JOURNAL OF MATERIALS SCIENCE 23 (1988) 3120–3124

Molybdenum effect on volume in Fe–Cr–Ni alloys

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By X-ray diffraction on powder specimens, we determined the unit-cell size for six face-centred-cubic Fe–Cr–Ni alloys, nominally Fe–19Cr–12Ni (at%). In these alloys, the molybdenum content ranged up to 2.4 at%. We found that molybdenum increases volume: 0.45% per at%. Usual models based on atomic volumes and elastic compressibilities fail to explain the large volume increase. We ascribe the discrepancy to changes in interatomic bonding, which we describe in terms of 3d-electron models.

1. Introduction

Foremost among a solid's most important physical properties is the atomic volume, which relates directly and inextricably to fundamental interatomic forces. The usual models of cohesion deal principally with three physical quantities: cohesive energy, bulk modulus, and atomic volume. Consider, for example, a Mie–Grüneisen interatomic potential

$$U(r) = Ar^{-n} - Br^{-m} \qquad (1)$$

where r denotes interatomic spacing; A and n are coefficients of the repulsive energy and B and m are coefficients of the attractive energy. In this model, one obtains for the bulk modulus (reciprocal compressibility) [1]

$$B_0 = V_0(\partial^2 U/\partial V^2)_{V=V_0} = mnU_0/9V_0 \qquad (2)$$

where U denotes internal energy, V volume, U_0 cohesive energy and V_0 equilibrium atomic volume. (Do not confuse B and B_0.)

More than fifty years ago, the strong effect of atomic size on solid-state alloy properties, especially solid solubility, was established by Hume-Rothery *et al.* [2–3]. Even earlier, Wasastjerna [4] and Goldschmidt [5] had realized the importance of establishing the elements' atomic radii. Pauling [6] found the concept of atomic radius essential for understanding molecular and crystal structures, which play vital roles in determining properties. Pauling [7] argued that a resonating-covalent-bond concept combined with atomic radii gives qualitative explanations of many properties: magnetic, heat capacity, hardness, compressibility, and thermal expansion. Waser and Pauling [8] related compressibilities and force constants to interatomic distance; they ascribed behavioural deviations to a change in bond type (electronic structure). Friedel [9] explained the non-linear volume dependence of alloys as arising from the constituents' compressibility differences. Rudman [10] reviewed the atomic volumes of the metallic elements. He reported a range of atomic volumes from 8.1 × 10^{-3} nm^3 for beryllium to 116.0 × 10^{-3} nm^3 for caesium. The 3d transition metals from chromium to nickel show a narrow range between 10.9 × 10^{-3} and 12.2 × 10^{-3} nm^3.

The atomic-volume/elastic-constant interrelationship is well established (see the Waser and Pauling study mentioned above). At least since Fuchs [11], we have known that the bulk modulus that arises from the free-electron gas varies as r^{-5}, where $V_0 = \frac{4}{3}\pi r_0^3$. Gilman [12] showed that B varies as r^{-n}, where n equals 4 for alkali metals, 4 for covalent tetrahedrally bonded crystals, 8 for fcc carbides, 4 for fluorite-type crystals, 4 for ionic crystals and 3 for solid rare gases. No simple B–r relationship arises for the transition metals. The explanation of why B decreases with increasing r clearly lies at some level more fundamental than the interatomic potential, which imposes no constraint on $[\partial^2 U(V)/(\partial V^2)]_{V=V_0}$ and V_0. If the interatomic-potential minimum shifts to another equilibrium volume, why should its curvature change?

In discussing cohesive forces in metals and alloys, Mott [13] cited experimental and theoretical reasons why the energy of an atom depends on the volume available to it rather than on the coordination number or its surroundings. Mott empahsized that atomic volume is more important than interatomic distance, which depends on coordination number.

The present study considers the volume change caused by alloying molybdenum, a body-centred-cubic element, into a face-centred-cubic Fe–Cr–Ni alloy. Iron, chromium, and nickel are 3d transition elements. Molybdenum is a 4d transition element with much larger atomic volume: V(Mo)/V(Fe) = 15.50 × 10^{-3} nm^3/11.78 × 10^{-3} nm^3 = 1.32.

2. Measurements

2.1. Materials

We obtained alloys from the research laboratory of a major molybdenum manufacturer. Table I shows their chemical compositions. Alloys were prepared in a vacuum induction furnace, cast into round ingots 13.3 cm in diameter and 21.8 cm long, cropped and forged at 1100° C to billets 7.6 cm in cross-section,

0022-2461/88 $03.00 + .12

TABLE I Chemical compositions (wt %)

Alloy	Mo	Cr	Ni	Mn	C	N	S	Si	P
1	2.05	18.5	13.8	1.05	0.021	0.180	0.004	0.30	0.002
2	2.06	18.0	12.0	1.00	0.024	0.188	0.004	0.30	0.003
3	2.98	18.2	14.0	1.02	0.022	0.188	0.005	0.30	0.002
4	3.00	18.0	11.8	1.01	0.023	0.200	0.005	0.29	0.002
5	4.02	17.9	14.2	1.00	0.022	0.196	0.004	0.30	0.002
6	4.08	18.2	12.1	1.03	0.020	0.204	0.005	0.28	0.002

rolled at 1100° C to 2.5 cm plate, annealed for 30 min at 1000° C, and water quenched. To prepare materials for X-ray diffraction, we filed the plates, sieved the powders to 0.053 to 0.150 mm, and annealed the powders in evacuated quartz ampules at 1050° C for 35 min.

2.2. X-ray diffraction

We prepared specimens by pressing the powders into viscous silicone grease in a flat sample holder. Specimens were placed in a commercial horizontally polarized Bragg–Brentano X-ray diffractometer. A 0.3 mm (0.18°) receiving slit at the goniometer radius of 22.5 cm was step scanned in 0.02° 2θ increments at 60 sec per step. The radiation consisted of Cu $K\beta(1, 3)$, wavelength $1.392\,25 \times 10^{-3}$ nm, excited at 44 kV and 40 mA. Using a germanium solid-state detector, we measured each specimen twice. During measurements, temperature varied between 307 and 310 K.

We determined peak positions by fitting to a Lorentzian

$$I = I_{\max}\left(1 + \frac{(\theta - \theta_{\max})^2}{2W^2}\right)^{-2}$$

where, $I_{\max}$ denotes maximum intensity, θ diffraction angle, and W full peak width at half-maximum intensity. We obtained nine fcc diffraction lines: 1 1 1, 2 0 0, 2 2 0, 3 1 1, 2 2 2, 4 0 0, 3 3 1, 4 2 0, 4 2 2. To determine the unit-cell size, we used the 4 2 2 diffraction line calibrated against silicon (NBS Standard Reference Material SRM-740A). For Cu $K\beta$ radiation, the 4 2 2 line appears at 143° in 2θ.

3. Results

Fig. 1 shows the principal results: measured unit-cell size, a, together with a linear-least-squares best-fit line (in nm):

$$a = a_1 + bc = 0.359\,26 + 0.053\,85c \qquad (3)$$

where a_1 denotes the zero-molybdenum intercept, b the slope $\mathrm{d}a/\mathrm{d}c$, and c the atomic fraction of molybdenum. For our purposes, we shall rewrite Equation 3 as

$$\frac{a - a_1}{ca_1} = \frac{\Delta a}{ca_1} = \frac{b}{a_1} = 0.1499 \qquad (4)$$

We shall try to estimate this quantity using simple models. For cell-size measurements, we estimate the systematic uncertainty as 6×10^{-5} nm and the random uncertainty as 1×10^{-5} nm. For the slope $\mathrm{d}a/\mathrm{d}c$, we estimate the uncertainty as 0.005 nm. From this result, it follows that the volume change equals

$$\frac{V - V_1}{cV_1} = 0.4504 \qquad (5)$$

Thus, the volume increases approximately 0.5% per atomic per cent molybdenum. If volume followed a linear rule-of-mixture, this result implies that the effective atomic volume of molybdenum exceeds the average Fe–Cr–Ni-alloy atomic volume by 45%.

In Table I, one sees two sets of alloys differing in nickel content by approximately 2%. The measurement results in Fig. 1 show a difference between the low- and high-nickel alloys. Compared with molybdenum, the nickel effect on volume is negligible; and we ignore it. Thus, the line in Fig. 1 represents the average nickel content: 13.0 wt %.

4. Discussion

First, we note that the measurements shown in Fig. 1 suggest that the nickel content affects the slope $\mathrm{d}a/\mathrm{d}c$; lower nickel content gives a lower slope. This effect is hardly unexpected. Nickel, with ten electrons outside the argon shell, represents the transition metal that differs most from molybdenum (with six outside electrons). Along with copper, nickel represents a prototype fcc metal. Thus, we expect its reluctance to accept molybdenum as a companion alloying element.

Second, we shall consider whether existing simple

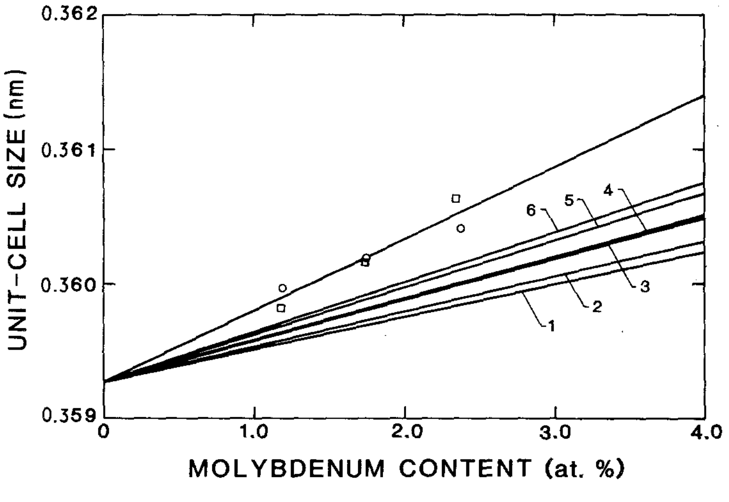

Figure 1 Compositional variation of unit-cell dimension, a. Curve through measurement points represents a linear-least-squares fit to six values. Open circles represent lower nickel alloys; open squares represent higher nickel alloys. Lower curves represent six model predictions: (1) sphere-in-hole; (2) Vegard; (3) Gschneidner and Vineyard; (4) Friedel; (5) Zener; (6) volume.

TABLE II Model predictions of $(1/a)\ (\mathrm{d}a/\mathrm{d}c)$

Model	Prediction
Sphere-in-hole	0.069
Vegard	0.073
Gschneidner and Vineyard	0.086
Friedel	0.087
Zener	0.099
Volume	0.104
Observed	0.150

models explain the volume change shown in Fig. 1. We consider six models, use them to calculate $(d - d_1)/cd_1$, (where d is the nearest-neighbour spacing) and show the results in Table II. Subscript 1 denotes the molybdenum-free Fe–Cr–Ni alloy, the reference state. Other measures of interatomic spacing include the unit-cell size, a, where

$$d = (\sqrt{2}/2)\, a \tag{6}$$

and the effective atomic volume

$$V = (4\pi/3)r^3 = a^3/4 \tag{7}$$

Among these, we find the relationships

$$\frac{\Delta d}{d} = \frac{\Delta a}{a} = \frac{\Delta r}{r} \tag{8}$$

Some of the models calculate $\Delta V/V$ rather than $\Delta d/d$. To compare these, we used the relationship

$$\frac{\Delta V}{V_1} = \frac{d^3 - d_1^3}{d_1^3} = 3\left(\frac{d - d_1}{d_1}\right) + 3\left(\frac{d - d_1}{d_1}\right)^2 + \left(\frac{d - d_1}{d_1}\right)^3 \tag{9}$$

4.1. Vegard's model

In 1921, Vegard [14] proposed that the unit-cell size follows a linear rule-of-mixture

$$d = (1 - c)d_1 + cd_2 \tag{10}$$

where the subscript 1 denotes the solvent, subscript 2 the solute, and c the atomic fraction. Thus,

$$\frac{\Delta d}{cd_1} = \frac{d_2 - d_1}{d_1} \tag{11}$$

4.2. Volume model

A simple alternative to Equation 10, which was adopted by Zen [15], substitutes atomic volume for interatomic distance

$$V = (1 - c)V_1 + cV_2 \tag{12}$$

In discussing cohesion in metals and alloys, Mott [13] argued that atomic volume rather than interatomic distance tends to remain constant. Thus,

$$\frac{\Delta d}{cd_1} \approx \frac{1}{3}\frac{\Delta V}{cV_1} = \frac{V_2 - V_1}{3cV_1} \tag{13}$$

4.3. Sphere-in-hole model

The above two models focus on atomic size and neglect atomic compressibility, or the elastic-stiffness constants. An isotropic material possesses two independent elastic constants, often chosen as bulk modulus (reciprocal compressibility) B and shear modulus G. Related to these is the Poisson ratio

$$\nu = \frac{1}{2}\frac{3B - 2G}{3B + G} \tag{14}$$

The sphere-in-hole model originated with Bitter [16] and received much elaboration by Eshelby [17]. This model simulates a point defect as either a rigid or an elastic sphere forced into a spherical cavity whose volume is smaller by $\Delta V'$. The elastic state possesses spherical symmetry with respect to the inclusions's centre. For the key equations, we take those given by Teodosiu [18]:

$$\Delta V = \frac{1 + (4G_1/3B_1)}{1 + (4G_1/3B_2)}\Delta V' \tag{15}$$

Here, $\Delta V'$ represents the solvent-atom–solute-atom volume difference:

$$\Delta V' = (4\pi/3)\,(r_2^3 - r_1^3) \tag{16}$$

4.4. Friedel model

Based on a modified Eshelby model, Friedel [9] gives the basic relationship

$$\frac{d - d_1}{cd_1} = \frac{d_2 - d_1}{d_1} + \frac{x + 1}{x + B_1/B_2} \tag{17}$$

If ν denotes the Poisson ratio defined in Equation 14 then

$$x = (1 + \nu)/[2(1 - 2\nu)] \tag{18}$$

4.5. Zener's model

Both the sphere-in-hole model and the Friedel model depend on atomic volumes and on elastic constants, the second-order elastic constants B and G. The large strains suggest that third-order elastic constants may enter the problem. In 1942, Zener [19] developed a model that contains one third-order elastic constant: $\mathrm{d}G/\mathrm{d}P$, the shear-modulus pressure derivative. Zener used an atomic-volume rule-of-mixture, Equation 12, and found two volume-change components:

$$\Delta V = \Delta V^{(1)} + \Delta V^{(2)} \tag{19}$$

The two components are given by

$$\Delta V^{(1)} = 12\pi r_1^2 \Delta r(1 - \nu_1)/(1 + \nu_1) \tag{20}$$

and

$$\Delta V^{(2)} = \frac{2\Delta r}{r_1}\left(\frac{\mathrm{d}G_1}{\mathrm{d}P} - \frac{G_1}{B_1}\right)\Delta V^{(1)} \tag{21}$$

4.6. Gschneidner–Vineyard model

Another model containing a third-order elastic constant arose in a study by Gschneidner and Vineyard [20]. They found that

$$\Delta V = c(1 - c)\, 8\pi\bar{r}(\Delta r)^2 \tag{22}$$

where

$$\bar{r} = (1 - c)r_1 + cr_2 \tag{23}$$

Note that this relationship contains a c^3 term. For dilute concentrations, $c \ll 1$, Gschneidner and Vineyard found

$$\frac{d - d_1}{cd_1} = \frac{d_2 - d_1}{d_1} + 2\left(\frac{\mathrm{d}G_1}{\mathrm{d}P} - \frac{G_1}{B_1}\right)\left(\frac{\Delta d}{d_1}\right)^2 \tag{24}$$

Table II shows results from the above six models. As input for the calculations, we used $r_1 = 0.253\,89\,\mathrm{nm}$, $r_2 = 0.272\,52\,\mathrm{nm}$, $B_1 = 158\,\mathrm{GPa}$, $B_2 = 260\,\mathrm{GPa}$, $\nu_1 = 0.275$, $G_1 = 83.5\,\mathrm{GPa}$, $G_2 = 260\,\mathrm{GPa}$, and $\mathrm{d}G/\mathrm{d}P =$

1.75. The second-order elastic constants for the molybdenum-free state were reported by Ledbetter and Kim [21] and dG/dP by Gerlich and Hart [22]. We took the remaining input from standard sources.

The results in Table II, ranging from 0.073 to 0.099, fall far below the observed value: 0.15. For molybdenum, if we adopt the Pauling radius for coordination number twelve [23], 0.2792 nm replacing 0.272 52 nm, the model calculations improve, however they remain well below observation.

The measurement-model discrepancy suggests that alloying molybdenum into Fe–Cr–Ni involves electron-structure changes. This observation contains no suprise for several reasons. First, we are placing an element that prefers the bcc structure into an fcc structure. From a chemical-bond viewpoint, an electron cloud with lobes in {1 1 1} directions must adjust to electron clouds with lobes in {1 1 0} directions [24]. Second, molybdenum represents not an ordinary bcc metal, but a paradigm. Among the 4d elements, molybdenum shows the highest melting point. Outside the metallic orbital, Pauling [23] assigns molybdenum a valence of 5.0, exactly the number of bonding electrons for maximum cohesion. The potency of molybdenum as a bcc stabilizer emerged in Pfeil's [25] studies on zirconium alloys. Altmann *et al.* [26] point out that the bcc stabilizing effect "should be more marked for molybdenum and tungsten, where we have a peak of the d weight". Altmann *et al.* also point out that, despite favourable size factors, molybdenum shows practically no solid solubility in silver, and chromium and none in copper. Thus, when alloyed into an fcc Fe–Cr–Ni alloy, we expect molybdenum to cause strong physical-property changes.

In trying to understand the physical properties of these alloys, we confront one of solid state physics's most difficult problems: quantum-mechanical theory of d electrons. Despite enormous effort – for example Mott [27], Pauling [28], Zener [29], Bader *et al.* [24], Goodenough [30], Friedel *et al.* [31] – the problem remains unsolved. Herring [32] gave an elementary critique of the state of d electrons in transition metals. He concluded that elements in the 3d row should resemble the free atoms and that most of these metals possess itinerant electrons. This reference contains Herring's much-cited remark on the electronic theories: "It is like mixing a few liquors in various proportions to get a variety of different cocktails". Mainly from the view of d-band theory, Brooks [33] reviewed the subject. In his review, Brooks disputes ideas based on crystal-field theory and separation of d levels into E_g and T_{1g} subbands. (However, a recent successful tight-binding calculation of iron's elastic constants invokes the E_g orbitals [34].)

In general, we expect that whatever increases volume will decrease cohesion and elastic stiffness. The present alloy system violates this precept. Ledbetter and Kim [21] showed that alloying molybdenum into Fe–Cr–Ni increases the bulk modulus. Thus, to understand these alloys, we must identify an electronic effect that simultaneously increases volume and increases bulk modulus, the V_0 and B_0 in Equation 2.

A theory by Ducastelle [35] leads to simple relationships for the volume and the bulk modulus. He assumed that the total energy arises from two sources: d-band energy calculated by a tight-binding approximation and Born–Mayer repulsive energy. Although this model is too simplified to explain present results, it displays the principal features necessary for an improved calculation. For the Wigner–Seitz radius, r_0, Ducastelle obtained

$$r_0 = \frac{1}{p-q} \ln \frac{pc}{qAW_0} \tag{25}$$

The bandwidth approximation is

$$W = W_0 e^{-qr} \tag{26}$$

The repulsive energy is

$$E_r = Ce^{-pr} \tag{27}$$

and

$$A = z(10-z)/20 \tag{28}$$

where, p and q are constants and z denotes the average number of electrons per atom in the d band. For the bulk modulus, Ducastelle obtained

$$\begin{aligned} B_0 &= V_0 \left(\frac{\partial^2 E}{\partial V^2} \right)_{V=V_0} = \frac{r_0^2}{9} \left(\frac{\partial^2 E_c}{\partial r_0^2} \right)_{r=r_0} \\ &= pqr_0^2 E_c/9 \end{aligned} \tag{29}$$

Thus, Ducastelle's model predicts that increased atomic volume ($V_0 = 4\pi r_0^3/3$) leads to decreased bulk modulus because E_c represents cohesive energy per unit volume.

Aside from the complications of 3d electrons, another factor arises in these alloys: magnetization. Even though the alloys show macroscopic paramagnetism, disordered local atomic moments may affect the physical properties. The usual view is that magnetization increases volume and decreases bulk modulus [36, 37]. However, several recent studies [38–41] show that the bulk modulus may increase with magnetization and increasing volume. Based on their model, Friedel and Sayers [40] expect such bulk modulus increases to occur in elements with a high electron-density-of-states, transition elements to the right: iron, cobalt, and nickel.

Another viewpoint is that molybdenum added to iron and nickel tends to form compounds. In these dilute alloys, we expect the same tendency. Thus, molybdenum increases cohesion and bulk modulus, but with ligands that impose a looser volume arrangement.

Faced with these different views, it seems reasonable to adopt an interim viewpoint. Molybdenum alloyed into fcc Fe–Cr–Ni alloys causes unspecified electronic changes that increase volume, increase resistance to dilatation, but decrease resistance to shear.

5. Summary

By X-ray diffraction, we measured the volume change accompanying molybdenum alloying into an Fe–Cr–Ni alloy. In volume, molybdenum atoms are approximately 30% larger than iron atoms. We found that molybdenum increases volume by 45%. Existing models based on atomic volume and elastic compressibility fail to explain the large volume increase. We ascribe this large increase to electronic effects associated with substituting molybdenum, which prefers a bcc crystal structure, into an f.c.c. crystal structure. Another study showed that the alloy's bulk modulus increases with increasing volume. This unexpected result – increased volume, increased bulk modulus – is consistent with some recent theoretical studies.

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Received 2 June
and accepted 16 December 1987