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Mechanical properties of Co_3Ti containing boron, carbon and beryllium

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The mechanical properties of the recrystallized Co_3Ti alloys doped with boron, carbon and beryllium were investigated by tensile testing. The addition of boron significantly improved the strength of the Co_3Ti alloys below the peak temperature of yield stress whereas the addition of carbon or beryllium was not so effective. The yield stresses obtained were evaluated as a sum of three temperature-dependent terms. The addition of boron and beryllium reduced the activation energy for the thermal stress to promote the anomalous positive temperature dependence whereas the addition of carbon enhanced this energy. The addition of boron to Co_3Ti alloys reduced the elongation values at all temperatures while the addition of beryllium increased the values at 700 to 800 K and also at room temperature. The addition of carbon did not affect the elongation values. The fracture patterns correlated well with the levels of elongation, depending on the alloys and testing temperatures. The higher the elongation values, the more fractional area of the transgranular fracture modes increased.

1. Introduction

It has been shown by the present authors that the Co_3Ti alloy has very unique properties among many $L1_2$-type ordered alloys; this alloy is deformable at a wide range of temperatures and shows high flow strength at elevated temperatures. In order to improve further the mechanical properties of the Co_3Ti alloy and to understand the deformation mechanism of this alloy, ternary Co_3Ti alloyed with the addition of substitutional elements was studied, using polycrystals [1] and also single crystals [2].

In the present work, the flow strengths and the ductility of the Co_3Ti alloys doped with the small diameter atoms of boron, carbon and beryllium are reported. In the preceding work [3], it was proposed that boron behaved as an interstitial element while carbon and beryllium behaved as a substitutional element in the perfect lattice of the Co_3Ti alloy. The recrystallized samples, the grain sizes of which were controlled to be mostly the same, were used to exclude the microstructural effect and then to determine the doping (alloying) effect on the mechanical properties of these alloys. The main objectives are devoted to understanding the effect of the concentration of the dopants and testing temperature on the present phenomenon. The mechanical properties were characterized by tensile testing and fractographic observation. It is anticipated that the results obtained in these alloys could be correlated with some structural features observed in the preceding work [3].

2. Experimental procedure

The alloy systems and their chemical compositions of the ternary Co_3Ti alloys used in this work were almost the same as those used in the preceding work [3] and are shown in Table I. It is again noted that the chemical compositions of alloys doped with beryllium were prepared assuming; (1) that beryllium occupies the interstitial site, independent of the mother lattices and (2) that beryllium substitutes for the component atoms of titanium. Agreement between the nominal and analysed chemical compositions was extremely good for each element and each alloy.

Rectangular buttons of dimensions $\sim 15\,mm \times 15\,mm \times 80\,mm$ were prepared by the same method as described in the preceding work [3]. These samples were homogenized for 1 day at 1323 K under a vacuum better than 6.7×10^{-3} Pa, followed by furnace cooling. These were then rolled to a reduction of $\sim 50\%$ at 673 K. The tensile specimens with gauge dimensions of $1.0\,mm \times 2.0\,mm \times 14\,mm$ were prepared from these buttons using a multi-wire saw and an electro-erosion machine. The faces of the samples were abraded on SiC paper.

To prepare the recrystallized microstructure, the tensile specimens were encapsulated in a silica tube and then heat treated at 1273 K for desired times for each alloy. Microstructures were observed using an etching solution of 20 ml HCl, 4 g $CuSO_4$ and 20 ml H_2O. The grain size was measured by the conventional line intercept method where the twin boundaries were excluded from the measurements.

The tensile tests were carried out using an Instron-type testing machine at a nominal strain rate of $1.2 \times 10^{-3}\,sec^{-1}$. The test temperatures were from 77 to 1173 K. The tests at 77 K were performed with an apparatus suspended in a Dewar filled with liquid nitrogen. The tests at room and elevated temperatures were conducted in a special vessel in which a niobium plate heater was furnished and

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TABLE I Alloy compositions used for the tensile test

Alloy	Analysed composition (at % (mass %))			
	Ti	B	C	Be
Co23Ti	22.96			
Co23Ti–0.1 mass % boron	–	–		
Co23Ti–0.2 mass % boron	22.77	1.04(0.20)		
Co23Ti–0.05 mass % carbon	22.80		0.26(0.06)	
Co23Ti–0.05 mass % beryllium	22.91			0.26(0.04)
Co23Ti–0.1 mass % beryllium	22.85			0.57(0.09)
Co22.7Ti–0.3 at % beryllium	22.68			0.27
Co22.4Ti–0.6 at % beryllium	22.29			0.56

a vacuum better than 1.3×10^{-3} Pa was maintained. After tensile testing, the fracture surfaces of the specimens were examined by a scanning electron microscopy (SEM).

3. Results

3.1. Microstructure and grain size

All the alloys which were recrystallized showed similar microstructures consisting of equiaxed grains containing many annealing twins and their grain sizes are shown in Table II. By heat treatment at 1273 K for 1 day, grain sizes of 13 to 14 μm were obtained for alloys doped without and with boron and carbon, and 24 to 26 μm for alloys doped with beryllium. Hence, in order to obtain the same grain size, the alloys doped with beryllium were heat treated at 1273 K for the shorter time of 4 h. By this heat treatment, a grain size of 14 μm was obtained for the alloys doped with 0.05 mass %, 0.3 and 0.6 at % beryllium.

3.2. The yield stress behaviour

The temperature dependence of the yield stress in the alloys doped with various additives is shown in Figs 1 to 4. First, in alloys doped with boron (Fig. 1), the yield stress level at test temperatures below the peak of the yield stress–temperature curves increased with increasing boron concentration. At sufficiently high temperatures above the peak temperature, the strengthening effect of boron addition almost disappeared. Here, it is noted (1) that the increases of the yield stress with decreasing temperature from room temperature are remarkable in the alloys doped with boron, and (2) that the peak temperature decreases with increasing boron concentration.

Next, it is seen in Fig. 2 that the addition of 0.05 mass % carbon slightly reduced the yield stress at temperatures below the peak temperature.

TABLE II Grain size in the recrystallized alloys

Alloy	Grain size (μm)
Co23Ti	13
Co23Ti–0.1 mass % boron	13
Co23Ti–0.2 mass % boron	14
Co23Ti–0.05 mass % carbon	16
Co23Ti–0.05 mass % beryllium	24(14)
Co23Ti–0.1 mass % beryllium	26
Co22.7Ti–0.3 at % beryllium	14
Co22.4Ti–0.6 at % beryllium	14

In alloys doped with beryllium which were prepared assuming interstitial alloying (Fig. 3), it is shown that the addition of a small amount of beryllium (0.05 mass %) reduces the yield stress at all testing temperatures while the addition of beryllium of 0.1 mass % enhances the yield stress at temperatures above 600 K and reduces it at temperatures below 600 K. These softenings are not due to the difference in the grain size between the unalloyed samples (13 μm) and the alloyed samples (24 to 26 μm) because the alloyed samples (14 μm) consisting of exactly the same grain size with the unalloyed samples showed a similar trend. These data are compared in Fig. 3. On the other hand, as for alloys doped with beryllium which were prepared assuming substitutional alloying (Fig. 4), it is shown that the additions of 0.3 and 0.6 at % beryllium do not actually affect the yield stress–temperature curves of the unalloyed Co_3Ti.

It has been proposed that the yield stress–temperature curve in the Co_3Ti alloy is regarded as a sum of three temperature-dependent terms [2] and the

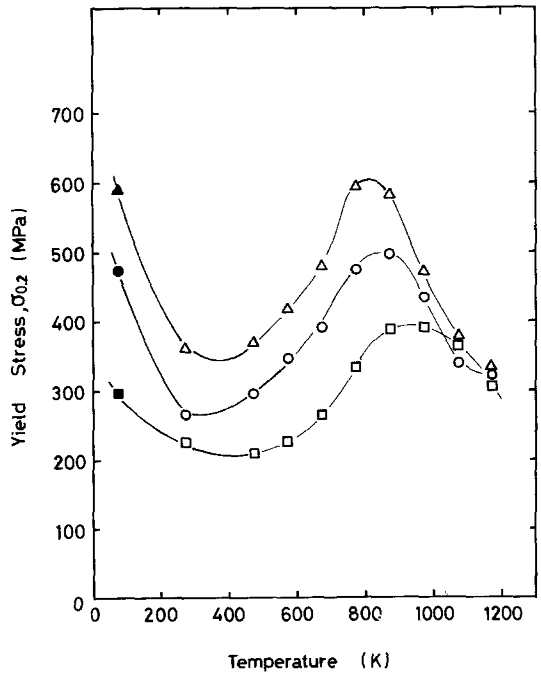

Figure 1 Temperature dependence of the yield stress in the Co_3Ti alloys doped with boron. (□) Co23Ti, (○) Co23Ti + 0.1 mass % B, (△) Co23Ti + 0.2 mass % B. (Solid symbols – tests in liquid nitrogen; unfilled symbols, – tests in vacuum.)

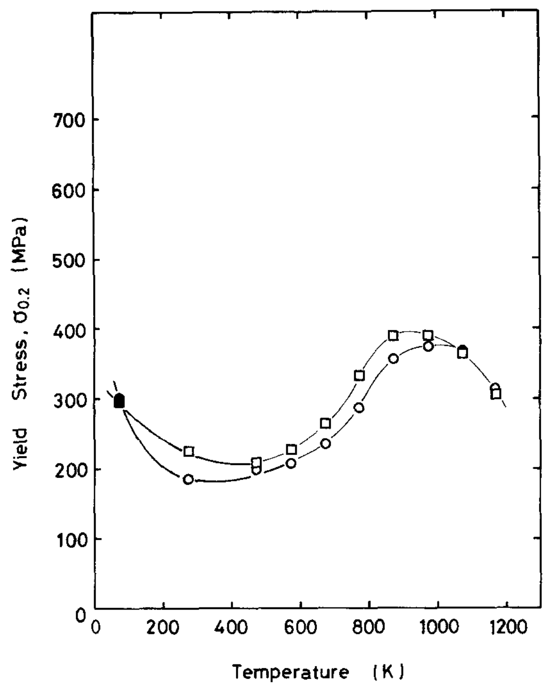

Figure 2 Temperature dependence of the yield stress in the Co_3Ti alloys doped with carbon. (□) Co23Ti, (○) Co23Ti + 0.05 mass % C.

observed yield stress, σ_y, is expressed as

$$\sigma_y = \sigma_{ath} + \sigma'_{th} + \sigma''_{th} \quad (1)$$

$$\sigma_{ath} = \sigma_o(1 - BT) \quad (2)$$

$$\sigma_{th} = A \exp(-U/kT) \quad (3)$$

where U is defined as the activation energy for the thermally activated process, R is the gas constant, T is temperature, and A and B are constants.

The stress component, σ_{ath}, has the ordinary negative temperature dependence of stress arising from shear modulus change with temperature and correlates with the solid solution hardening by the additives. On the other hand, σ_{th} involves further two terms; σ'_{th} is the term corresponding to the anomalous negative temperature dependence of the stress which is dominantly operative at low temperatures, while σ''_{th} is the term corresponding to the anomalous positive temperature dependence of the stress caused by the micro cross-slip mechanism which is dominantly operative at high temperatures [2]. The degree of strengthening

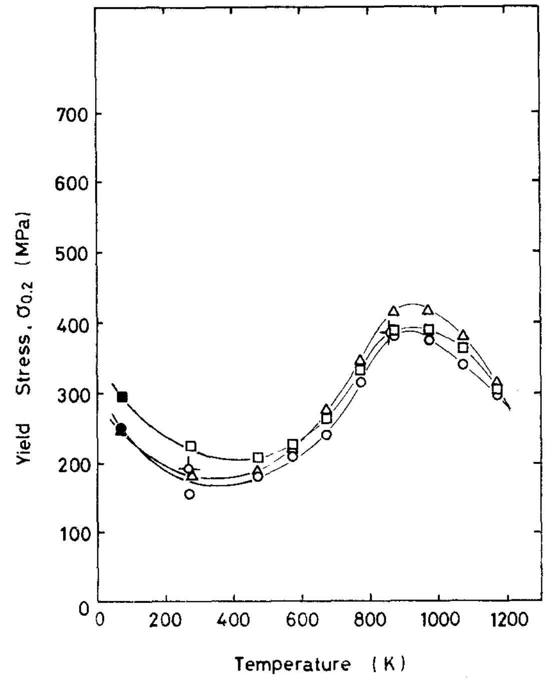

Figure 3 Temperature dependence of the yield stress in the Co_3Ti alloys doped with beryllium which were prepared assuming it was interstitial atom. Note that the grain size effect was checked for alloys doped with 0.05 mass % beryllium which consisted of the grain size (○) 24 μm and (-◇-) 14 μm. (□) Co23Ti, (-◇-, ○) Co23Ti + 0.05 mass % Be, (△) Co23Ti + 0.1 mass % Be.

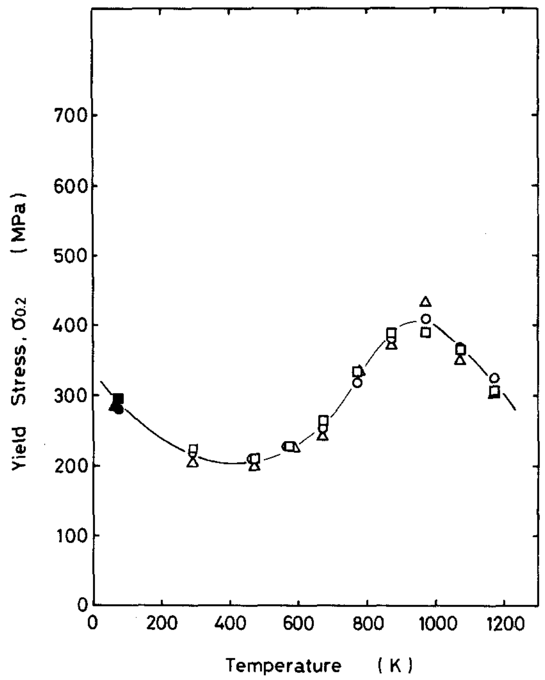

Figure 4 Temperature dependence of the yield stress in the Co_3Ti alloys doped with beryllium which were prepared assuming it was substitutional atom. (□) Co23Ti, (○) Co22.7Ti + 0.3 at % Be, (△) Co 22.4Ti + 0.6 at % Be.

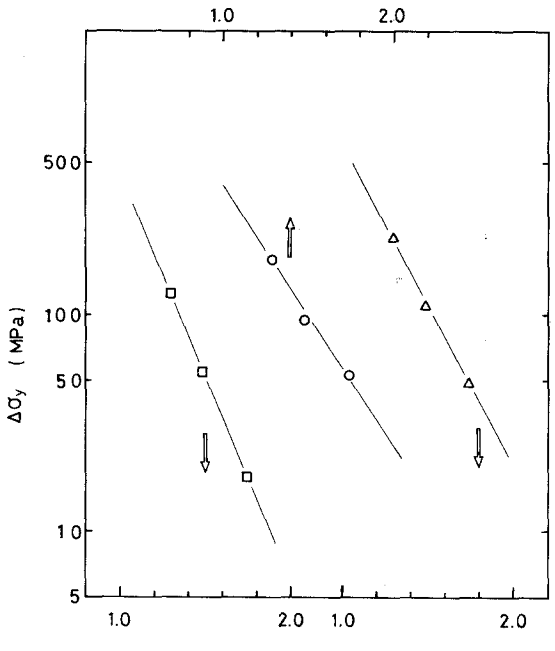

Figure 5 Arrhenius plots of the stress increment ($\sigma_T - \sigma_{473\,K}$) against reciprocal temperature for the alloys doped with boron. (□) Co23Ti, (○) Co23Ti + 0.1 mass % B, (△) Co23Ti + 0.2 mass % B, in vacuum.

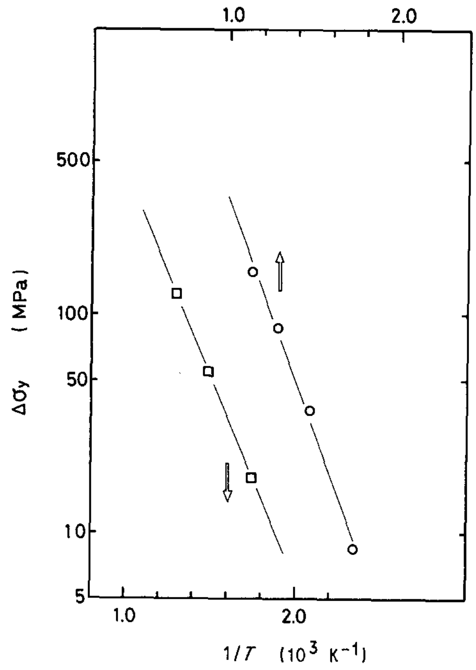

Figure 6 Arrhenius plots of the stress increment ($\sigma_T - \sigma_{473\,\text{K}}$) against reciprocal temperature for the alloys doped with carbon. (□) Co23Ti, (○) Co23Ti + 0.05 mass % C, in vacuum.

at high temperatures is evaluated as the σ''_{th} in the total yield stress by subtracting σ_{ath} and σ'_{th}; similarly, that at low temperature could be evaluated as the σ'_{th} in the total yield stress by subtracting σ_{ath} and the σ''_{th}.

Based on the assumption that σ_{ath} is independent of temperature and σ'_{th} is not operative at high temperatures, the activation energy, U, for the thermal component σ''_{th} of the yield stress was evaluated. The Arrhenius plots of the yield stress were carried out for $\ln \sigma_T - \sigma_{473\,\text{K}}$ with reciprocal testing temperature, as shown in Figs 5 to 8. Here, $\sigma_{473\,\text{K}}$ corresponds to the yield stress at the minimum temperature in the yield stress–temperature plots. It is apparent in these figures that the Arrhenius plot of the σ''_{th} and $1/T$ for each addition of the dopant holds a well-defined linear relation. The activation energy from the slope of the Arrhenius plot was calculated using a least squares plot. Thus, the effect of each dopant on the activation energy for the thermally activated process at high temperatures is shown in Fig. 9 as a function of concentration of the dopants. The value obtained for the unalloyed Co_3Ti polycrystals ($36\,\text{kJ}\,\text{mol}^{-1}$) is almost identical to that obtained for the single crystals of the binary alloy ($40\,\text{kJ}\,\text{mol}^{-1}$) [4]. It is shown in this

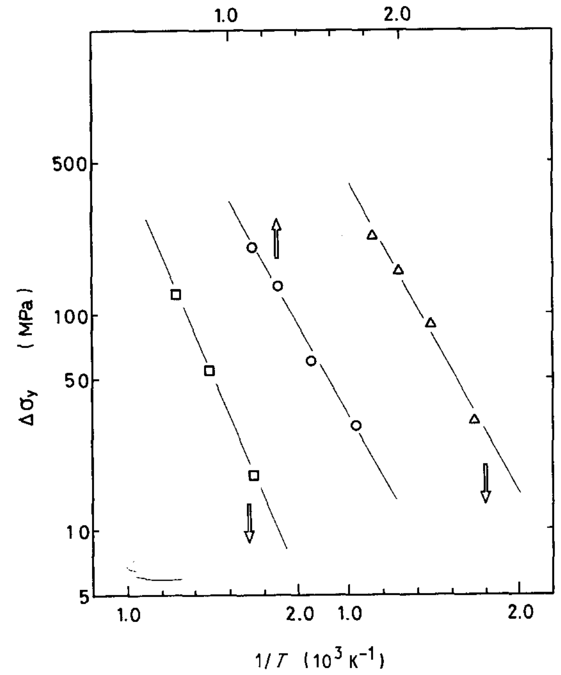

Figure 7 Arrhenius plots of the stress increment ($\sigma_T - \sigma_{473\,\text{K}}$) against reciprocal temperature for the alloys doped with beryllium. Note that beryllium was doped assuming it was interstitial atom. (□) Co23Ti, (○) Co23Ti + 0.05 mass % Be, (△) Co23Ti + 0.1 mass % Be, in vacuum.

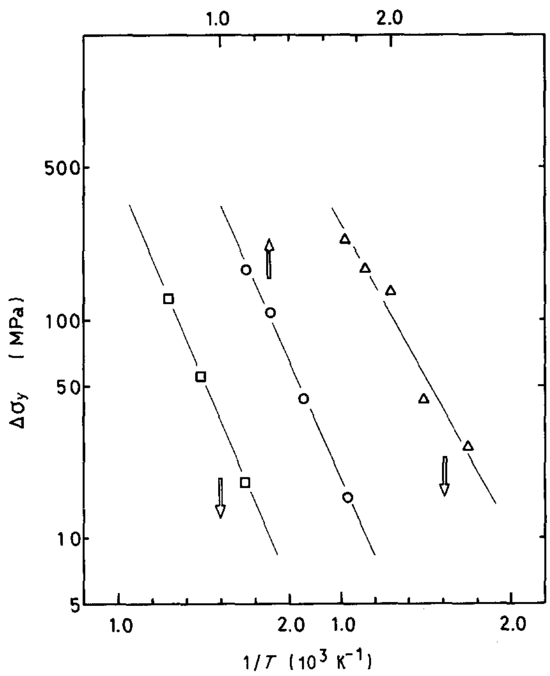

Figure 8 Arrhenius plots of the stress increment ($\sigma_T - \sigma_{473\,\text{K}}$) against reciprocal temperature for the alloys doped with beryllium. Note that beryllium was doped assuming it was the substitutional atom. (□) Co23Ti, (○) Co22.7Ti + 0.3 at % Be, (△) Co22.4Ti + 0.6 at % Be, in vacuum.

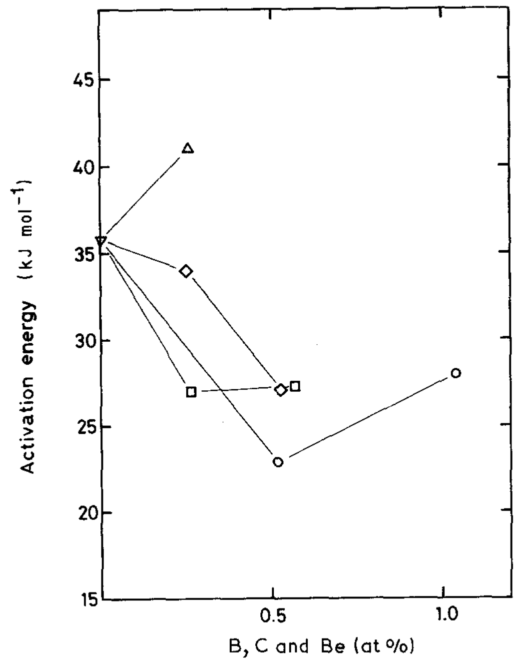

Figure 9 Effect of additives on the activation energies for the stress term to produce an anomalous positive temperature dependence, in vacuum. (▽) Co23Ti, (○) Co23Ti + B, (△) Co23Ti + C, (□) Co23Ti + Be, (◇) Co23(Ti, Be).

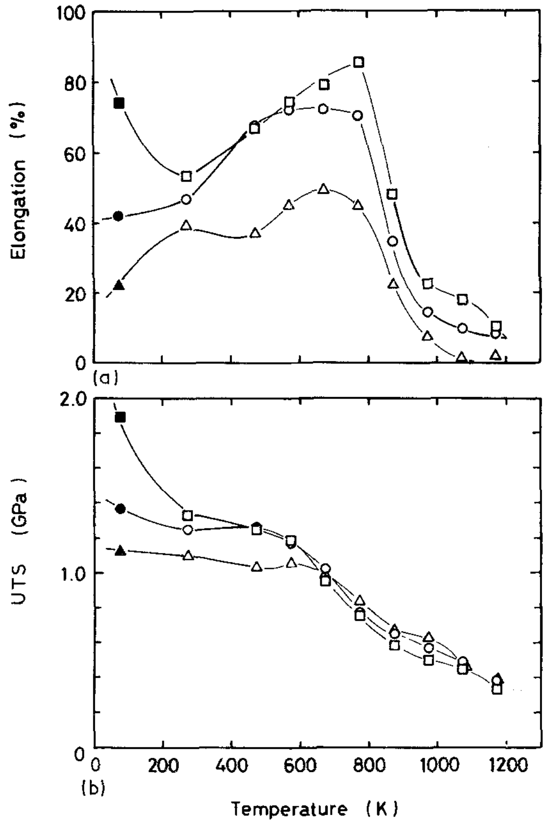

Figure 10 Variations of (a) elongation and (b) ultimate tensile stress with test temperature for alloys doped with boron. (□) Co23Ti, (○) Co23Ti + 0.1 mass % B, (△) Co23Ti + 0.2 mass % B.

figure that the addition of carbon to the Co$_3$Ti alloy enhanced the activation energy while the additions of boron and beryllium reduced the activation energy.

Similarly, the evaluation of the activation energy, U, for the thermal component, $\sigma'_{\rm th}$, of the yield stress is basically possible. However, the data points at this temperature are not so many, as shown in Figs 1 to 4 and therefore this estimation was not done. On the other hand, the evaluation of the solid solution strengthening term, $\sigma_{\rm ath}$, is very difficult. Although this stress term contributes greatly to the yield stress at the minimum temperature (approximately at 473 K), the other two stress terms are still operating at this temperature [2].

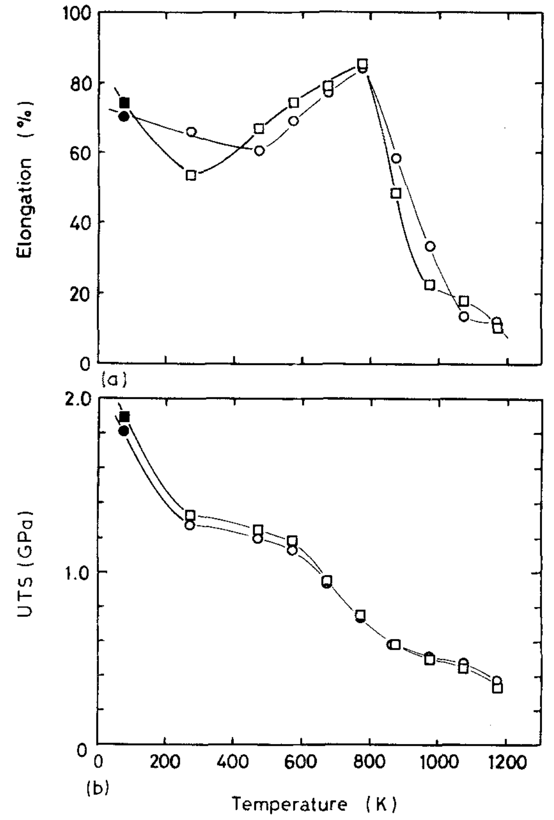

Figure 11 Variations of (a) elongation and (b) the ultimate tensile stress with test temperature for alloys doped with carbon. (□) Co23Ti, (○) Co23Ti + 0.05 mass % C.

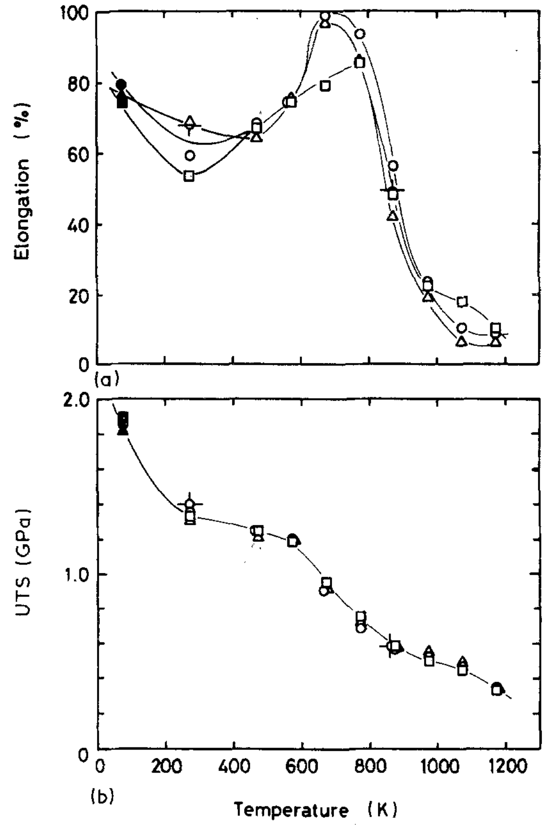

Figure 12 Variations of (a) elongation and (b) the ultimate tensile stress (UTS) with test temperature for alloys doped with beryllium. Note that beryllium was doped assuming it was interstitial atom. (□) Co23Ti, (⌖, ○) Co23Ti + 0.05 mass % Be, (△) Co23Ti + 0.1 mass % Be. (⌖) Grain size = 14 μm.

3.3. The ductility behaviour

Figs 10 to 13 illustrate the changes of elongation and the ultimate tensile stress (UTS) with test temperature for the additions of boron (Fig. 10), carbon (Fig. 11) and beryllium (Figs 12 and 13). The curves of the elongation–temperature generally show a minimum around room temperature and a maximum around 700 to 800 K. On the other hand, the UTS basically decreases monotonically with increasing temperature, although the curves show a shallow decrease or depression at room temperature.

First, the addition of boron reduces the elongation values almost at all temperatures. The reductions in elongation at the lowest temperature tested (77 K) are most remarkable. On the other hand, the addition of boron reduces the UTS values at temperatures below the peak temperature of the yield stress (Fig. 1) and slightly enhances these values at temperatures above the peak temperature.

Next, the addition of carbon does not actually affect the elongation values, nor the UTS values, as shown in Figs 11a and b.

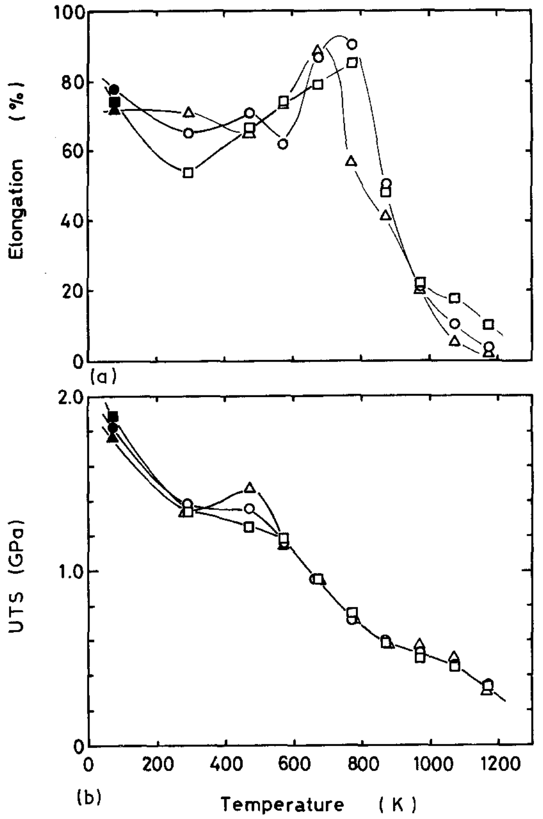

Figure 13 Variations of (a) elongation and (b) the ultimate tensile stress with test temperature for alloys doped with beryllium. Note that beryllium was assuming it was the substitutional atom. (□) Co23Ti, (○) Co22.7Ti + 0.03 at % Be, (△) Co22.4Ti + 0.6 at % Be.

Last, the addition of beryllium apparently increases the elongation around 600 to 800 K and also at room temperature, regardless of the alloying methods whether interstitial (Fig. 12) or substitutional (Fig. 13). On the other hand, UTS is not affected by the addition of beryllium.

3.4. Fractography

Fractographic observations for the alloys doped with the various additives will be shown in the following paper [5], and compared with those for the alloys which were tested in air. Here, only the fractographs of the unalloyed Co_3Ti and the boron-doped Co_3Ti alloys are shown in Figs 14 and 15, respectively, as a function of testing temperature.

For the unalloyed Co_3Ti, the fractographs observed at temperatures below the peak temperature show patterns consisting of transgranular fracture accompanying dimple patterns, although that observed at room temperature exhibits a trace amount of intergranular fracturing. The fractographs observed at 1073 K show the intergranular facets on which a large number of small cavities are distributed. For the alloys doped with boron, the fractograph observed at 77 K exhibits more intergranular fracture patterns than that observed in the unalloyed Co_3Ti, corresponding well to the elongation values described above. Thus, the fracture mode is primarily rationalized by the degree of the elongation itself; as the elongation values decreases, the fracture mode changes from transgranular fracture patterns to the intergranular patterns. In other words, the elongation is basically controlled by the competition between the intergranular and the transgranular fracture modes.

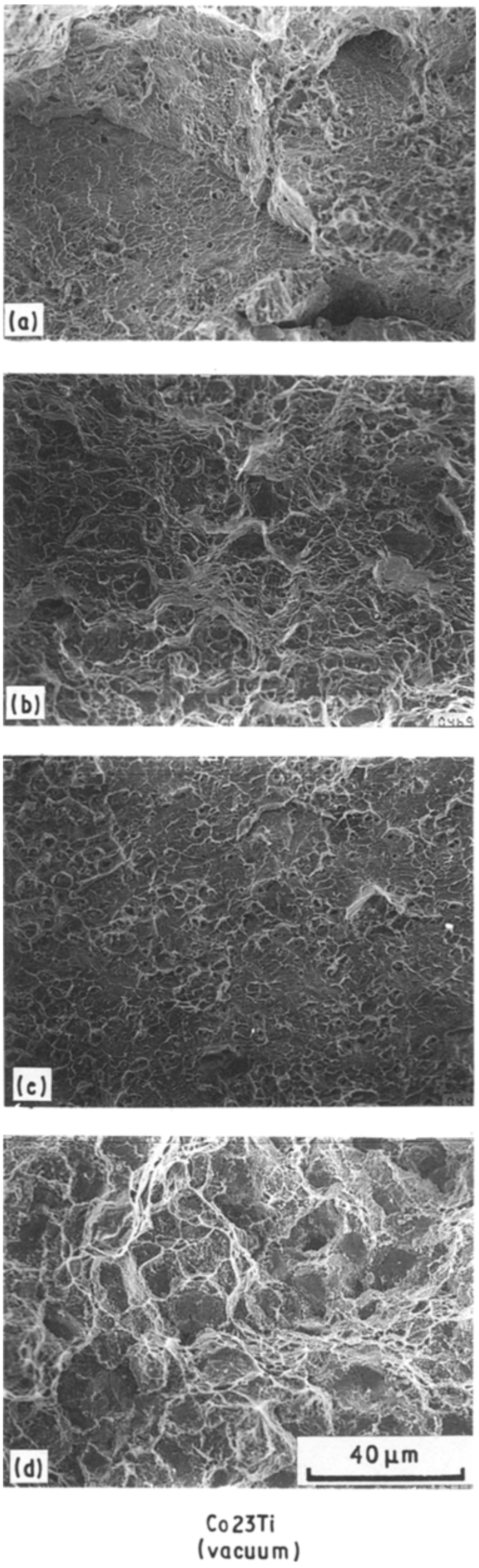

Figure 14 Variation of the fractographs for the unalloyed Co_3Ti with test temperature. (a) 77 K, (b) 293 K, (c) 673 K, (d) 1073 K.

4. Discussion

4.1. Strength property

The deformation mechanism of the Co_3Ti alloy has been investigated using binary Co_3Ti [4] and $(Co\text{-}3\,at\,\%\,Ni)_3Ti$ single crystals [2]. The sharp increase in the yield stress with decreasing temperature below

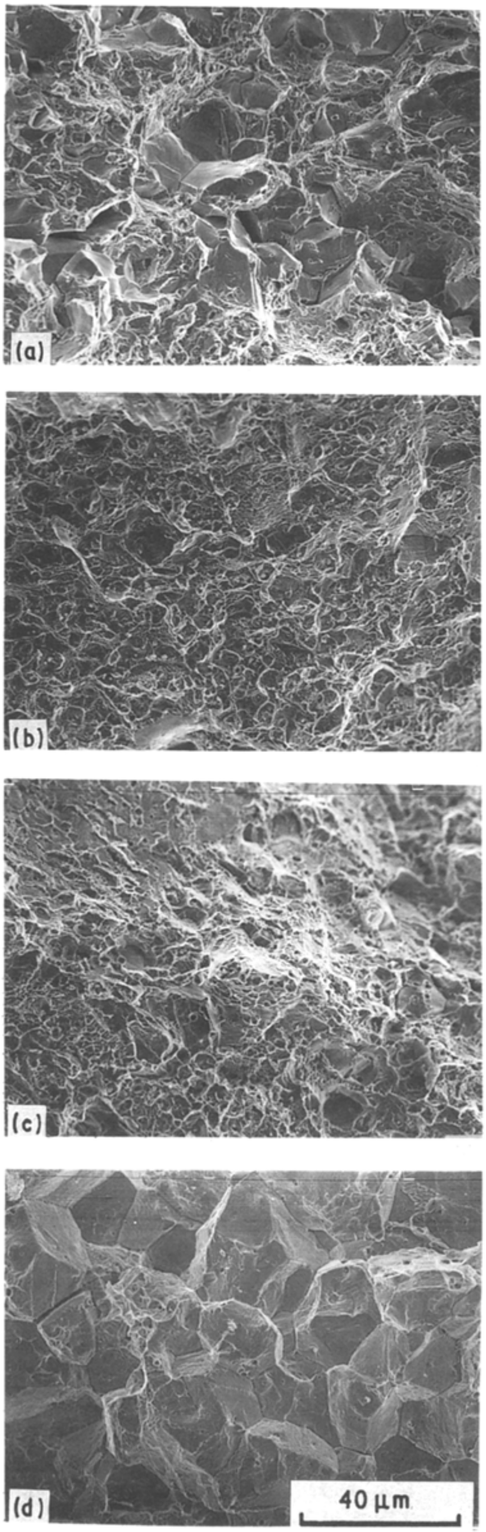

Figure 15 Variation of the fractographs for the Co_3Ti alloys doped with boron with test temperature. (a) 77 K, (b) 293 K, (c) 673 K, (d) 1073 K.

room temperature was suggested to be due to the non-planar core of the superlattice intrinsic stacking fault (SISF) dissociated superdislocation [6]. On the other hand, it was suggested, based on the orientation dependence of the critical resolved shear stress (CRSS) and transmission electron microscopy (TEM) observation of the dislocation structure, that the micro cross-slip mechanism operates at elevated temperatures in this material [2, 7]. It has also been shown that the decrease of the yield stress at higher temperature is due to the operation of {0 0 1} slip instead of {1 1 1} slip. It was thus concluded that the yield property of Co_3Ti intermetallic compounds is attributed to the unique structure of the dislocation core.

The results of Figs 1 to 4 clearly show that the significant strengthening below the peak temperature was brought about by the interstitial atom, boron [3], but not by the substitutional atoms, carbon and beryllium [3]. It is suggested that the strengthening in the former alloys is primarily due to the solid solution strengthening of the stress term, σ_{ath}.

Boron might also affect the other two thermal stress terms, σ_{th}; the stress increases at temperatures below and above the minimum temperature by the addition of boron are evident, as shown in Fig. 1 and as evaluated by the activation energy of the associated process (Fig. 9). This implies that boron affected the flow behaviour through modifying the core structure or the transformation of the superdislocation, i.e. by changing the energies of the antiphase boundary (APB) or the SISF combining with superpartials. Boron may increase the energy of APB and then promote the micro cross-slip, resulting in a decrease of the activation energy for the σ''_{th}, and may stabilize the SISF decomposed superdislocation, promoting the stress increase at low temperature (77 K). Indeed, the increase of the long-range order parameter, *S*, by the addition of boron [3] suggests the increase of APB energy. On the other hand, the fact that boron did not affect the yield stress at temperatures above the peak temperature means that boron does not influence the flow behaviour by {0 0 1} deformation mode. Thus, the effect of the boron addition on the strength property of the Co_3Ti alloys is possibly similar to that in the Ni_3Al alloys [8].

Carbon and beryllium were not so effective in solid solution strengthening because of their substitutional occupations in the lattices of the Co_3Ti [3]. However, the alloying effects on the positive temperature stress term were recognized; the activation energy corresponding to this stress term increased on addition of carbon but decreased on addition of beryllium, as shown in Fig. 9. However, no explanation of this change can be given at the present time.

4.2. Ductility property

Before discussing the doping effect on the elongation of the Co_3Ti alloys, the ductility behaviour of the binary Co_3Ti alloys is briefly described. The curves of the elongation–temperature plots generally showed a minimum around room temperature and a maximum around 700 to 800 K. It was suggested that the elongation reduction at ambient temperatures was associated with hydrogen embrittlement [9, 10]; when the samples were tensile-tested under vacuum, the residual hydrogen contained in the samples affected the grain-boundary cohesion and also the associated plastic flow with a propagating microcrack [10], resulting in easier propensity of grain-boundary fracturing. This embrittlement occurs more severely when the samples were tensile-tested in air and hydrogen gas and correspondingly hydrogen is injected into the sample under these circumstances. A detailed description of this will be given in the following paper [5]. On the other hand, the falls in elongation at temperatures above the peak temperature of the yield stress were attributed to high stress concentration at the grain-boundary plane caused by the activation of $\{100\}$ slips.

The additions of boron reduced the elongation values almost at all temperatures. However, the fractographic observation for this alloy suggests that this decrease is not due to the decrease in the grain-boundary cohesion, at least at temperatures above room temperature (293 K), because the transgranular fracture still operates in this temperature range. Consequently, this may be due to the hardening of the matrix by the addition of boron, resulting in a reduction of the elongation. On the other hand, the elongation reductions at the lowest temperature (77 K) on the addition of boron may be due to the promotion of intergranular fracturing through decreasing the relative strength of the grain-boundary strength to the fracture strength of the matrix. Thus, whether boron enhances the grain-boundary cohesion of the Co_3Ti alloys is not clear at the present time. However, it may be said that boron in the Co_3Ti alloys is not harmful in the least.

The additions of the substitutional atoms, carbon and beryllium had no effect or were slightly beneficial in the elongation of the alloys. The addition of beryllium enhanced the elongation value at room temperature. Thus the beryllium atom has the ability to prohibit harmful effects of hydrogen in this temperature region. On the other hand, the obvious increases of the elongation around 700 to 800 K may be attributed to two reasons: (1) the grain-boundary slidings were accelerated by this doping and (2) the grain-boundary cavitations were inhibited by this doping. However, more detailed studies will be necessary to clarify this result.

5. Conclusions

The mechanical properties of the yield stress, the elongation and the fracturing in the recrystallized Co_3Ti alloys doped with boron, carbon and beryllium were investigated by tensile testing. The following results were obtained.

1. The addition of interstitial atoms of boron produced a significant strengthening below the peak temperature of the yield stress whereas the addition of the substitutional atoms carbon and beryllium did not produce marked strengthenings at whole temperatures.
2. The yield stresses obtained were evaluated as a sum of three temperature-dependent terms, i.e. one athermal term and two thermal terms to produce the anomalous negative temperature dependence of the stress and to produce the anomalous positive temperature dependence of the stress.
3. The activation energy measured from the Arrhenius plot of thermal stress, required to produce the anomalous positive temperature dependence, was calculated. The additions of boron and beryllium to the Co_3Ti alloy reduced the activation energy while the addition of carbon enhanced the activation energy.
4. The addition of boron into the Co_3Ti alloys reduced the elongation values almost at all temperatures. The addition of carbon did not actually affect the elongation values. The addition of beryllium created an apparent increase in the elongation around 700 to 800 K and also at room temperature.
5. The fracture mode was primarily rationalized by the degree of elongation itself; as the elongation decreases the fracture mode changed from transgranular to intergranular fracture modes.

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