

Thermoelastic properties of 350 grade maraging steel

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The elastic moduli of 350 grade maraging steel in the annealed and hardened states have been determined in the temperature range 4.2 to 300 K. Thermal expansion of these steels and pure iron are given for the range 2 to 800 K. The elastic moduli show a normal temperature dependence, increasing with decreasing temperature, and a zero temperature derivative at 0 K. The low-temperature thermal expansion coefficient is the sum of a linear and cubic term, the former having a negative sign for the steels, which is probably due to magnetic effects. The elastic moduli increase by about 10% on hardening, and this increase is correlated with the structural changes caused by the hardening process.

1. Introduction

The thermoelastic properties of austenitic stainless steels have been investigated extensively over the past years [1, 2]. A number of them exhibit striking anomalies at low temperatures ascribed to magnetic interactions between the iron, chromium and nickel atoms [1, 2]. Another class of very important structural materials are the maraging steels [3]. Their main constituents are iron, nickel, cobalt and molybdenum, and they are already martensitic in the annealed (soft) state. The hardening is achieved by a precipitation process, presumably of Ni_3Mo [3]. Their advantages as structural materials are their high degree of hardness, strength and toughness, as well as their very simple hardening procedure (heating in air at 485°C for 3 h [4]). The elastic moduli and their temperature dependence between 77 and 400 K for grades 200, 250 and 300 maraging steel have recently been reported by Ledbetter and co-workers [5, 6].

The present paper describes measurements of the elastic moduli from 4.2 K to room temperature and the thermal expansion between 2 and 800 K for annealed and hardened grade 350 maraging steel. Thus the effect of the hardening process on the elastic moduli and the thermal expansion may be explored. For comparison we have also measured the thermal expansion of pure iron as there was a lack of data, particularly below 300 K.

2. Experimental details

The maraging steel was obtained from a commercial source [4] and contained (wt %) 63 Fe, 18.5 Ni, 12.0 Co, 4.8 Mo, 1.4 Ti and 0.1% each of Al, Si and Mn.

The elastic moduli were determined by measuring velocities of ultrasonic longitudinal and shear waves in cylinders 15 mm long \times 20 mm diameter. The ultrasonic waves were generated by means of crystal-line quartz transducers, operating at 10 MHz. At

room temperature, phenyl salicylate (salol) was used as the bonding agent, while at low temperatures, petroleum ether was employed. The sound velocities were measured by a pulse echo system, utilizing unrectified waves [7].

In the temperature range 2 to 77 K, the thermal expansion was determined in a three terminal capacitance dilatometer [8] on cylinders 50 mm long \times \sim 20 mm diameter. In the range 77 to 300 K a push-rod dilatometer was employed [9] and at higher temperatures a commercial silica push-rod dilatometer (Adamel Lhomargy, France) was used with samples of 50 mm length \times 6 mm diameter. The iron was spark-cut from the same 99.95% Fe used in earlier work [10].

3. Results

The sound velocities and the resulting elastic moduli for the annealed and hardened steels at room temperature are compared with iron [11] in Table I. v_L and v_T are the velocities of the longitudinal and shear waves, c_L and G the longitudinal and shear elastic moduli, defined as ρv_L^2 and ρv_T^2 , ρ being the density (8100 kg m^{-3} at 300 K). $B (= c_L - 4G/3)$, E and σ are, respectively, the bulk modulus, Young's modulus and Poisson's ratio. No distinction is made between adiabatic and isothermal moduli, because the difference is much smaller than the experimental error. As can be seen, the process of hardening causes c_L and G to increase by about 10%. A similar effect is also observed in the other grades of maraging steel [6], and the change becomes larger on going from 200 to 350 grade.

In Figs 1 and 2, the temperature dependences of c_L and G are shown in the annealed and hardened state, respectively. The dots are the measured data points, while the lines are a non-linear least-squares fit [12] to the Varshni equation [13]. The temperature

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TABLE I Sound velocities and elastic moduli at room temperature for annealed and hardened 350 maraging steel (iron data included for comparison)

	v_T (10^3 m sec^{-1})	v_L (10^3 m sec^{-1})	G (GPa)	c_L (GPa)	B (GPa)	E (GPa)	σ
Annealed	2.810	5.586	63.17	249.6	165.4	168.1	0.33
Hardened	3.010	5.783	72.51	270.9	174.2	191.0	0.32
Iron (approx)	3.25	5.96	84	284	168	215	0.29

dependence in both states is normal, a small increase with decreasing temperature, and a zero derivative at 0 K. The low-temperature anomalies found in the temperature dependence of the elastic moduli of the austenitic stainless steels [1] 304 and 316 are absent here.

The smoothed values of the linear expansion coefficient, α , are shown in Fig. 3 and Table II. At temperatures below 20 K, corresponding to $T < 0.04\theta_D$ (θ_D is Debye characteristic temperature), we also plot α/T against T^2 in order to separate the lattice vibrational and electronic contributions (Fig. 4). The steel data may be represented in the range 2 to 20 K by expressions

$$\alpha = -7 \times 10^{-10} T + 13.5 \times 10^{-12} T^3 \text{ (annealed)} \quad (1)$$

$$\alpha = -28 \times 10^{-10} T + 9.8 \times 10^{-12} T^3 \text{ (hardened)} \quad (2)$$

compared with

$$\alpha = +32 \times 10^{-10} T + 7.5 \times 10^{-12} T^3 \text{ (for pure iron)} \quad (3)$$

4. Discussion

4.1. Thermal expansion

At normal temperatures, the coefficient $\alpha(T)$ for the maraging steels is about 10% smaller than for pure iron, while the bulk modulus is rather similar to that of iron. At low temperature the α behaviour is more complicated and below 10 or 20 K there is evidence of negative expansivity in the alloys. Negative values occur in many Fe-Ni-Cr (and Mn-) alloys and are usually attributed to magnetostrictive effects [2]. They are often sensitive to small changes in composition [10]. In some alloys, notably 304 stainless steel, there appears to be an additional contribution to α due to

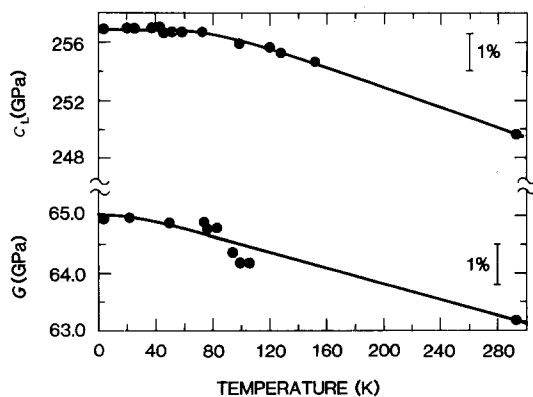


Figure 1 Longitudinal and shear elastic moduli as a function of temperature for annealed 350 maraging steel.

magnetic clustering which causes departures from the $AT + BT^3$ dependence mentioned above. This is not apparent in the present Fe-Ni-Co-Mo alloys.

Values of the Grüneisen parameter

$$\gamma = 3\alpha B^s V/C_p \quad (4)$$

where B^s is the adiabatic bulk modulus and C_p is the heat capacity at constant pressure per volume, V , cannot be calculated accurately as we have no heat-capacity data on the alloys. At room temperature, we may suppose C_p is similar to that of iron [14, 15], and hence deduce $\gamma \approx 1.4_5$.

We can also calculate a limiting value, θ_0 , for the Debye temperature from the measured elastic moduli using

$$\theta_0 = \frac{h}{k} \left(\frac{3 N \rho}{4\pi M} \right)^{1/3} v_a \quad (5)$$

where the average sound velocity

$$v_a = \left[\frac{1}{3} \left(\frac{2}{v_T^3} + \frac{1}{v_L^3} \right) \right]^{-1/3} \quad (6)$$

Thence $v_a = 3.15 \text{ km sec}^{-1}$ for annealed and 3.37 km sec^{-1} for hardened steel.

Using $\rho = 8.1 \text{ g cm}^{-3}$, $M = 57$, $N = 6 \times 10^{23}$ atoms/mole we calculate $\theta_0 = 411 \text{ K}$ for annealed and 440 K for hardened steel (cf $\theta_0 \approx 470 \text{ K}$ for Fe). We may use these values of θ_0 to calculate the lattice contributions to the heat capacity in the low-

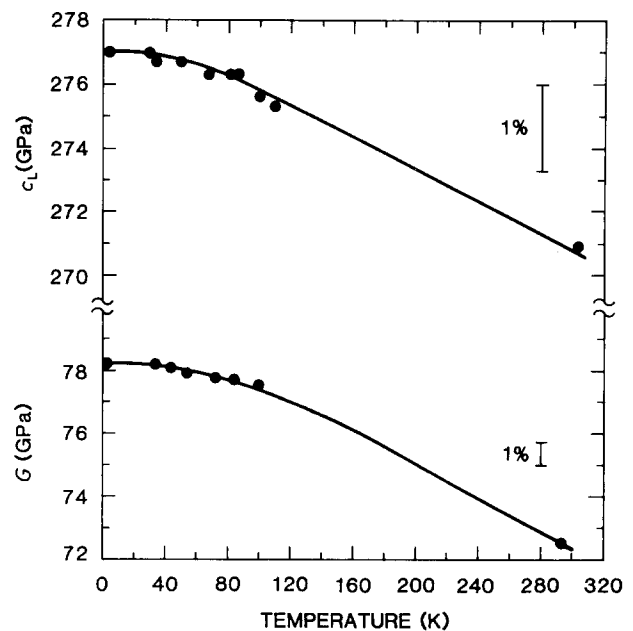


Figure 2 Longitudinal and shear elastic moduli as a function of temperature for hardened 350 maraging steel.

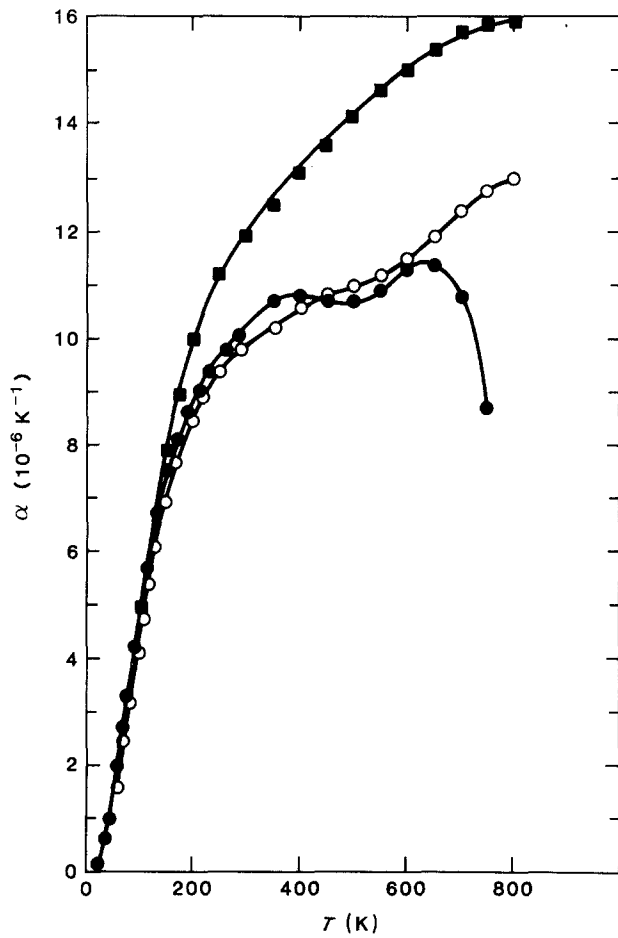


Figure 3 Linear thermal expansion coefficient as a function of temperature for (●) annealed and (○) hardened 350 maraging steel and (■) iron.

temperature limit from the Debye expression

$$c_L \approx 1944(VT/\theta_0)^3 \quad (7)$$

and compare these T^3 terms with the equivalent terms in the $\alpha(T)$ polynomial. These lead to limiting values

TABLE II Linear thermal expansion coefficient as a function of temperature for 350 maraging steel

Temperature (K)	Linear thermal expansion coefficient ($10^6 K^{-1}$)		Iron
	350 maraging		
	Annealed	Hardened	
3	-0.0015	-0.0081	0.0100
5	-0.0020	-0.0130	0.0167
10	0.0058	-0.0190	0.039
15	0.035	-0.0111	0.073
20	0.095	0.024	0.123
30	0.345	0.211	0.310
40	0.81	0.61	0.71
50	(1.50)	1.10	(1.4)
75	3.35	3.05	3.45
100	5.0	4.7	5.45
150	7.6	7.3	7.9
200	8.9	8.6	10.0
250	9.7	9.5	11.2
293	10.1	9.8	11.8
400	10.8	10.6	13.1
500	10.7	11.0	14.1
600	11.3	11.5	15.0
700	10.8	12.4	15.7
800	~6	13.0	15.9

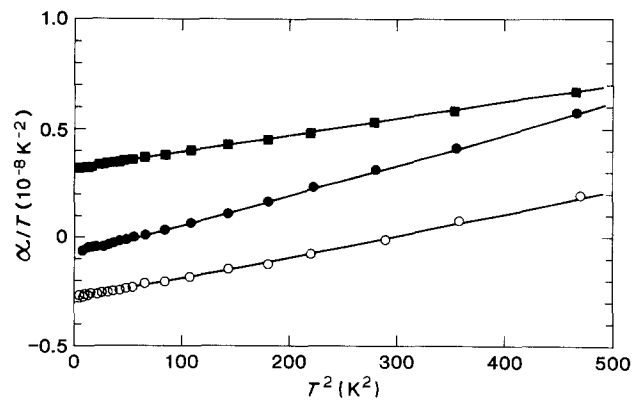


Figure 4 Plot of α/T against T^2 in the low-temperature range for (●) annealed and (○) hardened 350 maraging steel and (■) iron.

of the lattice Grüneisen parameter of ~ 1.7 (annealed Marsteel), 1.6 (hardened) and 1.4_s (Fe).

It is apparent that magnetic interactions are responsible for the differences in behaviour of $\alpha(T)$ at low temperatures compared with iron. The negative component is not as marked as in invar [10] or in some 18/8 stainless steels [2] but is clearly sensitive to the amount of nickel in solution. Hardening increases the negative component considerably (Fig. 4).

We note that the high-temperature values of α do not represent true equilibrium conditions. Particularly in the case of the annealed material, on heating above about 500 K the precipitation processes are in progress while the sample is being measured. Hence the result obtained is dependent on heating rate (in this case $2 K min^{-1}$).

4.2. Hardening effects

Hardening causes an increase in c_L and G in all four grades, 200, 250, 300 and 350, the effect becoming larger on going from 200 to 350 [5, 6], being the order of 10% in the case of 350 maraging steel. Most investigators claim that the hardening process causes Ni_3Mo to precipitate on dislocations which were formed during the martensitic transformation [3, 16]. Assuming that in the annealed state all the nickel, cobalt and molybdenum are in solution, while on hardening all the molybdenum and part of the nickel precipitate as Ni_3Mo , one may try to correlate the measured changes in the elastic moduli and α , by invoking simple models suggested by Zener [17] and Klemens [18].

Zener's model ascribes the lowering of the elastic modulus to the residual strain energy during solution caused by the difference in size between the solute and solvent atoms [17]. Because the atomic radii of iron and nickel are very close (0.128 and 0.125 nm), all of the effect may reasonably be ascribed to the molybdenum atoms (0.140 nm atomic radius) [19]. The change in the elastic modulus, M , of the solvent matrix on alloying, may be related to the temperature derivative of M as follows [17]

$$\frac{1}{M} \frac{\partial M}{\partial c} = 4 \left(\frac{\Delta R^2}{R} \right) (Nk_B)^{-1} \frac{\partial M}{\partial T} \quad (8)$$

where c is the atomic fraction of the solute, N the total number of atoms in the sample, R the atomic radius of

TABLE III Calculated and measured changes in G and E due to hardening for four maraging steels.

Material	$\frac{\partial G}{\partial T}$ (10^7 Pa K^{-1})	$\frac{\partial E}{\partial T}$ (10^7 Pa K^{-1})	$\frac{1}{G} \frac{\partial G}{\partial c}$ calc.	$\frac{1}{E} \frac{\partial E}{\partial c}$ calc.	$\frac{1}{G} \frac{\partial G}{\partial c}$ meas.	$\frac{1}{E} \frac{\partial E}{\partial c}$ meas.
200	-2.15	-5.30	-0.64	-1.58	-2.35	-2.05
250	-2.25	-5.45	-0.82	-1.62	-2.73	-2.45
300	-2.20	-5.40	-0.66	-1.61	-3.39	-3.07
350	-2.97	-6.35	-0.93	-1.95	-4.09	-4.12

the solvent, and ΔR the difference between the atomic radii of solvent and solute. Measured and calculated values from Equation 8 for G and E in various grades of maraging steel are shown in Table III. As can be seen, the agreement is within a factor of 2 to 4. This is of the same order of magnitude as in the data for the various copper alloys [20] on which Zener's model was based.

We can only speculate on the reasons for the small differences in α as there are at least three contributing factors. Firstly, an increase in bulk modulus will have the effect of reducing the expansivity if other factors remain unchanged. That is, if the internal pressure generated by temperature changes due to anharmonic or electron effects is similar for annealed and hardened materials, then α will be controlled by B as seen in the Grüneisen relation (Equation 4). Secondly, the magnetostrictive effect chosen clearly at low temperatures may persist at ambient temperatures and reduce α for the hardened material. Thirdly, we can consider the hardened material as a composite consisting of a Fe-Ni-Co matrix containing inclusions of Ni_3Mo . If these inclusions have a smaller expansivity, then this will reduce α for the composite to an extent roughly proportional to the volume fraction [18].

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