



An electron work function based mechanism for solid solution hardening

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ABSTRACT

Solid solution hardening is one of common methods to increase hardness of metals by adding solute atoms. The mechanism for solution hardening is ascribed to the differences in atomic size and elastic modulus between the host and the solute. However, the theory is somehow ambiguous without clear clues for optimizing the balance between the two effects towards maximized hardening effectiveness. Current selection of alloying elements for solution hardening is largely based on experience. In this study, we re-examine the conventional mechanism and propose a single-parameter model using electron work function (EWF) as an indicator to evaluate the capability of solute atoms in solid solution hardening. With relevant experiments, we demonstrate the correlation between electron work function and solution hardening effectiveness. The prediction from the proposed EWF model is consistent with the experimental observations.

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1. Introduction

The resistance of a metal to plastic deformation depends on its barrier to dislocation movement. Microstructure constituents, e.g., interphase boundaries, grain boundaries and precipitates, are used to generate barriers to dislocation motion [1]. The basic principle for strengthening metallic materials is to block dislocation motion [1]. Solid solution hardening is another mostly used method to increase hardness of metals by adding solute atoms without forming second phases. The solute atoms tend to stay around the dislocation to reduce the local strain energy, leading to the pinning effect, i.e., the solute atoms result in barriers to dislocation motion. The solute atom also affects the local atomic bonding, thus influencing the hardening effectiveness.

Although solution hardening is widely used to strengthen materials, the selection of alloying elements is largely based on experience. Trial-and-error experiments are generally needed, which are time-consuming and costly. Considerable studies have been conducted to investigate the mechanism for solution hardening [2–8]. The strengthening of metals by solute atoms is often attributed to the difference in atomic size between solute and host atoms, which helps reduce the strain introduced by

dislocations and thus pin the dislocations. The classic theory proposed by Mott and Nabarro [2,3] analyzes the average magnitude of stress/strain in the matrix of a dilute solid solution with the alloying element having its atomic size different from that of the host. The effectiveness of solution hardening is related to the magnitude of local distortion, caused by atomic size misfit as $\delta_b = \left(\frac{1}{b}\right) \cdot \left(\frac{db}{dc}\right)$, where b is the lattice constant and c is the concentration of the solute. As mentioned earlier, another contributing factor is the modulus misfit [4] or the difference in elastic modulus between the host and the solute. By taking into account the interaction between dislocation and solute atoms with different values of stiffness [4,5], Fleisgher indicated that the effectiveness of solution hardening through the interaction between dislocation and solute atom was governed by the differences in both rigidity and atomic size between the solute and solvent elements. The effect of modulus misfit on the solution hardening is evaluated as defined as $\delta_G = \left(\frac{1}{G}\right) \cdot \left(\frac{dG}{dc}\right)$, where G is shear modulus. It is suggested that $\delta_h = |\delta_G - \alpha\delta_b|$ is a measure of the solution hardening effectiveness, where α is an experimentally determined constant through data fitting and α value is also influenced by the type of dislocations [6,7]. The model indicates the solute-hardening mechanism, but does not show the mutual influences of these two factors and how to maximize the hardening effectiveness by selecting an appropriate solute. It

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should also be noted that the modulus misfit $\delta_G = \left(\frac{1}{G}\right) \cdot \left(\frac{dG}{dc}\right)$ may be experimentally measurable but it is difficult to be theoretically calculated, since the modulus misfit is influenced by not only the electron-nuclei interactions but also the size misfit δ_b , which distorts the crystal lattice and thus affects the resistance of the crystal to plastic deformation. Although considerable studies were conducted to identify effective approaches to optimally balance the size misfit and modulus misfit such as application of the formula, $\delta_h = |\delta_G - \alpha\delta_b|$, for different categorized conditions [6], it still does not provide clear guidelines for optimal solute selection. Due to the uncertainty of the constant α and complex dislocation-solute interactions, it is difficult to determine how the size misfit and the modulus misfit synergistically influence the solution hardening [8]. Inaccurate or incorrect predictions could occur.

Furthermore, it is often stated that both larger and smaller solute atoms, relative to the solvent or host atom, can strengthen metals. A larger solute may stay in the tensile region of an edge dislocation while the smaller one may stay in its compressive region, so that the dislocation can be pinned [1]. However, it must be indicated that metals of elements with small atomic sizes are generally stronger with high elastic modulus than those with larger atomic sizes [9], meaning that the size factor and modulus factor are intrinsically related. Thus, these two factors cannot be taken into account separately. This often results in conceptual misinterpretation and makes it difficult to determine the optimal balance between the two factors for maximized strengthening effectiveness. It is therefore highly desired to have a more straightforward theory or approach to guide element selection for solid solution hardening with more precise understanding.

The intrinsic mechanical behavior of metallic materials is fundamentally determined by their electron behavior, which governs the atomic bond strength [10]. Efforts have been made to correlate solution hardening to electron configurations based on quantum mechanics with the help of first-principles calculation [11,12] and classic approaches [13,14]. These treatments are however complicated and difficult to be used in material design. Identifying a simple but fundamental parameter which characterizes the electron behavior of materials would be greatly helpful. The authors have conducted considerable studies on mechanical properties and electron work function (EWF) [9,15–20] and foreseen that EWF could be such a parameter for looking into the effectiveness of solid solution hardening. EWF is the minimum energy required to extract electrons at Fermi level from the interior of a solid to its surface without kinetic energy, which reflects the metallic bond strength [19–22].

$$\varphi^6 = \xi \cdot \frac{\epsilon_b}{r_e^3} \quad (1)$$

where φ is the electron work function, ϵ_b is the atomic bond energy and r_e is the bond length, and ξ is the fitted constant based on experiment data for pure metals. The value of ξ is dependent on the crystal structure, e.g., equal to 104.42 for BCC structure and 470.66 for FCC structure. The unit for the electron work function is eV and that for the bond length, r_e , is nm.

Our previous studies have shown clear correlations between the work function and mechanical properties of metallic materials, such as Young's modulus, hardness, toughness and thermal expansion [9,15–20]. It has been demonstrated that Young's modulus and hardness of pure metals show a six power relation with electron work function, and the reciprocal of thermal expansion coefficient obeys a sixth power relationship with the work function. As for fracture toughness, when the work function

is smaller than 4.6 eV, the fracture toughness of transition metals increases with work function. However, as the work function is larger than 4.6 eV, the fracture toughness decreases quickly with the work function.

Moreover, work function is also related to the atomic size of elements [9].

$$r = 6.7\varphi^2 - 76.1\varphi + 349.4 \quad (2)$$

where r is the atomic radius.

It is therefore possible to use EWF as a bridge to connect the size misfit and modulus misfit in order to obtain clues for maximized hardening effectiveness. Confirmation of this hypothesis and development of a corresponding theoretical base are objectives of this study. In this article, a single-parameter model based on EWF is proposed to evaluate the capacity of solute atoms in solution hardening and to understand the mechanism behind. Predicted hardening effectiveness using the model is consistent with experimental data reported in the literature and also our experimental observations of Cu hardened by Ni, Zn and Ga with different EWFs.

2. Experimental methods

Pure copper, nickel, zinc and gallium, provided by Alfa Aesar and Strem Chemicals with at least 99.9% purity, were used to make Cu-X solid solution samples ($X = \text{Ni, Zn, Ga}$) with solute atomic concentrations of 2%, 5%, 10%, up to 20%, respectively. The reason of using Ni, Ga, and Zn as sample solutes to strengthen Cu is attributed to their relatively high solubility in copper, which makes it easy to fabricate solid solutions without forming secondary phases. Fig. 1 illustrates reproduced phase diagrams of Cu-X alloys ($X = \text{Ni, Zn, Ga}$) [23]. The samples were made using an induction furnace provided by MTI Corporation (U.S.). Pure copper and solute nickel (or zinc, gallium) were mixed together and melted under vacuum. All samples were made under the same condition and melted twice in order to reduce the microstructural inhomogeneity. All samples were then annealed (homogenization) in argon atmosphere at 600 °C for 3 h and slowly cooled down in the furnace. Rockwell hardness tests using a 1/16" tungsten carbide ball were performed under a load of 15 kg. Two samples for each alloy and at least five different regions on each sample were analyzed for statistically reliable results. Microstructures of the alloys were characterized using a Vega-3 TESCAN Scanning Electron Microscope and a Rigaku X-ray diffractometer with Cu $K\alpha$ radiation (Scanning speed: 0.02° per step and 2° per minute) in order to make sure the alloys are homogeneous solid solutions without the formation of second phases.

3. Results and discussion

3.1. Solid-solutions of copper with Ni, Zn and Ga

X-Ray diffraction patterns of all samples and the Scanning Electron Microscope backscattered electron images of the samples with the highest concentration of solute atoms are illustrated in Figs. 2 and 3, respectively. No second phases were observed in the XRD patterns of all samples. SEM examination also confirms that the samples are homogeneous without patches resulting from possible second phases or compositional inhomogeneity (Fig. 3), indicating that the samples are solid solutions. Since all as-cast samples were made under the same condition, the strengthening discussed below should result from solution hardening without other strengthening mechanisms being involved.

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