JOURNAL OF MATERIALS SCIENCE 25 (1990) 4239-4246

Environmental effects on the mechanical properties of Co_3Ti containing boron, carbon and beryllium

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The environmental effects on Co_3Ti polycrystals doped with boron, carbon and beryllium were investigated by tensile testing in air at 293 to 1173 K and the results were compared with those tested in vacuum. The yield stresses of the alloys observed were independent of the test environment. The elongation and ultimate tensile strength of the alloys observed were strongly dependent on the test environment and also the test temperatures. Ductility losses were found for the samples which were tested in air at temperatures below 473 K. The losses were accompanied by a change in fracture mode from transgranular to intergranular. It was suggested that this embrittlement was due to the hydrogen absorbed from air. Neither species boron, carbon nor beryllium were observed in this work to affect the environmental effects on the ductility behaviour of Co_3Ti alloys.

1. Introduction

Recent studies to find intrinsically ductile intermetallic compounds and to render the intermetallic compounds ductile led to the introduction of some fabricable intermetallic compounds. An example of these is the $L1_2$-type Co_3Ti alloys which are currently being studied by the present authors. However, as more information on these ductile intermetallic structural alloys has been published, it has been known that the mechanical properties of these alloys are very much influenced by the testing environment. So far it has been shown in some ductile $L1_2$-type intermetallic compounds that the tensile ductility and the associated fracturing strongly depend upon the test environment, with the worst ductility in cathodic charging of hydrogen or hydrogen gas exposure, and with lower ductilities observed in air than in vacuum. A strong effect of strain rate on ductility was also found with lower ductilities observed at a lower strain rate than at a higher strain rate. These embrittlements are accompanied by an intergranular crack path which is postulated to be associated with hydrogen atoms. This kind of environmental effect has been described in various review papers [1-3].

Hydrogen-related embrittlement has been reported to occur in the intermetallic compounds at ambient temperatures. Recently, a different kind of environmental effect has been reported. Oxygen, absorbed from the air during high-temperature testing, has been shown to embrittle the Ni_3Al compounds ductilized by the addition of boron [4]. The tensile ductilities measured at 600° C were found to be a strong function of test environment, whether in air or in vacuum. The samples tensile tested in air showed a severe loss of ductility. This kind of embrittlement also depended upon strain rate and produced grain-boundary fracture paths. In addition, it is pointed out that the oxygen-related embrittlement is phenomenologically very similar to the hydrogen-related embrittlement, although the species and operative temperature are different.

In the preceding work [5], the flow strength and the ductility of the Co_3Ti alloys doped with three small diameter atoms (boron, carbon and beryllium) were reported. All the data were taken from tensile tests in vacuum. In the present work, the same alloys as those tested in vacuum were tensile tested in air. The results obtained in this work were compared with the previous work [5] from the point of view of environmental effects. The tests were performed at room temperature to 1173 K.

2. Experimental details

The alloy systems and their chemical composition in the ternary Co_3Ti alloys used in this work are shown in Table I of the previous paper [5]. However, the alloys doped with 0.05, 0.1 mass % and 0.3 at % beryllium are excluded in this paper for simplicity.

The procedures of alloy preparation, heat treatment (for homogenization and recrystallization), tensile specimen preparation and tensile testing were exactly the same as those performed in the previous work [5]. The tensile samples were held for about half an hour at the testing temperature in an air environment before pulling. After tensile testing, the fracture surfaces of the specimens were examined by scanning electron microscopy (SEM).

3. Experimental results

3.1. The yield stress behaviour

The yield stresses in the alloys doped with various additives are shown in Figs 1 to 5 as a function of testing temperature, and compared with those tested

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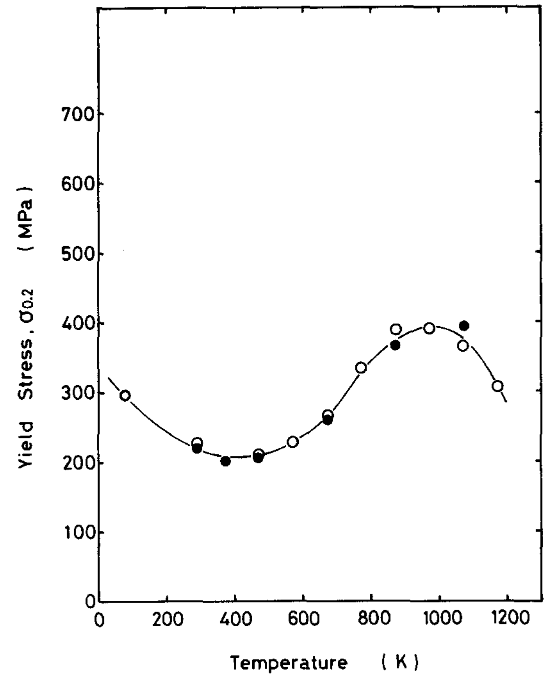

Figure 1 Temperature dependence of the yield stress in unalloyed Co_3Ti which was tested in air (●). Data obtained in vacuum (○) are also included for comparison.

in vacuum. As for all of the alloy systems, compositions and testing temperatures, the yield stresses obtained by the tests in an air environment were basically identical to those obtained by the test in vacuum. Consequently, it is suggested that the environmental medium did not affect the yield stress property not only at low temperatures but also at high temperatures. However, it must be noted that the slight increases of the yield stress were found in the alloys doped with boron and beryllium at temperatures above the peak temperature.

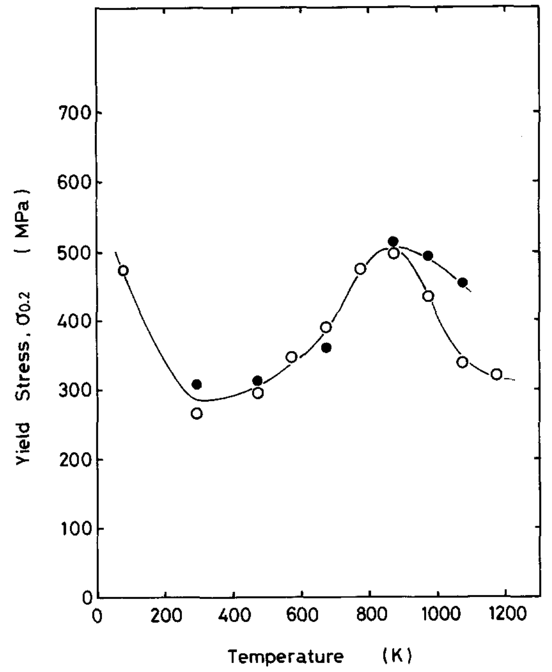

Figure 2 Temperature dependence of yield stress in the Co_3Ti alloys doped with 0.1 mass % boron (Co23Ti + 0.1 mass % B) which was tested in air (●). Data obtained in vacuum (○) are also included for comparison.

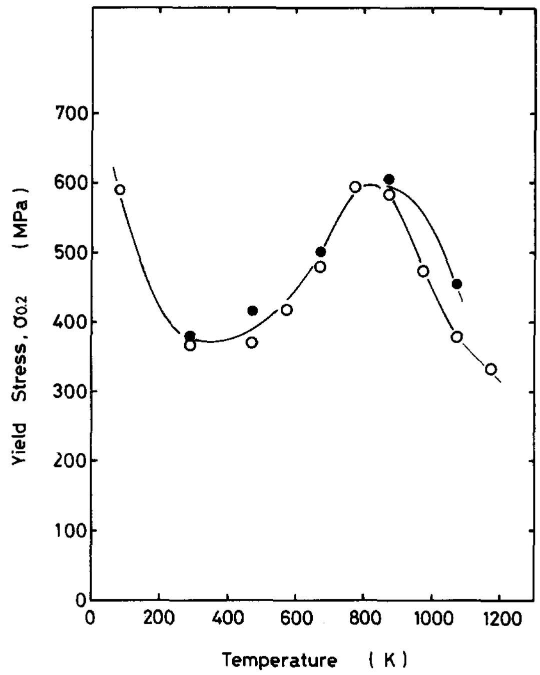

Figure 3 Temperature dependence of yield stress in the Co_3Ti alloys doped with 0.2 mass % boron (Co23Ti + 0.2 mass % B) which was tested in air (●). Data obtained in vacuum (○) are also included for comparison.

3.2. The ductility behaviour

Figs 6 to 10 illustrate the changes in elongation and the ultimate tensile stress (UTS) with test temperature for the unalloyed Co_3Ti (Fig. 6), the alloys doped with boron (Figs 7 and 8), carbon (Fig. 9) and beryllium (Fig. 10). All were again compared between the two different environmental conditions.

For the ductile behaviour of the unalloyed Co_3Ti, the discrepancy in the elongation and UTS values between the two environmental media was significant at ambient temperatures. The data at 77 K were

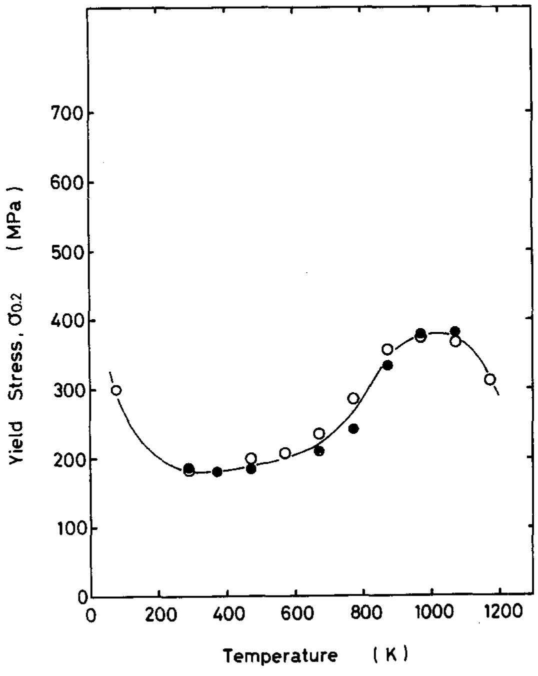

Figure 4 Temperature dependence of yield stress in the Co_3Ti alloys doped with carbon (Co23Ti + 0.05 mass % C) which was tested in air (●). Data obtained in vacuum (○) are also included for comparison.

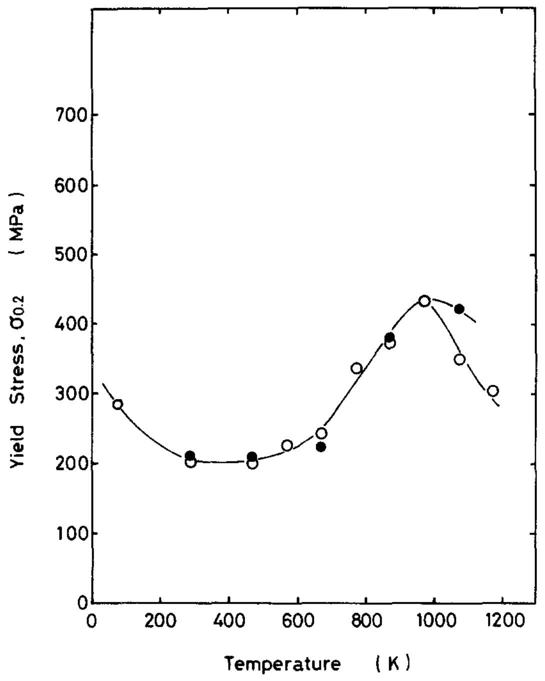

Figure 5 Temperature dependence of yield stress in the Co_3Ti alloys doped with beryllium (Co22.4Ti + 0.6 at % Be) which was tested in air (●). Data obtained in vacuum (○) are also included for comparison.

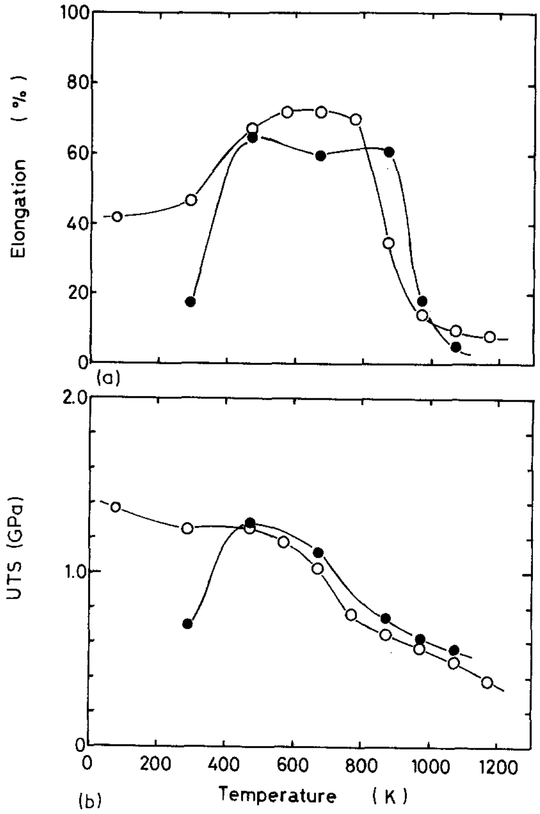

Figure 7 Temperature dependences of (a) elongation and (b) ultimate tensile stress (UTS) for the Co_3Ti alloys doped with 0.1 mass % boron (Co23Ti + 0.1 mass % B) which were tested in air (●). Data obtained in vacuum (○) are also included for the comparison.

obtained by tensile testing in liquid nitrogen medium, which is neither vacuum nor air. However, there is a likelihood that the test in liquid nitrogen is equivalent to the test in vacuum, because the penetration of hydrogen into the sample interior is impossible in both tests. Therefore, the data points at 77 K were connected with data points which were obtained in vacuum at 293 K. At room temperature, the elongation value was about 55% when the sample was tested in vacuum whereas that was about 15% when the sample was tested in air. Similarly, the UTS value decreased from about 1.4 to about 0.5 GPa when the test environment

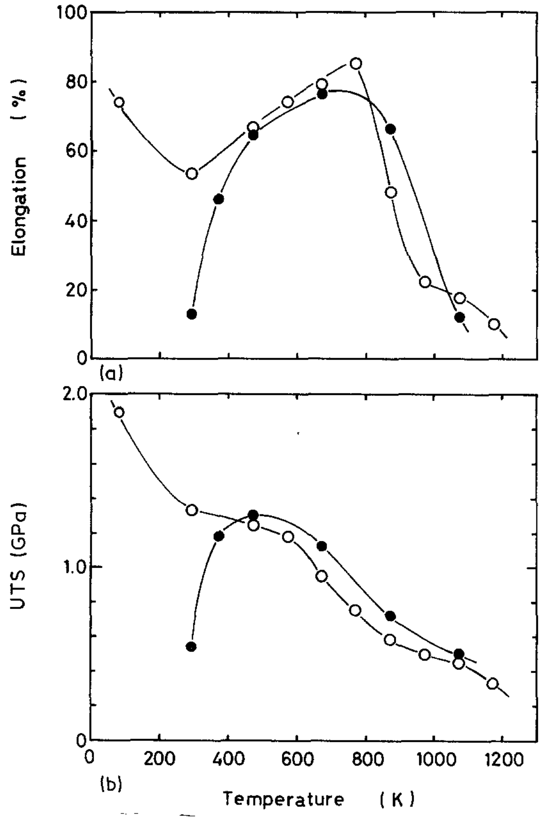

Figure 6 Temperature dependences of (a) elongation and (b) ultimate tensile stress (UTS) for unalloyed Co_3Ti (Co23Ti) which was tested in air (●). Data obtained in vacuum (○) are also included for comparison.

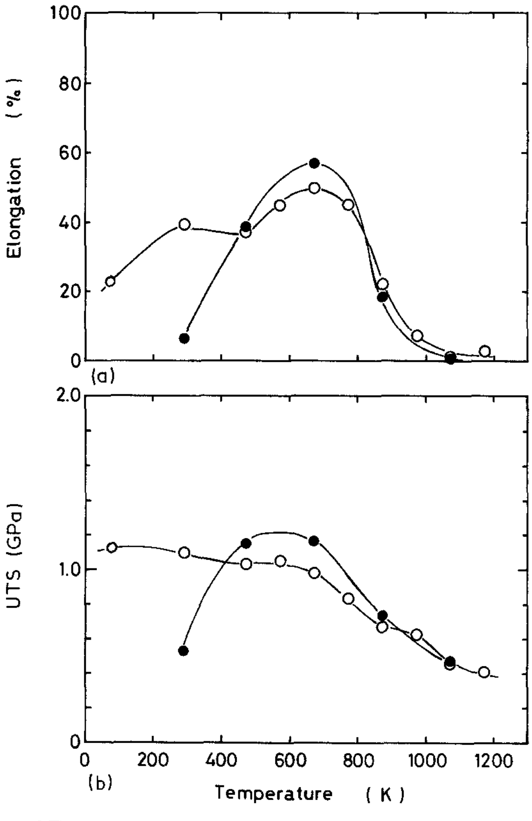

Figure 8 Temperature dependences of (a) elongation and (b) ultimate tensile stress (UTS) for the Co_3Ti alloys doped with 0.2 mass % boron (Co23Ti + 0.2 mass % B) which were tested in air (●). Data obtained in vacuum (○) are also included for comparison.

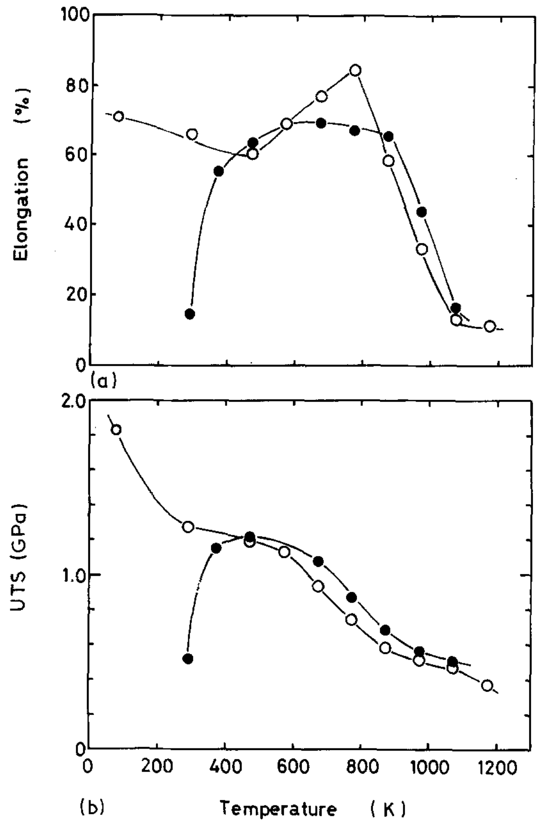

Figure 9 Temperature dependences of (a) elongation and (b) ultimate tensile stress (UTS) for the Co_3Ti alloys doped with carbon (Co23Ti + 0.05 mass % C) which were tested in air (●). Data obtained in vacuum (○) are also included for comparison.

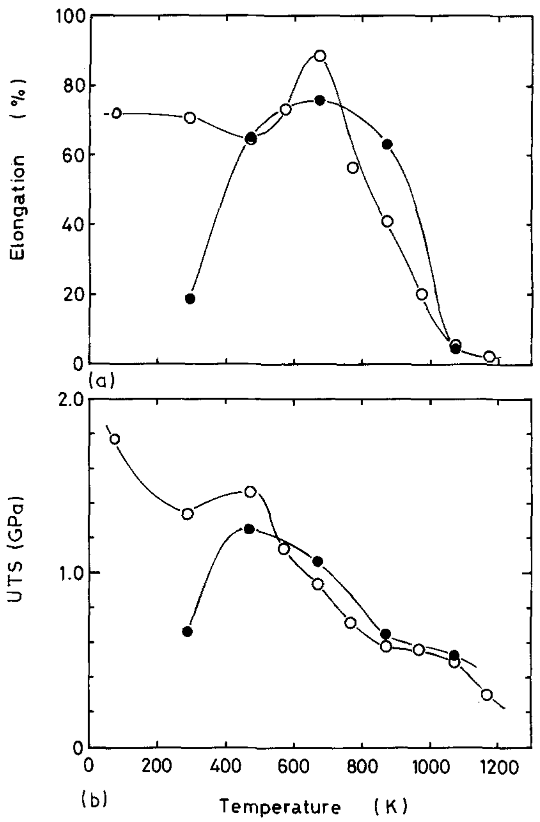

Figure 10 Temperature dependences of (a) elongation and (b) ultimate tensile stress (UTS) for the Co_3Ti alloys doped with beryllium (Co22.4Ti + 0.6 at % Be) which were tested in air (●). Data obtained in vacuum (○) are also included for comparison.

changed from vacuum to air. This behaviour is quite consistent with the previously reported result [6]. However, an important result found in this figure is that as test temperature increases the elongation and UTS increase and at 473 K (200° C) are completely restored to the values tested in vacuum. On the other hand, at high temperatures, meaningful differences were not recognized for the two properties in the two environmental media although the UTS values obtained in vacuum were slightly, but consistently, higher than those obtained in air.

The environmental effect on the ductile behaviour of the alloys doped with boron at two concentration levels was basically similar to that of the unalloyed Co_3Ti; the embrittlements due to the test in air were limited to temperatures below 473 K (200° C) and did not occur at high temperatures.

In alloys doped with carbon and beryllium, the observed environmental effects on ductility were basically similar to that of the unalloyed Co_3Ti and boron-doped Co_3Ti alloys. However, elongation peaks at 673 K (400° C) which appeared in the samples tested in vacuum became less evident when these samples were tested in air.

3.3. Fractography

In the preceding paper [5], the fractographs of the unalloyed Co_3Ti and the boron-doped Co_3Ti which were tested in vacuum were shown. Therefore, for these two alloys, fractographs of samples tested in air are shown here in Figs 11 and 12, respectively. For the carbon-doped Co_3Ti alloys and beryllium-doped Co_3Ti alloys, fractographs are shown for the samples tested in both environments (Figs 13a and b, and 14a and b, respectively). The fractographs are shown for samples tested at various temperatures.

In the undoped Co_3Ti alloys, a comparison of Fig. 11 in this paper with Fig. 14 in the preceding paper [5] clearly indicates that the samples tested at 673 and 1073 K showed the same fractographic patterns under the two environmental conditions, whereas samples tested at room temperature (293 K) showed very different fracture patterns. At 293 K, the samples tested in vacuum showed almost 100% ductile transgranular fracture patterns, while the sample tested in air showed a mixture of transgranular fracture patterns with intergranular fracture patterns. Thus, this result corresponds well with the elongation and UTS behaviour observed for the samples tested in the two environmental conditions. It should also be noted that although the fractographs observed at 1073 K showed grain-boundary facets in both environmental conditons, the test in air produced grain-boundary facets with less cavitation, i.e. flatter surface patterns. Such fractographic patterns may indicate that the exposure of the fractured surfaces to air changed the mobility of the atoms on the cracked grain-boundary surfaces during or after fracturing, and thus the ridges of the cavities disappeared.

The environmental effects observed in the fractographs of the boron-doped Co_3Ti alloys were similar to those of the undoped Co_3Ti alloys; comparison of Fig. 12 in this paper with Fig. 15 in the preceding paper [5] again indicates that the samples tested at 673 and 1073 K showed the same fractographic patterns in the two environ-

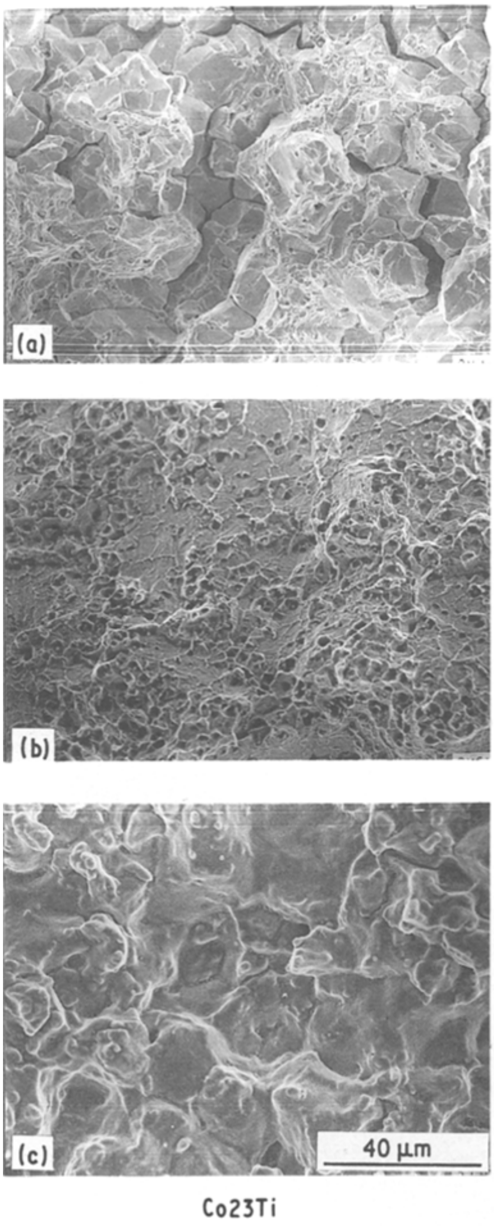

Figure 11 Temperature dependence of the fractographs for the unalloyed Co_3Ti which was tested in air at (a) 293 K, (b) 673 K and (c) 1073 K.

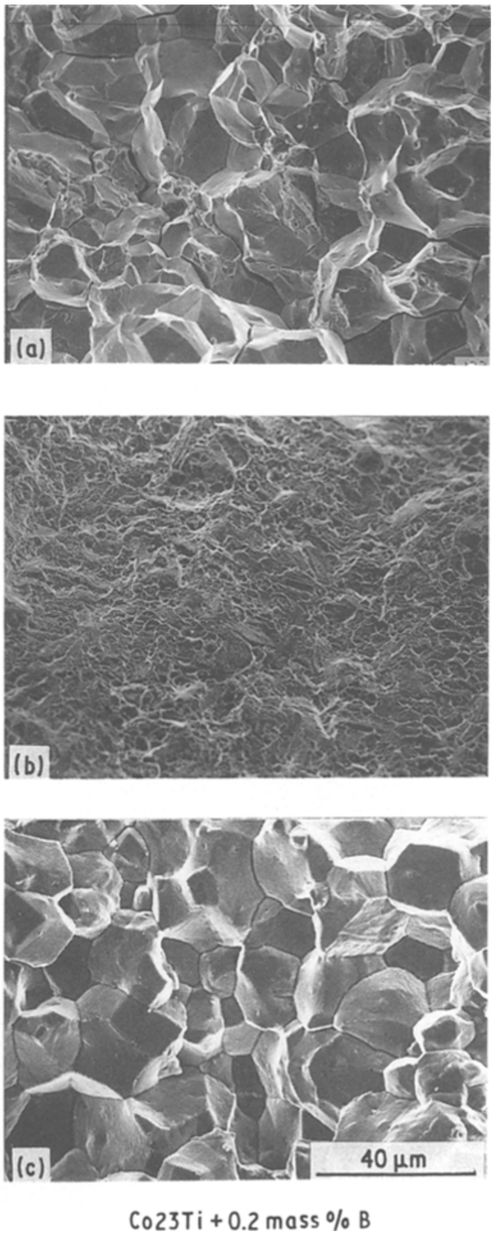

Figure 12 Temperature dependence of the fractographs for the Co_3Ti alloys doped with 0.2 mass % boron which were tested in air at (a) 293 K, (b) 673 K, (c) 1073 K.

mental conditions. However, at 293 K, the sample tested in vacuum showed almost 100% ductile transgranular fracture patterns while the sample tested in air showed a larger portion of intergranular fracture patterns.

Environmental effects on Co_3Ti alloys doped with carbon and beryllium, seen in the fractographs were basically similar to those of the unalloyed Co_3Ti and boron-doped Co_3Ti alloys.

4. Discussion

The results observed for the Co_3Ti alloys with or without various additives demonstrate that environmental effects at low temperatures were evident as expected, but that at high temperatures no effects were found. It has been suggested that the effects at low temperature are associated with embrittlement due to hydrogen, while the effects at high temperature are associated with embrittlement due to oxygen. Thus, both environmental effects are attributed to the gaseous species existing in the air medium.

First, let us discuss the environmental effect associated with hydrogen which was operative at ambient temperatures. The previous observations [6, 7] indicated that the embrittlement in the binary Co_3Ti alloys was reversible (recoverable) after a degassing treatment of hydrogen injected by cathodic charging [6] or absorbed by hydrogen gas exposure [7]. The recovery of elongation was simply established at room temperature. This result suggested that the reduced ductilities could not be attributed to the introduction of swelling or a hydride. Indeed, TEM observation for this alloy did not indicate any formation of hydride either after fracturing or during stressing of the sample [7]. Also, the embrittlements were caused by intergranular fracturing. Based on these experimental results, an associated micro mechanism with this phenomenon was proposed [6, 7]; the dynamic and

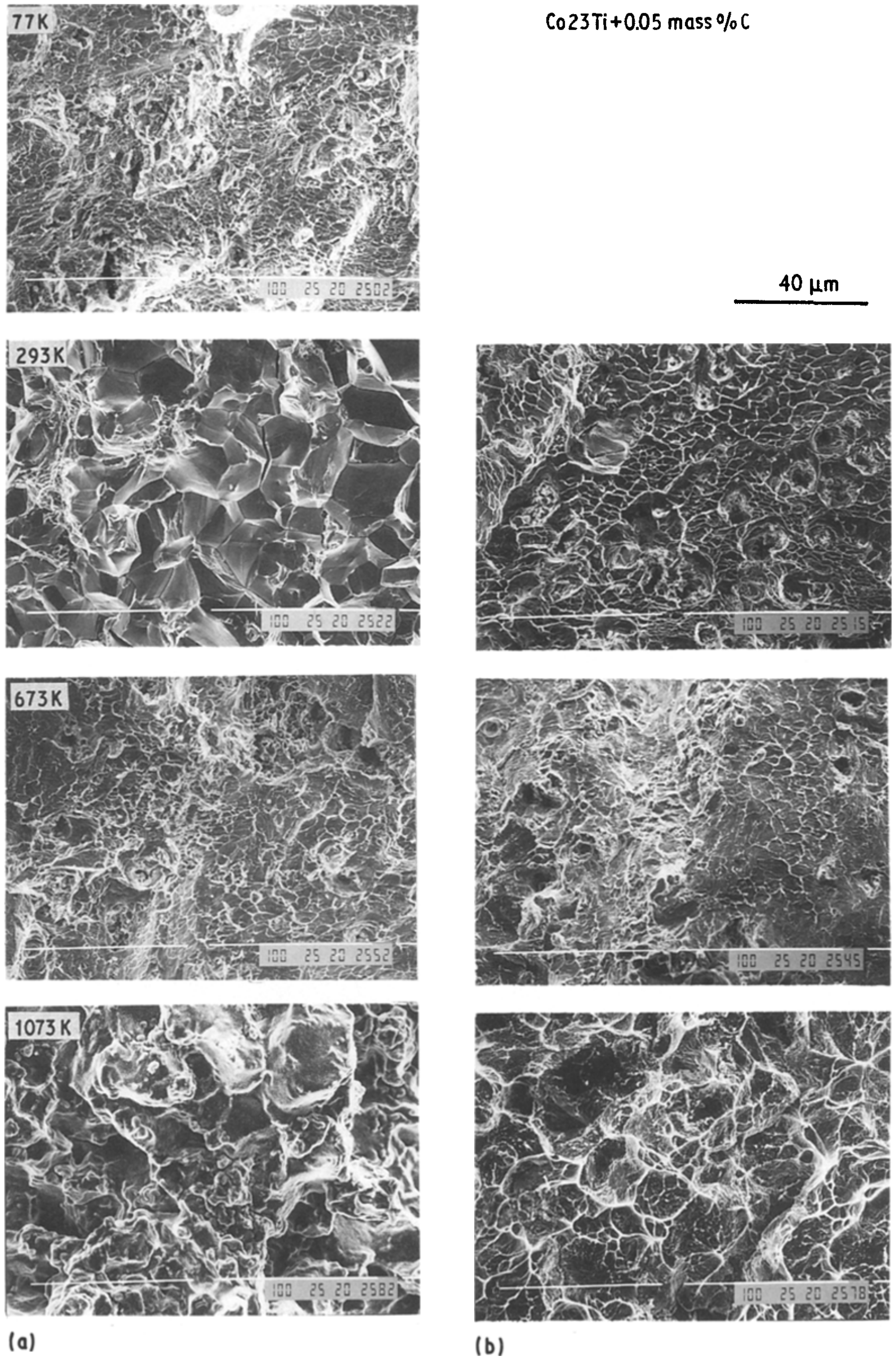

Figure 13 Temperature dependence of the fractographs for the Co_3Ti alloys doped with carbon which were tested in (a) air, and (b) vacuum. Note that the fractograph at 77 K was taken after testing in a liquid nitrogen medium.

atomistic mechanism by which the cohesive strength of the grain boundary and the associated plastic flow around micro crack was affected by the hydrogen, was proposed.

As the test temperature increases, the tensile ductilities of the samples tested in air increased and eventually at 473 K reached the same value as the samples tested in vacuum. This change was predicted in the previous paper [6]. As the test temperature increases, the mobility of hydrogen is supposed to increase, but the enrichment of hydrogen into the region of a propagating micro crack will be alternatively reduced, due to the entropy effect. As a result, this kind of embrittlement disappears at high temperatures. Naturally, the temperature at which the embrittlement disappears depends on the test strain rate, alloy composition, etc.

Even if the alloys were tested in vacuum, increases in tensile ductilities on increasing the temperature from room temperature were recognized. In other words, the elongation showed lower values at room temperature than at about 673 K. This temperature dependence of elongation could still be attributed to the hydrogen embrittlement. In this case, "residual"

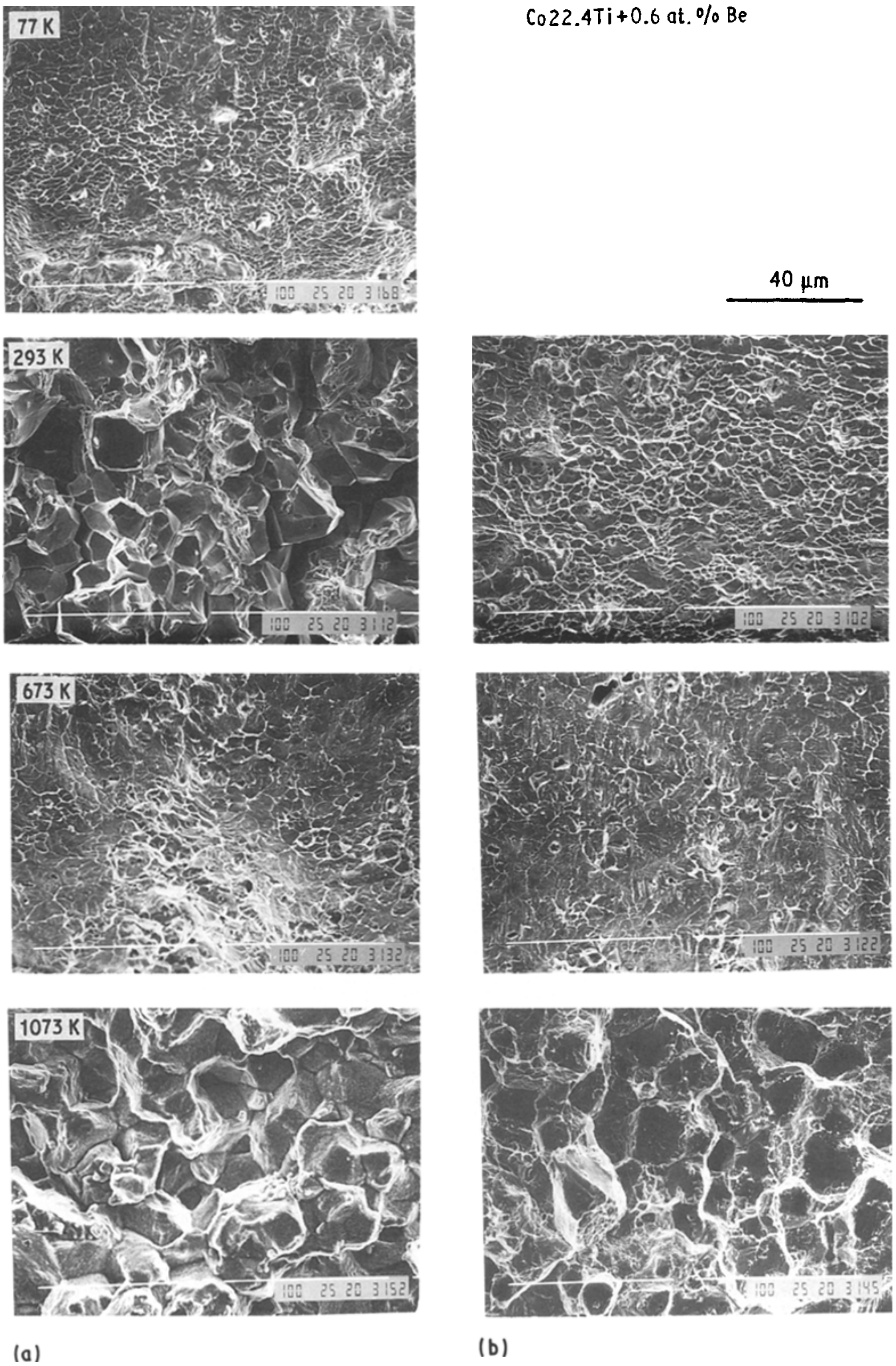

Figure 14 Temperature dependence of the fractographs for the Co_3Ti alloys doped with beryllium which were tested in (a) air, and (b) vacuum. Note that the fractograph at 77 K was taken after testing in liquid nitrogen medium.

hydrogen contained in the sample is supposed to affect the grain-boundary cohesion and also the associated plastic flow with a propagating micro crack. Therefore, when we investigate the tensile behaviour of extremely pure alloys at extremely high strain rates [6], or of the single crystals which do not provide the stressed sites condensed by hydrogen [8], it was observed that the curves of the elongation–temperature plots do not show a minimum around room temperature and therefore show a monotonic change with increasing temperature from 77 K.

For the environmental effect associated with oxygen which would be operative at high temperatures, the results obtained here are somewhat different from those obtained in the Ni_3Al alloys doped with boron [4]. The boron-doped Ni_3Al alloy did not show any environmental effect on tensile ductilities at room temperature either in air or in vacuum but did show an effect at high temperatures [4]. At high temperatures (~ 600° C), boron-doped Ni_3Al polycrystals showed lower tensile ductilities in air than in vacuum. The loss in ductility was accompanied by a change in fracture mode from transgranular to intergranular, a feature of which is quite similar to the loss in ductility due to hydrogen. It was suggested that this embrittlement was due to a dynamic effect simultaneously involving localized stress concentrations, elevated temperature, and gaseous oxygen. The difference is that the temperature guaranteeing their mobilities into the micro crack is high in the oxygen-related embrittlement and low in the hydrogen-related embrittlement.

However, the environmental effect associated with oxygen was not found in the Co_3Ti alloys. The process of oxygen (and even hydrogen) embrittlement has been considered to consist of several general steps, as described previously: (i) adsorption of gaseous molecules, (ii) dissociation of molecules to form atoms or ions, (iii) diffusion and enrichment of oxygen to the stressed region and/or grain boundary (or crack-free surface) near the crack tip, and (iv) loss of mechanical strength. Amongst these, step (iii) could be correlated with atomic solid solubility [9]. The general form of the relationship is that the enrichment factor of the atom is inversely proportional to the solid solubility of the atom. Previous observations on the Co_3Ti alloys [6] showed that dissolved oxygen and hydrogen were approximately 0.02 and < 0.0001 mass %, respectively. This implies, in the case of the Co_3Ti alloys, that the effect of enrichment on the stressed defect is high for hydrogen atom and low for oxygen. Hence, embrittlement due to hydrogen evidently occurred and embrittlement due to oxygen did not. On the other hand, the analysis of the Ni_3Al alloys showed that the amount of dissolved oxygen was 0.002 to 0.015 mass % [10] although the amount of dissolved hydrogen was little reported. Therefore, it might be expected that the effect of enrichment of oxygen into the stressed defect is high in the case of the Ni_3Al alloys, compared with the Co_3Ti alloys. As a result, it is suggested that embrittlement due to oxygen atoms severely occurred in the case of the Ni_3Al alloy. Details of dynamic embrittlement due to oxygen as well as hydrogen are not so simple, and therefore more research is needed to characterize this phenomenon and the differences between Co_3Ti and Ni_3Al alloys. The bonding nature between gaseous atoms and constituent atoms may also be responsible for this phenomenon. The decohesion is associated with Co–Ti or Ti–Ti bonds. Whether or not oxygen ad- (or ab-) sorptions at the crack tip actually affect these bond pairs must be understood.

Finally, let us consider the interaction between the gaseous atoms and additive solid atoms in the environmental effects on the Co_3Ti alloys. Results observed here clearly indicated that no solid species (boron, carbon or beryllium) observed in this work had any envrionmental effect on the ductile behaviour, although substitutional atoms such as iron and aluminium have been shown to prohibit hydrogen embrittlement in the Co_3Ti alloys [8, 12]. In other words, no solid species prohibited either hydrogen embrittlement or created oxygen embrittlement in the Co_3Ti alloys. It has been reported in the Ni_3Al alloy that boron prohibited environmental embrittlement in air through competing with hydrogen for site occupation at grain boundaries [10]. Therefore, it is very likely that the solid species of boron, carbon and beryllium do not segregate to the grain boundary of the Co_3Ti alloys.

5. Conclusions

The Co_3Ti polycrystals doped with boron, carbon and beryllium were tensile tested in air and compared with the results of tensile testing in vacuum [5]. The following results were obtained.

1. The yield stresses of all the alloy systems investigated were independent of the test environment at all test temperatures.
2. The tensile elongation and the UTS of all the alloy systems investigated were found to be strongly dependent on the test environment at ambient temperatures (below 473 K) but independent of the test environment at high temperatures (above 473 K).
3. Ductility reduction is accompanied by a change in fracture mode from transgranular to intergranular.
4. It was suggested that this embrittlement was due to the hydrogen absorbed from air and to the dynamic effect involving the weakening of grain-boundary cohesion and the change of the corresponding plastic flow in a crack tip.
5. No solid species observed in this work produced any environmental effect on the ductile behaviour of the Co_3Ti alloys.

Acknowledgement

This research was partly supported by a Grain-in-Aid for Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control, The Ministry of Education, Science and Culture, Japan.

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Received 13 March
and accepted 30 August 1989