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Effects of alloying elements on hardness improvement and damping capacity of low thermal expansion cast irons

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The effects of alloying elements vanadium and molybdenum on hardness and the linear thermal expansion coefficient of the Invar-type austenitic cast irons were investigated. A combined addition of vanadium and molybdenum was found to be the most effective for the improvement of hardness without causing an increase in the thermal expansion coefficient. Without heat treatment, the hardness value increased up to 180 HB, and the thermal expansion coefficient was kept at a relatively low value of $4.6 \times 10^{-6}\ K^{-1}$ with a combined addition of 4.6 wt% V and 3.8 wt% Mo. The effects on the damping capacity of graphite morphology, the magnetic domain, and the combined addition of vanadium and molybdenum were also investigated. The good damping capacity of Invar-type cast irons was mainly the result of stress absorption in graphite. As the amounts of vanadium and molybdenum increased, the damping capacity decreased. This is caused by an increase in the amount of carbides. © *1998 Kluwer Academic Publishers*

1. Introduction

It is well known that Invar and Superinvar alloys have low thermal expansion coefficients. As the temperature increases, most metallic alloys show volumetric expansion due to the inharmonic thermal vibration effect of the crystal lattice. The linear expansion coefficient, α, of Invar alloys is about $1.2 \times 10^{-6}\ K^{-1}$ at room temperature, while those of common steel and iron alloys are in the range of $10\text{–}20 \times 10^{-6}\ K^{-1}$. In the case of Invar alloys, volume contraction occurs, due to a spontaneous magnetostriction below the Curie temperature, which results in a low thermal expansion coefficient [1].

Austenitic cast irons containing carbon and silicon exhibit relatively low thermal expansion coefficients, which are in the range of one-half to one-third of those for common cast irons and steel castings. Furthermore, these types of alloyed cast irons have other useful engineering properties, such as good castability, machinability and vibration damping capacity, while their hardness is relatively low.

Recently, several studies have focused on the development of new cast materials, which have both thermal expansion coefficients and appropriate mechanical properties [2]. Cast irons containing a high nickel content, similar to that of Invar, are being considered for practical applications as machine tool parts because of their excellent properties, such as low thermal expansion characteristics and good castability, in spite of their poor mechanical properties caused by high graphite content [3].

However, no work has been carried out to solve the problem of low hardness in Invar-type cast irons. The hardness of austenitic flake graphite cast irons is in the range of 90–140 HB. Hence, in order to use austenitic cast iron for machine tool parts, its low hardness due to the austenite matrix should be improved. In addition, in cases of structural materials used in dynamic states, the vibrational damping capacity is one of the most important characteristics to be considered. It is, therefore, necessary to analyse the relationship between the effect of alloying elements on hardness and the damping capacity of these alloys.

In the present study, the effects of alloying elements on the hardness of austenitic cast irons were investigated in regard to thermal expansion characteristics and vibration damping capacity. In order to improve hardness without causing an increase in the thermal expansion coefficient, the effects of the combined use of vanadium and molybdenum were also investigated.

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2. Experimental procedure

Two strengthening mechanisms on the austenite matrix can be considered: interstitial and the substitutional solid-solution hardening. In general, the reinforcing effect of interstitial atoms on the austenite matrix is considered to be superior to that of substitutional atoms. However, strengthening by interstitial atoms results in a harmful effect on magnetic properties and thermal expansion characteristics. In this study, substitutional carbide-forming elements were chosen as alloying elements for improving the hardness of austenitic cast irons, because they have low solubility in the austenite matrix.

Austenitic cast irons were produced from pure iron, pig iron, electrolytic nickel and ferroalloys using a high-frequency roll-over induction furnace. Argon gas was used for purging during the melting process to prevent surface oxidation of the molten metal. After detecting the pouring temperature by a dip–tip type thermocouple, a sand mould was placed over the furnace crucible and clamped. Then, pouring was completed by turning the crucible over. A stepped block cast specimen was made in order to observe the effects of the cooling rate on graphite size and damping capacity.

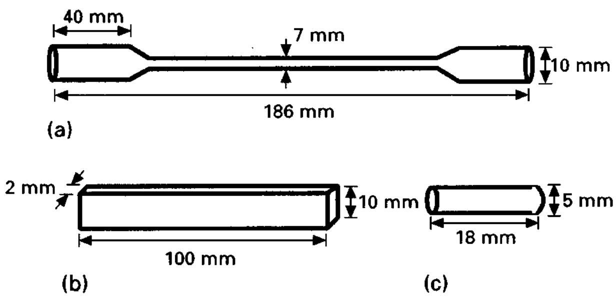

Figure 1 Geometries of the test specimens for the measurement of (a) specific damping capacity, (b) Young's modulus, and (c) thermal expansion coefficient.

The shape and dimensions of the various specimens are shown in Fig. 1. Hardness was measured by the Brinell Hardness Tester (load 1000 kg, steel ball 10 mm diameter, and time 30 s). The test specimens were cut and prepared for microstructural observation by polishing and etching with 3% Nital or 5% Picral +2% Nital. Microstructures were observed using an optical microscope and scanning electron microscopy. A wavelength-dispersive X-ray spectrometer (WDX) was used to analyse the distributions of alloying elements. The stoichiometry of the carbide was detected using an X-ray diffraction analyser (XRD) with CuK_α radiation at 40 kV and 30 mA. Linear expansion coefficients of the alloys were measured under an inert gas atmosphere using thermomechanical analyser (TMA). The heating rate between room temperature and 250 °C was 3 °C min^{-1}. Saturation magnetization of the specimen was investigated using a vibrating sample magnetometer (VSM). Table I shows the compositions of the castings.

3. Results and discussion

3.1. Effects of vanadium and molybdenum on hardness and the thermal expansion coefficient, α

As shown in Fig. 2, there is an increase in hardness with increasing molybdenum content. Molybdenum is

TABLE I Compositions (wt %) of the castings

Alloys	Ni	C	Si	Mn	V	Mo	Fe	Classification of tests
1	32.10	2.25	1.54	0.25	–	0.46	Bal.	Thermal
2	32.52	2.20	1.55	0.23	–	0.90	Bal.	expansion
3	32.37	2.25	1.65	0.24	–	1.40	Bal.	coefficient
4	32.83	2.20	1.64	0.24	–	1.77	Bal.	
5	32.67	2.16	1.64	0.24	–	2.15	Bal.	
6	32.50	2.27	1.64	0.24	–	2.65	Bal.	
7	32.49	2.22	1.55	0.24	–	2.96	Bal.	
8	32.49	2.22	1.55	0.24	–	2.96	Bal.	
9	33.80	2.35	1.15	0.21	2.08	–	Bal.	
10	33.80	2.25	1.07	0.22	–	–	Bal.	
11	33.80	2.24	1.13	0.23	0.55	–	Bal.	
12	33.80	2.26	1.02	0.22	0.83	–	Bal.	
13	33.80	2.25	1.08	0.21	1.30	–	Bal.	
14	33.80	2.30	1.14	0.23	1.98	–	Bal.	
15	34.45	2.04	1.36	0.20	3.30	2.30	Bal.	
16	34.55	2.03	1.36	0.20	3.30	2.30	Bal.	
17	35.38	1.95	1.40	0.24	4.00	2.00	Bal.	
18	33.50	2.45	1.07	0.22	–	–	Bal.	Specific
19	33.50	2.45	1.07	0.22	–	–	Bal.	damping
20	33.50	1.52	1.15	0.22	–	–	Bal.	capacity
21	33.50	1.75	1.05	0.22	–	–	Bal.	
22	33.50	2.66	1.20	0.22	–	–	Bal.	
23	33.50	2.78	1.15	0.22	–	–	Bal.	
24	33.50	2.45	1.07	0.22	–	–	Bal.	
25	33.50	2.10	1.34	0.20	2.00	2.10	Bal.	
26	33.50	2.20	1.15	0.20	–	1.90	Bal.	
27	33.50	2.20	1.15	0.20	0.55	1.78	Bal.	
28	33.50	2.20	1.15	0.20	0.93	1.91	Bal.	
29	33.50	2.20	1.15	0.20	2.09	1.88	Bal.	
30	33.50	2.20	1.15	0.20	2.04	3.71	Bal.	

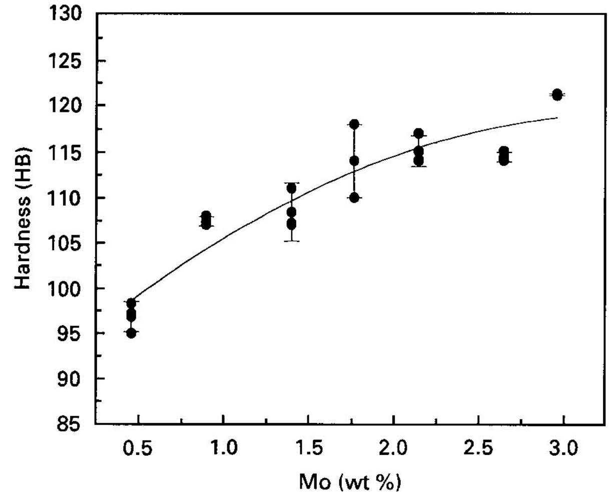

Figure 2 Effect of molybdenum content on hardness of an Fe–(32.49 ± 0.39)%Ni–(2.22 ± 0.06)%C–(1.61 ± 0.07)%Si–*X*%Mo alloy.

a weak carbide stabilizer, and it does not greatly affect graphite morphology because it reduces both the stable austenite/graphite eutectic and the metastable austenite/cementite eutectic temperature [4]. In high-nickel cast irons, molybdenum also prevents the formation of eutectic cells, resulting in fine eutectic graphites. Fig. 3 shows the shape and distribution of molybdenum carbides formed with eutectic graphites during solidification. However, the increase in hardness caused by the addition of molybdenum is not sufficient for practical application, even though the linear thermal expansion coefficient is constant, as shown in Fig. 4. The rate of increase in the linear thermal expansion coefficient per 0.1 wt % Mo is about 0.048×10^{-6} in the range 0–2.06 wt % Mo. Consequently, a proper hardness for practical use cannot be achieved by molybdenum addition alone.

Vanadium is generally considered to be an alloying element for the improvement of the hardness of austenitic cast irons, and is also known to increase the number of eutectic cells in cast irons. The stable austenite/graphite eutectic temperature increases with increasing vanadium content, while the metastable eutectic temperature decreases, which results in the formation of fine eutectic graphites and carbides. The vanadium carbides were found both in the eutectic cells and primary austenite dendrites, as shown in Fig. 5. These randomly dispersed carbides effectively promote the hardness of the austenite matrix. Fig. 6 shows the variation of the hardness value with various amounts of vanadium. With an increase in vanadium content up to 1.98 wt %, the hardness value increases from 116HB to 142HB. The rate of this increase was about 1.3HB per 0.1% V addition. As shown in Fig. 7, the rate of increase in the linear thermal expansion coefficient with the addition of vanadium was 0.028×10^{-6} per 0.1% V between room temperature and 100 °C, which is much smaller than that of the molybdenum addition. Fig. 8 shows a low nickel concentration in the carbide particle, which affects the magnetic properties. It was found that vanadium is an effective element for the improvement of hardness without raising the thermal expansion coefficient.

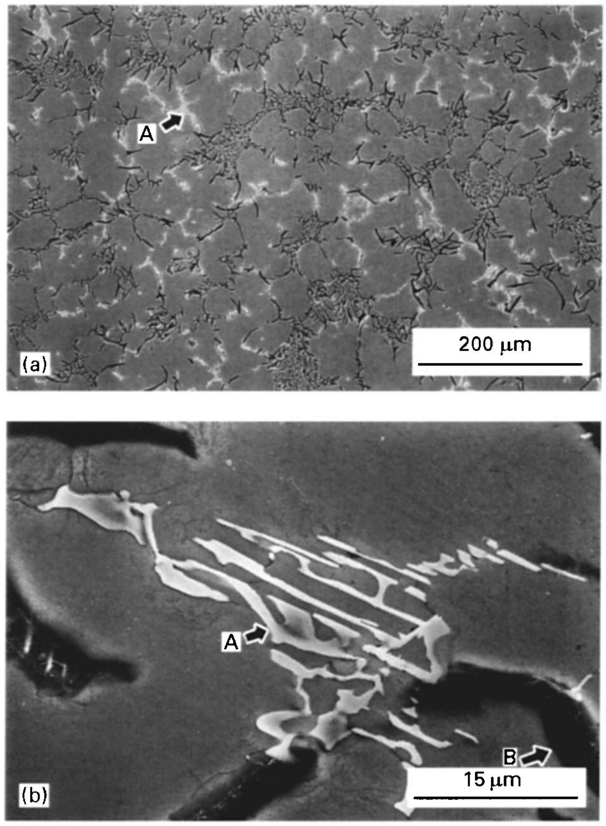

Figure 3 (a) Distribution and (b) shape of molybdenum carbides for a Fe–32.49%Ni–2.22%C–1.55%Si–2.96%Mo alloy: A, carbides; B, graphites.

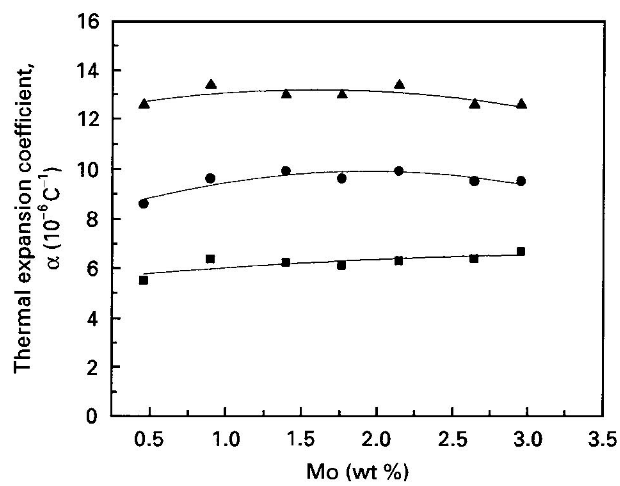

Figure 4 Effect of molybdenum content on thermal expansion coefficient of an Fe–(32.49 ± 0.39)%Ni–(2.22 ± 0.06)%C–(1.61 ± 0.07)%Si–*X*%Mo alloy: (▲) 200–250 °C, (●) 100–200 °C, (■) RT–100 °C.

In order to enhance the effect of alloys elements on the hardness value, combined additions of alloying elements were considered. It was found that the combined use of vanadium with molybdenum can improve the hardness value. Furthermore, it does not cause any serious increase in the linear thermal expansion coefficient. Fig. 9 shows the contour map of the hardness values as functions of vanadium and molybdenum contents, based on the experimental results. In the present experimental conditions the maximum and

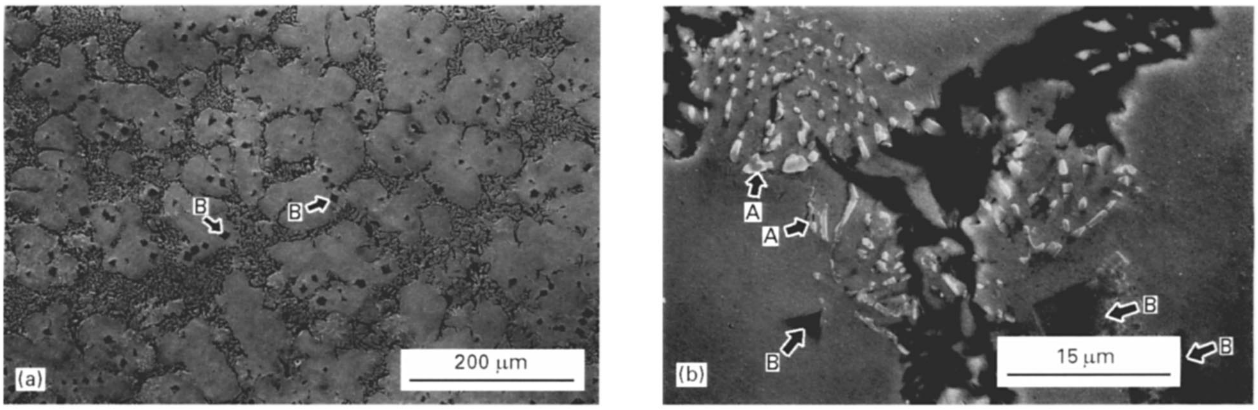

Figure 5 (a) Distribution and (b) shape of vanadium carbides for an Fe–33.3% Ni–2.35% C–1.15% Si–2.08% V alloy: A, eutectic carbides and graphites in the eutectic cells; B, large carbides in the austenite matrix.

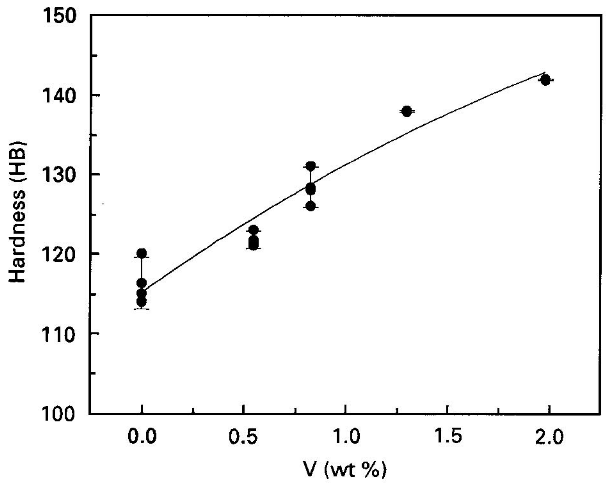

Figure 6 Effect of vanadium content on hardness of an Fe–(33.94 ± 0.46) % Ni–(2.22 ± 0.07) % C–(1.12 ± 0.02) % Si–*X* % V alloy.

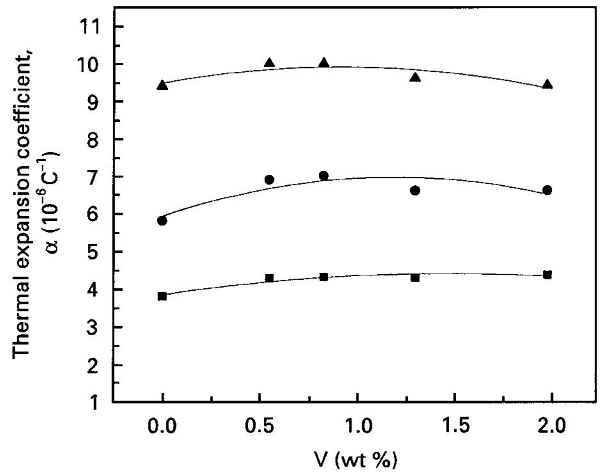

Figure 7 Effect of vanadium content on thermal expansion coefficient of an Fe–(33.49 ± 0.46) % Ni–(2.22 ± 0.07) % C–(1.12 ± 0.02) % Si–*X* % V alloy: (▲) 200–250 °C, (●) 100–200 °C, (■) RT–100 °C.

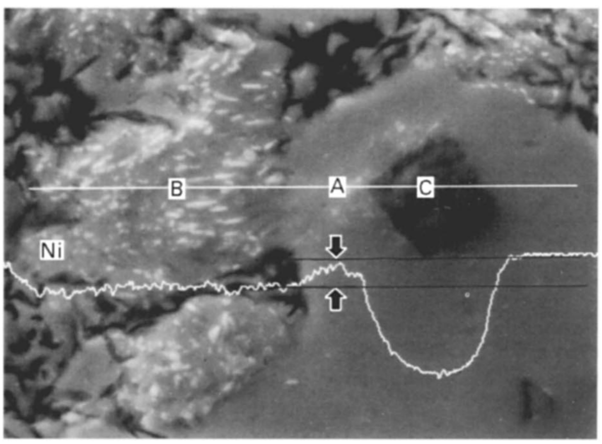

Figure 8 Redistribution of nickel concentration in the matrix for an Fe–33.80% Ni–2.35% C–1.15% Si–0.21% Mn–0.004% S–2.08% V alloy: A, the austenite region; B, the eutectic (carbide + graphite) region; C, the vanadium carbide particles.

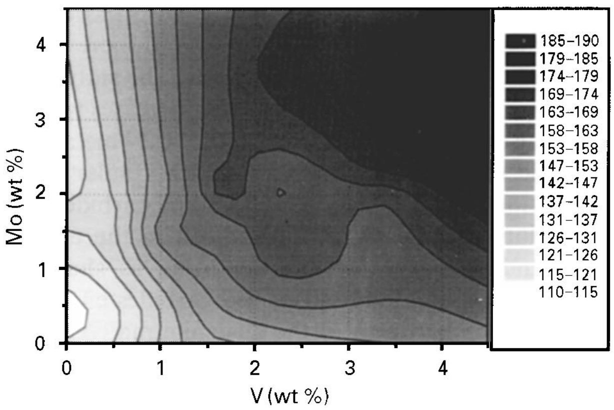

Figure 9 Contour map of hardness as functions of vanadium and molybdenum contents for an Fe–(34.29 ± 0.04) % Ni–(2.17 ± 0.13) % C–(1.16 ± 0.17) % Si–*X* % V–*Y* % Mo alloy, as drawn from the experimental results.

minimum hardness values were 180HB and 116HB, respectively. A synergistic effect on the improvement of the hardness value caused by the combined use of vanadium with molybdenum can be seen in this figure.

Fig. 10 indicates the distribution and shape of the carbides formed with the combined addition of vanadium and molybdenum. With an adequate addition of vanadium and molybdenum carbides appeared, which resulted in an increase in hardness.

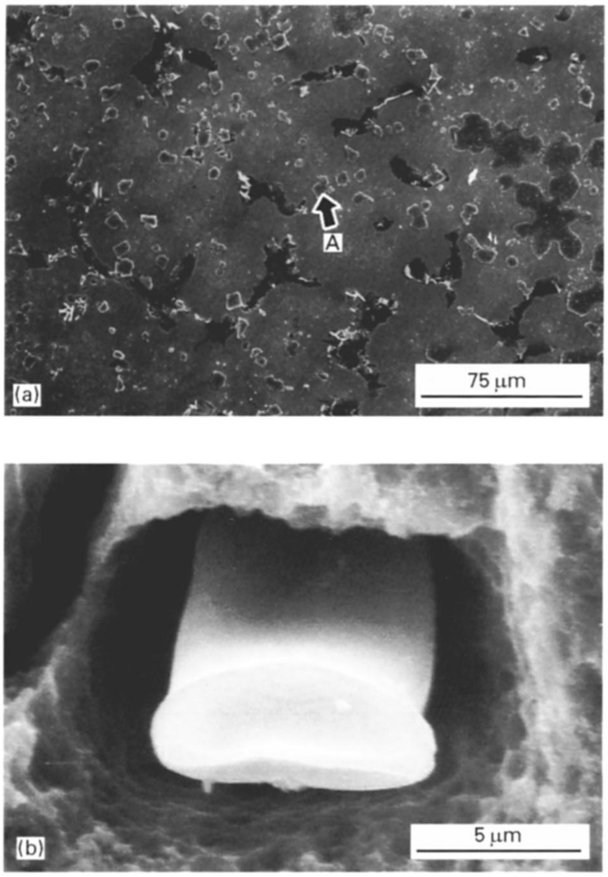

Figure 10 (a) Distribution and (b) shape of carbides in the case of the combined addition of vanadium and molybdenum in an Fe–34.45%Ni–2.04%C–1.36%Si–0.2%Mn–3.3%V–2.3%Mo alloy: the single carbide shown in (b) was revealed by etching with 3% Nital for 1 d.

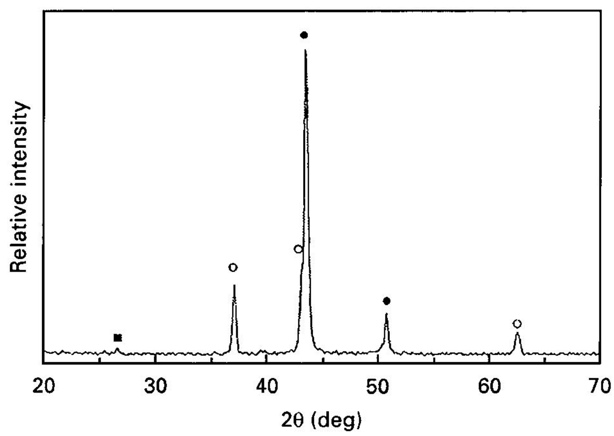

Figure 11 XRD analysis for an Fe–34.55Ni–2.03C–1.36Si–0.2Mn–3.3V–2.3Mo alloy: (●) austenite, (○) V_8C_7, (■) C.

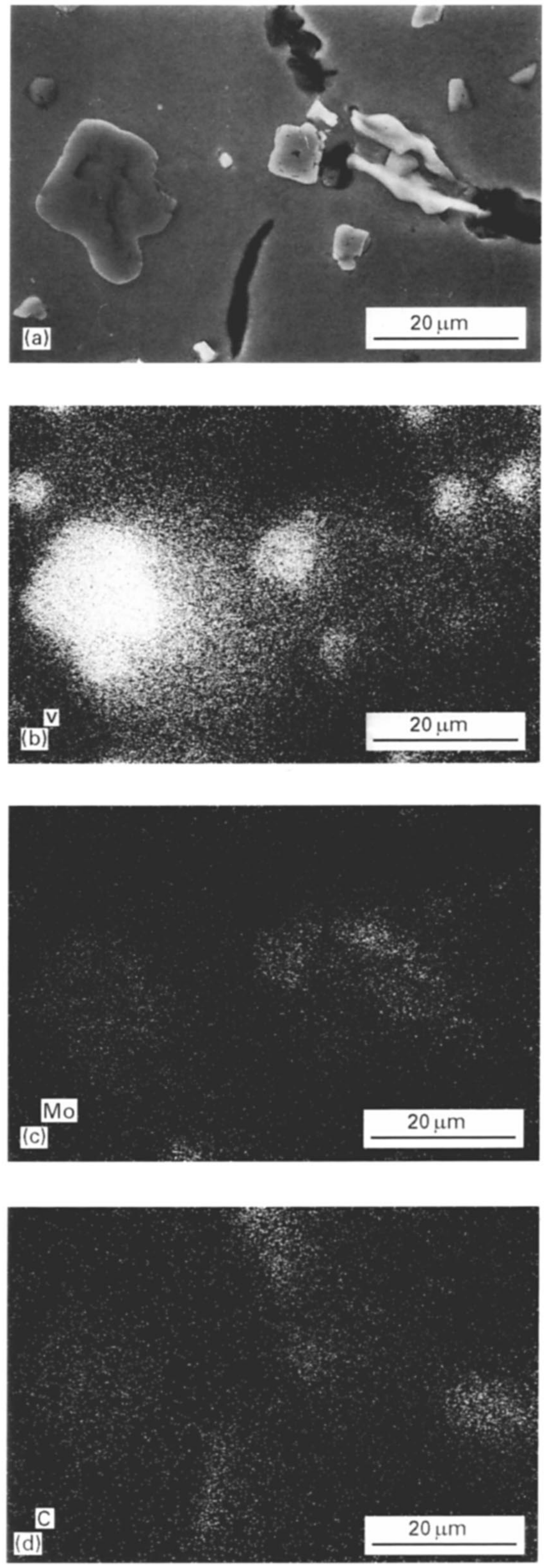

Figure 12 Distribution of alloying elements in carbides and the matrix for an Fe–35.38%Ni–1.95%C–1.40%Si–0.24%Mn–4.00%V–2.00%Mo alloy: (a) microstructure, (b) vanadium mapping, (c) molybdenum mapping, and (d) carbon mapping.

These carbides were revealed to be V_8C_7, including substitutionally soluble atoms molybdenum, iron and nickel by XRD as shown in Fig. 11. The solubilities of atoms in these carbides were affected by the alloy composition. The atomic percentages of soluble atoms in carbide V_8C_7 were detected at 7.5% Mo, 6.5% Fe and 2.6% Ni, while in the case of an alloy with the composition of 33.2%Ni–1.48%C–1.12%Si–0.2%Mn–3.6%V–2.5%Mo, the atomic percentages in carbide V_8C_7 were detected at 8.2% Mo, 13.6% Fe and 5.2% Ni. Fig. 12 shows the concentration distribution of the elements. Distributions of vanadium, molybdenum and carbon in the austenite matrix are rather random, but concentrated in carbide particles. This photograph shows that molybdenum is associated with vanadium carbide V_8C_7.

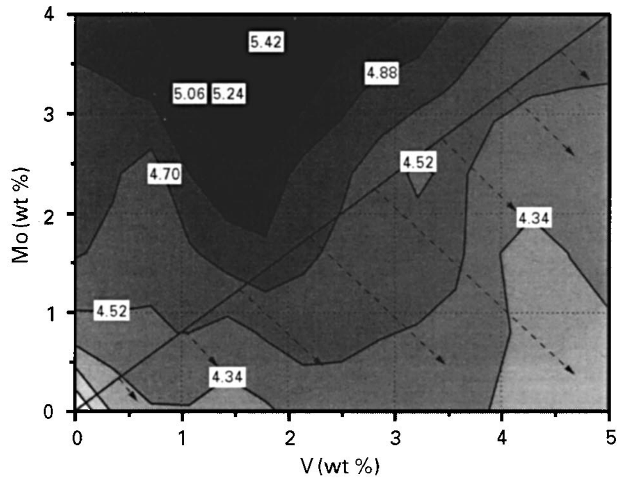

Figure 13 Contour map of thermal expansion coefficient as function of vanadium and molybdenum contents for an Fe–(34.35 ± 1.14)%Ni–(2.17 ± 0.17)%C–(1.19 ± 0.20)%Si–(0.21 ± 0.03)%Mn–(0.01 ± 0.002)%S alloy in the temperature range 23–100 °C.

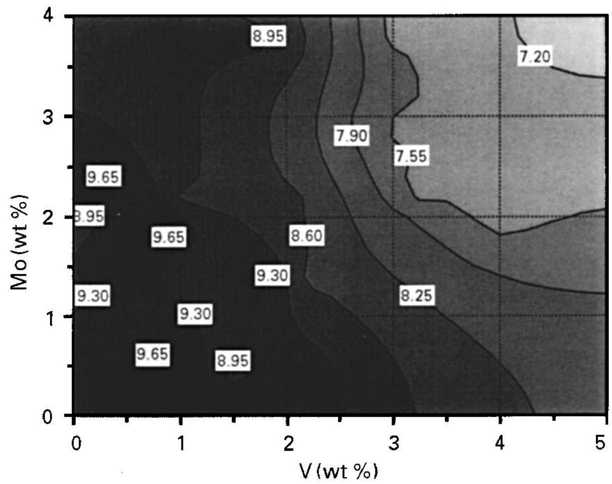

Figure 14 Contour map of thermal expansion coefficient as functions of vanadium and molybdenum contents for an Fe–(34.35 ± 1.14)%Ni–(2.17 ± 0.17)%C–(1.19 ± 0.20)%Si–(0.21 ± 0.03)%Mn–(0.01 ± 0.002)%S alloy in the temperature range 100–200 °C.

The effect of the combined use of vanadium and molybdenum on the linear thermal expansion coefficient was also studied. Fig. 13 represents the contour map of the thermal expansion coefficient in the temperature range 23–100 °C for various contents of vanadium and molybdenum, based on the experimental results. The measured maximum and minimum thermal expansion coefficients were $5.58 \times 10^{-6}\,K^{-1}$ and $3.80 \times 10^{-6}\,K^{-1}$, respectively. It can be seen from these figures that the rate of increase in the thermal expansion coefficient with the increase in the contents of vanadium and molybdenum is relatively low. However, the effect of molybdenum on the increase in the thermal expansion coefficient is greater than that of vanadium. This is considered to be caused by the fact that the solubility of molybdenum in the austenite phase at room temperature is higher than that of vanadium [5]. As shown in Fig. 14, in the temperature range 200–300 °C, the variation of the thermal expansion coefficient with the addition of alloying elements shows a different tendency. The thermal expansion coefficient decreases with increasing molybdenum or vanadium contents. This is because the suppression effect of thermal expansion by magnetostriction decreases while the thermal expansion effect due to the atomic thermal vibration increases inversely with an increase in temperature.

3.2. Effects of graphite and magnetic domains on the specific damping capacity (SDC) of Invar-type cast irons

Generally, the damping capacity of grey cast irons depends not on the matrix structure but on the graphite structures [6]. This can be explained by the following process: the damping capacity of cast irons is caused by energy loss due to the stress absorption in the graphite itself [7] and by plastic deformation of the matrix around the graphite due to stress concentration [6]. In order to estimate which process plays a dominant role in improving the damping capacity, the effects of morphology and graphite size on the damping capacity were investigated.

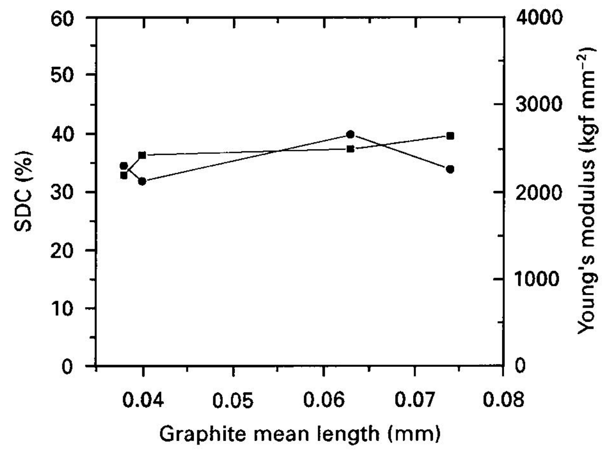

Figure 15 Effect of the mean length of graphite on (■) specific damping capacity and (●) Young's modulus for an Fe–33.50%Ni–2.45%C–1.07%Si–0.22%Mn alloy.

The effects of the mean length of the graphite on damping capacity and Young's modulus were studied, and the results are shown in Fig. 15. The mean length was changed by varying the cooling rate using a step-block casting. However, the amount of graphite was kept uniform throughout the test specimen by maintaining the same composition. The variation of graphite size is shown in Fig. 16. As shown in Fig. 15, there was no significant variation in the damping capacity with variation in the mean length of the graphite. The interfacial area between the austenite matrix and the graphite increases with a decrease in the mean length of the graphite. Thus, it can be said that the internal friction between the matrix and the graphite does not play an important role in improving the damping capacity. The effect of the amount of graphite on damping capacity was also studied. The amount of graphite was controlled by changing the amount of carbon and silicon contents. As shown in Fig. 17, the

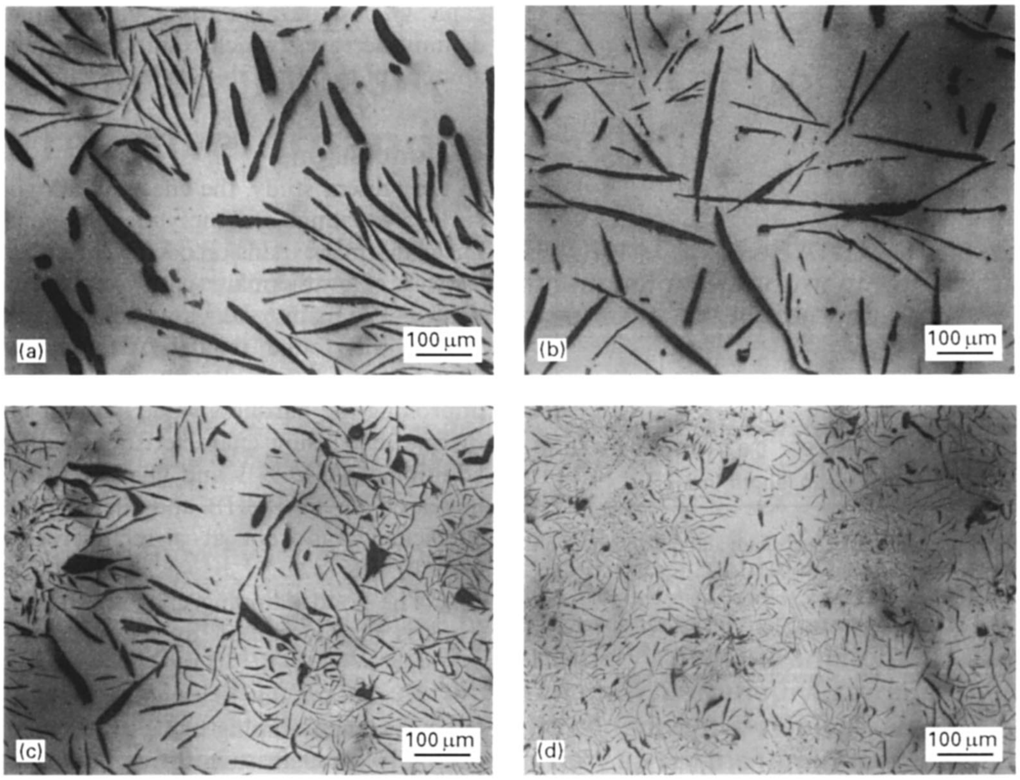

Figure 16 Variations of shape and size of graphites for various casting thicknesses for an Fe–33.50%Ni–2.45%C–1.07%Si–0.22%Mn alloy: (a) 90 mm, (b) 60 mm, (c) 30 mm, and (d) 15 mm.

damping capacity increases with an increase in the amount of graphite.

Based on these results, it can be said that the damping property of austenitic cast irons is caused by the stress absorption in the graphite itself through the movement and resonance of dislocation and by the plastic deformation at the matrix/graphite interface.

Invar-type cast irons have a relatively uniform austenite matrix structure, which exhibits ferromagnetism. The effect of magnetic domain boundary movement on the damping capacity was studied. Fig. 18 shows the effect of saturization magnetization on the damping capacity for cast irons with and without the combined addition of molybdenum and vanadium. The saturated magnetic flux intensity was measured using the VSM below the Curie temperature, and was about 0.5 T. The effect of the magnetic domain was removed by applying a magnetic field of 1.7 T. The composition of the specimens was in the range 1.52–2.45 wt % C, 1.05–1.07 wt % Si, 33.5 wt % Ni and 0.22 wt % Mn. The presence of a magnetic field resulted in a 1.1%–2.8% decrease in the damping capacity. This is because when a cyclic external stress acts on ferromagnetic materials, the movement and growth of magnetic domains will absorb energy. However, the effect of the magnetic domain structure on the increase in damping capacity is much smaller than that of the graphite.

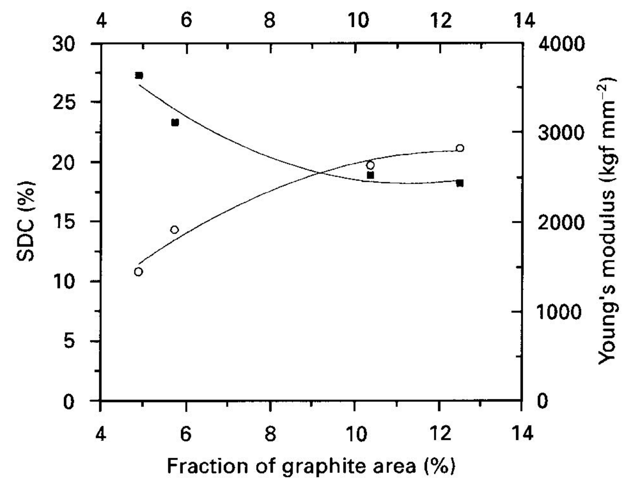

Figure 17 Effect of the amount of graphite on damping capacity for an Fe–33.50%Ni–(1.52–2.78)%C–(1.05–1.15)%Si–0.22%Mn alloy: (○) SDC, (■) Young's modulus.

3.3. Effects of vanadium and molybdenum on specific damping capacity

The effects of carbide-forming elements vanadium and molybdenum on damping capacity were also investigated. The specific damping capacity of the specimen is much greater in the absence of vanadium and molybdenum than that obtained with the addition of these elements. With an increase in the amount of vanadium and molybdenum the amount of graphite decreases, while the amount of carbides increases. When external stress is applied to the material, stress concentrates on the carbide particles, and the effective stress distribution by the graphite is suppressed. In addition, the solution hardening effect of vanadium and molybdenum causes an increase in Young's modulus of the matrix. Fig. 19 shows the effect of the amount of vanadium and molybdenum on the specific damping

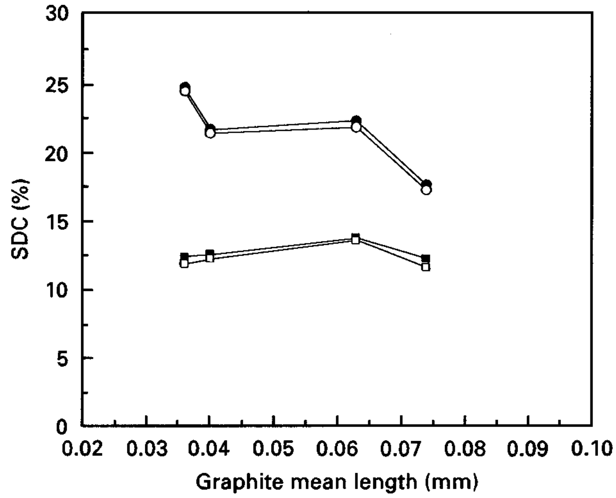

Figure 18 Effect of the addition of vanadium and molybdenum on damping capacity for an Fe–35.00%Ni–2.10%C–1.34%Si–0.20%Mn–2.00%V alloy with and without magnetic field: (○) without vanadium and molybdenum, (○) without vanadium and molybdenum under a magnetic field, (□) with 2.1% Mo and 2.0% V, (□) with 2.1% Mo and 2.0% V under a magnetic field.

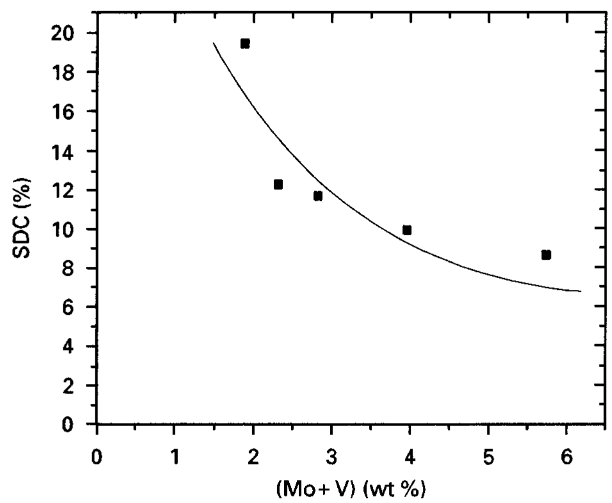

Figure 19 Effect of (vanadium plus molybdenum) content on specific damping capacity for an Fe–33.50%Ni–2.20%C–1.15%Si–X%Mo–Y%V alloy.

capacity. As the amount of vanadium and molybdenum increases, which results in an increase in the amount of carbides, the damping capacity decreases.

4. Conclusions

In the present study, the effects of alloying elements, such as vanadium and molybdenum, on hardness, the linear thermal expansion coefficient and the damping capacity of low thermal expansive cast irons were investigated. The main results are summarized as follows.

1. It was found that the combined addition of vanadium and molybdenum was most effective for improving the hardness value without impairing the thermal expansion characteristics. With a combined addition of 4.6 wt % V and 3.8 wt % Mo, the hardness increased up to 180HB and the thermal expansion coefficient was kept at a relatively low value of $4.6 \times 10^{-6}\ K^{-1}$.

2. The good damping capacity of Invar-type cast irons is mainly caused by the stress absorption in graphite.

3. As the amount of vanadium and molybdenum increases, the damping capacity decreases, which is caused by an increase in the amount of carbides.

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