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The effect of iron additions on the microstructure and properties of the "Tribaloy" Co–Mo–Cr–Si wear resistant alloys

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The effect of iron additions in the range 5 to 15 wt % iron inclusive on the microstructure and properties of two Co–Mn–Cr–Si wear resistant alloys ("Tribaloys" T400 and T800) has been investigated. Iron additions were found to stabilize the f c c form of the cobalt solid solution, to give a fully eutectic matrix and to decrease the volume fraction of the primary Laves phase. These microstructural modifications have little effect on the plane strain fracture toughness but result in a significant increase in the modulus of rupture. The addition of iron induces only minor changes in the corrosion and oxidation resistance of T800, whereas the performance of T400 deteriorates.

1. Introduction

The cobalt based "Tribaloys"[†], T400 and T800, form part of a group of wear resistant alloys that rely on a large percentage of a hard intermetallic Laves phase dispersed in a cobalt solid solution for their properties [1, 2].

Table I gives the compositions of T400 and T800 and Figs. 1 and 2 show the microstructures of the as-cast alloys. T800 has a larger percentage of the intermetallic phase and a higher chromium content which results in a harder alloy with a better corrosion resistance than T400. T400 (Fig. 2) exhibits a larger proportion of fine lamellar eutectic which is composed of the secondary Laves and cobalt solid solution. In addition to the primary Laves phase and the lamellar eutectic, both alloys contain areas of solid solution which are essentially free from secondary Laves phase particles.

As a result of the hard brittle nature of the Laves phase, the alloys possess a relatively low resistance to brittle crack propagation with a fracture toughness of about 20 $\mathrm{MN\,m^{-3/2}}$. However, recent work [3] has shown that the alloys' resistance to crack initiation and growth is considerably influenced by microstructure. The microstructure may be varied in these alloys due to the allotropic nature of the cobalt solid solution and a precipitation phenomenon that occurs on annealing in the temperature range 600 to 1100° C [4].

Pure cobalt has a hexagonal close packed (h c p) structure at room temperature. At 417° C, the h c p structure transforms to the higher temperature face centred cubic (f c c) form. The nature of the transformation has been classified as martensitic [5]. Additions of alloying elements change the temperature at which the martensitic transformation occurs and alters the range of thermodynamic stability of the f c c and h c p phases.

Fig. 3 shows the binary phase diagram for the Co–Mo system, where the dashed lines indicate the effect of the addition of molybdenum on the temperature at which the martensitic reaction occurs and the continuous lines indicate the diffusion controlled nucleation and growth mechanisms. In alloys containing more than 12% Mo, as both the "Tribaloys" do, the f c c form can occur as a metastable phase at room temperature. In the

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[†] Trademark of Cabot Corporation (Wear Technology Division).

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TABLE I Nominal composition (wt %) and % Laves phase in the cobalt based "Tribaloys"

Tribaloy	Co	Mo	Cr	Si	C	Vol % Laves
T400	61–63	27–29	7.5– 8.5	2.2–2.6	< 0.08	40–50
T800	51–53	27–29	16.5–17.5	3.0–3.5	< 0.08	40–60

Co–Cr system (Fig. 4) the fcc→hcp transformation lies above room temperature for alloying additions up to 50% Cr and so the fcc form would not be retained.

T400 and T800 have similar high weight percentages of molybdenum which will favour the retention of fcc cobalt at room temperature. However, the addition of chromium will increase the likelihood of the high temperature fcc transforming to hcp at room temperature. It follows that both "Tribaloys" could be expected to have a certain amount of hcp present in the as-cast condition with T800 having the greater proportion and this has been confirmed by X-ray diffraction [4].

When T400 or T800 are heat treated in the range 600 to 900° C, the regions of metastable fcc transform to hcp and a Widmanstätten precipitate, whereas the regions of hcp present at room temperature show evidence of a spherical precipitate [4]. The Widmanstätten precipitate has a particularly adverse effect on the fracture behaviour, but even the presence of the hcp and spherical precipitate gives a worse performance than the fcc form without a precipitate [3]. It would, therefore, be beneficial to identify an alloying addition to stabilize the fcc form of cobalt solid solution and to prevent, or at least reduce, the precipitation reaction.

As shown in Fig. 5, iron enlarges the fcc phase field and work carried out by Schumann [7] on a series of Co 5 to 15% Fe alloys demonstrated that all the alloys were completely fcc after being annealed at 1100° C and water quenched, except for the 5% Fe alloy which contained 10% hcp. In view of this information and bearing in mind that iron is inexpensive, it was decided to study the effect of iron on the microstructure and properties of the "Tribaloys". Such an investigation is also relevant to the use of "Tribaloys" as a hardfacing alloy. Steels are commonly the substrate in hardfacing operations and dilution of the "Tribaloy" coating with iron inevitably takes place.

2. Experimental procedure

Iron additions of 5, 10 and 15% by weight were made to both T400 and T800 by arc melting and recasting in ingots approximately 160 × 12 × 6 mm^3. Several tests were carried out on the new alloys in an attempt to assess the effect of the additions on the microstructure, mechanical properties and corrosion/oxidation resistance.

2.1. Microstructural studies

The new alloys were sectioned, ground and polished before being etched in Marbles Reagent (200 ml HCl, 30 g $CuSO_4$ and 100 ml distilled

Figure 1 T800 as-cast microstructure with coarse lamellar eutectic, primary Laves phase dendrites and Laves phase free regions of cobalt solid solution.

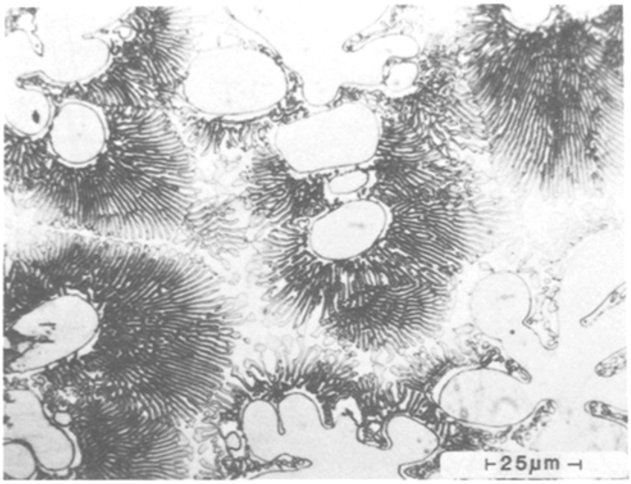

Figure 2 T400 as-cast microstructure with lamellar eutectic, primary Laves phase dendrites and Laves phase free regions of cobalt solid solution.

water) and examined by light microscopy. A linear intercept method was used to quantitatively assess the microstructure in terms of the volume fraction and average size of the primary Laves phase.

A Philips diffractometer (utilising Cu$K\alpha$ radiation) was used to obtain diffraction traces from the as-cast alloys, and also from the alloys after they had been given a 20 h heat treatment at 800° C, in order to identify the structure of the cobalt solid solution.

2.2. Mechanical properties

The hardness was determined using a Vickers machine with a 50 kg load. In addition, microhardness data were measured using a 100 g load on the primary Laves phase and 50 g on the eutectic.

Fracture toughness (K_{IC}) and modulus of rupture were chosen as the two fracture properties to evaluate the performance of the new alloys. Both tests used specimens of 37 x 5 x 2.5 mm^3, notched in the former case and un-notched and polished to a 1 µm finish in the latter. Testing took place under three-point bend loading conditions.

The two parameters have previously been measured for T400 and T800 and details regarding the testing procedure and analysis of the results are given in [3].

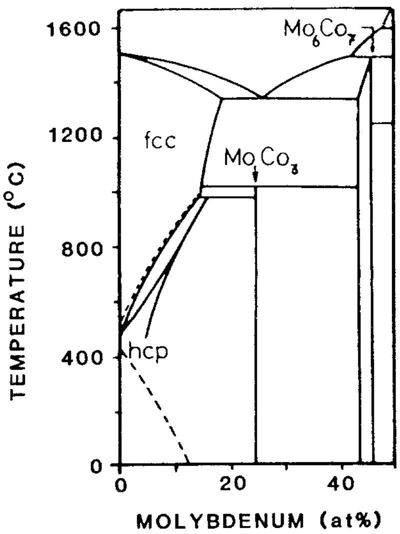

Figure 3 Cobalt-rich end of the Co–Mo phase diagram showing the martensitic – – – –, and equilibrium ———, modes of the h c p ⇌ f c c cobalt transformation [6].

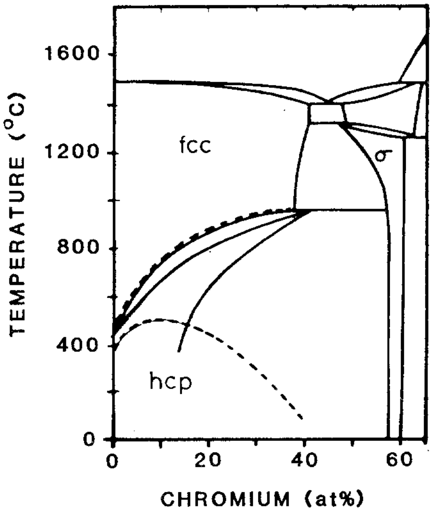

Figure 4 Cobalt-rich end of the Co–Cr phase diagram showing that the equilibrium and martensitic modes of the f c c ⇌ h c p transformation are above room temperature for chromium contents of less than ~ 40% [6].

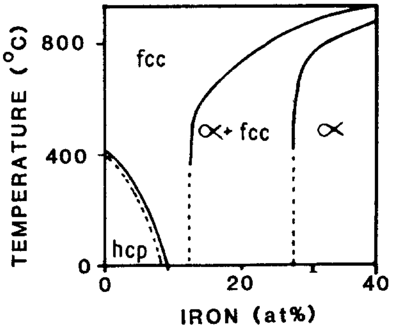

Figure 5 Cobalt-rich end of the Co–Fe phase diagram showing how iron suppresses the h c p form of cobalt [6].

2.3. Oxidation and corrosion resistance

It is important that any modification to the composition of "Tribaloy" does not seriously impair any of the major properties. One of these is the outstanding oxidation resistance due to its ability to form adherent oxides at elevated temperature.

A cyclic experiment was chosen to simulate an extreme type of oxidation which would be representative of very harsh service conditions. Specimens 5 x 3 x 10 mm^3 were polished to 1 μm and cleaned and tested in the apparatus shown in Fig. 6. The specimen was driven horizontally into the furnace and retracted to stand within a water cooled jacket. The temperature cycle which the specimen was subjected to is shown in Fig. 7. The apparatus was run at 1050° C continuously for 200 cycles. Periodically the specimens were removed during the cooling cycle and weighed.

Specimens for corrosion testing were of approximate size 4 x 10 x 6 mm^3 and were prepared in a similar manner to the specimens for the oxidation investigation. They were suspended in concentrated solutions of H_2SO_4, HNO_3 and HCl for 7 days prior to being re-weighed.

3. Results

3.1. Microstructure and hardness

Table II lists the results of the quantitative metallography and the X-ray diffraction. From Table II and Figs. 8 to 11, the addition of the iron can be seen to significantly reduce the volume fraction of the primary Laves phase: for T400 the reduction is from 42% to 17% and for T800 from 70% to 26% as the iron addition is increased up to 15% Fe. Comparing the micrographs of the modified alloys to those of T400 and T800 (Figs. 1 and 2), the areas of cobalt solid solution free from Laves phase are no longer evident and the new alloy

TABLE II Effect of iron additions on microstructure and mechanical properties of Tribaloy

Test and units	T400 arc melt	T400 5% Fe	T400 10% Fe	T400 15% Fe
VHN as-cast	685 ± 25	646 ± 15	611 ± 10	597 ± 32
VHN after 20 h, 800° C	729 ± 9	686 ± 9	619 ± 12	597 ± 13
Microhardness Laves, 100 g	1068 ± 90	1018 ± 100	1013 ± 90	1018 ± 70
Microhardness eutectic, 50 g		588 ± 70	590 ± 60	575 ± 50
Quantitative vol % fraction Laves	42.8 ± 8	35 ± 7	25 ± 3	17 ± 7
Size Laves (μm)	6 ± 7	8 ± 6	5 ± 10	5 ± 12
K_{IC} (MN m$^{-3/2}$)	22.3 ± 2.0	20.8 ± 2.0	24.8 ± 1.2	22.9 ± 1.5
MOR σ_f (MN m^{-2})	917 ± 54	965 ± 55	1280 ± 90	1279 ± 113
Flaw size (mm^2)	0.17	0.11	0.07	0.05
X-ray cobalt solid solution as-cast	f c c	f c c	f c c	f c c
X-ray cobalt solid solution after 20 h at 800° C	h c p/trace f c c	f c c	f c c	f c c
Test and units	T800 acc melt	T800 5% Fe	T800 10% Fe	T800 15% Fe
VHN 50 kg as-cast	627 ± 15	668 ± 10	654 ± 20	629 ± 12
VHN after 20 h 800° C	809 ± 8	748 ± 20	676 ± 21	661 ± 16
Microhardness Laves, 100 g	1081 ± 70	1017 ± 50	1027 ± 70	1020 ± 90
Microhardness eutectic, 50 g		610 ± 60	589 ± 50	590 ± 40
Quantitative vol % fraction Laves	70 ± 12	57 ± 7	43 ± 8	26 ± 6
Size Laves (μm)	9 ± 7	8 ± 10	8 ± 12	4 ± 20
K_{IC} (MN m$^{-3/2}$)	19.2 ± 1.8	20.9 ± 2.3	19.1 ± 2.8	19.8 ± 1.4
MOR σ_f (MN m^{-2})	752 ± 35	746 ± 60	809 ± 55	871 ± 82
Flaw size (mm^2)	0.21	0.31	0.15	0.13
X-ray cobalt solid solution as-cast	f c c/trace h c p	f c c	f c c	f c c
X-ray cobalt solid sol after 20 h at 800° C	h c p/f c c	f c c	f c c	f c c

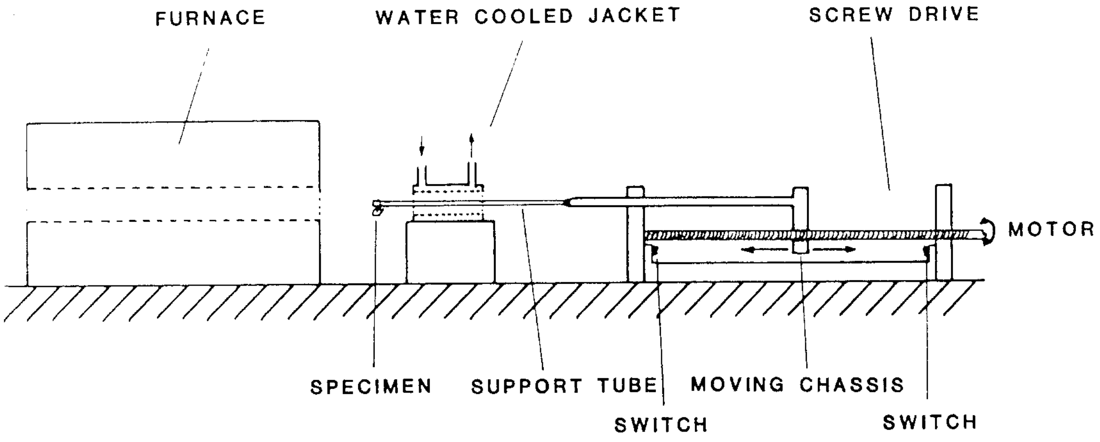

Figure 6 Diagram of the cyclic oxidation rig.

structures consist solely of primary Laves and a very fine lamellar eutectic of secondary Laves and cobalt solid solution.

Increasing the amount of iron does not affect the microhardness of the constituent phases to any measurable extent as the values in Table II reflect.

The as-cast "Tribaloys" T400 and T800 show a substantial hardness increase of approximately 50 VHN and approximately 150 VHN, respectively, when given a heat treatment of 20 h at 800° C. The addition of iron reduces this hardening effect (Table II) and in the case of T400 with 15% Fe no change in hardness is observed. Some hardening takes place in the iron bearing T800 alloys, but not to such an extent as in the as-cast T800 "Tribaloy".

X-ray data from the modified alloys before and after heat treatment revealed only the face centred cubic form of the cobalt solid solution to be present. However, due to the sensitivity of X-ray diffraction, it is possible that a small amount of h c p is present in these alloys.

3.2. Mechanical properties

The fracture toughness is, within statistical deviation, independent of the iron content (Table II). In the iron containing alloys the cracks propagate through the material cleaving the primary phase and eutectic. Even in the case of T400 + 15% Fe, where there is only a small percentage of the primary phase, no additional resistance is provided by the fine lamellar eutectic and cracks propagate straight through without differentiating between the different regions of the structure (Fig. 12). In contrast to the crack growth resistance as

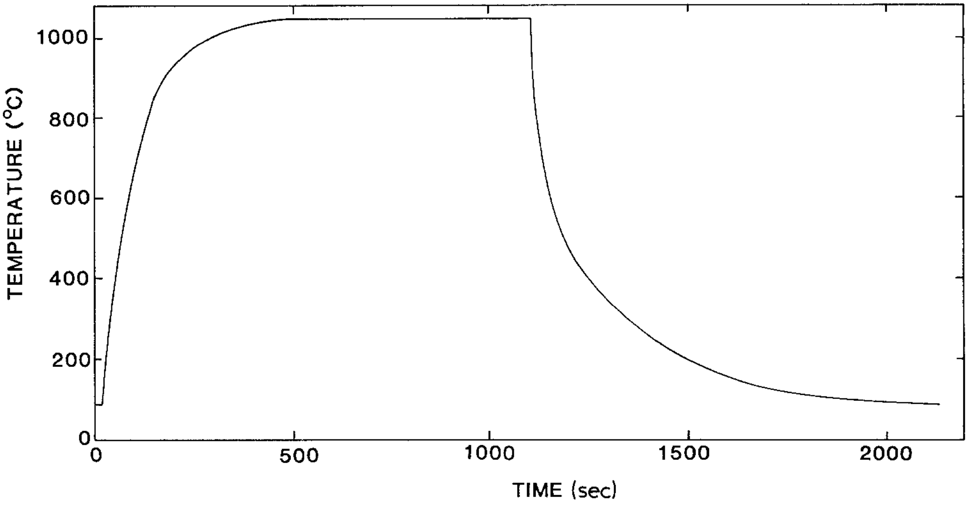

Figure 7 Temperature variation over one complete 1050° C oxidation cycle.

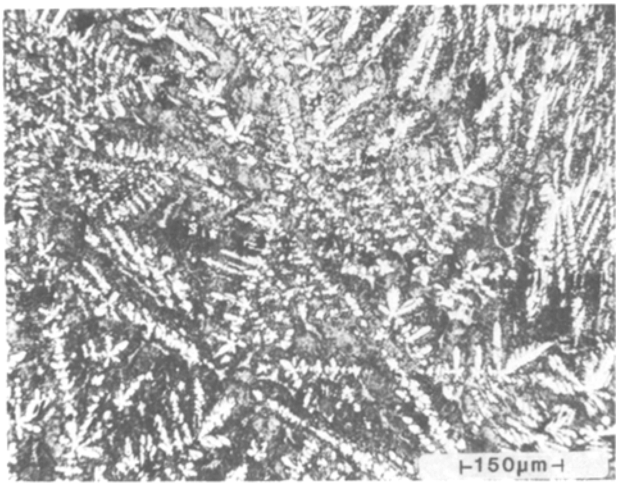

Figure 8 T400–5% Fe as-cast microstructure.

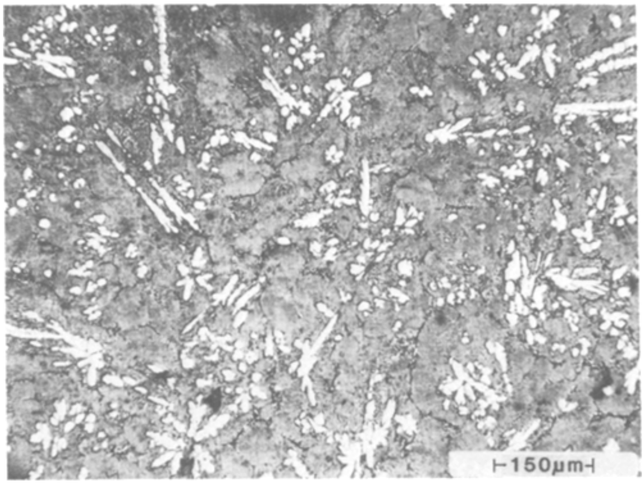

Figure 9 T400–15% Fe as-cast microstructure.

Figure 10 T800–5% Fe as-cast microstructure.

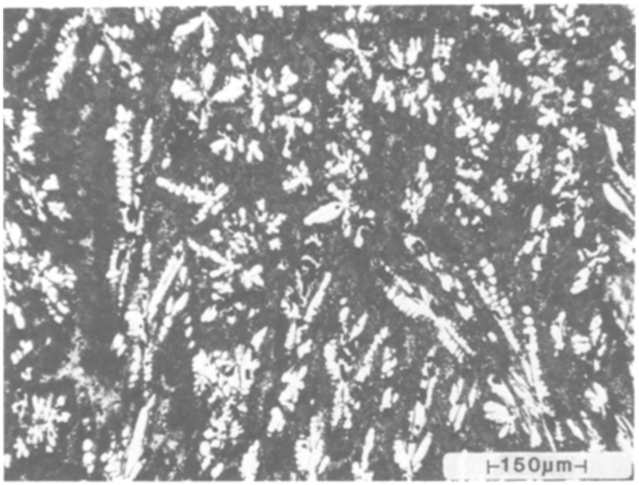

Figure 11 T800–15% Fe as-cast microstructure.

quantified by the fracture toughness, the modulus of rupture increases markedly as iron is added.

The critical flaw size was calculated from the MOR and K_{IC} data using the following modified form of the fracture equation which takes into account that the inherent flaws are normally elliptical and not through-the-thickness in nature [8]:

$$\mathrm{MOR} = \frac{1.68 K_{IC}}{Y A_C^{1/4}},$$

where Y is a constant depending on the geometry of the specimen and the loading conditions and A_C is the area of the critical inherent flaw. Thus, flaw size relates the modulus of rupture and the fracture toughness, giving a single parameter with which to compare the alloys. The smallest critical inherent flaw size will always be exhibited by the alloy with the best overall fracture properties. The improvement that the addition of iron imparts to T400 and T800 is indicated by the reduction in flaw size (Table II).

3.2. Oxidation and corrosion resistance

The results of the cyclic oxidation tests carried out at 1050° C are shown in Figs. 13 and 14. Attention is drawn towards the variations in the vertical scale of the two curves with T400 showing a loss in weight of 20 times greater than T800. Addition of iron to T400 can be seen to increase the weight loss of 200 cycles as more iron is added. T800 changes very little with the addition of iron and maintains an excellent oxidation resistance which is far superior to that of T400.

The corrosion results are presented in Table III. With the exception of T400 in HNO_3 the data demonstrate that the corrosion resistance is not sensitive to the iron content of the alloys.

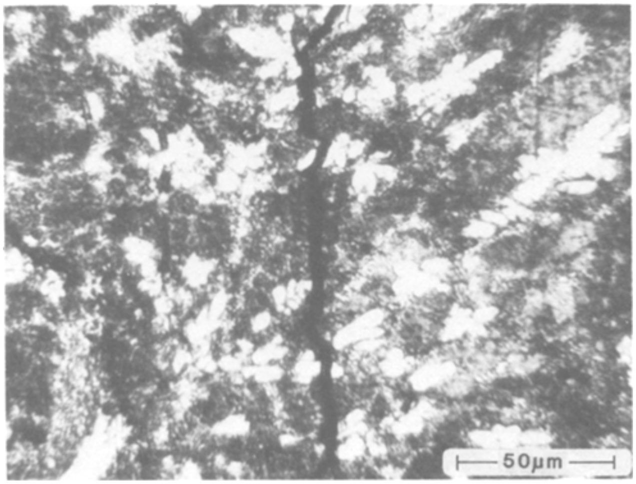

Figure 12 T400–15% Fe micrograph showing a crack traversing the primary Laves phase dendrites and the fine lamellar eutectic without deviating.

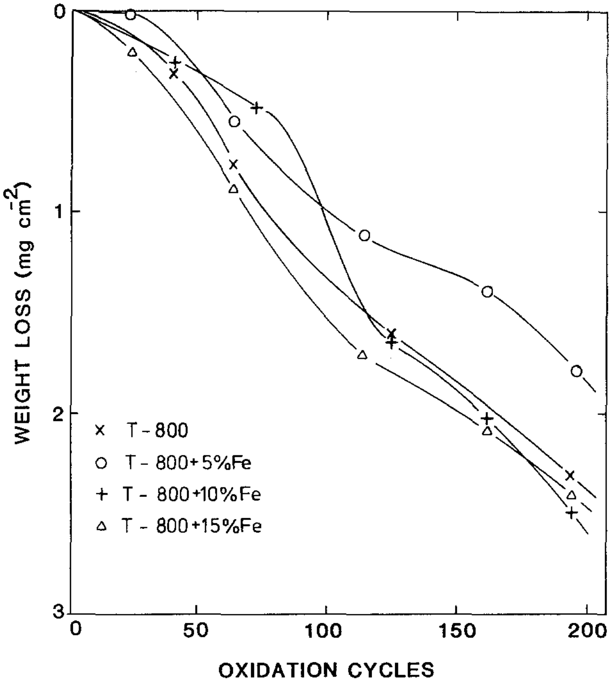

Figure 13 Cyclic oxidation results demonstrating that similar oxidation behaviour is obtained from T800 with and without iron additions.

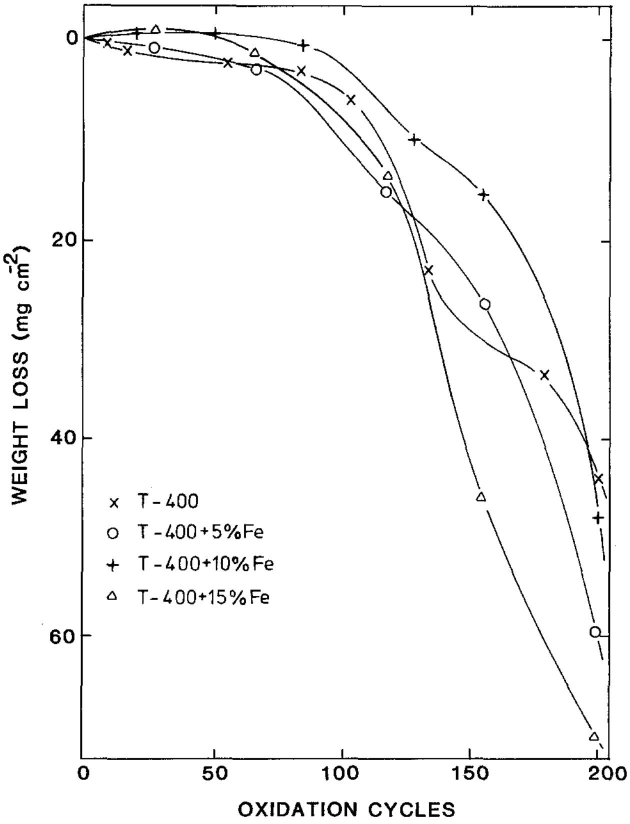

Figure 14 Cyclic oxidation results demonstrating that at 200 cycles the oxidation resistance of the iron bearing alloys is less than that of the unalloyed T400.

TABLE III Corrosion resistance of Tribaloy with and without Fe additions

Specimen	Weight loss (mg cm^{-2} day^{-1}) in conc. acid		
	HCl	H_2SO_4	HNO_3
T400	2.78	0.04	2.66
400 5% Fe	2.02	0.06	5.64
T400 10% Fe	2.00	0.03	9.3
T400 15% Fe	2.09	0.08	13.01
T400 13 days, 800° C	3.32	0.14	4.43
T800	1.80	0.03	1.70
T800 5% Fe	2.19	0.1	1.17
T800 15% Fe	2.20	0.05	1.66
T800 13 days, 800° C	2.21	0.00	2.04

4. Discussion

In the iron bearing "Tribaloy" alloys only the face centred cubic form of cobalt is detected both before and after heat treatment. Iron additions reduce the size of the h c p phase field in the Fe–Co system (Fig. 5) and, therefore, stabilizes the f c c form. This is because iron increases the stacking fault energy in cobalt alloy systems which in turn prevents their formation and maintains the f c c structure [9]. The relationship between stacking-fault energy and the allotropic transformation is that as the fault energy becomes vanishingly small the f c c will transform to h c p as the partial dislocations constituting the fault boundaries become independent.

In addition, as iron reduces the number of stacking faults, the number of suitable sites for preferred precipitation is decreased so hindering any precipitation process. This may account for the reduced hardening effect after 20 h at 800° C found for the iron containing alloys. Indeed similar results have been reported for a fully annealed Co–Ni–Cr–Mo alloy: with a single f c c phase, there was no evidence of precipitation but the peritectoid form of the transformation led to the h c p form being present with a precipitate [10].

It appears then that the precipitation effect in "Tribaloy" is directly linked to the f c c→h c p allotropic transformation. As a slight hardening effect is still evident in some of the alloys, it is reasonable to suppose that a small percentage of h c p is present at room temperature or that there is some metastable f c c. The fact that T800, which is the alloy with the higher percentage of chromium and therefore the alloy most likely to transform to h c p, shows the greater evidence of a hardening effect gives support to this suggestion.

As well as stabilizing the f c c form of the cobalt solid solution the addition of iron significantly reduces the volume fraction of the primary phase in a linear manner as shown in Fig. 15. This figure predicts that about 25% Fe would produce completely eutectic microstructures in both the "Tribaloys".

The constancy of the K_{IC} values shows that there is no change in the alloys' resistance to crack propagation on increasing the iron content despite the fact that the volume fraction of the primary Laves phase is substantially decreased and that the f c c form of the solid solution is stabilized. Our previous work on unalloyed T400 and T800 [3] indicated that K_{IC} was controlled by the volume fraction of the primary Laves particles, but also that the f c c structure slightly improved the fracture toughness. If these factors were applicable to the iron bearing alloys the microstructural changes associated with the addition of iron would be expected to lead to an increase in K_{IC} and this was not experimentally observed. This apparent discrepancy is due to the absence of the Laves phase free solid solution regions in the iron containing "Tribaloys": it is deemed that these ductile regions, which separate the easily cleaved primary Laves particles from the lamellar eutectic and sub-divide the lamellar eutectic (see Figs. 1 and 2) are required to provide crack growth resistance. This proposal is consistent not only with the present results but with the previously reported [3] fall in K_{IC} when the Laves phase free regions in "Tribaloys" are embrittled by precipitation in a Widmanstätten morphology. Thus the primary Laves particles are important in determining K_{IC} only in the presence of the ductile solid solution regions. In the absence of these regions a crack may propagate with almost equal ease through either the primary phase or the fine lamellar eutectic.

It can be seen (Table II) that retaining an f c c solid solution and reducing the volume fraction of the primary Laves phase has a significant effect on the MOR, e.g. the MOR for T400 + 15% Fe is some 40% higher than for the unalloyed "Tribaloy". As the microhardness of the components of both T400 and T800 differ very little and do not change with increasing iron content, these results can be analysed simply in terms of the volume fraction of the Laves

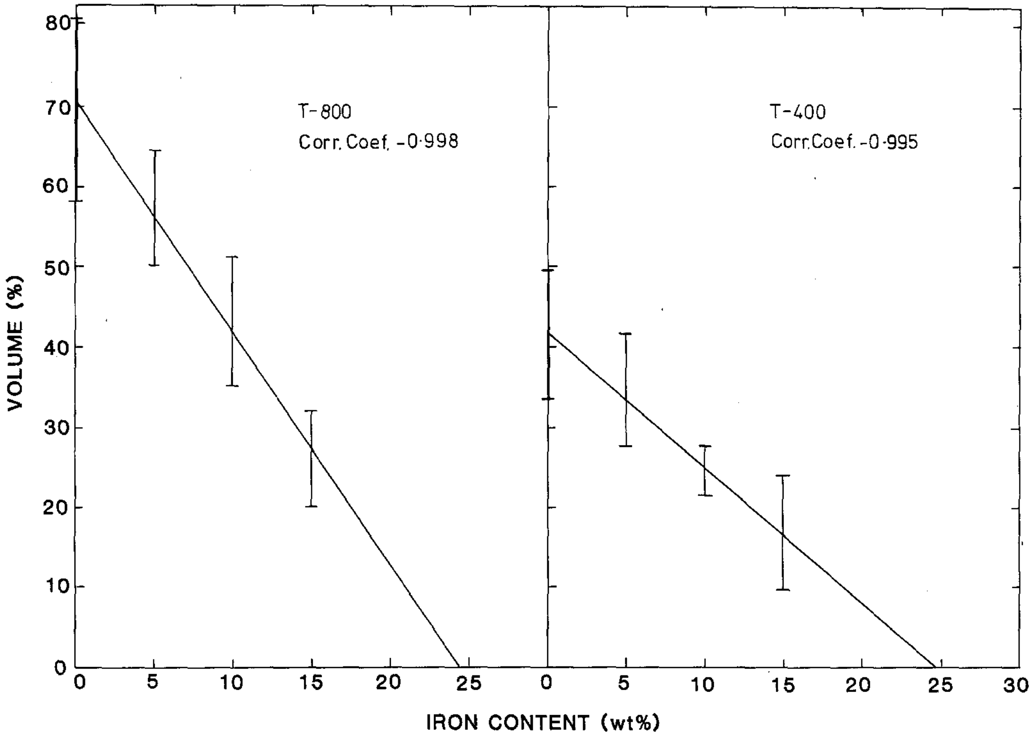

Figure 15 Effect of iron additions on the volume fraction of primary Laves phase.

phase. The graph of MOR against volume fraction of primary Laves phase (Fig. 16) shows that the alloys lie on a common curve with the MOR increasing as volume fraction decreases. The one deviation that occurs is between T400 + 10% Fe and T800 + 15% Fe: both have comparable volume fraction of primary phase but even considering the nearest values at one standard deviation from the mean, a difference of $237\,\mathrm{MN\,m^{-2}}$ exists. A possible explanation is the anomalous long thin primary Laves dendrites found in the crack path of T800 + 15% Fe even though this alloy had a low average volume fraction of the Laves phase (Fig. 16).

These results show the strength for a constant matrix microstructure (in this instance f c c cobalt solid solution/Laves phase eutectic) is controlled by the volume fraction of the primary particles. At high volume fractions the particles can cleave and link easily between themselves attaining the critical flaw size and failure results. At low volume fractions, although the large particles can cleave the

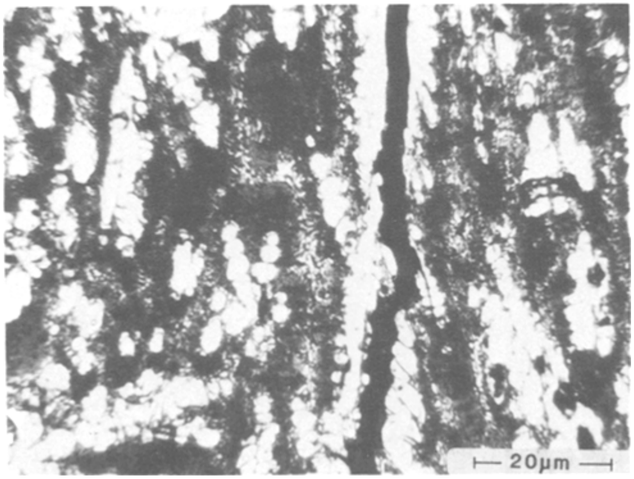

Figure 16 T800–15% Fe micrograph showing the anomalous long Laves phase dendrites in the crack path.

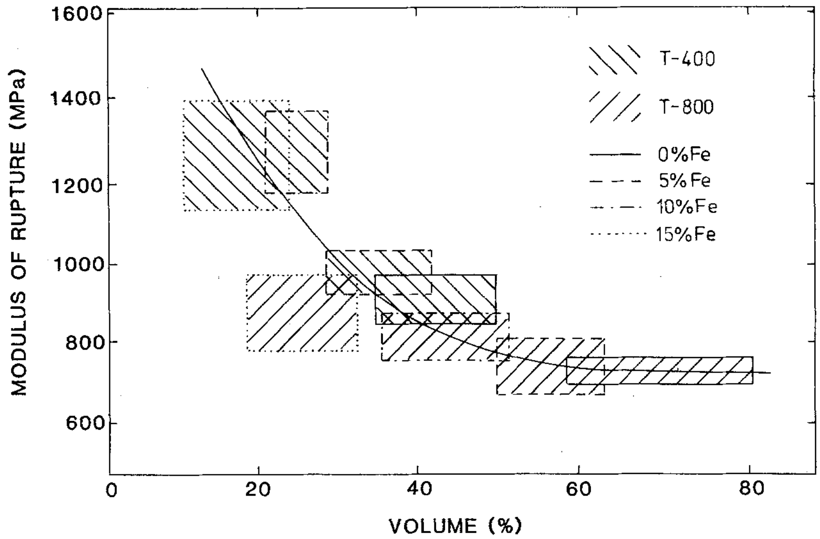

Figure 17 Effect of the volume fraction of primary Laves phase on the modulus of rupture.

cracks are not initiated easily within the lamellar eutectic and much higher stresses are needed to extend the cleavage cracks to the critical flaw size. So although a propagating main crack can traverse the eutectic without difficulty (as shown by the constant K_{IC} values), the modification in the microstructure does increase the tensile strength and resistance to crack initiation as seen by the reduction in critical flaw size.

In terms of corrosion and oxidation resistance very little change is detected between the iron bearing T800 alloys and the unalloyed "Tribaloy". In contrast, the performance of T400 does deteriorate slightly with increasing additions of iron. However, T400, due to its lower chromium content, is not the cobalt "Tribaloy" marketed for corrosion and high temperature oxidation resistance and it is thought unlikely that the reduced resistance associated with iron additions would be significant in the normal service situation.

5. Conclusions

1. Iron additions of between 5 and 15% stabilize the fcc form of the cobalt solid solution.

2. Iron reduces the hardening effect that occurs when the commercial T400 and T800 alloys are treated in the range 600 to 1100° C.

3. Additions of iron to "Tribaloy" reduce the volume fraction of primary phase from 42% to 17% in T400 and 70% to 26% in T800 up to additions of 15 wt% Fe. The microstructure of iron bearing "Tribaloys" consists solely of primary Laves phase in a matrix of a fine lamellar eutectic: no Laves phase free regions of solid solution are present.

4. Primary Laves particles and secondary Laves within the lamellar eutectic are equally detrimental in terms of the crack growth resistance of the alloys and iron additions do not affect the fracture toughness values of the "Tribaloys" which remain $20\,\text{MN}\,\text{m}^{-3/2}$.

5. The modulus of rupture and the alloys' resistance to crack initiation is substantially increased by iron additions, e.g. 15 wt% Fe increases the MOR of T400 by 40% and decreases the critical flaw size by 70%.

6. Iron additions of up to 15% do not affect the excellent oxidation and corrosion resistance of T800. Although the performance of T400 deteriorates as iron is added, the changes are not considered to be significant as far as normal service is concerned.

Acknowledgements

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