

The Influence of Oxygen and Carbon-Content on Aging of Ti-15-3

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Optical microscopy, analytical transmission microscopy and scanning electron microscopy, and hardness tests have been carried out on quenched samples of Ti-15wt.%V-3wt.%Cr-3wt.%Al-3wt.%Sn containing different levels of oxygen and carbon that were aged at temperatures between 400 and 600 °C. The increase of oxygen content and the addition of carbon (C) increase the kinetics and the magnitude of age hardening. The addition of C greatly reduces the coarse grain boundary precipitation of α . Room temperature deformation has been shown to override compositional differences, and all deformed alloys age harden similarly. The role of oxygen and carbon additions and deformation on aging kinetics are discussed in terms of the factors, such as ω , dislocations, and grain boundary oxygen content that influence α precipitation.

Keywords carbon, oxygen, Ti-15-3

1. Introduction

It has been shown recently that the addition of carbon (C) to Ti-25V-15Cr-2Al leads to a significant improvement in properties. The ductility of this alloy is reduced close to zero when it is exposed at 550 °C for 500 h, but with 0.2 C added the ductility is over 10% (Ref 1). The improvement in the properties of Ti-25V-15Cr-2Al through the addition of 0.2 C occurs because the Ti_2C that is formed acts as a getter, and reduces the oxygen content in the matrix alloy and in the grain boundary regions. This reduction of oxygen in the grain boundary region is particularly important in this alloy because it reduces the unwanted embrittling precipitation of α during exposure at an operating temperature of about 550 °C. In addition, and significantly, the carbides limit grain growth during processing, which will also result in a reduction in the oxygen content of grain boundaries.

Detailed work on a range of binary Ti alloys has shown that the formation of Ti_2C (rather than TiC) is a necessary but not a sufficient condition for it to act as a getter (Ref 2). It is also necessary that oxygen has some solubility in the Ti_2C , and this has been found to be the case for alloys containing V, Mn, Fe, and Cr.

The role of the addition of C to some commercial β Ti alloys has also been studied, and it has been found that the properties of Ti-15wt.%V-3wt.%Sn-3wt.%Cr-3wt.%Al (Ti-15-3) are significantly improved through the addition of C (Ref 3). Thus, it has been found the carbon addition has a significant effect on the age hardenability and thermal stability of the age-hardened

alloy. The presence of carbides in Ti-15-3 was found to accelerate the precipitation and to inhibit the growth of α phase, and to improve the homogeneity of α precipitation throughout the grains as well as reducing the tendency for coarser α precipitation at grain boundaries.

The present work was undertaken in an attempt to distinguish between the roles of the carbides themselves and the oxygen content in the matrix in influencing the kinetics of the precipitation of α . The presence of the hard carbides also leads to dislocation generation during quenching, and these dislocations act as sites for α precipitation (Ref 4). In addition, as noted above, the carbides remove some oxygen from the matrix, which will have a dual affect on α precipitation. First, oxygen is an α stabilizer, and any reduction in the level of oxygen could lead to a reduced tendency for the formation of α . Second, a reduction in oxygen content will lead to an increase in the amount of ω (which can act as a precursor for α precipitation) (Ref 5-7).

There is general agreement that deformation after quenching accelerates the precipitation of α , although the banding of precipitation (Ref 8) is seen, which leads to samples with heterogeneous properties. The role of deformation is not straightforward inasmuch as it has been argued that deformation reduces the amount of ω formed on subsequent aging (Ref 5, 9), which would be expected to decrease the aging response (Ref 5, 6).

In view of the dual role of C (i.e., the formation of carbides and the reduction of the oxygen content of the matrix and grain boundaries) the aging response of samples that do not contain the deliberate addition of C but have different oxygen levels has been examined and compared with the response of samples containing 0.2 or 0.15 C. In addition, the role of dislocations on α precipitation has been considered by comparing the age-hardening kinetics of samples that have been deformed after quenching with those of C-containing and as-quenched samples.

2. Experimental

One kilogram buttons of Ti-15-3, with and without the addition of C, were melted using elemental feedstock in a button

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Table 1 Showing the nominal compositions of the alloys

Ti	V	Cr	Al	Sn	C	O
Balance	15	3	3	3	<0.02	1300 ppm
Balance	15	3	3	3	0.2	1300 ppm
Balance	15	3	3	3	0.15	1300 ppm
Balance	15	3	3	3	<0.02	750 ppm
Balance	15	3	3	3	0.15	3500 ppm

Note: Values are in wt.%, unless otherwise indicated.

plasma melter. The standard alloy using the normal feed stock results in an O content of between 1150 and 1300 ppm. Low-oxygen feedstock was used to prepare a button with 750 ppm oxygen, and high-oxygen feedstock was used to produce a button with 3500 ppm oxygen. The nominal compositions of the V, Cr, Al, and Sn contents are shown in Table 1, together with the analyzed values of oxygen and carbon. Buttons were melted at least four times to ensure chemical homogeneity. Sections from the buttons were forged at 1050 °C at a strain rate of 5×10^{-3} s to break down the cast structure, and the samples cut from these buttons were heat-treated.

The samples for aging studies were solution treated at 900 °C (significantly above the β transus) for 1 h and water quenched before aging at 400, 450, and 600 °C for different times. After polishing, the samples that had been heat treated to different stages were etched using 7% HF, 10% HNO₃, and 83% H₂O for conventional optical observation. Both etched and unetched samples were examined in a scanning electron microscope (SEM). Samples of the quenched Ti-15-3 with and without the addition of C were deformed to about 20% strain at room temperature to introduce a significant density of dislocations.

Secondary electron imaging, back-scattered electron imaging, and composition analysis were carried out on a Philips XL30 SEM (Amsterdam, The Netherlands) interfaced to an Oxford Instruments energy dispersive x-ray (EDX) analysis system. Analysis for oxygen was done using a wavelength dispersion x-ray (WDX) detector fitted on an analytical SEM. Transmission electron microscopy (TEM) was carried out using a Philips CM20 interfaced to an Oxford Instruments EDX analysis system. Hardness tests have been carried out using a standard Vickers hardness tester with a load of 20 kg.

3. Results

3.1 Optical Microscopy

Optical micrographs of the cast and heat-treated samples show that the only important difference in the microstructures between the standard oxygen (1300 ppm) Ti-15-3 low-oxygen (750 ppm) sample and the C-containing samples is the carbides. After forging and quenching from 900 °C, these carbides, which have been broken down, act to limit grain growth so that the grain size in the C-containing samples is about a factor of 10 less than of that in the C-free samples. This is illustrated in Fig. 1, where the microstructures of the samples containing 1300 ppm oxygen are shown in Fig. 1(a) with no C addition and in Fig. 1(b) with 0.15 C.

Samples were aged at 400, 450, and 600 °C after quenching, and Fig. 2 shows the microstructures observed after aging at 600 °C. Figure 2(a) shows the microstructure of the low-oxygen (750 ppm) sample, Fig. 2(b) shows that of the 1300 ppm oxygen sample, and Fig. 2(c) and (d) show the 1300 ppm

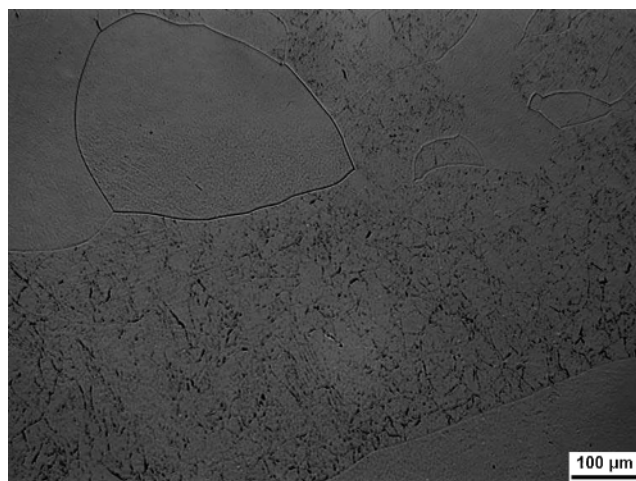
**(a)****(b)**

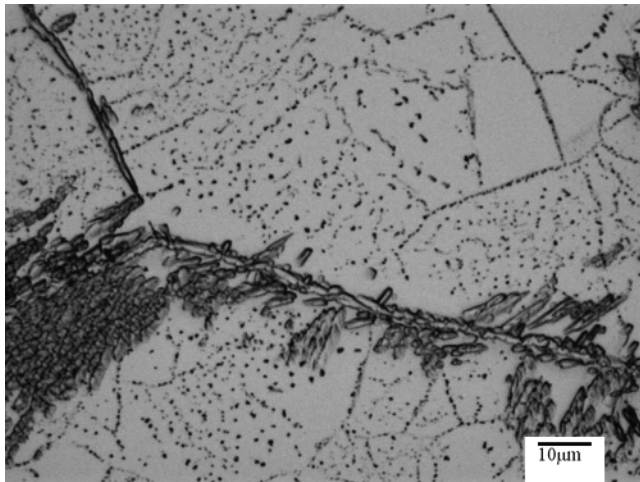
Fig. 1 Optical micrographs of samples forged and quenched from 900 °C: (a) standard oxygen (1300 ppm) Ti-15-3, and (b) a standard oxygen (1300 ppm) sample containing 0.15 C

oxygen sample with 0.15 and 0.2 C, respectively. It is clear that coarse grain boundary precipitation of α occurs in the C-free samples and that much finer precipitation occurs in the samples containing 0.15 and 0.2 C.

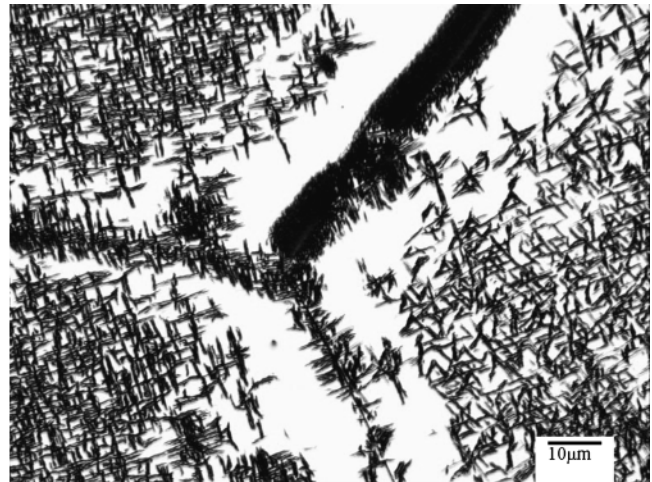
The microstructures of the low-oxygen sample and the standard oxygen sample with and without additions of C after aging for 8 h at 400 °C are shown in Fig. 3. Coarse grain boundary α is again obvious on the grain boundaries in both C-free samples, but all precipitation, including any at the grain boundaries, is too fine to resolve in the samples containing 0.15 and 0.2 C in these micrographs. Figure 4 shows the micrographs obtained from the samples aged at 600 °C, which were deformed to 20% strain in compression after quenching. The defects introduced by deformation have influenced the precipitation in all samples, so that optical microscopy is unable to resolve precipitates and the observable contrast appears to be caused by decorated slip.

3.2 Scanning Electron Microscopy

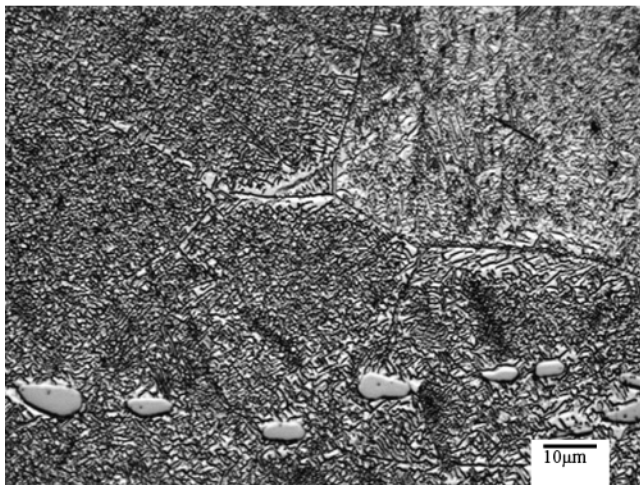
Examination of the as-quenched samples confirmed the findings of optical microscopy that they are all single phase



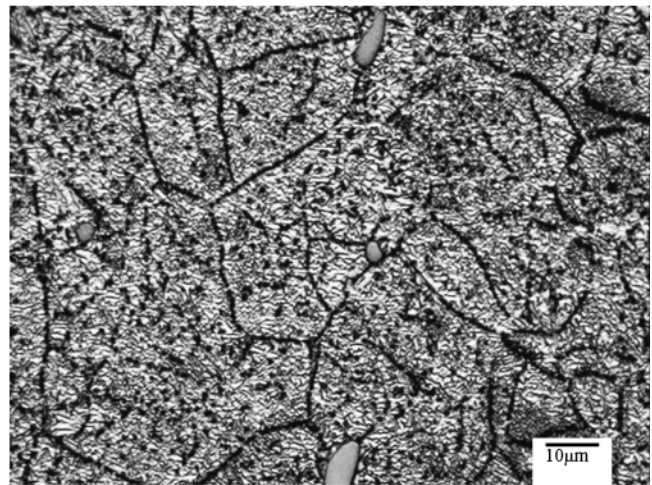
(a)



(b)



(c)



(d)

Fig. 2 Optical micrographs of Ti-15-3 quenched from 900 °C that was aged for 8 h at 600 °C (a) of the low-oxygen (750 ppm) sample and (b), (c), and (d) of the standard (1300 ppm) oxygen-content sample (b) C-free, (c) containing 0.15 C, and (d) containing 0.2 C

apart from the presence of carbides in the C-containing alloys.

Observations have been made after aging at 400, 450, 500, and 600 °C, and in all cases the trend was for the coarser precipitation of α at higher aging temperatures. As was found with optical microscopy (even for a higher aging temperature at which precipitation would be expected to be coarser), no obvious precipitation is apparent in aged, deformed quenched samples, and SEM observations added nothing to the optical microscopy.

Analytical SEM has been used to assess the extent of the removal of oxygen from the matrix by the titanium carbides formed in the C-containing samples. The number of counts in the oxygen peak was compared for identical electron optical conditions when the electron probe was on the matrix and on carbide particles. The number of oxygen counts obtained in a reasonable counting time was very low, between 100 and 200, which leads to x-ray data that are accurate to only about 20%. The counts obtained from matrix and carbides were indistinguishable within this accuracy so that the formula of these carbides is about $\text{Ti}(\text{C}_{0.95}\text{O}_{0.05})$. The magnitude of the gettering is thus slightly less than that in Ref 1. Because the carbides are present at about 4 vol.%, the oxygen level in the matrix has

been reduced to only about 1200 ppm in the case of the 1300 ppm sample. It is however significant that many of the carbides are in the β grain boundaries and that the precipitation of grain boundary α is virtually eliminated in the C-containing alloys. Thus, locally the carbides may have reduced the C content through rapid grain boundary diffusion of the carbon.

3.3 Transmission Electron Microscopy

TEM has been carried out with the aim of identifying the important factors governing the nucleation of α during aging. It was found that the density of α precipitates formed in different samples and at different aging temperatures follows the density of ω precipitates. This is illustrated in Fig. 5 where the density observed of α and ω (using dark-field imaging to image a single habit) decrease in parallel with the increase of aging temperature.

Even though ω is unstable at higher temperatures and longer aging times, observations have shown that ω is formed during heating up to the highest temperatures used, and this appears able to nucleate α . This has been confirmed by heating samples either rapidly or slowly to 600 °C where it has been found that

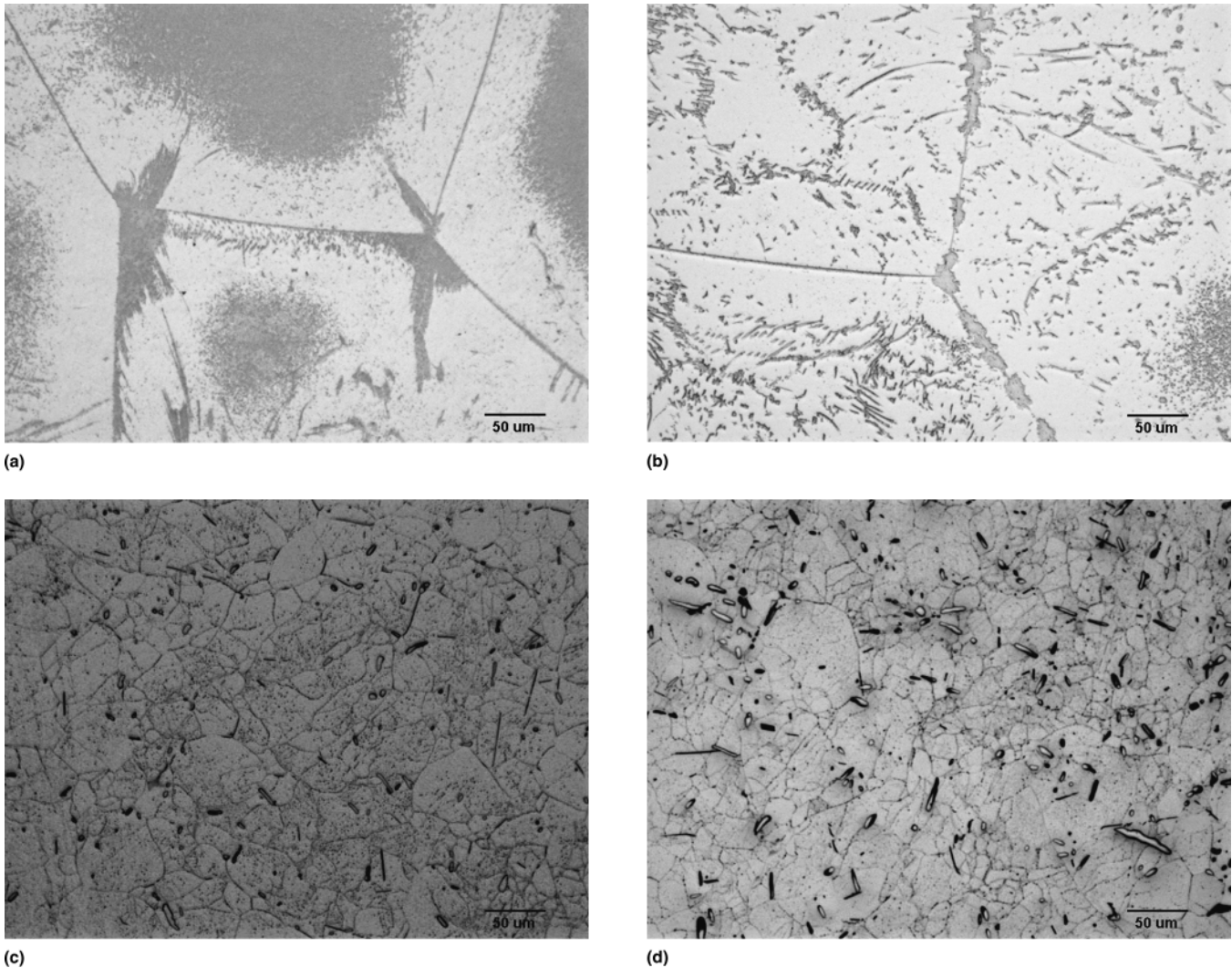


Fig. 3 Optical micrographs of samples aged 8 h at 400 °C quenched from 900 °C with (a) 750 ppm oxygen and (b), (c), and (d) 1300 ppm oxygen that were (b) C-free, and had (c) 0.15 C and (d) 0.2 C

rapidly heated samples do not harden significantly on subsequent aging, and slowly heated samples initially harden and then soften reaching a significantly higher final hardness than the rapidly heated samples. The slow heating allows ω to form, enabling α to precipitate, which gives rise to the longer-term hardening, while ω redissolves, causing softening. Direct observation using the dark field confirms that individual α precipitates are associated with individual ω precipitates.

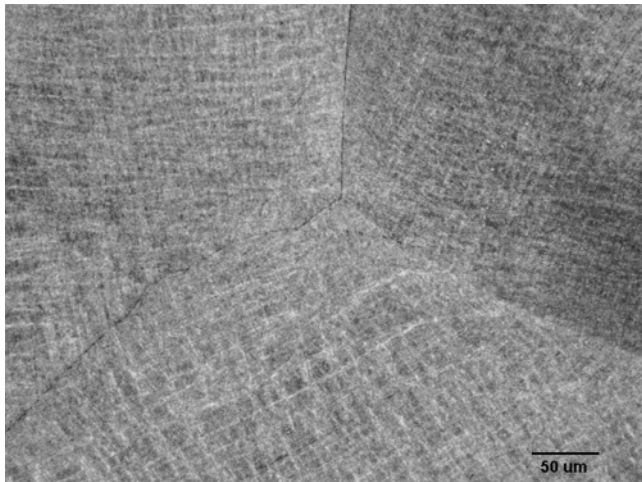
TEM shows that local stresses due to the carbides give rise to punched-out dislocations and that these dislocations act as sites for α precipitation. However, α precipitates are significantly more closely spaced than the punched out dislocations, and it is clear that additional nucleation sites are operative at all temperatures.

3.4 Hardness Tests

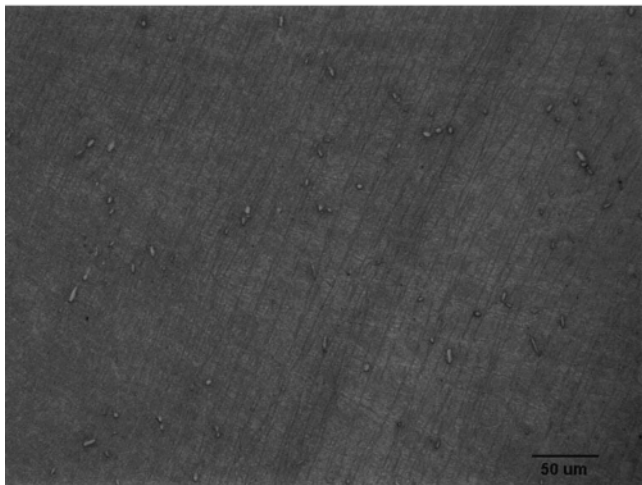
Comparisons of the hardening response of the alloys at 400, 450, and 600 °C, respectively, are shown in Fig. 6(a) to (c). Considering the two alloys without the addition of C (the two lowest curves on each figure), it is clear that the reduction of the O content from 1300 to 750 ppm has the same effect at all

three aging temperatures; it reduces the speed of age hardening and also reduces the maximum hardness that can be achieved. The addition of 0.15 or 0.2 C to the standard alloy containing 1300 ppm oxygen increases the hardening response at 400 and 450 °C but has a smaller effect at 600 °C. The 0.15 C addition improves the hardening response more than does the 0.2 C addition. From the comparison of the aging response of alloys containing this optimum amount of C it is also clear that the aging response of the high-oxygen (3500 ppm) alloy is better than that of the standard (1300 ppm) oxygen content alloy at all temperatures. The as-quenched hardness is highest for the samples containing C, and decreases as the C content and O content are reduced, with the C-containing alloy with 3500 ppm O having the highest value and the sample with no added C and low oxygen (750 ppm) having the lowest value.

The age-hardening curves at 400 °C for samples that had been deformed after quenching are shown in Fig. 7, which shows that the kinetics of age hardening are now similar for all alloys and that aging the deformed samples at this temperature has reversed the kinetics of the 0.2 C and the 0.15 C alloy seen in samples without deformation. The 0.2 C alloy now hardens more rapidly and to a slightly higher hardness than the



(a)



(b)

Fig. 4 Optical micrographs of (a) the low-oxygen (750 ppm) sample and (b) the 0.15 C sample. Samples were aged for 8 h at 600 °C after being deformed at room temperature.

0.15 C alloy, contrary to the behavior at 450 °C without deformation.

4. Discussion

The influence of the matrix oxygen level on the age-hardening response is apparent from the results shown in Fig. 6, where the samples containing 750 ppm oxygen age-harden much more slowly and reach a far lower ultimate hardness than the sample containing 1300 ppm. A further increase of oxygen to 3500 ppm in an alloy containing 0.15 C increases the hardening rate and ultimate hardness, and the most obvious interpretation of the role of oxygen is that it increases the driving force for α precipitation because it is an α stabilizer. The fact that an increase in oxygen level leads to a decrease in the amount of ω (Ref 5-7) appears not to be important, despite the fact that ω does nucleate for α .

The fact that the addition of 0.15 C to a sample containing 1300 ppm O accelerates the hardening kinetics and increases the ultimate hardness to well above that observed in C-free samples containing either 750 or 1300 ppm suggests a complex

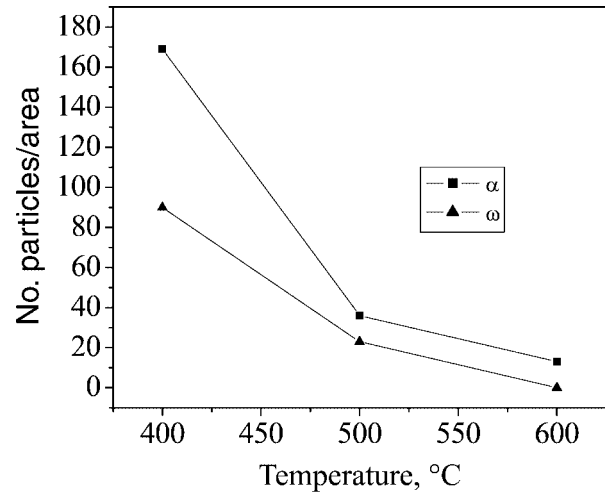
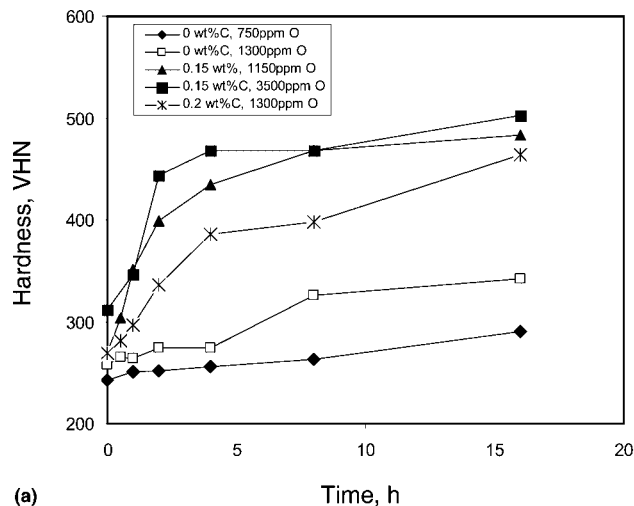


Fig. 5 Graph showing the changes in the numbers of ω and α precipitates observed as a function of aging temperature for Ti-15-3 containing 1300 ppm oxygen. Data were obtained using dark-field imaging in a transmission electron microscope using identical imaging conditions, in which one habit of each precipitate was imaged at all temperatures.

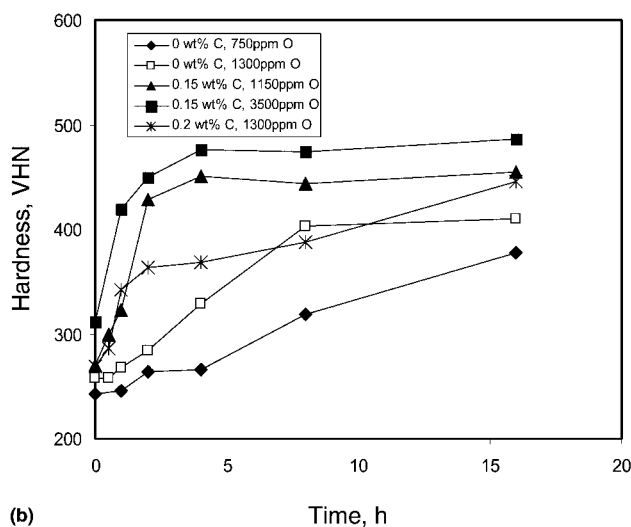
role for C. The slight reduction in the matrix oxygen level caused by gettering by the titanium carbide will increase the amount of ω (thus providing more nucleation sites for α), but the observations on the samples with different oxygen contents suggests that this effect is insignificant. The reduction in the oxygen level will decrease the driving force for α because oxygen stabilizes α , but the relatively small change in oxygen content caused by gettering will again not be significant. It thus appears that the role of C in changing the hardening kinetics and ultimate hardness is not the result of the small change in composition of the matrix and, thus, must be due either to the stresses generated by the carbides during cooling or to some complex interaction between C atoms in solution with point defects. The stresses that are present certainly generate dislocations, which do provide nucleation sites for α , but detailed TEM images show that the scale of the α precipitation is too fine to be accounted for by these punched out dislocations. Work on Ti-13Cr to which yttria particles have been added shows that the precipitation of α is refined by the presence of these inert particles and again that the punched out dislocations are on too coarse a scale to account for the refinement (Ref 10). This observation strongly suggests that unrelieved elastic stresses, caused by the differential contraction of the particles and the matrix, exert an influence on α precipitation.

TEM has also shown some evidence for β phase separation (Ref 11) in Ti-15-3, and at low-aging temperatures this may also influence α precipitation. The addition of C would be expected to reduce the tendency for α formation via this mechanism because the local oxygen content is slightly reduced, which would be expected to reduce the tendency for β phase separation. The present observations, however, provide no data that clarify any role that β phase separation may play in α precipitation.

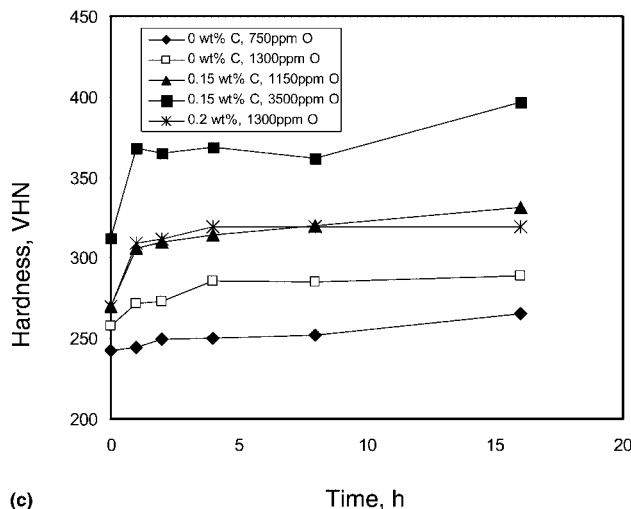
The most obvious and important effect of C is the reduction in grain size and a reduction in the amount of grain boundary α that is formed. The reduction in the grain size by a factor of about 10 will reduce the amount of oxygen in grain



(a) Time, h



(b) Time, h



(c) Time, h

Fig. 6 Age-hardening curves obtained at (a) 400 °C, (b) 450 °C, and (c) 600 °C for the low-oxygen Ti-15-3 alloy (◆), the standard oxygen alloy (1300 ppm) Ti-15-3 (□), the standard oxygen alloy containing 0.15 C (▲), the standard oxygen content alloy containing 0.2 C (✱), and the high-oxygen content (3500 ppm) alloy containing 0.15 C (■)

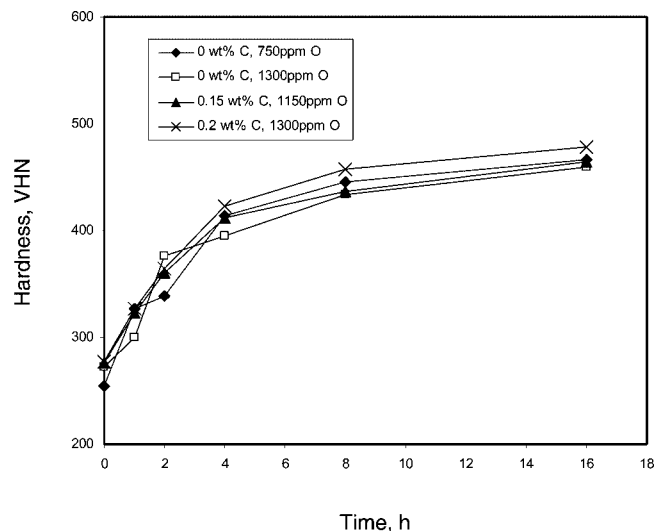


Fig. 7 Age-hardening curves obtained at 400 °C for samples that had been deformed after quenching showing the low-oxygen sample (750 ppm) (◆), the standard oxygen sample (1300 ppm) (□), the 0.15 C-containing sample (▲), and the standard oxygen content sample (1300 ppm) containing 0.2 C (✱)

boundaries by about the same factor, and this reduction, taken with a reduction of the oxygen content in the grain boundaries by the $Ti(C_xO_y)$, are the obvious causes of the reduction in the tendency to form grain boundary α , because oxygen is an α stabilizer and a reduction in the local oxygen level would reduce the driving force for α precipitation.

Further work is underway that is aimed at increasing our understanding of the complex role of C additions. In addition, an industrially supported program is underway in which the significance of the addition of C on commercially processed Ti-15-3 is being studied inasmuch as the reduction of aging times and the elimination of grain boundary α are commercially significant factors. These two aspects will be reported on later.

5. Summary

- Addition of C to Ti-15-3 accelerates hardening and refines α precipitation within the grains and at grain boundaries. Similarly, an increase of oxygen from 750 to 1300 ppm and to 3500 ppm results in an improved aging response in Ti-15-3.
- Deformation of the quenched samples leads to a similar aging response for all alloys for the various oxygen and carbon levels investigated.
- The role of carbides in α precipitation is complicated due to their role in slightly changing oxygen levels, which in turn influences ω precipitation and the driving force for α formation. Punching stresses also appear to be an important factor in influencing α precipitation.
- The most important effect of C is the very significant reduction in the amount of grain boundary α formed during aging.

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