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Heat treatment of cast Co–Cr–Mo for orthopaedic implant use

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Cast Co–Cr–Mo was heat treated to determine whether a significant improvement in the alloy's mechanical properties could be obtained without loss of corrosion resistance. Tensile, corrosion fatigue, and corrosion tests were carried out using individually cast test pieces. The effect on the tensile properties of solution treatment at 1240° C and of ageing at 720° C was determined for a large range of heat treatment times. In addition the effect of other heat treatments described in the literature was determined. Partial solution treatment gave the greatest improvement in corrosion fatigue behaviour. None of the heat treatments significantly affected the corrosion resistance. In spite of the improvements obtained, it was concluded that for orthopaedic implant applications requiring high corrosion fatigue strength, cast Co–Cr–Mo was less suitable than other currently available products.

1. Introduction

For almost 50 years cast Co–Cr–Mo has been used as a dental and orthopaedic implant material. Today it remains popular and of the estimated 30 000 total hip replacements performed in the UK each year [1], more than half are thought to be cast Co–Cr–Mo. For hip joints however, it is recognized that there is a small but significant incidence of component fracture [2], and this has raised doubts about the alloy's mechanical properties. Thus, although experience has shown that the alloy has adequate corrosion resistance, its low ductility and fatigue strength is now a matter of concern, especially since the introduction of newer alloys such as Ti–6 wt % Al–4 wt % V.

For this reason many manufacturers currently subject their castings to a short solution treatment in order to increase ductility. However previous studies, some of which were concerned with turbine blades, indicated that heat treatments could be expected to give even better results [3–6]. In 1955 Weeton and Signorelli [7] demonstrated that solution treatment followed by ageing increased hardness, and later Hollander and Wulff [8] confirmed that it improved the tensile properties, as did hot isostatic pressing [9, 10]. Recently Cohen *et al.* [11] demonstrated than an even greater improvement resulted from a three stage heat treatment process. These results are summarized in Table I.

Little fatigue data existed on the effect of heat treatment and there was no data to support the findings of Cohen *et al.* However, Lorentz *et al.* [12] obtained an improvement in fatigue strength resulting from solution treatment and from homogenization, but no such improvement was noted by Cox [13] who found that the best fatigue resistance was obtained by material in the as-cast condition. These results are summarized in Table II.

The corrosion of Co–Cr alloys has been reviewed recently by Kuhn [16], but little data exist on the effect of heat treatment on the corrosion of Co–Cr–Mo in aqueous chloride solutions at or near room temperature. Acharya *et al.* [17] measured open circuit potentials as a function of time in Ringer's solution and showed that the as-cast material was more noble than either homogenized or aged material. Syrett and Wing [18] showed using anodic polarization that the solution treatment did not significantly affect the corrosion

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TABLE I Tensile data for cast Co–Cr–Mo

Reference	Condition	Yield stress (MPa)	UTS (MPa)	Elongation (%)	Reduction (%)
Hollander and Wulff [8]	A/C	461	741	6.25	4.0
	A/C + 1 h at 1230° C WQ	468	813	11.5	9.5
	A/C + 1 h at 1230° C WQ + 20 h at 650° C	477	852	11.75	11.0
	A/C + HIP + 1 h at 1230° C WQ + 20 h at 650° C	496	926	16.0	15.0
Devine and Wulff [10]	A/C	544	699	8	9
Hodge and Lee [9]	A/C	547	650	5	7
	A/C + HIP + 2 h at 1230° C	484	761	17	17
Cox [13]	A/C	553	789	7.6	9.9
	A/C + 72 h at 1230° C WQ	387	616	10.2	12.2
	as above + 72 h at 700° C	540	664	3.0	3.0
Cohen *et al.* [11]	A/C	477	851	11	13
	A/C + 4 h at 815° C + 4 h at 1225° C WQ	498	1149	25	26
Lorentz *et al.* [12]	A/C	450	665	8	–

A/C = as-cast, WQ = water quench.

behaviour, whereas both Devine and Wulff [19] and Süry and Semlitsch [20] showed by means of long term immersion tests that solution treatment improved crevice and general corrosion resistance. A similar improvement was obtained for material that was hot isostatically pressed [8, 9]. These and other anodic polarization results are summarized in Table III.

Clearly contradictions and omissions existed among the fatigue and corrosion results and one purpose of the present work was to carry out a comparative study to resolve these differences. In particular, it was our aim to determine whether any of the heat treatments described in the literature provided a significant improvement in mechanical properties when compared with the as-cast material. Tensile, fatigue and corrosion tests were carried out since each gives information relevant to the survival and performance of implants. The effect on the tensile properties of solution treatment at 1240° C and of ageing at 720° C was determined for a large range of heat treatment times. Individually cast specimens were used throughout, since their performance was thought to be the most similar to that of actual cast components.

2. Materials and experimental procedures

Table IV lists the details of the Co–Cr–Mo alloy used. Tensile test pieces were individually cast to

TABLE II Fatigue data for cast Co–Cr–Mo

Reference	Condition	Test Method	Frequency (Hz)	Test Condition	Fatigue strength at 10^n cycles (MPa)
Hall and Morral [14]	A/C	*	*	Air	232[8]
Devine and Wulff [10]	A/C	RB	*	Air	284[8] notched
					346[7] notched
Hodge and Lee [9]	A/C	RB	167	Air	346[7]
	A/C + HIP + 2 h at 1230° C				346[8]
Cox [13]	A/C	RB	*	Air	335[6]
	A/C + 72 h at 1230° C, WQ				257[6]
	as above + 72 h at 700° C				230[6]
Hughes *et al.* [15]	A/C	AV	100	Air	249[8], 138[8] notched
				Saline	235[8], 48[8] notched
Lorentz *et al.* [12]	A/C	RB	*	Air	190–280[8]
	A/C + * h at 1240° C				220–280[8]
	A/C + 4–8 h at 1180° C				280–350[8]

A/C = as-cast, *Not known, RB = Rotating bending, AV = Amsler Vibrophore, HIP = Hot isostatic pressing.

TABLE III Anodic polarization data for cast Co–Cr–Mo (polished) in deaerated physiological solution at 37° C

Reference	Condition	Test Method	Step/Sweep Rate ($mV\ min^{-1}$)	E_{Corr} (mV) (SHE)	I_p/A ($\mu A cn^{-2}$)	E_B (mV) (SHE)	E_{Repass} (mv) (SHE)
Hoar and Mears [21]	A/C + Annealed	PS	5	87	3.2	870	–
Mueller and Greener [22]	A/C	PS (in air)	5	−25	0.50	700	–
Cahoon *et al.* [23]	A/C	PD	10	272	0.20	742	642
Devine and Wulff [19]	A/C	*	*	−128	0.06	567	–
Hodge and Lee [9]	A/C	PD	10	−300	1.5	842	342
	A/C + HIP + 2 h at 1230° C			−300	2.0	692	742
Brettle and Hughes [24]	A/C	PD	50	–	0.64	942	880
Süry and Semlitsch [20]	A/C	PD	10	−50 to −200	–	650–900	–
Syrett and Wing [18]	A/C	PD	10	339	–	805	805
	A/C + 1 h at 1230° C (Ar) WQ			372	–	783	783
Cornet *et al.* [25]	A/C	PS (mO_2)	*	50	~ 2	375	250

A/C = as-cast, PS = Potentiostatic, PD = Potentiodynamic, *not known, HIP = Hot isostatic pressing, SHE = Standard hydrogen electrode.

TABLE IV Details of alloy

Supplier	OEC Orthopaedic Limited
Manufacture	Vacuum melt, vacuum cast
Cast No.	RCL 130/10
Composition* (wt%)	0.24 C, 0.58 Si, 0.18 Mn, 1.81 Ni, 28.9 Cr, 5.58 Mo, 0.08 Al, 0.57 Fe, 0.11 Ti, Bal Co.

*Complies with BS 3531 (1980)

TABLE V Details of heat treatments

Condition	Heat treatment
As-cast	
Solution treated	2 h at 1240° C WQ
Solution treated and aged	2 h at 1240° C WQ + 16 h at 720° C WQ
Partially solution treated	1/4 h at 1225° C AC
Pretreated solution treated	4 h at 815° C WQ + 4 h at 1225° C WQ
Homogenized	4 h at 1170° C WQ

WQ = Water quenched AC = Air cool

size and were flaw detected by the manufacturer. They were heat treated in an electrical resistance tube furnace in high purity argon. The heat treatment consisted of a solution treatment at 1240° C for ½, 1, 2, 4 and 8 h followed by quenching in cold water. 1240° C was the maximum suitable temperature for solution treatment since above this temperature incipient melting occurred, as did substantial grain growth. Ageing of the solution treated material was carried out at 720° C for 6, 9, 16, 24 and 47 h. This temperature produces a satisfactory rate of precipitation. A minimum of two test pieces were used for each heat treatment time. Further experiments were carried out for the six conditions listed in Table V. Partial solution treatment at 1225° C was the treatment used by a UK manufacturer of orthopaedic implants. Pretreated solution treatment and homogenization were the treatments described by Cohen *et al.* [11] and Lorentz *et al.* [12], respectively.

Vickers hardness measurements were made on polished surfaces using a 20 kg load. Tensile tests were made using an Instron testing machine (Model TT-C) and a calibrated strain gauge extensometer (Instron Model G-51). The tensile test pieces were cylindrical, had a diameter of 5.7 mm and were tested with the as-cast surface finish, since this finish was known to be satisfactory for tensile tests. The strain rate in the elastic region was 0.005 min^{-1}.

Corrosion fatigue tests were conducted at 50 Hz using a Wohler reverse bending ($R = -1$) machine (GTG Engineering Ltd). Krouse test pieces were used. They had a tapered cylindrical section, 13 mm long and 3.81 mm in central diameter, with a 0.2 degree taper. They were prepared from individual castings, 1 mm oversize in diameter, heat treated as described and then machined and abraded longitudinally with SiC paper to a final grit size of 1200. Ringer's solution was applied to the test pieces by drip feeding it onto a cotton wick which, without touching the specimen, held a liquid film in contact with the centre of the tapered section (see Fig. 1). The diameter of each test piece was measured and the load to give the required stress was calculated using the appropriate formula.

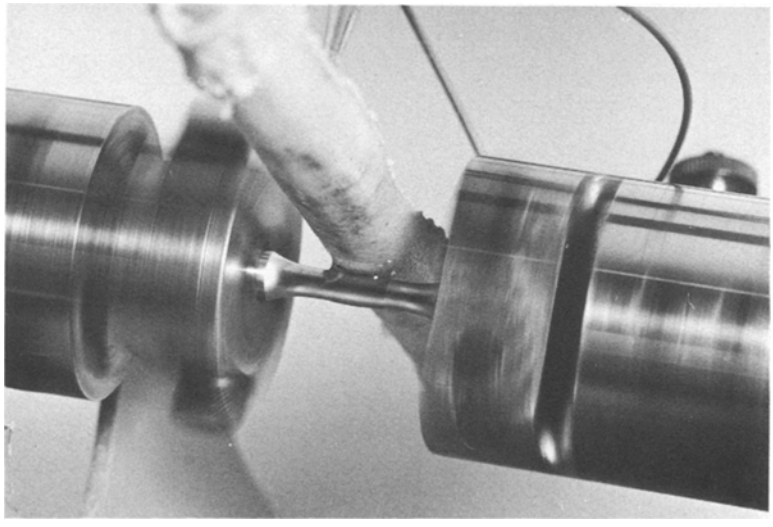

Figure 1 Wohler test showing liquid drop in contact with test piece.

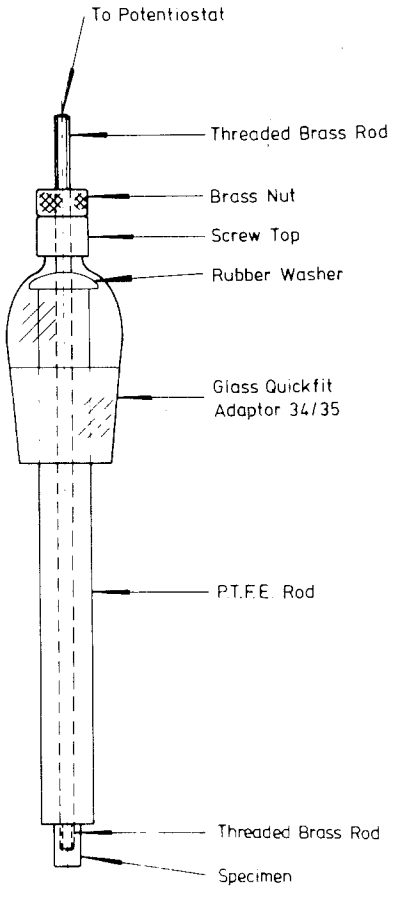

Figure 2 Schematic of working electrode.

In vitro corrosion behaviour was investigated by potentiodynamic cyclic polarization tests using a recognized experimental method [26]. The specimen was cylindrical, the average length and diameter being 11 mm and 7 mm, respectively. One end of the specimen was firmly attached to the cylindrical PTFE specimen holder giving a 270 mm^2 area of specimen exposed to the electrolyte. The attachment was by means of a threaded brass plug soldered into the specimen (cast Co–Cr–Mo could not be tapped) and screwed to a threaded brass rod as shown in Fig. 2. The test cell consisted of a 700 ml capacity reaction flask filled with the test solution. The cover had five ground glass openings into which were inserted the specimen holder, a platinum counter electrode, a Luggin probe, a gas bubbler and a thermometer. The cell was suspended in a water bath thermostatically controlled at 37° C and oxygen free nitrogen was passed through the test solution. The rest potential was measured after 30 min immersion and the specimen was then anodically

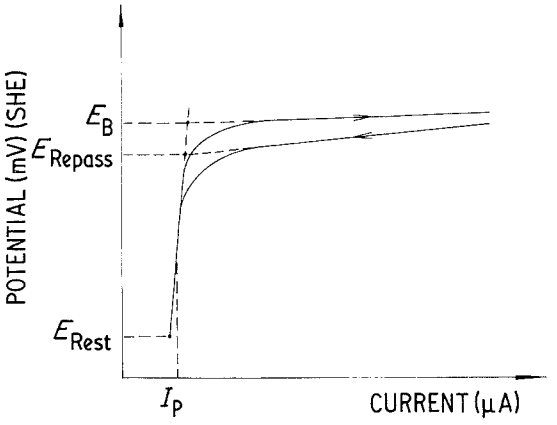

Figure 3 Anodic polarization curve for cast Co–Cr–Mo.

polarized at a rate of 10 mV min^{-1} using a potentiostat (Wenking 70 TS1) and a linear sweep generator (Chemical Electronics) until breakdown occurred. The sweep direction was then reversed. The reference electrode was a saturated calomel electrode and the sign convention adopted was that specimen potentials anodic to the reference electrode were positive (active), while cathodic were negative (noble). The test solution was Ringer's solution buffered to pH 7.4 by the addition of 0.874 g $NaH_2PO_4 \cdot 2H_2O$ + 2.044 g Na_2HPO_4 l. All the specimens were prepared by wet grinding with 600 grit SiC paper. Most specimens were passivated and steam sterilized since orthopaedic implants are normally treated in this manner. Passivation was by immersion in an aqueous solution of 30% HNO_3 for 30 min at room temperature in accordance with BS 3531. Steam sterilization was at 136° C and 31 psi for 5 min.

Fig. 3 shows a typical polarization curve obtained for cast Co–Cr–Mo. The curve shows the method by which the relevant parameters (rest potential, E_{Rest}; passive current density, I_p/A; breakdown potential; E_B; repassivation potential, E_{Repass}) were obtained.

Before and after heat treatment each tensile and fatigue specimen was examined metallographically to determine grain size and microstructure. Specimen ends were macroetched in a solution of 90% HCl + 10% H_2O_2 and the polished sections were etched either electrolytically in 50% C_2H_5OH + 50% HCl or chemically in Murakami's solution. Fracture surfaces were examined in a Jeol 35C scanning electron microscope.

3. Results

Figs. 4 and 5 show the effect of heat treatment

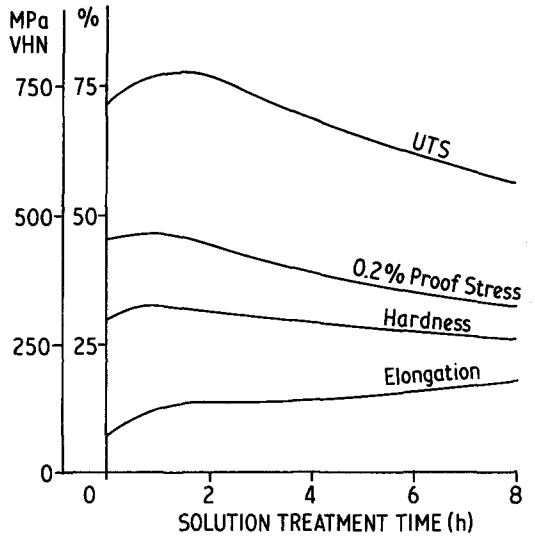

Figure 4 Effect of solution treatment at 1240° C on as cast Co–Cr–Mo.

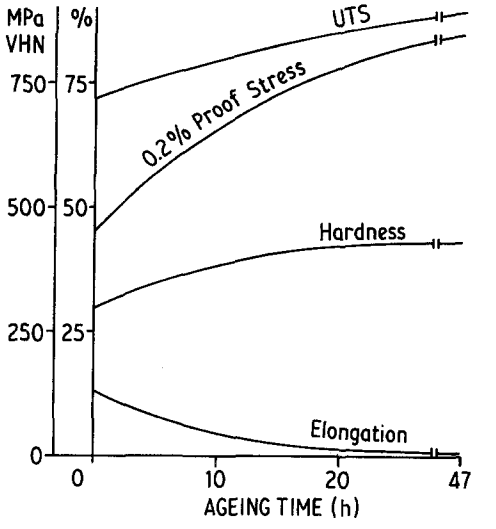

Figure 5 Effect of ageing at 720° C on Co–Cr–Mo solution treated for 2 h.

on the hardness and tensile properties, namely the 0.2% proof stress, the ultimate tensile strength (UTS), and the elongation to fracture. Fig. 4 shows the effect of solution treatment at 1240° C on as-cast material, while Fig. 5 shows the effect of ageing at 720° C on solution treated material. The results in Fig. 5 are for a material solution treated for 2 h, but similar results were obtained for a material solution treated for 1 h and for 4 h. It can be seen that solution treatment for not more than 2 h increased the UTS but did not significantly affect the proof stress. Elongation was almost doubled after 2 h. Treatment times greater than 2 h increased ductility but lowered both the proof stress and the UTS. Ageing improved both the proof stress and the UTS but caused embrittlement. After 47 h the proof stress almost doubled but after 5 h the elongation fell below 8%.

Table VI lists the results of the tensile tests for the six conditions given in Table V, and also shows the requirements of the relevent British Standard (BS 3531, 1980). It can be seen that most of the heat treatments gave an increase in the UTS as compared with the as-cast material, but some of the treatments failed to satisfy the BS proof stress requirement, and the solution treated and the aged material did not possess the necessary ductility.

Table VII lists the results of the corrosion fatigue tests at 367 MPa. In each case the heat treatment improved the median life, but the greatest improvement resulted from partial solution treatment (the median life was thirty times greater than for the as-cast material). The mean life was determined from the Weibull plots (not shown) and the values compared well with the median life values given in the table. Using the statistical method of Johnson [27] it could be shown at the 99% probability level that the

TABLE VI Results of tensile tests

Condition	0.2% Proof stress (MPa)	UTS (MPa)	Elongation $5.65\sqrt{So}$ (%)
As-cast	450	715	7.5
Solution treated	440	765	13.5
Solution treated and aged	745	835	2.0
Partially solution treated	503	839	15.3
Pretreated solution treated	431	812	14.6
Homogenized	419	805	15.6
BS 3531, 1980: as-cast	500 min	700 min	8 min
as heat treated	445 min	665 min	10 min

TABLE VII Results of corrosion fatigue tests at 367 MPa. Specimen surface polished (1200 SiC). Number of each type tested = 10

Condition	Median Life (cycles × 10^7)
As-cast	0.26
Solution treated	1.29
Solution treated and aged	0.84
Partially solution treated	7.41
Pretreated solution treated	1.70
Homogenized	0.79

mean life had in every case been improved by the heat treatment. In spite of this improvement there still remained a considerable scatter in the fatigue lives. For partially solution treated material, a typical example, the lives at 367 MPa ranged from 8×10^5 to $> 1 \times 10^8$ cycles. From the Weibull plot for this material it is evident that about 10% of these specimens would fail in a time shorter than the mean life of the as-cast material. Thus, the heat treatment did not entirely eliminate the possibility of early failures.

We also determined for the partially solution treated material how the median life varied with the applied stress level. The following median life values were obtained from five or more tests at each stress level: 310 MPa, 10^8 cycles; 367 MPa, 7.4×10^7 cycles; 420 MPa, 5.6×10^6 cycles; 450 MPa, 1.3×10^6 cycles; 460 MPa, 4×10^5 cycles. Thus it can be seen that the median life decreased steadily as the stress increased.

Table VIII lists the results of the polarization tests on material in the passivated and steam sterilized condition. The table gives the mean values of similar results obtained from two or more tests. It can be seen that the heat treatments did not significantly affect the corrosion behaviour. In similar experiments on partially solution treated material it was shown that passivation reduced the passive current density by a factor of five, whereas stream sterilization had little effect and neither of these treatments altered the breakdown potential. Furthermore, there was little change in corrosion behaviour as a result of small changes in pH (7.0 to 8.5) and as a result of using bovine serum instead of Ringer's solution.

The microstructure of the material in the heat treatment conditions listed in Table V is shown in Fig. 6. The as-cast alloy exhibited the typical microstructure, namely a cored cobalt-rich face centred cubic matrix with interdendritic carbides and grain boundary precipitates. Partial solution treatment did not alter the carbide size or morphology, but both the grain boundary precipitate and the coring were removed. After solution treatment for 2 h the carbides were considerably reduced in size and after 4 h they were eliminated. After ageing, transformation bands appeared. Both pretreated solution treatment and homogenization eliminated the grain boundary precipitate and the coring. In the former case the carbides were spherodized, and in the latter case they were unchanged and no further carbide precipitation occurred. The average grain size of the fatigue test pieces was 180 μm for the as-cast material and 390 μm for material after heat treatment.

Fig. 7 shows scanning electron micrographs of the fracture surfaces of typical fatigue test pieces in the six conditions listed in Table V. Each fracture surface exhibited a mixture of fracture modes and often it was difficult to locate the fracture origin. Heat treatment produces no obvious differences in fracture behaviour and porosity was evident in most cases.

4. Discussion

Our tensile tests demonstrated that the tensile properties of the as-cast alloy could be improved by heat treatment. Our results for solution treatment agree well with those of Hollander and

TABLE VIII Results of potentiodynamic polarization tests in deaerated Ringer's solution, pH 7.4, at 37° C and 10 mV min^{-1}, specimen surface polished (600 SiC), passivated and steam sterilized

Condition	E_{Corr}* (mV)	I_p/A (μAcm^{-2})	E_B* (mV)	E_{Repass}* (mV)
As cast	102	0.06	692	657
Solution treated	6	0.04	692	657
Solution treated and aged	64	0.05	679	647
Partially solution treated	91	0.04	687	712
Pre-treated solution treated	40	0.11	684	659
Homogenized	65	0.10	699	659

*Measured against the standard hydrogen electrode

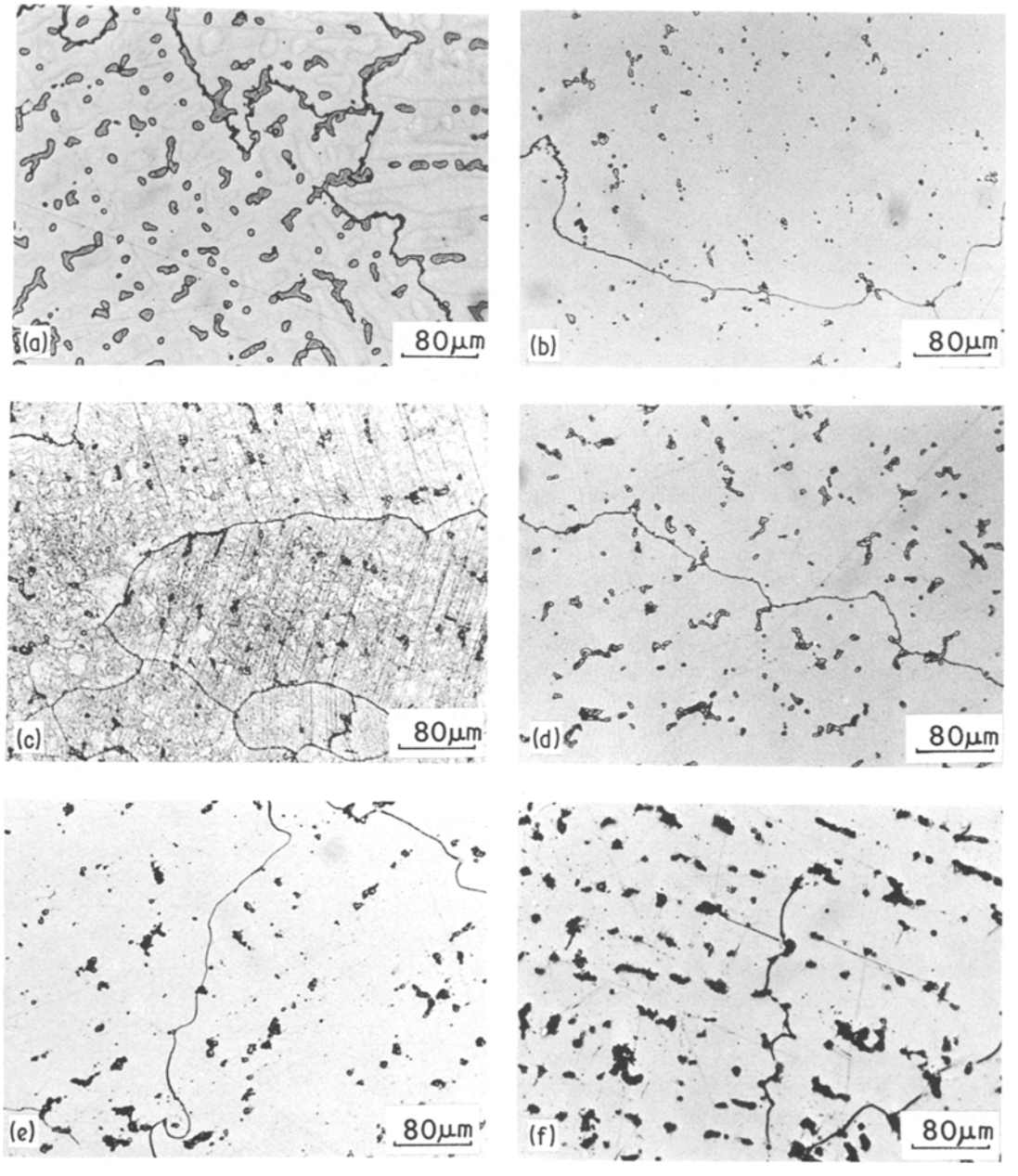

Figure 6 Microstructure of alloy before and after heat treatment. Co–Cr–Mo (cast): (a) as-cast, (b) solution treated, (c) solution treated and aged, (d) partially solution treated, (e) pretreated solution treated and (f) homogenized.

Wulff [8], but disagree with those of Cox [13], whose poor results suggest that in his experiments grain growth occurred. Our values for pretreated solution treatment compare well with those of Cohen *et al.* [11], although we obtained a smaller increase in UTS than they did. No comparison was possible for partial solution treatment or homogenization since to our knowledge no published data exist for these treatments.

The response of the tensile properties to heat treatment can be understood in terms of the microstructural changes which occur [28, 29]. In the as-cast state the carbides provided the major strengthening mechanism with solid solution strengthening being of lesser importance [30]. The grain boundary precipitates and the coring were responsible for brittleness. Solution treatment caused carbide dissolution [31, 32] and elimination

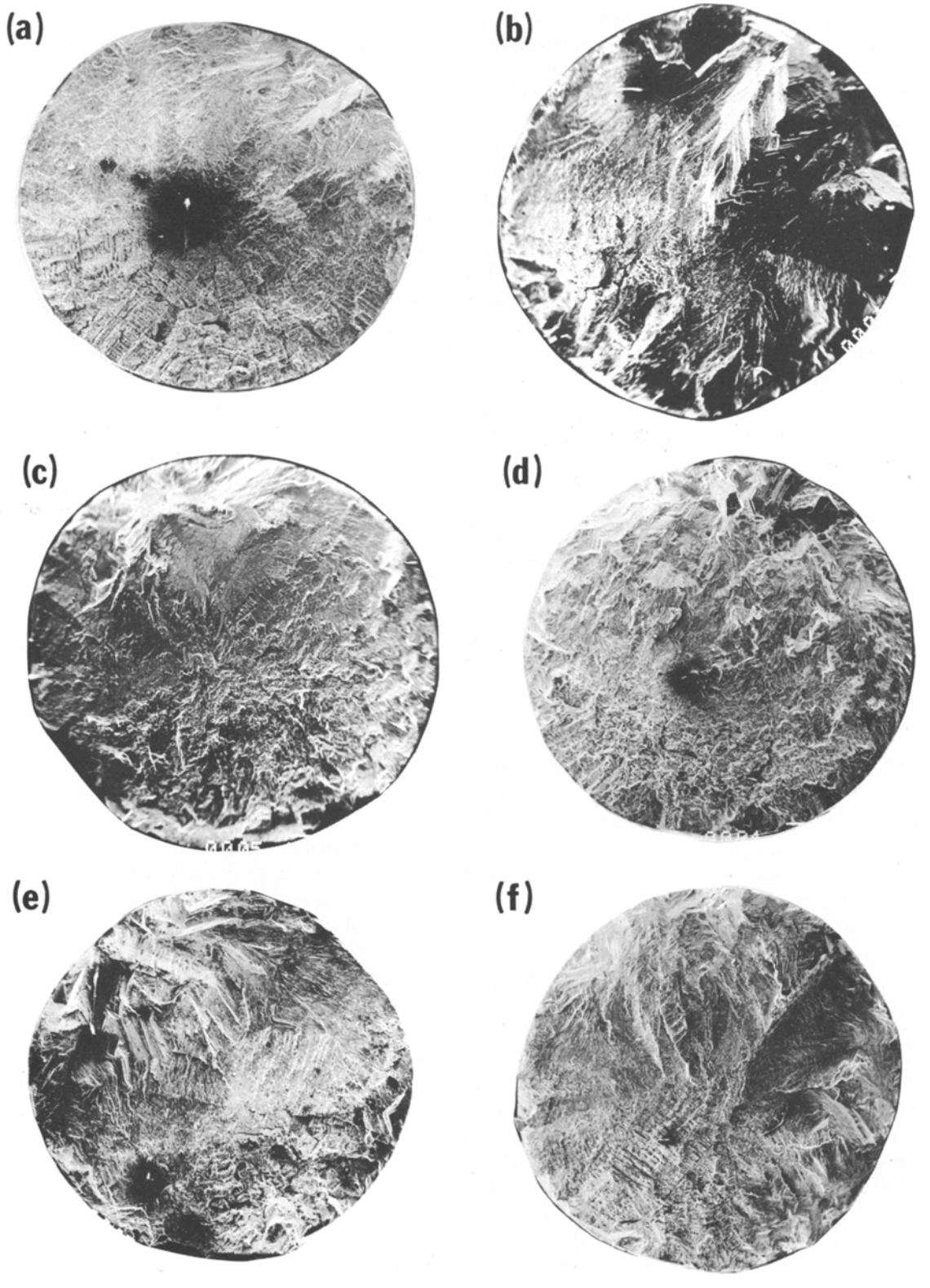

Figure 7 Appearance of fracture surfaces of fatigue test pieces. The test piece diameter was approximately 3.8 mm in each case. (a) As-cast, (b) solution treated, (c) solution treated and aged, (d) partially solution treated, (e) pretreated solution treated, (f) homogenized.

of both grain boundary precipitates and coring. Consequently, as shown in Fig. 4, fully solution-treated material had low strength and good ductility, whereas partially solution-treated material exhibited a satisfactory compromise in properties. Ageing produced carbide precipitation along slip lines, twin boundaries and stacking faults, formed on quenching [7]. These transformation bands acted as a further strengthening mechanism, producing increased hardness and decreased ductility as shown in Fig. 5. Both the pretreated solution treatment and the homogenization eliminated the grain boundary precipitate and the coring with the consequent improvement in properties.

Although heat treatment improved the fatigue properties, the results were disappointing. Only partial solution treatment produced a worthwhile improvement and pretreated solution treatment and homogenization behaved less well than anticipated [11, 12]. The results suggest that the most detrimental feature of the microstructure was the grain boundary precipitate. Once this was removed the fatigue life improved. The results also demonstrated that it was easier to improve the tensile strength than the fatigue life. One reason for this may be the influence of porosity, which is known to worsen fatigue behaviour.

The results of our corrosion tests on as-cast material compare well with those of other workers listed in Table III. In addition our results show that heat treatment had a relatively small effect on the corrosion behaviour. The passive current density was practically unaffected due perhaps to the fact that such small passive current densities are difficult to measure reliably [16]. On the other hand heat treatment, especially solution treatment, made the rest potential more noble, which is the expected result due to the passivating effect of the liberated chromium [17].

Using Faraday's law the quantity of corrosion products liberated into the body can be estimated from the *in vitro* results. Assuming a passive current density of 4×10^{-8} A cm^{-2} (typical of the passive region) and an implant surface area of 200 cm^2 (typical of a hip joint) we obtain a figure of 400 μm per day. This is probably an overestimate [33], but the figure serves as a reminder that cobalt and chromium are liberated into the body and that as a consequence detrimental effects can occur [34].

In summary, our experiments showed that heat treatment improved the mechanical properties of the alloy without loss of corrosion resistance. In particular, heat treatment increased the median fatigue life of the alloy by more than an order of magnitude as compared with the as-cast material. This represented a worthwhile improvement but the casting still remained inferior to wrought titanium or wrought or sintered Co–Cr–Mo as shown in later work [35]. Furthermore, although heat treatment improved the mean fatigue life, the scatter in the fatigue lives still remained, as mentioned above. Since much of this variability may be the result of minor casting defects, such as porosity, it is not clear that heat treatment alone would provide a cast product able to compete on mechanical grounds with the wrought or sintered products mentioned above. Additional improvements may result from hiping to eliminate defects (expensive) or from nitrogen incorporation to provide solid solution strengthening (of questionable value).

What then are the implications of these results for orthopaedic implants? It is our opinion that for those joint replacement applications where low corrosion fatigue strength is acceptable and where ease of fabrication and good wear resistance are required, cast Co–Cr–Mo may still be the material of choice. For other joint replacement applications requiring high corrosion fatigue strength (e.g. hip joints) the products mentioned above are more suitable.

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