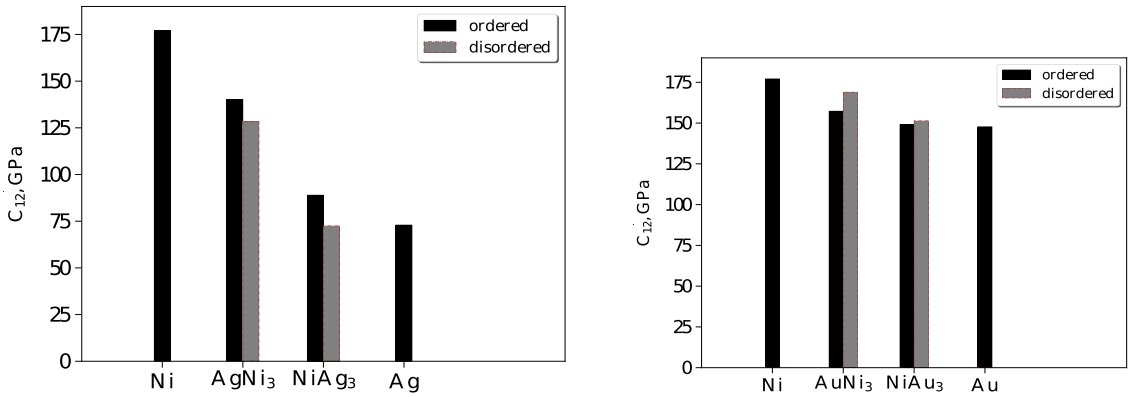


a *b*

Figure 3 – Comparison of elastic moduli of the ordered and disordered alloys: *a* – Ni -Ag; *b* – Ni-Au

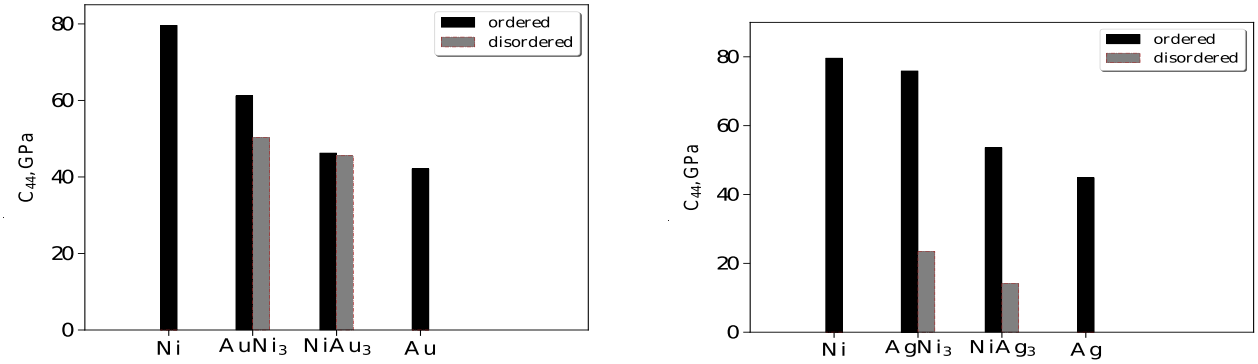
Table 2 – Chemically ordered alloys: C_{11}, C_{12}, C_{44}, B, G, H_{VT}, in GPa; K and σ are dimensionless quantities

Metal	C_{11}	C_{12}	C_{44}	B	G	H_{VT}	K	σ
Ni	230.8340	177.1365	79.6187	195.0357	51.54275	3.3027	3.7840	0.38
$AgNi_3$	196.6286	140.1696	75.9039	158.9892	51.06752	4.0960	3.1133	0.35
$NiAg_3$	129.4388	88.9563	53.6246	102.4505	36.29046	3.5946	2.8231	0.34
Ag	106.6456	72.9385	44.8804	84.17421	30.31093	3.2241	2.7770	0.34
$AuNi_3$	211.2794	157.3351	61.2112	175.3161	44.05635	2.7910	3.9794	0.38
$NiAu_3$	187.8893	149.1501	46.2503	162.0632	32.61945	1.7528	4.9683	0.40
Au	179.8710	147.7899	42.1339	158.4836	28.61083	1.4116	5.5393	0.41



a *b*

Figure 4 – Comparison of elastic moduli of the ordered and disordered alloys: *a* – Ni -Ag; *b* – Ni-Au

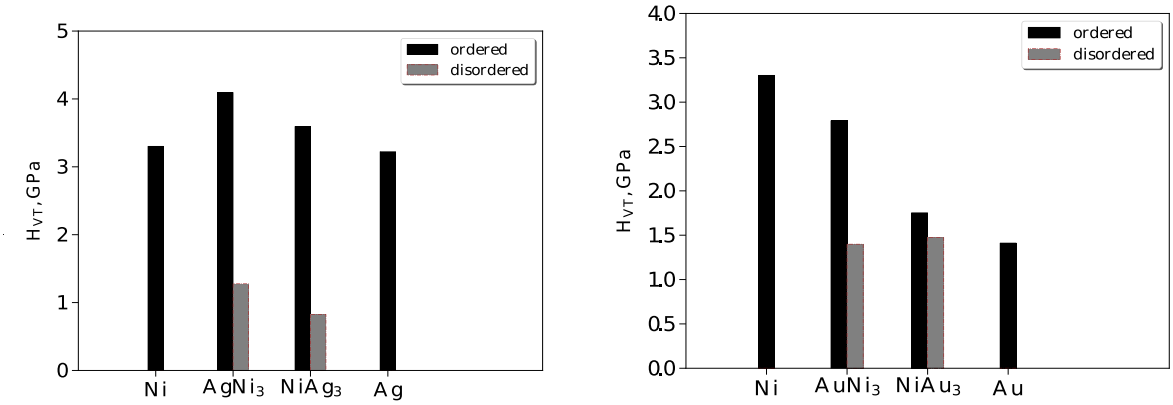


a *b*

Figure 5 – Comparison of elastic moduli of the ordered and disordered alloys: *a* – Ni -Ag; *b* – Ni-Au

Table 3 – Chemically disordered alloys: C_{11}, C_{12}, C_{44}, B, G, H_{VT}, in GPa; K and σ are dimension-less quantities

Metal	C_{11}	C_{12}	C_{44}	B	G	H_{VT}	K	σ
$AgNi_3$	157.4414	128.3508	23.4546	138.3015	24.9193	1.2773	5.5500	0.42
$NiAg_3$	103.7768	72.5192	14.1502	84.25555	14.4995	0.8262	5.8109	0.42
$AuNi_3$	195.0908	168.9585	50.3417	176.3558	30.4057	1.3986	5.8001	0.42
$NiAu_3$	183.7217	151.4620	45.5370	162.1504	29.7137	1.4747	5.4571	0.41



a *b*

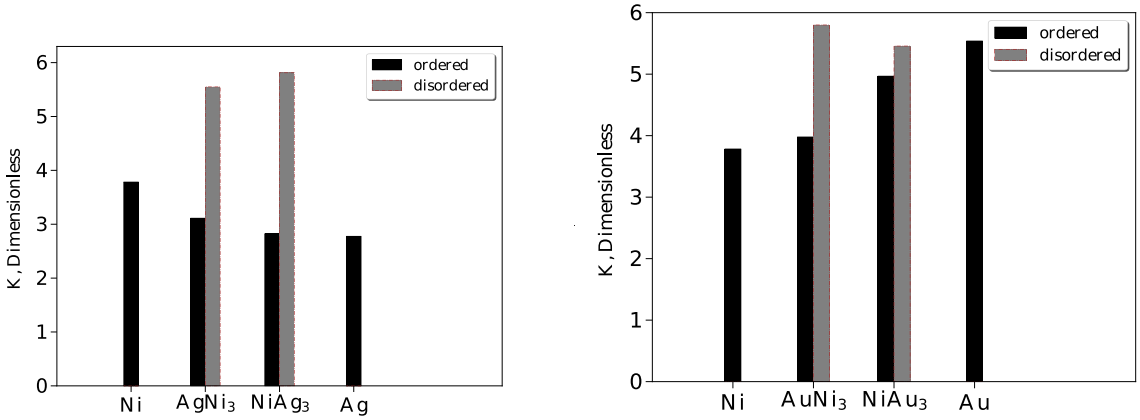
Figure 6 – Comparison of intrinsic hardness of the ordered and disordered alloys: a) Ni -Ag; b) Ni-Au

In all the alloy systems for both the ordered and disordered alloys, the elastic constants and moduli of the type $AgNi_3$ is greater than that of $NiAg_3$. The same can be said about the alloys $AuNi_3$ and $NiAu_3$. All the alloy systems investigated here satisfy the stability condition given in equation (4). Further, for all pure metals, ordered and disordered alloys, $C_{12} < B < C_{11}$.

The Poisson's ratio for the metals and ordered alloys falls in the interval 0:34 0:41 while for the disordered alloys it is approximately 0:41 or 0:42. We were able to estimate the intrinsic hardness of the metals and their alloys. For both ordered and disordered alloys, the hardness values of $AgNi_3$ is greater than $NiAg_3$. The value of hardness for the ordered $AuNi_3$ is greater than $NiAu_3$. For the disordered alloys, the hardness of $AuNi_3$ is less than $NiAu_3$.

As it can be seen from tables 2 and 3 the metals and their alloys have good ductility coefficients. The value for ordered alloys, the ductility coefficient, K, of alloy AgNi3 is greater than the ductility coefficient of $NiAg_3$. For the disordered alloys the reverse is true. For ordered alloys, the ductility coefficient of the alloy $AuNi_3$ is lower than that of $NiAu_3$. Again the opposite is true with regard the ductility coefficient of disordered alloys of $AuNi_3$ and $NiAu_3$.

It is worth noting that the hardness values of the pure metal A is less than the hardness values of the alloys of the type ANi3 and NiA3. The same can be said about the ductility coefficient except for the alloys AuNi3 and NiAu3 where the value is lower



a *b*

Figure 7 – Comparison of ductility coefficient of the ordered and disordered alloys: *a* – Ni -Ag; *b* – Ni-Au

than the ductility of pure gold.

The influence of chemical disorder is much higher in the Ni-Ag alloy system in comparison to Ni -Au. In general terms, the values of the elastic constants and moduli of the disordered alloys are less than the ordered counterparts except for the elastic constant C_{12} for the alloy system Ni-Au. In all the materials, intrinsic hardness decreased with disorder while coefficient of ductility increased. The highest influenced mechanical properties by chemically disorder are the shear modulus (G), the elastic constant C_{44}, intrinsic hardness and coefficient of ductility.

Conclusion

In the present work, we were able to estimate bulk and shear moduli, elastic constants, Poisson's ratio, intrinsic hardness and ductility coefficients of alloys using computer simulation. Further the extent of influence of chemical disorder on the mechanical properties of the alloys was estimated.

For binary ordered alloy of nickel with gold or silver, the alloy will have higher values of the elastic moduli and intrinsic hardness in comparison the pure metals Au or Ag. The higher the ratio of nickel in the alloy, the higher the values of the elastic moduli and intrinsic hardness is.

Generally, chemical disorder in the alloys decreases the values of elastic constants and moduli and intrinsic hardness while it increases the values of ductility coefficient and Poisson's ratio. The influence of chemical disorder is much higher in the al-

loys involving nickel and silver. Chemical disorder influences higher the shear modulus, elastic constant C_{44}, intrinsic hardness and coefficient of ductility.

References

1 Ezugwu, E. O. The machinability of nickel-based alloys: a review / E. O. Ezugwu, Z. M. Wang, A. R. Machado // Journal of Materials Processing Technology. – 1999. – Vol. 86. – № 1-3. – P. 1-16.

2 Ortiz-Roldan, M. J. Thermostructural behaviour of Ni-Cr materials : modelling of bulk and nanoparticle systems / M. J. Ortiz-Roldan, A. R. Ruiz-Salvador, S. Calero Sofia et al. // Physical Chemistry Chemical Physics. – 2015. – Vol. 17. – № 24. – P. 15912-15920.

3 Davoodi, J. Calculation of the Mechanical Properties of Cu-Ni Nanocluster / J. Davoodi, K. Ronasi // International Journal of Nanoscience and Nanotechnology. – 2009. – Vol. 5. – № 1. – P. 19-24.

4 Che, X. Ab initio Study on the Structural Stability and Magnetism of Metastable A3B Phases in Ni-Au (Cu, Zn, Al) Binary Systems / X. Che, J. Li, Y. Dai, B. Liu // Journal of the Physical Society of Japan. – 2009. – Vol. 78. – № 3. – P. 034720-034720.

5 Boucetta, S. Elastic and mechanical properties of Mg3Rh intermetallic compound : An ab initio study / S. Boucetta, G. U'gur // Journal of Magnesium and Alloys. – 2016. – Vol. 4. – № 2. – P. 123-127

6 Luan, X. The Mechanical Properties and Elastic Anisotropies of Cubic Ni3Al from First Principles Calculations / X. Luan, H. Qin, F. Liu et al. // Crystals. – 2018. – Vol. 8. – № 8. – P. 307-318.

7 Kong, G. Structural stability, elastic and thermodynamic properties of Au-Cu alloys from first-principles calculations / G. Kong, X. Ma, Q. Liu et al. // Physica B : Condensed Matter. – 2018. – Vol. 533. – P. 58-62.

8 Musa, S. M. Computational Finite Element Methods in Nanotechnology. Vol. 1. / S. M. Musa. – CRC Press, 2012. – 640 p.

9 Gale, J. D. The general utility lattice program (GULP) / J. D. Gale, L. A. Rohl // Molecular Simulation. – 2003. – Vol. 29. – № 5. – P. 291-341.

10 Khoei, A. R. An investigation on the validity of Cauchy-Born hypothesis using Sutton-Chen many-body potential / A. R. Khoei, M. J. MJ. A. Qomi, M. T. Kazemi, A. Aghaei // Computational Materials Science. – 2009. – Vol. 44. – № 3. – P. 999-1006.

11 Desta, O. G. Computer simulations of the influence of atomic structure disorder on thehardness of Cu-Ag and Au-Ag alloys / O. G. Desta, O M. I. Bykova,

Yu. K. Timoshenko // Journal of Physics : Conference Series. – 2020. – Vol. 1479. – P. 012027.

12 Деста, О. Г. Компьютерное моделирование влияния неупорядоченности атомной структуры на твердость сплавов Cu-Ag и Au-Ag / О. Г. Деста, М. И. Быкова, Ю. К. Тимошенко // Актуальные проблемы прикладной математики, информатики и механики. – 2020. – P. 793-799.

13 Arslan, H. Melting dynamics and isomer distributions of small metal clusters / H. Arslan, M. H. G'uven // New Journal of Physics. – 2005. – Vol. 7. – № 1. – P. 60(1-21).

14 Januszko, A Phonon spectra and temperature variation of bulk properties of Cu, Ag, Au and Pt using Sutton-Chen and modified Suttonв-Chen potentials / A. Januszko, S. k. Bose // Journal of Physics and Chemistry of Solids. – 2015. – Vol. 82. –P. 67-75.

15 Kart, H. H. Thermal and mechanical properties of Cu-Au intermetallic alloys / H. H. Kart, M. Tomak, T. Cagin // Modelling and simulation in materials science and engineering. – 2005. – Vol. 13. – № 5. – P. 657-669.

16 Rafii-Tabar, H. Long-range Finnis-Sinclair potentials for fcc metallic alloys / H. Rafii-Tabar, Ap. Sulton // Philosophical Magazine Letters. – 1991. – Vol. 63. – № 4. – P. 217-224.

17 Barsch, R. G. Relation between third-order elastic constants of single crystals and polycrystals / R. G. Barsch // Journal of Applied Physics. – 1968. – Vol. 39. – № 8. – P. 3780-3793.

18 Crosson, S. R. Voigt and Reuss prediction of anisotropic elasticity of unite / S. R. Crosson, L. Jia-Wen // Journal of Geophysical Research. – 1971. – Vol. 76 – № 2. – P. 570-578.

19 Edrees, J. S. First-principle analysis of the structural, mechanical, optical and electronic properties of wollastonite monoclinic polymorph / J. S. Edrees, M. M. Shukur, M. M. Obeid // Computational Condensed Matter. – 2018. – Vol. 14. – P. 20-26.

20 Toprek, D. Ab initio studies of the structural, elastic, electronic and thermal properties of NiTi2 intermetallic / D. Toprek, J. Belosevic-Cavor, V. Koteski // Journal of Physics and Chemistry of Solids. – 2015. – Vol. 85. – P. 197-205.

21 Gilman, J. Chemistry and physics of mechanical hardness. Vol. 5 / J. J. Gilman / John Wiley & Sons, 2009. – 203 p.

22 Teter, M. D. Computational alchemy : the search for new superhard materials / M. D. Teter // Mrs Bulletin. – 1998. – Vol. 23. – № 1. – P. 22-27.

23 Pugh, S. F. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals / S. F. Pugh // The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science. – 1954. – Vol. 45. – № 367. – P. 823-843.