JOURNAL OF MATERIALS SCIENCE 14 (1979) 1407–1412

Tempering of a beta quenched Zr–1.9 wt % Cr alloy

Part 3 *Tensile properties*

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The room temperature tensile properites of a Zr–1.9 wt % Cr alloy have been examined in the beta quenched as well as in tempered conditions and the results have been rationalized in terms of possible hardening mechanisms. The appearance of the fracture surfaces has been correlated to the microstructures developed in the alloy after various heat-treatments.

1. Introduction

Little work appears to have been performed to date on the dependence of the strength of dilute zirconium–chromium alloys on their microstructure. Since a variety of phase transformations can occur in these alloys, there is a possibility of obtaining various types of microstructures which, in turn, are likely to have a considerable influence on the strength properties. Keeler's study [1] on the effect of $ZrCr_2$ precipitation on the tensile properties of zirconium–chromium alloys containing up to 18 at.% chromium has shown that while chromium additions do not cause any significant solid-solution hardening in zirconium, there exists a linear relation between the flow stress of the alloys and the volume fraction of the $ZrCr_2$ precipitates and that the precipitation-hardening effect increases with strain over a wide range. He has also found that although the hardening contribution of the precipitates decreases with increasing temperature, the fractional increase in the strength compared to that of the precipitate-free matrix is essentially constant. A more recent study [2] has indicated that the chromium content and the rate of quenching from the beta phase have a marked influence on the strength of zirconium–chromium alloys through the formation of the metastable martensite and omega phases. The omega phase is associated with extremely high strengths and low ductilities. The martensitic transformation also brings about a good deal of hardening although the enhancement in strength and the reduction in ductility are not as drastic as in the case of omega formation. Moreover, it is only the internally twinned martensite and not the dislocated lath martensite (the former replaces the latter as the chromium content increases) that is associated with a significant hardening. On tempering the martensitic or the omega structures, which are unstable at high temperatures, the $ZrCr_2$ phase precipitates and the strengthening effect associated with these precipitates could be maximized by suitably controlling their size and their distribution through a judicious choice of alloy composition and heat-treatment schedule. These authors have suggested that the structures obtained on tempering the omega phase would be associated with a very much more uniform dispersion of $ZrCr_2$ precipitates as compared to those produced by tempering the martensite and are thus likely to exhibit superior properties during high-temperature service.

In the work reported in this paper, the effect of tempering a beta quenched Zr–1.9 wt % Cr alloy on its room temperature tensile properties has been examined.

2. Experimental details

As mentioned in Part 1, the alloy was received in the form of a 1 mm thick strip which was cold-rolled to about 0.3 mm thickness. The tensile test specimens were punched out in such a manner that the gauge length was perpendicular to the final rolling direction. These specimens were then subjected to the desired heat-treatments and tested at room temperature. The tests were conducted (in a floor model Instron machine) at a strain-rate of 6.5×10^{-5} sec^{-1}. The topography of the fracture surfaces of the tested specimens was examined by scanning electron microscopy (secondary electron imaging).

TABLE I Yield strength and ultimate tensile strength of the Zr–1.9 wt% Cr alloy after different heat-treatments

Treatment	0.2% offset yield strength (kg mm^{-2})	Ultimate tensile strength (kg mm^{-2})
Beta quenched	75.29	90.59
Aged for 2 h at 350° C	88.26	100.7
Aged for 4 h at 350° C	74.59	92.83
Aged for 2 h at 550° C	75.34	99.75
Aged for 16 h at 550° C	64.36	77.73
Aged for 2 h at 700° C	51.49	71.66
Aged for 16 h at 700° C	46.19	63.80

3. Results and discussions

3.1. Tensile properties

Room temperature tensile properties of the alloy were examined after various heat-treatments. Some of the observed values of the 0.2% offset yield strength and the ultimate tensile strength are given in Table I while the corresponding true stress versus true plastic strain plots are shown in Fig. 1. It was seen that for a given ageing time, the strength of the alloy decreased with increasing ageing temperature. Again, at low tempering temperatures, the strength first increased and then decreased with increased period of tempering while the alloy softened continuously when the ageing temperature was higher. These observed trends suggested that precipitation hardening was a primary source of strength in this alloy, precipitate coarsening being associated with a fall in strength.

The beta quenched alloy was found to be much stronger than pure zirconium. The major factors which could have led to this enhancement in strength were: (i) solid-solution hardening, (ii) hardening due to the martensite substructure, (iii) hardening due to the formation of the omega phase, and (iv) hardening due to $ZrCr_2$ precipitation during quenching.

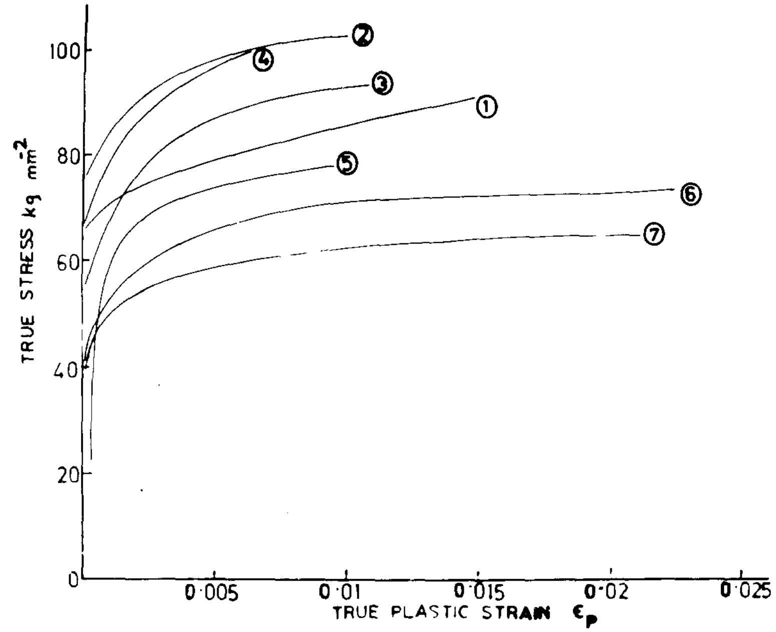

Figure 1 True stress versus true plastic strain plots corresponding to various heat-treatments. The tests were carried out at room temperature. 1, beta quenched; 2 beta quenched and aged at 350° C for 2 h; 3, beta quenched and aged at 350° C for 4 h; 4, beta quenched and aged at 550° C for 2 h; 5, beta quenched and aged at 550° C for 16 h; 6, beta quenched and aged at 700° C for 2 h; 7, beta quenched and aged at 700° C for 16 h.

The equilibrium solubility of chromium in alpha zirconium being extremely restricted, there would be a strong tendency for excess chromium atoms to be thrown out of the alpha zirconium lattice. The fact that even rapid beta quenching could not suppress the precipitation of the $ZrCr_2$ phase testified to this catharsis. The extent of solute supersaturation in the martensite in the quenched alloy was certainly much smaller than that implied by the alloy composition. Apart from this, in view of the physical theories of solid-solution hardening developed by Stern [3] and by Collings and Gegel [4], chromium ([Ar] $3d^5 4s^1$) is unlikely to be a strong solid-solution hardener in zirconium ([Kr] $4d^2 5s^2$). Significant solid solution strengthening is expected only when the perturbation of the wave function of the solvent due to the presence of the solute is large [3] – a situation obtained when the solvent and the solute belong to columns of the periodic table that are far apart. This condition is obviously not satisfied in the case of zirconium and chromium and thus one may expect only a weak interaction. On the basis of these considerations, it appeared unlikely that solid-solution hardening was a major factor contributing to the strength of the beta quenched alloy. The martensite substructure must have brought about some strengthening, the plate boundaries and the dislocations within the plates acting as obstacles to the motion of glissile dislocations. At the same time, it should be borne in mind that this hardening must have been much smaller than what would be obtained in an internally twinned martensite of small plate size because in the latter the interfaces obstructing dislocation motion are more impenetrable and more numerous [5]. The formation of the omega phase is known to be associated with the spectacular hardening effect [6]. However, in the present case, the presence of this phase could not be detected either in the beta quenched or in the tempered alloy. If omega formation did occur, its volume fraction and, therefore, its contribution to the strength of the alloy must have been small. In the light of these considerations it appeared that the strength of the beta quenched alloy was derived, to a very large extent, from the observed fine dispersion of $ZrCr_2$ precipitates.

Ageing at 350° C for short periods would lead to further expulsion of chromium from the matrix and a consequent increase in the precipitate density. At the same time, no significant growth of the pre-existing precipitates would occur during these short tempering treatments, the growth kinetics being slow at low temperatures. As a result, these treatments would lead to a further enhancement in strength. This was observed. On prolonged ageing, however, precipitate coarsening would take place and cause softening (as in the case of tempering at 350° C for 4 h). A similar situation seemed to prevail when tempering was carried out at 550° C. At these temperatures, the martensite substructure remained more or less unaltered (with reference to the beta quenched alloy) so that the strengthening contribution from this source was also available. Ageing at 700° C, however, corresponded to a much faster precipitate growth kinetics; the larger precipitates coarsened rapidly at the expense of the smaller particles. This led to a significant drop in the strength of the alloy. Some loss in strength must also have occurred due to the recovery and recrystallization of the martensite structure.

These considerations make it clear that the strength of the alloy depended greatly on the size and the distribution of $ZrCr_2$ precipitates. Although a substantial strengthening could be obtained in this dilute zirconium–chromium alloy in the quenched and in the tempered conditions by obtaining a fine precipitate dispersion, the uniform elongation was observed to be prohibitively low: between 1% and 2% on beta quenching and on tempering at 350° C, between 3% and 4% on tempering at 550° C and between 4% and 5% on tempering at 700° C. Since tensile tests at high temperatures were not carried out, it could not be ascertained whether this poor elongation persisted at such temperatures.

The low uniform elongation in this alloy pointed to a rapid work-hardening. This was qualitatively consistent with Ashby's theory of the deformation of plastically inhomogeneous materials [7] which is applicable to a situation where a dispersion of hard particles exists in a relatively soft matrix. This theory predicts that when the interparticle spacing is in the submicron range (as in the present case), the work-hardening rate is higher, the smaller the particle spacing (i.e. the geometric slip distance).

3.2. Fractography

Fractographic studies were made on the fracture surfaces of tensile specimens fractured at room temperature. It was found that the fracture

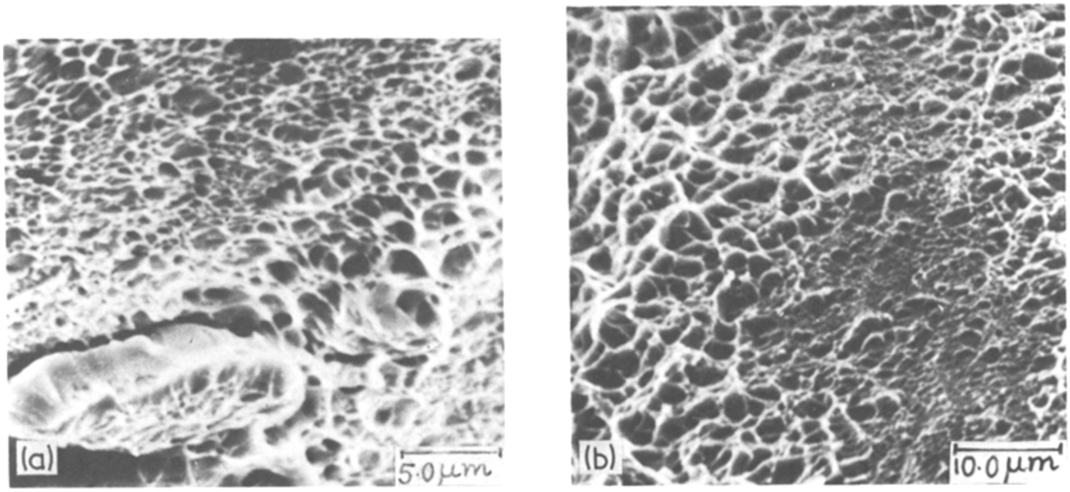

Figure 2 Dimple appearance of fracture surface suggesting a fracture mechanism involving microvoid coalescence. (a) Beta quenched; (b) beta-quenched and aged at 350° C for 4 h.

surfaces of the beta quenched samples as well as of the samples tempered at 350° C exhibited, in general, a clear dimple appearance characteristic of the microvoid coalescence mechanism (Fig. 2). However, facets showing only a small density of dimples were also encountered occasionally (Fig. 3). It can be recalled that the samples corresponding to these treatments showed very little uniform elongation. It was surprising how a predominantly ductile fracture mode could operate in a situation where the elongation was so limited. The apparently contradictory observations of a low uniform elongation and a ductile failure mode implied that although the fracture travelled a path where a considerable amount of plastic deformation occurred, the lengths through which the cracks had to traverse in order to join up with the neighbouring ones were very small. Such a situation is likely to prevail in a structure where fine, hard particles are distributed in a relatively soft matrix, the particle density being very high. In the present case, it was plausible that numerous microvoids nucleated at the interfaces between the hard $ZrCr_2$ particles and the softer α-Zr(Cr) matrix at a low level of plastic strain and because of the small interparticle spacing, they joined up rapidly, leading to failure. The fine microvoids observed in the beta quenched and the low-temperature tempered samples did point to easy and extensive nucleation of these at the precipitate–matrix interfaces.

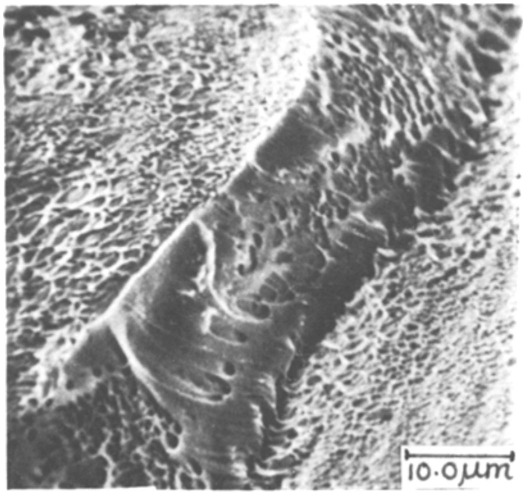

Figure 3 Zr–1.9 wt % Cr, beta quenched. The density of microvoids is smaller in the facet running diagonally.

Specimens tempered at higher temperatures (550° C and above) showed a relatively high uniform elongation and the fractographic features were correspondingly coarse (Fig. 4). The coarser and more widely spaced precipitates in these samples reduced the frequency of microvoid nucleation. Consequently, the fracture path length was larger.

Another interesting fractographic feature frequently encountered in samples tempered at 700° C was the appearance of "parallel striations" (Fig. 5). The formation of similar features under monotonic loading conditions has been reported in alpha titanium by Chessnutt and Williams [8] and in zirconium and zirconium alloys by Aitchison and Cox [9]. These workers have

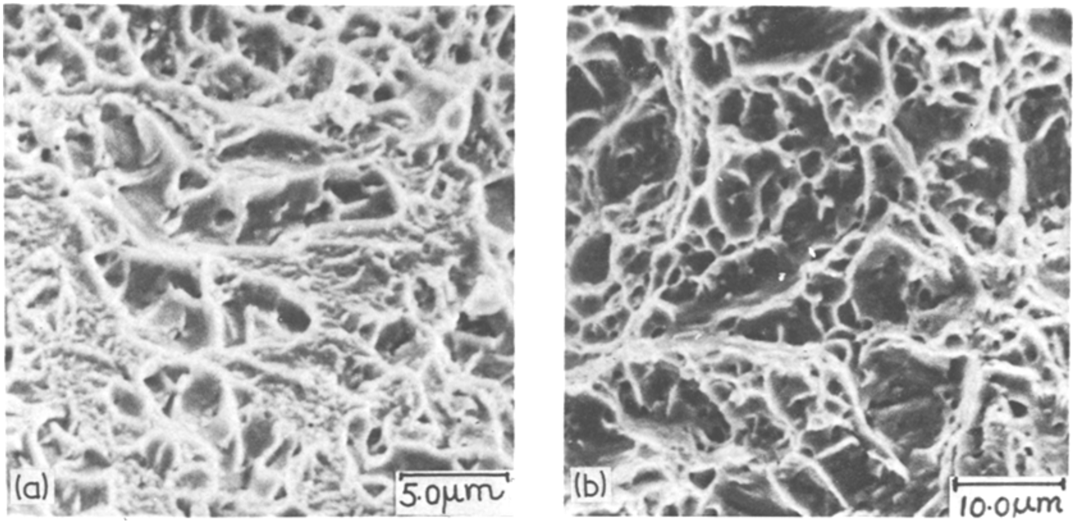

Figure 4 Typical appearance of fracture surfaces in the alloy aged at (a) 550° C for 16 h, and (b) 700° C for 2 h.

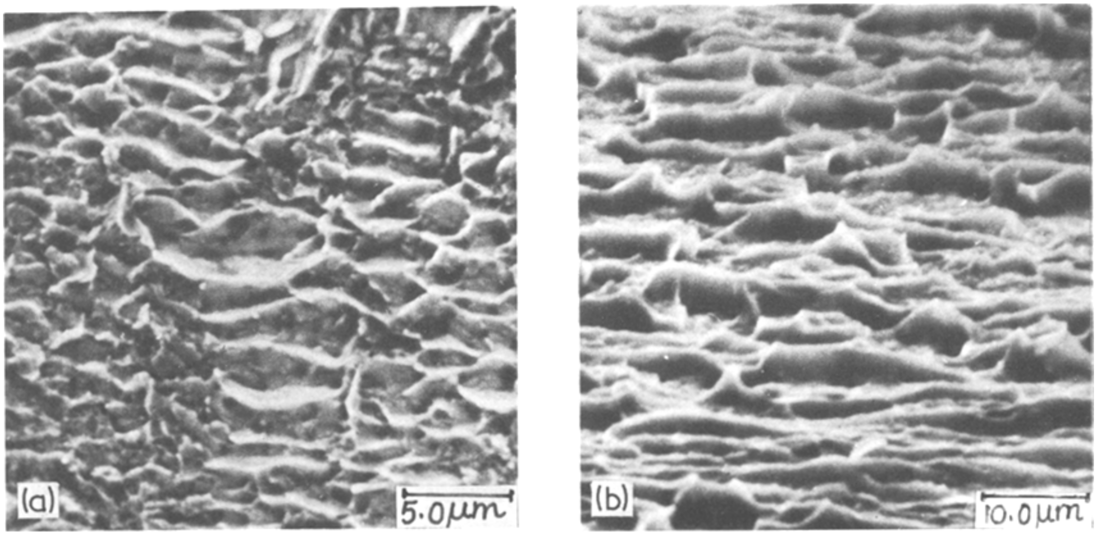

Figure 5 Typical appearance of "parallel striations" in fracture surfaces of samples aged at high temperatures. (a) 700° C for 2 h; (b) 700° C for 4 h.

shown, by stereomicroscopic techniques, that these features are not complementary on the mating halves of the fracture surface but are mirror images of one another. In this respect, these striations could be distinguished from typical fatigue striations and have been designated by a special name: "flutes". Chessnutt and Williams [8] have also noticed that flutes, in conjunction with slip-line markings along their sides, are associated with extensive plastic deformation. The appearance of flutes in the present case, corresponding to treatments that imparted a relatively high ductility to the alloy, was in conformity with these earlier observations.

4. Conclusions

The Zr–1.9 wt % Cr alloy is very strong in the beta quenched and in the low temperature tempered conditions, presumably due to the fine dispersion of $ZrCr_2$ precipitates and to the martensite substructure. Tempering at higher temperatures leads to softening due to the coarsening of the precipitates and the recovery and recrystallization of the martensite structure. The ductility of the alloy is poor at room temperature.

Acknowledgements

The authors are grateful to Dr V. M. Padmanabhan and Dr M. K. Asundi for their interest in this work and to Mr M. Sundararaman for useful discussions.

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Received 9 August and accepted 20 October 1978.