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Elastic constants of four Fe–Cr–Ni–Mn alloys

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Using ultrasonic methods, the complete polycrystalline elastic constants of four Fe–Cr–Ni–Mn alloys were measured. Combining these results with those reported previously for five similar alloys, the focus was on the alloying effects of chromium, nickel, and manganese. The alloys contained 16 to 23 at% chromium, 7 to 28 at% nickel, and 0 to 13 at% manganese. Only manganese produced regular effects, consistent with volume changes. Both chromium and nickel produced surprising increases in the bulk modulus and equally surprising decreases in the shear modulus. It is hypothesized that changing the bonding electrons from a d-character to an s-character explains such irregularities. The measurements were examined with Ducastelle's model, which contains two terms: a band-structure term and a repulsive-energy term.

1. Introduction

In cryogenic applications, austenitic stainless steels are used extensively for storage and handling because they resist corrosion and show relatively high strength, stability and toughness.

Austenitic stainless steels are formed by adding face-centred cubic (f.c.c.) stabilizing elements such as nickel or manganese to the Fe–Cr system. Nickel in Fe–Cr systems not only acts as a strong austenite stabilizer, it also improves the material properties [1]. Nickel shortage during World War II forced manufacturers to reduce or replace nickel with other elements such as manganese and nitrogen. Many questions arose. How do these replacements affect mechanical properties such as tensile strength, yield strength, elongation, weldability, formability, machinability and corrosion resistance? Many researchers [2–4] have considered these effects.

Elastic-constant changes caused by decreasing or replacing nickel with manganese in Fe–Cr–Ni have been studied recently [5, 6]. Elastic constants interrelate fundamental physical properties. They also provide key design parameters. For cryogenic-equipment design, for example, the thermal expansivity, β, and the thermal conductivity, κ, are important variables to consider. Both $\beta = \beta(\gamma, \rho, C_V, B)$ and $\kappa = \kappa(\theta, \rho, \gamma, T)$ can be related to the elastic constants. Here, γ is the Grüneisen parameter, ρ is the mass density, C_V is the specific heat, θ is the Debye characteristic temperature, T is the temperature and B is the bulk modulus. The elastic constants can also be closely related to plastic-deformation properties.

In this study, the elastic constants of four Fe–Cr–Ni–Mn alloys were determined. These results are combined with our previous results for five similar alloys. From the set of nine results, the alloying effects of Cr, Ni and Mn are deduced.

2. Measurements

2.1. Materials

The alloys were prepared at the Institute of Metal Research (Shenyang). Table I shows the chemical compositions. The alloys received the following heat treatments. The Fe–16Cr–28Ni alloy was annealed for 1 h at 1253 K, quenched in water to 993 K and cooled in air for 16 h. The Fe–23Cr–12Ni–5Mn alloy was annealed for 1 h at 1338 K and quenched in water. The Fe–21Cr–9Ni–9Mn and Fe–21Cr–7Ni–9Mn alloys were annealed for 1 h at 1323 K and quenched in water.

2.2. Sound-velocity measurements

Room-temperature ultrasonic velocities were determined by a pulse-echo-superposition technique. Quartz piezoelectric crystals with fundamental resonances between 3 and 9 MHz were used as transducers. X-cut and ac-cut transducers were used to produce longitudinal and shear waves. A transducer was rigidly cemented to a specimen's flat and parallel surface using phenyl salicylate as the bonding agent. The experimental details and the methods of obtaining the correct transit time are reported in [7]. The ultrasonic sound velocity, v, was computed from

$$v = \frac{2l}{t} \tag{1}$$

Here, l denotes the specimen length and t denotes the round-trip transit time.

2.3. Density measurement

The specimen's density was determined using distilled water as a standard and Archimedes's method.

$$\rho = \frac{\rho_w}{1 - (m_w/m_a)} \tag{2}$$

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TABLE I Chemical compositions

Alloy	Chemical composition (at %)													
	Cr	Ni	Mn	N	C	Si	P	S	Mo	V	Cu	Al	Ti	Fe
Fe-16Cr-28Ni-0Mn[a]	16.36	28.08	0.19	< 0.02	0.11	0.34	0.02	0.01	0.89	0.29	-	0.41	2.16	Balance
Fe-23Cr-12Ni-5Mn[b]	23.48	12.04	4.97	1.22	0.21	0.57	0.04	0.01	1.49	0.24	-	-	-	Balance
Fe-21Cr-9Ni-9Mn	20.62	8.86	8.94	0.97	0.14	0.64	0.03	0.01	-	-	0.05	0.14	0.06	Balance
Fe-21Cr-7Ni-9Mn	21.36	7.05	9.07	1.01	0.17	0.99	0.04	< 0.01	-	-	0.07	< 0.06	0.06	Balance

[a] Also contains 0.01 at % B.
[b] Also contains 0.17 at % Nb.

Here, ρ_w is the density of water, m_w is the specimen mass in water and m_a is the specimen mass in air.

3. Results

The elastic moduli are related to the longitudinal and transverse sound velocities, v_l and v_t by

longitudinal modulus

$$C_l = \rho(v_l)^2 \tag{3}$$

shear modulus

$$G = \rho(v_t)^2 \tag{4}$$

Young's modulus

$$E = \frac{3\rho(v_t)^2(v_l)^2 - \frac{4}{3}(v_t)^2}{(v_l)^2 - (v_t)^2} \tag{5}$$

bulk modulus

$$B = \rho[(v_l)^2 - \tfrac{4}{3}(v_t)^2] \tag{6}$$

Poisson's ratio

$$\nu = \frac{1}{2}\frac{(v_l)^2 - 2(v_t)^2}{(v_l)^2 - (v_t)^2} \tag{7}$$

Table II shows the room-temperature elastic constants and mass density.

The estimated error in the velocity measurements is $d(\ln v) = [(d(\ln l))^2 + (d(\ln t))^2]^{1/2}$. For both v_l and v_t, $|d(\ln v)| < 0.08\%$ is expected. For mass-density measurements, it was estimated that $|d(\ln \rho)| < 0.01\%$. The uncertainties in the elastic moduli are therefore

$$\begin{aligned}\tfrac{3}{2}|d(\ln C_l)| &= |d(\ln G)| \simeq |d(\ln B)| \simeq |d(\ln E)| \\ &\simeq \tfrac{1}{2}|d(\ln \nu)| < 0.3\%\end{aligned}$$

By linear least-squares analysis, $C = C_0 + ax_{Cr} + bx_{Ni} + cx_{Mn} + e$ (where e is the residual error associated with the response C), the separate effects of chromium, nickel, and manganese were determined. Table III shows the results, which reflect the measured values when corrected for both C + N and Mo content using results reported previously [8, 9]. The mean square error, s^2, is calculated from the error sum of squares with five degrees of freedom; s^2 for C_l, G, B, E and ν is 3.89, 2.70, 11.9, 10.1 and 5.6×10^{-5}, respectively. Variations in the other alloying elements were neglected.

4. Discussion

A simple sphere-in-hole model (Bitter [10], Eshelby [11]) leads to the expected elastic-stiffness changes related to volume changes, dV. Focusing on the bulk and shear moduli, it follows that for these materials [8]

$$\frac{\Delta B}{B} = -1.69\frac{dV}{V} \tag{8}$$

and

$$\frac{\Delta G}{G} = -2.06\frac{dV}{V} \tag{9}$$

taking $\nu = 0.290$ and the values of the other parameters as reported previously [8]. From the values in Table IV it is expected that Mn will lower the values of B and G, that chromium will cause a smaller reduction and that nickel will increase the values of both B and G. Four of these six expectations are met. Against expectation, chromium increases the value of B, and nickel decreases the value of G. Thus, a simple

TABLE II Elastic constants of Fe-Cr-Ni-Mn alloys corrected for C + N and Mo

Alloy	Density ($kg\,m^{-3}$)	C_l (GPa)	G (GPa)	B (GPa)	E (GPa)	ν
Fe-16Cr-28Ni-0Mn	8029	269.1	72.77	172.2	191.5	0.3149
Fe-23Cr-12Ni-5Mn	7879	259.8	72.96	162.6	190.3	0.3048
Fe-20Cr-9Ni-9Mn	7825	253.8	76.94	151.2	197.3	0.2826
Fe-21Cr-7Ni-9Mn	7802	254.9	76.51	153.0	196.7	0.2858
Fe-19Cr-1Ni-12Mn	7734	253.3	74.7	153.7	192.8	0.291
Fe-19Cr-3Ni-13Mn	7817	247.2	75.1	147.1	192.6	0.282
Fe-22Cr-6Ni-9Mn	7838	252.8	75.4	152.3	194.1	0.288
Fe-22Cr-12Ni-5Mn	7884	257.9	73.9	159.4	192.1	0.299
Fe-20Cr-9Ni-2Mn	7860	260.5	77.7	156.9	200.1	0.287

TABLE III Compositional variation of the elastic constants based on nine Fe–Cr–Ni–Mn alloys: $C = C_0 + ax_{Cr} + bx_{Ni} + cx_{Mn}$; x in at %; C_0 and a, b, c are in GPa; ν is dimensionless

C	C_0	ax $1000C_0$	bx $1000C_0$	cx $1000C_0$
C_l	264.7	− 0.7682	1.025	− 3.526
G	84.11	− 2.556	− 3.190	− 3.412
B	152.3	0.5837	4.180	− 3.569
E	213.9	− 2.203	− 2.354	− 3.495
ν	0.2651	2.675	4.946	0.2591

TABLE IV The properties of the constituent atoms and one reference alloy

	V (nm^3)	B (GPa)	E (GPa)	G (GPa)	ν
Fe	0.01170	166.9	212.4	82.4	0.288
Cr	0.01194	161.9	279.5	115.3	0.212
Ni	0.01087	186.0	220.6	84.7	0.302
Mn	0.01222	124.4	197.7	76.5	0.292
Fe–18Cr–8Ni[a]	0.01159	158.2	199.6	77.4	0.290

[a] [7, 12].

sphere-in-hole model, based on volume, fails to explain the alloy behaviour. This suggests strong electronic changes.

The effect of manganese, for B and G, is similar to that found previously for the Fe–Cr–Ni alloys [13] where manganese varied up to 6 at %. Those alloys contained a lower nitrogen content, averaging at 0.6 at %. Despite the many peculiar elemental properties of manganese, including a large change of this system's Néel temperature [14], it affects the elastic properties in a regular, expected way. It is interesting that manganese contains seven bonding electrons which is close to the alloy's number of 7.8. Thus, among all possible d-electron alloying elements, manganese may least disrupt the alloy's electronic structure. As discussed by Pettifor [15], manganese prefers a close-packed hexagonal (c. p. h.) or an f. c. c. crystal structure to a body-centred cubic (b. c. c.) crystal structure.

Considering chromium the unexpected result is found that B increases and that B and G change in opposite directions. Almost all elastic-constant models predict the same sign for $(1/x)$ $(\mathrm{d}B/B)$ and $(1/x)$ $(\mathrm{d}G/G)$. A sign difference signals an interatomic-bonding change that affects (in this case) the dilatational modes more than the shear modes. Ledbetter and Kim [9] reported similar behaviour for molybdenum alloyed into Fe–Cr–Ni. Chromium and molybdenum are isoelectronic; both represent b. c. c. paradigms. Both are expected to disrupt the f. c. c. electronic structure (interatomic bonds) strongly, and to produce unusual changes in the physical properties of the f. c. c. alloys. Also, note that chromium, despite possessing a shear modulus 50 per cent larger than the Fe–Cr–Ni alloy, decreases the alloy's shear modulus. Molybdenum, with a 60 per cent larger shear modulus, also decreases the alloy's shear modulus. Thus, rule-of-mixture models fail drastically for these d-electron alloys. Alloying sharply alters the electronic state.

Considering nickel, a typical f. c. c. element except for its magnetism, its alloying effects are found to be surprisingly large and hard to understand, especially the sign difference in $(1/x)$ $(\mathrm{d}B/B)$ and $(1/x)$ $(\mathrm{d}G/G)$. Again, this suggests an interatomic-bonding change, in this case affecting the shear modes more than the dilatational modes. Thus, electronically, nickel behaves differently to chromium. Even though both are 3d-electron transition metals, chromium possesses only six bonding electrons while nickel possesses ten.

The present results for nickel differ from those found in another study [16] in Fe–21Cr–xNi–9Mn (at %) where nickel varied from 4 to 11 at % and the alloys contained a lower nitrogen content, averaging at 0.8 at %. For the shear modulus, that study found $(1/x)$ $(\mathrm{d}G/G) = 0.861 \times 10^{-3}$, which is much smaller than the present result. The reason for this difference remains under study.

The irregular responses of B and G (which reflect dilatational and shear stiffness, respectively) to alloying were described above. Irregular means inconsistent with the responses expected from volume effects, Equations 8 and 9. Some understanding of these irregular responses can be achieved by realizing that B and G mainly reflect changes in the s-electrons and the d-electrons, respectively. The s-electrons represent a wide, spherically symmetrical distribution. In contrast, the d-electrons represent a narrow, localized, highly directional distribution. The shear modulus, G, represents resistance to changes in interatomic-bond angles (the d-electrons). The bulk modulus, B, represents resistance to changes in interatomic-bond lengths (both in s-electrons and d-electrons). For transition metals, Pettifor [17] showed that the bulk modulus arises largely from the s-electron contribution, a contribution enhanced strongly by the ion-core orthogonality constraint. Pettifor also emphasized that the s-electrons figure prominently in transition-metal cohesion; they provide a repulsive pressure that counters the strong d-electron attraction. Thus, the d-electrons often contribute negatively to the bulk modulus. The negative contribution of d-electrons to the bulk modulus also arises in the renormalized-atom transition-metal cohesive-energy model of Gelatt *et al.* [18]. They found four components for the cohesive energy, $E(r)$: (i) renormalization energy, (ii) s-band formation energy, (iii) d-band broadening energy, and (iv) s–d hybridization energy. Combined and expressed as $E(r)$, the last two terms show a negative curvature with r. The bulk modulus is related to $E(r)$ by the following equation [19]

$$B = \frac{1}{12\pi r_0}\left(\frac{\partial^2 E(r)}{\partial r^2} - \frac{2}{r}\frac{\partial E(r)}{\partial r}\right)_{r=r_0} \qquad (10)$$

The renormalization and s-band terms show a positive curvature; thus they contribute positively to B. As electrons change from a d-character to an s-character, the bulk modulus is expected to increase and the shear modulus to decrease. The present study shows that both chromium and nickel cause such changes. A previous study [9] showed the same result for molybdenum. It remains undetermined whether changing the d-electron character from e_g to t_{2g} [20] affects the elastic constants. These two subbands possess a different wave-function symmetry. The e_g subband shows six lobes along $\langle 1\,1\,1\rangle$ directions. For these f.c.c. alloys, the Young's modulus maxima occur along the $\langle 1\,1\,1\rangle$ directions.

The opposite changes in the bulk and shear moduli suggest focusing on the Poisson's ratio

$$\nu = \frac{1}{2}\frac{3B - 2G}{3B + G} \tag{11}$$

In differential form

$$\begin{aligned}\frac{\mathrm{d}\nu}{\nu} &= \frac{9BG}{(3B+G)(3B-2G)}\left(\frac{\mathrm{d}B}{B} - \frac{\mathrm{d}G}{G}\right)\\ &= 0.624\left(\frac{\mathrm{d}B}{B} - \frac{\mathrm{d}G}{G}\right)\end{aligned} \tag{12}$$

The factor 0.624 applies to the Fe–18Cr–8Ni reference alloy. From Equation 12, the opposite changes in B and G combine to produce a larger $\mathrm{d}\nu/\nu$. This reminds the authors of the Köster–Franz [21] view that "Poisson's ratio depends to a much greater extent on the conditions of bonding than do the other elastic constants." Considering the Voigt bound, Ducastelle [22] derived the following simple relationship:

$$\nu_V = \frac{1}{2}\frac{3-\bar{x}}{6-7\bar{x}} \tag{13}$$

Here, $\bar{x} = q/p$, the ratio of the band-structure-energy and repulsive-energy exponential coefficients, with $p > q$. This model can be extended to the Reuss bound:

$$\nu_R = \frac{9-4\bar{x}}{33-38\bar{x}} \tag{14}$$

Finally, the physically more realistic Hill-model result can be obtained:

$$\nu_H = \frac{87-34\bar{x}}{333-386\bar{x}} \tag{15}$$

Solving for $\bar{x}$

$$\bar{x} = \frac{333\nu - 87}{386\nu - 34} \tag{16}$$

Thus, the Poisson's ratio leads directly to the Ducastelle-model q/p ratio, which gives the relative contribution of the band-structure energy, U_b, and the repulsive energy, U_r, to cohesion [9]:

$$\left|\frac{U_b}{U_r}\right| = \frac{p}{q} \tag{17}$$

Ducastelle's model represents almost the simplest possible equilibrium model of a transition metal with two terms: a repulsive term and an attractive band-structure term. Better models have more terms. For example, the renormalized-atom model of Gelatt *et al.* contains four principal energy terms. Positive contributions to the bulk modulus arise from two terms: a renormalization and an s-band term. The renormalization energy relates to the free-atom wave functions. The s-band energy is given by

$$\Delta E_s = E_0 + \tfrac{3}{5}E_f - E_s^r \tag{18}$$

Here, E_0 denotes the bottom of the s-band, E_f denotes the Fermi energy, and E_s^r denotes the renormalized-atom, one-electron energy. Negative contributions to the bulk modulus arise from the combined d-band broadening and s–d-hybridization. Neither the renormalization energy nor the d-band terms show large curvature near the equilibrium volume. Thus, the s-band term dominates the bulk modulus. However, for copper, for example, considering only Equation 18 predicts a bulk modulus which is approximately 50% too high. Thus, the d-band terms, which contribute negatively, cannot be neglected. The large positive curvatures of E_0 and E_f near the equilibrium volume result from an effective compression caused by s–d-hybridization. (In the 3d-row, potassium and copper possess atomic volumes of 0.0714 and 0.0117 nm^3, respectively!)

Table V shows the results of fitting Ducastelle's model for our nine alloys to an 18Cr–8Ni alloy [7], and to seven f.c.c. elements. Columns 2–4 show the

TABLE V Ducastelle-model parameters

Material	ν	B (GPa)	U (GJ m^{-3})	U_b/U	B_b/B	q/p	$(p+q)r$	pqr^2
Ag	0.364	101.2	27.8	0.76	0.30	0.32	13.3	32.7
Au	0.424	173.5	35.9	0.71	0.34	0.42	14.5	43.5
Co	0.310	188.9	63.8	0.84	0.23	0.19	14.1	26.6
Cu	0.341	135.3	47.5	0.79	0.28	0.27	12.3	25.6
Fe	0.314	188.3	58.7	0.83	0.24	0.20	14.4	28.9
Ni	0.302	186.0	65.0	0.86	0.22	0.17	14.6	25.8
Pt	0.395	282.7	62.2	0.73	0.32	0.38	14.4	40.9
Fe–18Cr–8Ni	0.290	158.2	58.6	0.89	0.19	0.12	15.8	24.3
Alloy 1	0.315	172.2	59.5	0.83	0.24	0.20	13.6	26.1
Alloy 2	0.305	162.6	58.1	0.85	0.23	0.17	14.2	25.2
Alloy 3	0.283	151.2	58.4	0.91	0.16	0.09	17.2	23.3
Alloy 4	0.286	153.0	58.2	0.90	0.18	0.11	16.5	23.7
Alloy 5	0.291	153.7	57.8	0.89	0.19	0.13	15.5	23.9
Alloy 6	0.282	147.1	57.9	0.92	0.16	0.09	17.2	22.9
Alloy 7	0.288	152.3	58.2	0.90	0.18	0.12	15.9	23.6
Alloy 8	0.299	159.4	58.1	0.87	0.21	0.15	14.6	24.7
Alloy 9	0.287	156.9	58.7	0.90	0.18	0.11	16.3	24.1

input: ν is the Poisson's ratio, B the bulk modulus and U the cohesive energy. Columns 5 and 6 show the percentage band-structure contributions to U and to B. Columns 7–9 show various forms of the p and q coefficients. As described by Fürth [23], pqr^2 correlates with harmonic properties such as the bulk modulus; and $(p+q)r$ correlates with anharmonic properties such as the thermal expansivity, the thermal-expansivity temperature derivative, the bulk-modulus temperature derivative, and the bulk-modulus pressure derivative.

Although the band-structure energy dominates the cohesive energy, it contributes only 16 to 34% to the bulk modulus. For our nine alloys, a larger variation was noted in $(p+q)r$ than in pqr^2. Thus, these alloys would show larger variations in thermal expansivity than in elastic stiffness, and the usual elastic-stiffness/thermal-expansivity empirical interrelationships should be less reliable.

5. Conclusions

Four conclusions were reached concerning the elastic constants of these quaternary Fe–Cr–Ni–Mn alloys.

1. Manganese lowers all the elastic stiffnesses and the Poisson's ratio. This agrees with expectations based on volume changes.

2. Both chromium and nickel increase the bulk modulus and decrease the shear modulus. This agrees with results reported previously for molybdenum. Such opposite alloying effects for B and G disagree with most theoretical models. A qualitative explanation arises by invoking a change in bonding electrons from a d-character to an s-character.

3. The strong nickel alloying effects differ from those found previously for lower nickel concentrations.

4. Except for manganese, which behaved regularly, the other alloying elements, chromium and nickel, caused unusually large changes in the Poisson's ratio, an elastic constant that reflects changes in the type of interatomic bonding.

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