First-Principles Study on Solution Strengthening Effect of Cu and Zn in Ag Alloy

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Abstract: A first-principles plane-wave pseudopotential method based on the density functional theory was used to investigate the mechanical properties and electronic properties of AgCu and AgZn solid solution. The VCA models have been set up for solid solution, and elastic constants, bulk modulus and shear modulus, Young modulus and density of states of Cu or Zn doped Ag system were also analysed. The results show that Cu and Zn in Ag alloy play a role of solution strengthening, the solid solution strengthening effect was obviously improved by adding a small amount of Cu(less than 2at.%) or Zn(less than 1at.%). The total DOS of AgCu(Zn) Solid solution is mainly constituted by the Ag 4d and Cu(Zn) 4d states. The AgZn Solid solution has a more stable structure than AgCu solid solution.

1.Introduction

Ag-Cu-Zn alloys are widely used for sliding electrical contact materials, jewelry, coins, silverware[1-3]due to their high hardness and strength and good performances of electrical conductivity，thermal conductivity and wear resistance. Nowadays, Ag-Cu-Zn alloys researches are mainly focused on the effects of Zn on microstructure and mechanical properties of materials, corrosion resistance, anti-tarnishing and strengthening mechanism [4-8] etc. However, many properties (including elastic properties, as well as electronic properties) of AgCu and AgZn solid solution still need to be understood at an atomic level. The maximum solid solubility of Cu and Zn in Ag is about 14 and 30wt, respectively. In the practical application, the content of Cu is 3-6wt. % and Zn is 1-2wt. % while the Ag-Cu-Zn alloys used for electrical contact materials, jewelry and coins. Here, we performed first principles calculations to investigate the elastic properties and electronic properties for AgCu and AgZn solid solution added less than 10at. % Cu and 10at. % Zn, in order to understand the solution strengthening effect of Cu and Zn on Ag Alloy.

2. Details of the Calculations

2.1 Computational Method

The crystal structure of metal Ag and Cu is the face-centered (FCC), and Zn is the hexagonal close packed (hcp),The cell model of face centered cubic crystals were build based on the virtual crystal approximation (VCA), the adding atoms (Cu and Zn) and Ag atoms are indefinite position, each position can be viewed as a mixture of two kind atoms, the atomic percentage show the probability of one kind atom appearing in that position .The VCA method was widely used to calculate the structure properties of disordered solid solution and ordered solid solution. The mass fraction of Cu and Zn added in Ag alloy are from 0 to 10at. %, the crystal cell of Ag-Cu and Ag-Zn alloy as shown in Figure 1.

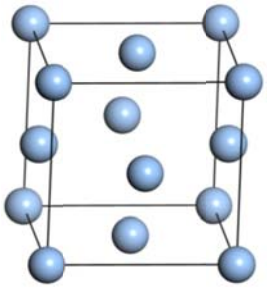

Figure 1. Crystal cell of Ag-Cu and Ag-Zn alloy

In order to research the electronic properties, the 2X2X2 supercell of substitution solid solution of Cu and Zn in Ag was structured, as shown in Figure 2.

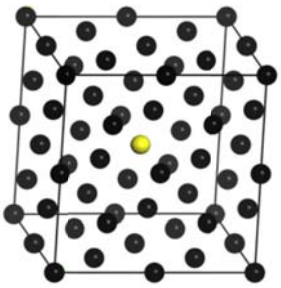

Figure 2. Crystal cell of substitution solid solution of Cu and Zn in Ag

2.2 Calculation Methods

All calculations were performed with Cambridge serial total energy package (CASTEP) code based on the first-principles method within the framework of density function theory (DFT).Through calculating in many times and the calculation results were compared with experimental data (such as lattice), Finally, the calculation parameters were determined as follows: the periodic boundary condition was used in the whole process. Interactions of electrons with an ion core were represented by the Vanderbilt-type ultrasoft pseudopotential. The electronic exchange-correlation energy was treated under the generalized gradient approximation (GGA-PBE). The plane-wave basis set cutoff was 460 eV for all calculations. The special k-points sampling integration over the Brillouin zone was employed by using the Monkhorst-Pack method with a 10×10×10 special k-point mesh. The energy tolerance is 5×10−7eV/atom. These parameters were sufficient to lead to convergences of total energy and geometrical configuration. Before calculation, the Cell Geometry was optimized by Broyden-Fletcher-Goldfarb-Shanno (BFGS) method to obtain the local stable structure.

3. Results and Discussion

3.1Mechanical Properties

The elastic constants of solids are closely related to its mechanical properties. It can be used to characterize the response of crystals to external stresses and as the interaction between atoms standard. Therefore, to research the elastic constants of Ag-Cu and Ag-Zn solid solution alloys is of great importance to understanding the mechanical properties of alloys. In the case of cubic crystals, there are three independent elastic constants (C_{11}, C_{12} and C_{44}). According to the Voigt-Reuss-Hill arithmetic approximation, the bulk modulus (B), shear modulus (G) and Young's modulus (E) can be obtained from the following equation[9]:

$$B_0 = B_V = B_R = \frac{c_{11}+2c_{12}}{3} \quad (1)$$

$$G_V = \frac{c_{11}-c_{12}+3c_{44}}{5} \quad (2)$$

$$G_R = \frac{5c_{44}(c_{11}-c_{12})}{4c_{44}+3(c_{11}-c_{12})} \quad (3)$$

$$G = \frac{G_V+G_R}{2} \quad (4)$$

$$E = \frac{9GB}{3B+G} \quad (5)$$

Where B_V is Voigt elastic modulus, B_R is Reuss elastic modulus, G_V and $G_R$are Voigt shear modulus and Reuss shear modulus, respectively.

The calculation result of the elastic constants, bulk modulus, shear modulus and Young's modulus of Ag-Cu and Ag-Zn are showed in Table 1 and Table 2. It can be seen that the mechanical constants of pure Ag are close to the calculated value of ref.[10] and experimental values of ref.[11], so the calculation result is credible.

Table 1. Mechanical property parameters of Ag-Cu alloys (GPa)

Composition	C_{11}	C_{12}	C_{44}	B	G_V	G_R	G	E
Ag	131.67	80.43	58.41	97.51	45.29	38.63	41.96	110.09
Ag-1Cu	147.48	89.05	61.84	108.52	48.79	42.75	45.77	120.38
Ag-2Cu	157.66	95.29	59.13	116.08	47.95	43.53	45.74	121.29
Ag-3Cu	157.91	99.87	54.39	119.22	44.24	40.30	42.27	113.40
Ag-4Cu	157.39	103.20	50.72	121.26	41.27	37.60	39.44	106.74
Ag-5Cu	157.87	106.71	47.94	123.77	39.00	35.52	37.26	101.58
Ag-6Cu	158.60	108.44	46.57	125.16	37.97	34.68	36.33	99.37
Ag-7Cu	159.81	110.40	45.77	126.87	37.35	34.13	35.74	98.01
Ag-8Cu	160.69	110.62	45.57	127.31	37.35	34.31	35.83	98.28
Ag-9Cu	160.35	111.57	45.49	127.83	37.05	33.80	35.42	97.29
Ag-10Cu	160.11	111.92	45.87	127.98	37.16	33.69	35.43	97.30

Table 2. Mechanical property parameters of Ag-Zn alloys (GPa)

Composition	C_{11}	C_{12}	C_{44}	B	G_V	G_R	G	E
Ag	131.67	80.43	58.41	97.51	45.29	38.63	41.96	110.09
Ag-1Zn	144.78	84.02	59.71	104.27	47.98	43.08	45.53	119.23
Ag-2Zn	143.11	85.33	59.60	104.59	47.32	41.82	44.57	117.07
Ag-3Zn	135.80	83.47	57.97	100.91	45.25	39.01	42.13	110.95
Ag-4Zn	130.09	84.30	56.78	99.56	43.23	35.67	39.45	104.53

Ag-5Zn	130.23	83.04	51.08	98.77	40.09	34.84	37.47	99.78
Ag-6Zn	128.77	81.41	52.83	97.20	41.17	35.40	38.29	101.53
Ag-7Zn	113.25	85.07	47.59	94.46	34.19	24.39	29.29	79.64
Ag-8Zn	108.92	79.43	40.14	89.26	29.98	23.77	26.87	73.27
Ag-9Zn	99.38	81.39	36.74	87.39	25.64	16.45	21.04	58.44
Ag-10Zn	94.91	79.44	35.25	84.60	24.24	14.55	19.40	54.06

The bulk modulus is usually used to describe the ability of materials on resistance to volume deformation under external force. The larger bulk modulus means that the volumetric deformation resistance of crystal is stronger. Shear modulus is a measure of the resistance to form change of crystal. It can reflect the anti-plastic-deform capacity of materials. It was suggested that the Young's modulus E and shear modulus G have close relations with the hardness of materials because it has a strong correlation with the cohesion energy or binding energy of atoms in crystal. It indicates that the higher the Young's modulus E and shear modulus G, the higher the hardness of materials. The hardness and shear modulus between different materials are not the exactly same, but generally speaking, with B, G and E increase, the hardness of the material increase accordingly.

Figure 3 is curve which reflect the change of B, G and E with the copper content in Ag-Cu solid solution alloy,it can be seen from the graph that the bulk modulus increases with the increase of copper content, the bulk modulus increase sharply atfirst, when the copper content is above 8at.%, the bulk modulus still rise but the trend becomes very slow, it shows that the processing difficulty increases with the increase of copper content, as well as ,the higher the Cu content, the higher the resistivity, it seriously affect the performance of electrical contact materials. In practical application, in order to obtain higher conductivity,the content of added elements is minimized under the condition of guaranteeing strength. For AgCu electrical contact materials that we commonly used, such as AgCu4Ni0.5. AgCu5, AgCu6Zn, the Cu content of them are about 6wt. % or less than 6wt. %,it also shows that the calculated results are in good agreement with the practical application, the physical model and parameters of simulation is reasonable, the result is credible.

It also can be seen from Figure 3, that the Young's modulus and shear modulus first increase then decreasewith the increase of Cu content, when Cu content rise to 2%at. %, the two modulus reach a maximum value and then drops down sharply.It shows that adding a small amount of Cu (2at. %) in Ag can effectively improve the strength and hardness of Ag, increasing the amount of Cu results in performance decreased instead.

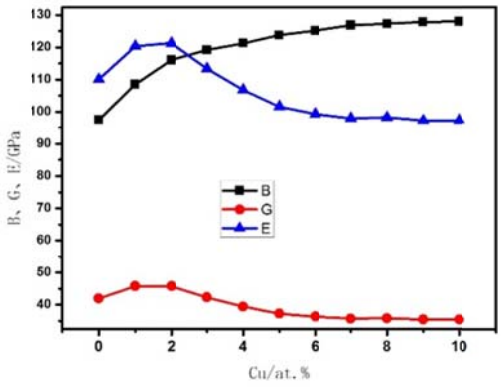

Figure 3. The relationship between Young's modulus (E), shear modulus (G) and bulk modulus (B) with the content of Cu.

The relationship between Young's modulus (E), shear modulus (G) and bulk modulus (B) with the content of Zn as shown in Figure 4.It can be seen that the three elastic modulus first increase then decreasewith the increase of Zn content, when Zn content rise to 1%at. %, the three elastic modulus reach a maximum value and then drops down sharply.It shows that adding a small amount of Zn

(1at. %) in Ag can effectively improve the strength and hardness of Ag, such as the Zn Content of wear-resisting silver based electrical contact material (AgCu6Zn1Ni0.5) and 925Ag are about 1wt. %, increasing the amount of Zn results in performance degradation. So the actual application is in good agreement with the calculation results.

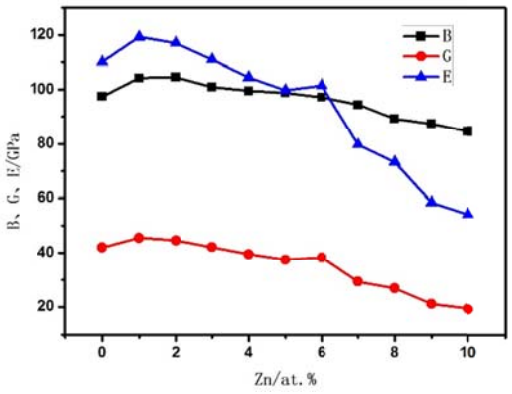

Figure 4. The relationship between Young's modulus (E), shear modulus (G) and bulk modulus (B) with the content of Zn.

3.2 Electronic Properties

Almost all the macro-properties of materials, such as hardness, elasticity, and conductivity, originate from their electronic structure properties as well as the nature of the chemical bonding. Therefore, it is necessary to perform the electronic structure analysis of AgCu Solid solution and AgZn Solid solution. The DOS is an important quantity for understanding the bonding in a compound. After geometry optimization, the total and partial DOS at equilibrium lattice constants forAgCu Solid solution and AgZn Solid solutionare calculated, as shown in Figure 5. In Figure 5(a) it is shown that the total DOS of AgCu Solid solutionis mainly constituted by the Ag 4d and Cu 4d states.In Figure 5(b) it is shown that the total DOS of AgZn Solid solutionis mainly constituted by the Ag 4d and Ag 4p and Zn 4d states.The density of states at the Fermi level, N(EF) is oftenused as a good indicator for the structural stability, and thevalues are 7.6 and 6.5 state·eV $^{-1}$ perSupercellfor AgCu Solid solution and AgZn Solid solution, respectively, so the AgZn Solid solution has a more stable structure than AgCusolid solution ,thisconclusion is in agreement with the phase diagram of Ag-Cu and Ag-Zn, that the solid solubility of Zn in Ag is much larger than that of Cu in silver.

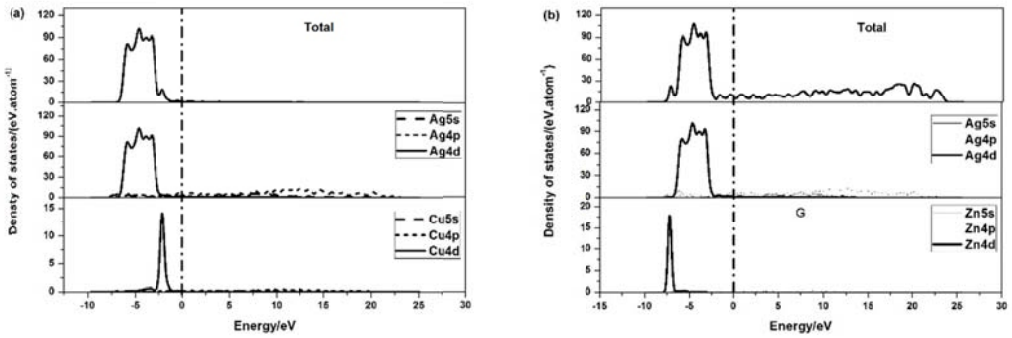

Figure 5. Calculated total and partial density of states for Solid solution(a)Ag31Cu,(b)Ag31Zn

4. Conclusions

(1)Cu and Zn in Ag alloy play a role of solution strengthening, the solid solution strengthening effect was obviously improved by adding a small amount of Cu(less than 2at.%) or Zn(less than 1at.%).

(2)The total DOS of AgCu(Zn) Solid solutionis mainly constituted by the Ag 4d and Cu(Zn) 4d states. The AgZn Solid solution has a more stable structure than AgCusolid solution.

5.Acknowledgement

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6. References

[1] Editor Team of Precious Metal Materials Process Handbook.Precious Metal Materials Machining Manual [M].Beijing:Metallurgical Industry Press, 1978: 14 (in Chinese).
[2]Yu Chaoqing, Wang Liqiong. *Small & Special Machines*[J], 2003(2): 31 (in Chinese).
[3]Lei Zhuo, Bai Xiaojun, Xiang Xiongzhi et al. *MaterialsReview* [J], 2006, 20(5): 434 (in Chinese)
[4]Bo Hairui, Yuan Junping, Zhou Yongheng et al. *Special Casting & Nonferrous Alloys* [J], 2011, 31(7): 680 (in Chinese).
[5] Yang Qingqing, XiongWeihao, Shen Dingjie et al. *Rare Metal Materials and Engineering* [J], 2008, 37(6): 947(in Chinese).
[6]YangQingqing, XiongWeihao, Yang Zhen et al. *Rare Metal Materials and Engineering* [J], 2010, 39(4): 578(in Chinese).
[7]Eccles P A. US Patent, US 6726877[P], 2004.
[8]Tang Youzheng, Xiang Xiongzhi, Bai Xiaojun et al. *RareMetal Materials and Engineering* [J], 2012, 41(5): 929 (in Chinese).
[9] Rong Yang,Bin Tang,Tao Gao. *Zeitschrift für Naturforschung A*[J],2017,72(6): 527-534.
[10]Wang Y，Aurtarolo S，Jiang C. *Ab initio lattice stabilityin comparison with CALPHAD lattice stability* [J].Calphad，2004，28: 79-90.
[11] Kittel C. Introduction to Solid State Physics [M]. 6th ed. New York: John Wiley＆Sons Inc，1986: 55-144.