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Influence of zirconium and heat treatment on the structure of heat-resistant cobalt casting alloys of MAR-M509 type

Z. OPIEKUN
Institute of Mechanical Engineering, Technical University in Rzeszów, Wincentego Pola 2, 35-959 Rzeszów, Poland

The article presents the importance of zirconium as an alloy addition introduced in different amounts into six cobalt cast alloys of MAR-M509 type. The tests concerning effect of various heat treatment processes on structural changes and mechanical properties are also presented. Based on the alloy structure observations by optical microscopy, TEM and diffraction pattern, as well as distribution of alloying elements using SEM with auxiliary energy device "Kevex-Ray" and Debye–Scherrer method, primary and secondary phases have been identified. It has found that zirconium resulted in vanishing of dendritic nature of the alloys, primary carbides refining, creating carbo-nitrides of M(C, N) type, strengthening of the alloy matrices, prohibiting the tendency to coarsening of secondary carbides $Cr_{23}C_6$ and increasing their creep strength.

1. Introduction

Cobalt-base alloys, characterized by very high heat resistance, are used for parts of aircraft turbine engines and rockets such as combustion chambers and vanes [1]. In most cases, the parts from cobalt-base alloys are made from precision castings.

Cobalt casting alloy structure is characterized by an inclination to produce large dendritic grains in the matrix, and at the same time, to segregation of carbide phases. In most cases, the matrix of these alloys is composed of so-called cobalt austenite γ (f c c lattice of cobalt α, stabilized chiefly with nickel) [2].

Cobalt casting alloys contain many elements, and zirconium is one of special importance. It occurs (0.1 to 2.25 wt %) in alloys of type: Al-Resist 215, HS-224, WS-25, WAZ-NASA and MAR-M [3], placing these alloys among the best modern cobalt casting alloys. Zirconium is present also in precipitation-hardened alloys of TD-cobalt type [4]. Zirconium additions in cobalt alloys seems to be very advantageous; however its influence on alloys of MAR-M509 type is not fully explained. Only a few papers [5–7] provide more full information on MAR-M509 type alloys.

The intention of this paper is to show the influence of zirconium additions on the structure of MAR-M509 type cobalt alloys, as well as the influence of heat treatment on the mechanical properties of these alloys.

2. Experimental material

The heat treatment of heat-resistant cobalt-base casting alloys of MAR-M509 type, with various contents of zirconium, were carried out using an induction crucible furnace of Type Asec 15 and an alundum crucible.

In the first step, from pure alloying components, the ingots were cast into investment moulds. At the end of every heating step zirconium was added to the liquid alloy, using Ni–Zr master alloy.

After the mould was broken, the ingot was sand-blasted and remelted, in the same induction crucible furnace. Before remelting the crucible was rinsed with liquid cobalt.

After melting the alloy was heated up to 1600° C, as measured with an immersion thermocouple Pt–PtRh 13, and poured into a mould for shaft-shaped specimens. The investment mould containing the set of specimens was placed in a moulding box filled with cement material. Before alloy pouring the mould was kept at 1000° C for about 10 h.

Altogether six heat-resistant alloys were used, 44 specimens of each (10 mm diameter, about 75 mm

TABLE I Compositions of experimental alloys

Alloy No.	Compositions (wt %, balance cobalt)							
	Cr	Ni	W	Ta	Ti	Zr	C	S
1	23.70	10.05	7.13	1.82	0.20	–	0.72	0.0030
2	23.37	9.96	6.75	2.03	0.21	0.17	0.71	0.0030
3	23.52	9.64	7.47	1.90	0.19	0.43	0.74	0.0028
4	23.61	9.00	7.65	1.95	0.20	1.09	0.72	0.0030
5	23.62	9.40	7.00	1.86	0.20	1.68	0.71	0.0029
6	23.40	9.52	7.20	1.95	0.19	2.72	0.73	0.0030

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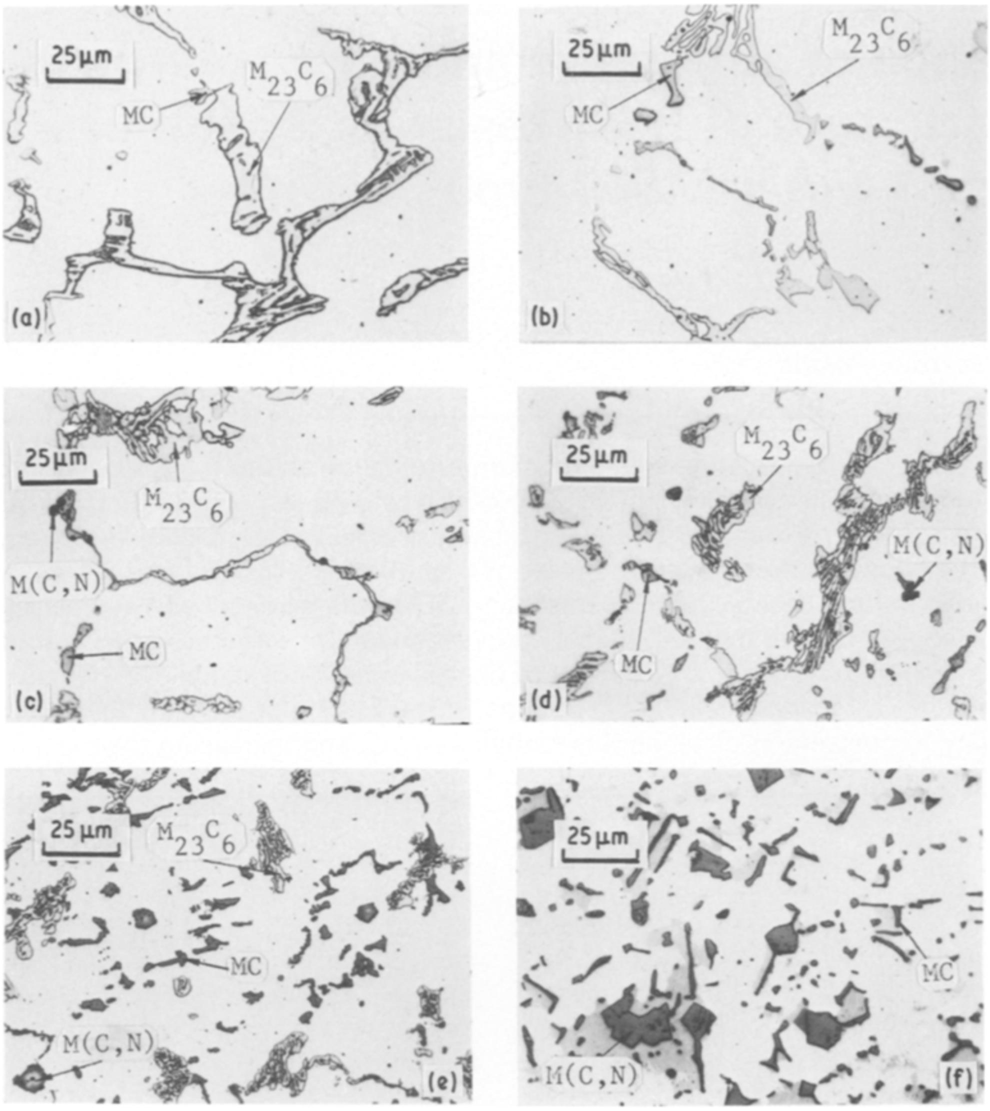


Figure 1 As-cast microstructure of MAR-M509 type alloys. Etch: 50% HNO_3, electrolytic. (a) Alloy 1, (b) Alloy 2, (c) Alloy 3, (d) Alloy 4, (e) Alloy 5, (f) Alloy 6.

length). The specimens were tested with X-rays and no faults were found. Compositions of the alloys are listed in Table I.

A typical composition of MAR-M509 alloy is as follows (wt %): 21.5 Cr, 10 Ni, 7 W, 3.5 Ta, 0.2 Ti, 0.5 Zr and 0.6 C. The tested alloys, besides significant differences in zirconium content, have a tantalum content about 1.5% less and carbon content about 0.1% more.

3. Experimental results

Results presented hereafter have been obtained from tests on bars of 10 mm diameter and 75 mm length, as-cast and after various heat treatments (see Table II).

3.1. Microstructure

3.1.1. As-cast condition

Structure analysis of cobalt alloys tested in the as-cast condition was made on metallographic specimens using optical microscopy. The surface distribution of alloying elements was also studied using scanning electron microscopy with an auxiliary energy device "Kevex-Ray".

The primary carbides present in the alloys were identified by the Debye–Scherrer method using Cu*K*α radiation. The carbides were electrolytically extracted from the matrix, using a solution of 90 cm^3 alcohol, 10 cm^3 HCl, tartaric acid 1 wt % and a current of about 0.3 A. The structures of the alloys in the as-cast condition are shown in Fig. 1.

Diffraction patterns obtained enable one to state that in Alloys 1 and 2 there were carbides of MC and $M_{23}C_6$ types, in Alloys 3, 4 and 5 there were carbides

TABLE II Heat treatment applied to experimental alloys

Alloy No.	Heat treatment
1	All Alloys: solution heat-treatment 1260° C for 4 h in air + ageing at 900° C for 25 h in air + ageing at 975° C for 200, 300 or 400 h in air
2	
3	
4	
5	
6	
1	As-cast + ageing at 850° C for 720 h in air
5	
1	Solution heat-treatment at 1270° C for 5 h in air + ageing at 975° C for 25, 75, 160, 260, 390 or 450 h in air
5	

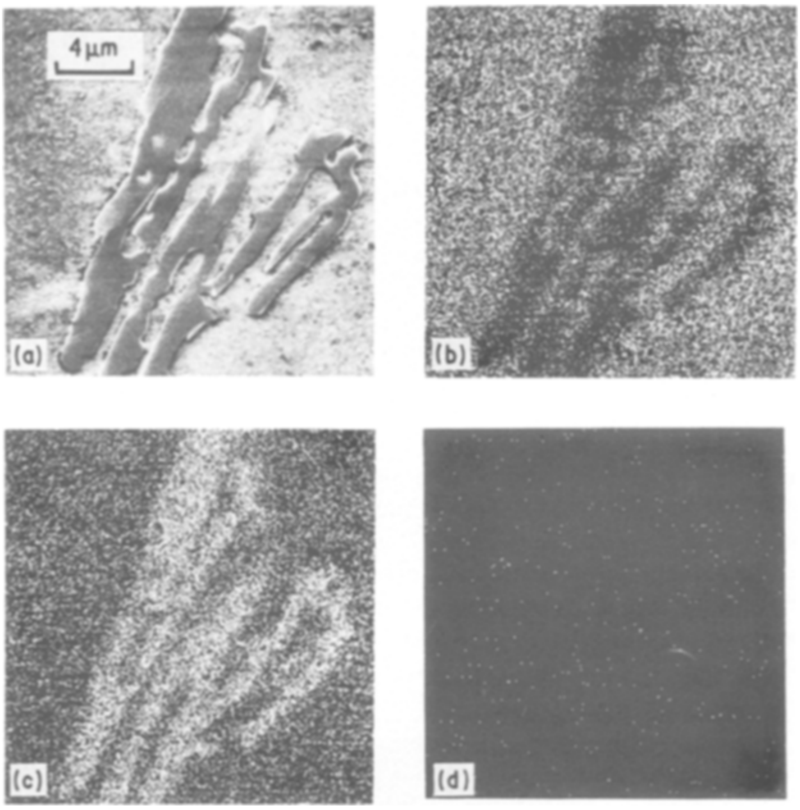


Figure 2 (a) Structure of Alloy No. 1 in the as-cast condition. Images of alloying element distributions: (b) cobalt, (c) chromium, (d) tungsten.

of MC and $M_{23}C_6$ types and carbonitrides of M(C, N) type were present.

Figs 1a and b show the structure of Alloys 1 and 2 in the as-cast condition. In interdendritic areas of γ solid solution there are large carbides of $M_{23}C_6$ type and smaller carbides of MC type. Figs 1c, d and e present the structure of Alloys 3, 4 and 5 in the as-cast condition. In these alloys, besides the carbides of $M_{23}C_6$ and MC types, there are also the carbonitrides of M(C, N) type. As the zirconium content in the tested alloy increased, it was observed that the sizes and amount of primary carbides of $M_{23}C_6$ type decreased and, at the same time, the sizes and amount of carbonitrides of M(C, N) type increased. The carbonitrides have the shape of polygons. In Alloy 6 in the as-cast condition (Fig. 1f), in which the zirconium

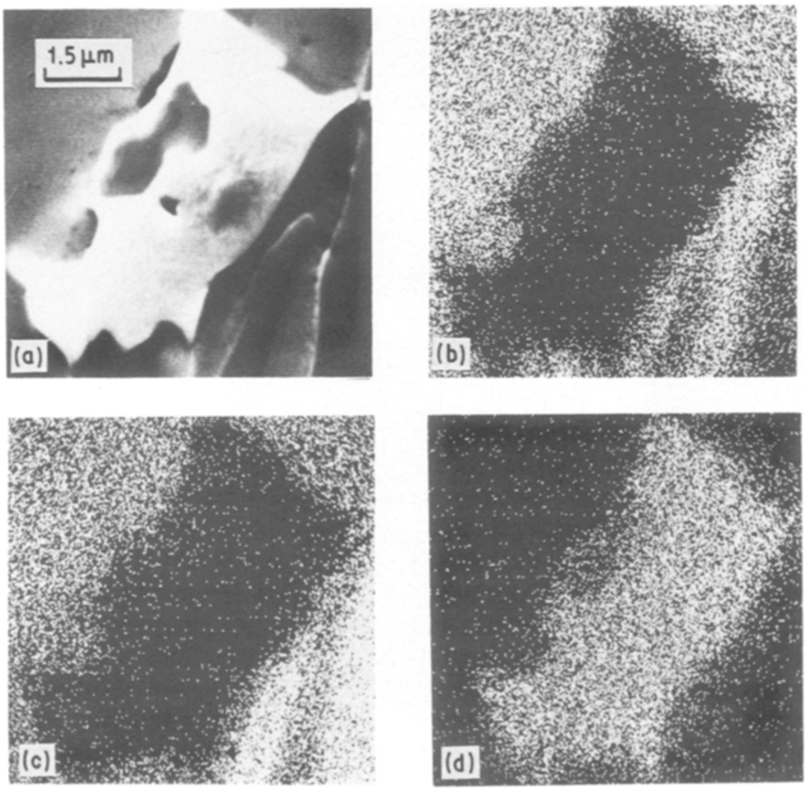


Figure 3 (a) Structure of Alloy No. 3 in the as-cast condition. Images of alloying element distributions: (b) cobalt, (c) chromium, (d) tantalum, (e) zirconium, (f) titanium.

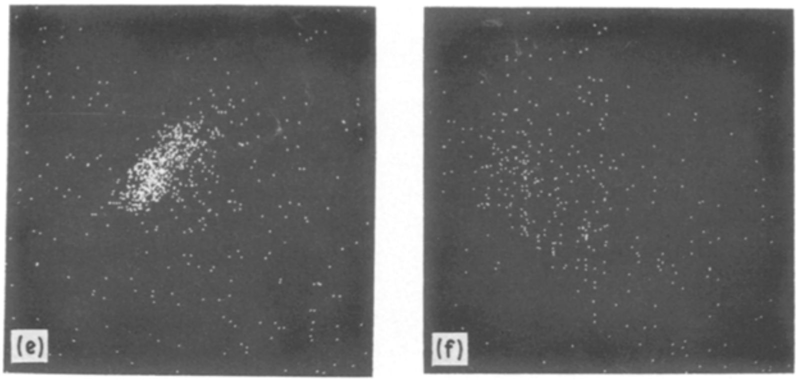


Figure 3 Continued.

content is the largest, in the γ matrix there are carbides of MC type and large carbonitrides of M(C, N) type. The dentritic nature of this alloy has vanished.

The distributions of alloying elements (Figs 2, 3 and 4) show that primary carbides, yielding dark contrast after exposure to the electron beam, contain mainly chromium and cobalt and can be descripted as (Cr, Co)$_{23}$C$_6$. In the matter of primary carbides of MC type, yielding bright contrast, these are phases of high tantalum content, and there is also tungsten. So these carbides can be described as (Ta, W)C. Grey primary carbonitrides of the M(C, N) type are rich in zirconium, and also contain titanium, so they can be described as (Zr, Ti)(C, N).

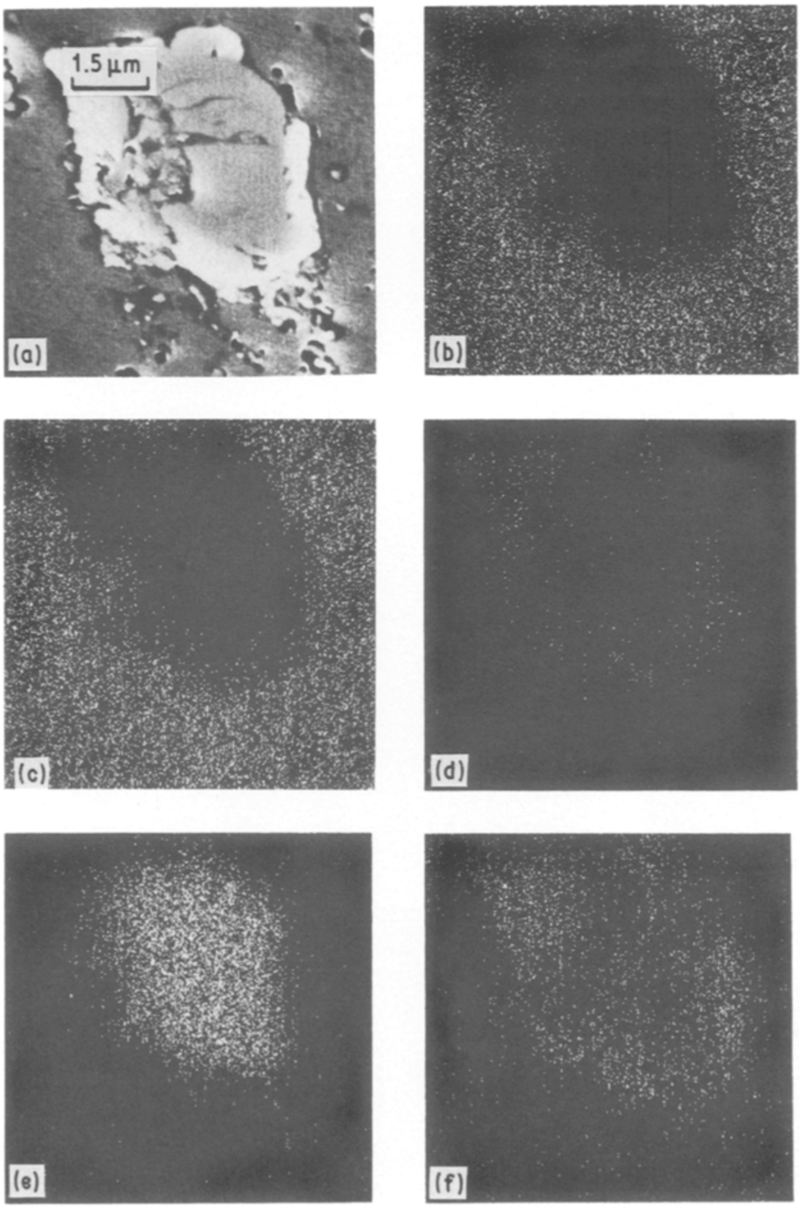
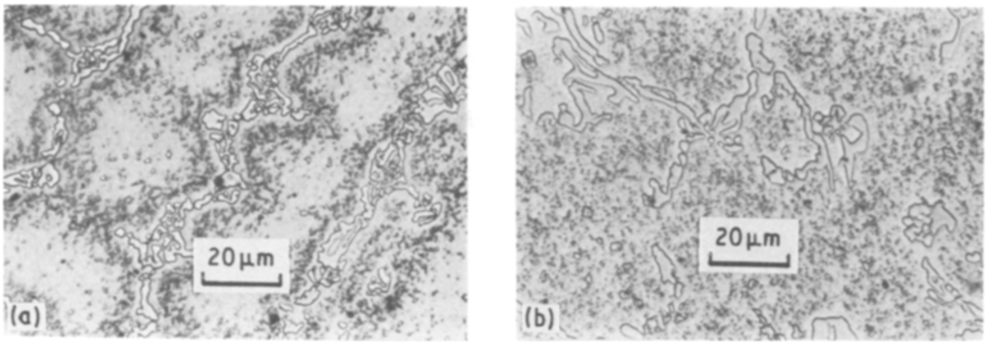


Figure 4 (a) Structure of Alloy No. 5 in the as-cast condition. Images of alloying element distributions: (b) cobalt, (c) chromium, (d) tantalum, (e) zirconium, (f) tungsten.



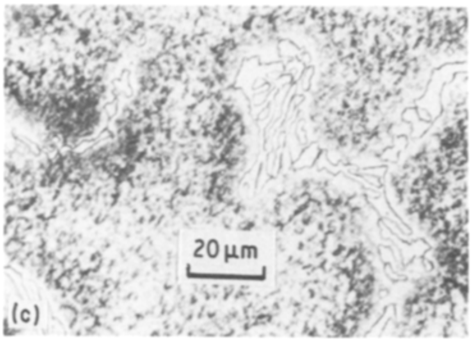


Figure 5 Optical micrographs of Alloy No. 1. Etch: Kalling's reagent (2 g $CuCl_2$, 40 cm^3 HCl, 60 cm^3 alcohol). (a) After solution heat-treatment at 1260° C for 4 h in air + ageing at 900° C for 25 h in air. (b) After solution heat-treatment at 1260° C for 4 h in air + ageing at 900° C for 25 h in air + ageing at 975° C for 200 h in air. (c) After ageing, from as-cast condition, at 850° C for 720 h in air.

3.1.2. Heat-treated alloys

Structural examination of the alloys after various heat treatment (Table II) were carried out with optical microscopy and transmission electron microscopy (JEM 100B). Test preparations for TEM were thin foils, obtained by electrolytic polishing of thin plates (thickness 0.01 to 0.02 mm) using as electrolyte 1 part of H_2SO_4 (concentrated) + 7 parts of methanol, and 35 V. Electrolytic polishing was done by the Bollman method. Figs 5 and 6 present examples of structures of the alloys examined by optical microscopy.

After solution heat-treatment at 1260° C for 4 h the primary carbides have not dissolved entirely in γ solid solution. After ageing at 900° C for 25 h and at 975° C for 200, 300 or 400h, secondary phases have precipitated in solid solution. Alloys 1 and 5, after ageing at 850° C for 720 h (Figs 5c and 6c) also have secondary phases precipitated in the matrix. These phases, shown in Figs 5 and 6, constitute fine spot precipitates.

Structural analysis of the alloys, using TEM and electron diffraction, enables one to identify secondary carbides $Cr_{23}C_6$ (Fig. 7).

The secondary carbides $Cr_{23}C_6$, that provide dispersion-hardening of the matrix of MAR-M509 cobalt-base casting alloys, precipitate at $\{1\,1\,1\}$ planes, nucleating at stacking faults. In the case of the austenitic matrix of the investigated cobalt alloys, the energy of stacking faults (ESF) is very small, so a large density of these lattice defects is observed. A long time of annealing (720 h at 850° C) has caused – in the Alloy No. 1 not containing zirconium addition – a coarsening of the $Cr_{23}C_6$ secondary carbides, but in the matrix of Alloy No. 5 the $Cr_{23}C_6$ secondary carbides have much less tendency toward coarsening (Fig. 8).

Heat treatment of Alloys 1 to 6, consisting of solution heat-treatment at 1260° C for 4 h in air, and ageing at 900° C for 25 h in air and ageing at 975° C for 200, 300 or 400 h, caused $Cr_{23}C_6$ secondary carbides to precipitate in their matrix (Fig. 9); however, in the

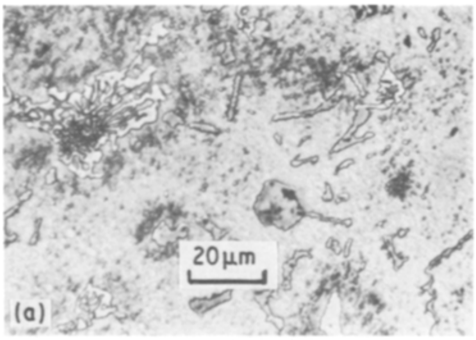
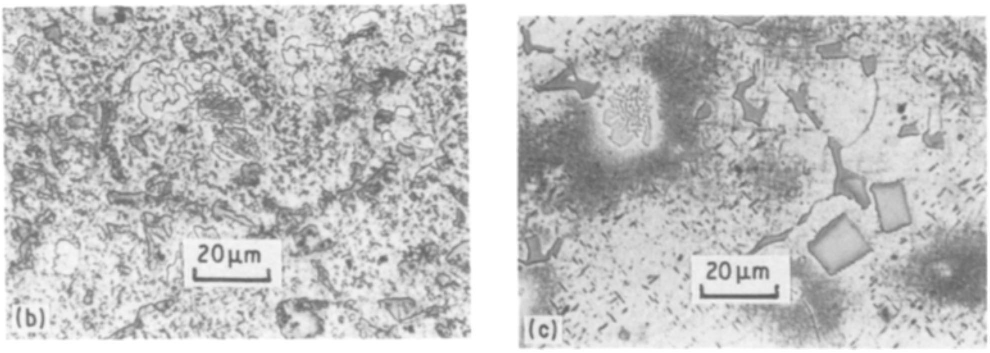


Figure 6 Optical micrographs of Alloy No. 5. Etch: Kalling's reagent (2 g $CuCl_2$, 40 cm^3 HCl, 60 cm^3 alcohol). (a) After solution heat-treatment at 1260° C for 4 h in air + ageing at 900° C for 25 h in air. (b) After solution heat-treatment at 1260° C for 4 h in air + ageing at 900° C for 25 h in air + ageing at 975° C for 200 h in air. (c) After ageing, from as-cast condition, at 850° C for 720 h in air.



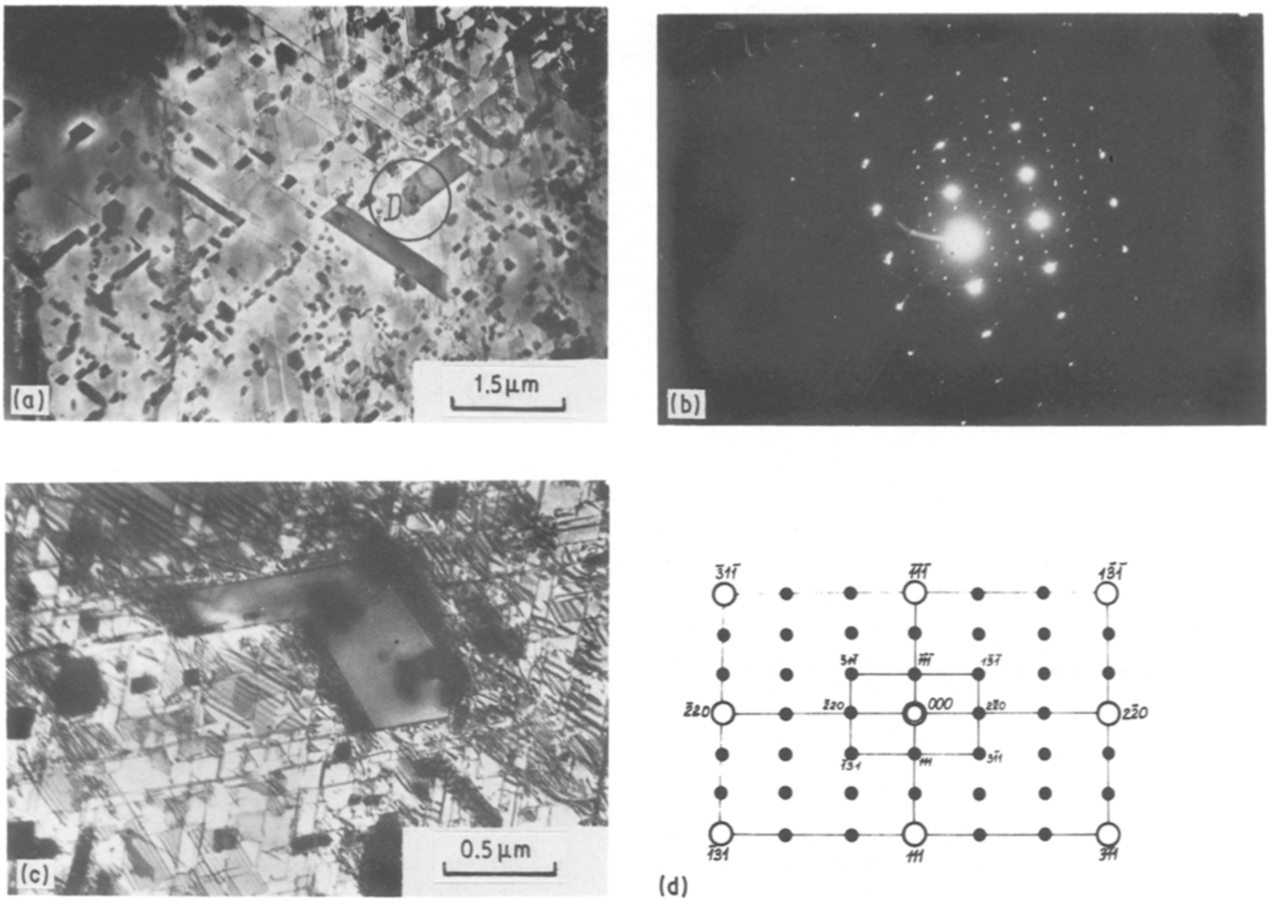


Figure 7 Microstructure of Alloy No. 1 in as-cast condition and after ageing at 850° C for 720 h. (a) Electron micrograph; (b) diffraction pattern of $Cr_{23}C_6$ carbides from area D in (a); (c) electron micrograph; (d) indexed diffraction pattern: (○) matrix $\{\bar{1}\,\bar{1}\,\bar{2}\}$, (●) $Cr_{23}C_6$ $\{\bar{1}\,\bar{1}\,\bar{2}\}$.

matrix of Alloy No. 6 $Cr_{23}C_6$ secondary carbides scarcely exist. A long time (200 to 400 h) of annealing at 975° C also caused coarsening of the $Cr_{23}C_6$ secondary carbides, but carbide growth was less intense in the alloys containing zirconium (Fig. 10).

Figs 11 and 12 show electron diffraction of primary carbides TaC and primary carbonitrides of Zr(C, N).

Identification of primary carbides and carbonitrides by the electron diffraction method has confirmed results that had been obtained by the Debye–Scherrer method. MC type primary carbides of high tantalum content, and M(C, N) type carbonitrides of high zirconium content, have dislocations that are shown in Figs 11a and 12a.

3.2. Mechanical properties

3.2.1. Microhardness of the matrix

Alloy matrix modifications in the as-cast condition, resulting from the addition of such a highly carbide-forming element as zirconium, were recorded by microhardness measurements. Microhardness was measured with a microhardness tester of Type Micro-SA (Matsuzawa Seiki Co. Ltd, Tokyo), using a Vickers pyramid indenter and 100 g load. The effect of zirconium content on alloy matrix microhardness is shown in Fig. 13.

The increase of alloy matrix microhardness in the as-cast condition resulting from zirconium addition

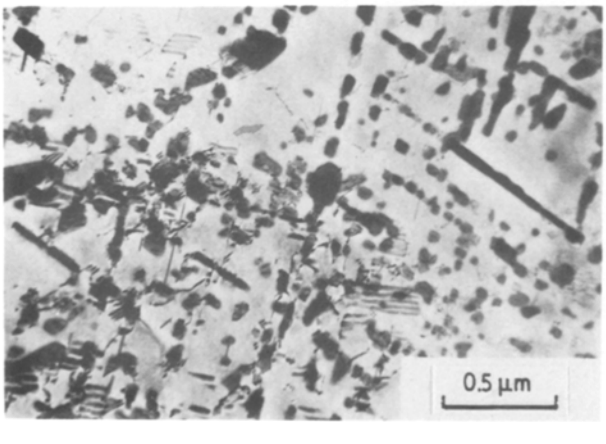


Figure 8 Microstructure of Alloy No. 5 in the as-cast condition and after ageing at 850° C for 720 h.

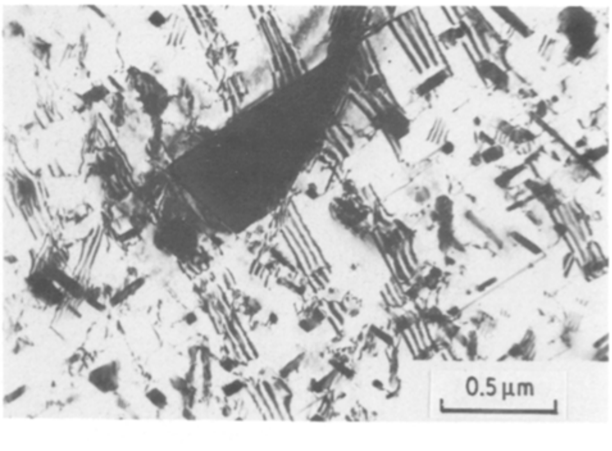


Figure 9 Electron micrograph of Alloy No. 1, after solution heat-treatment at 1260° C for 4 h in air and ageing at 900° C for 25 h in air and ageing at 975° C for 200 h.

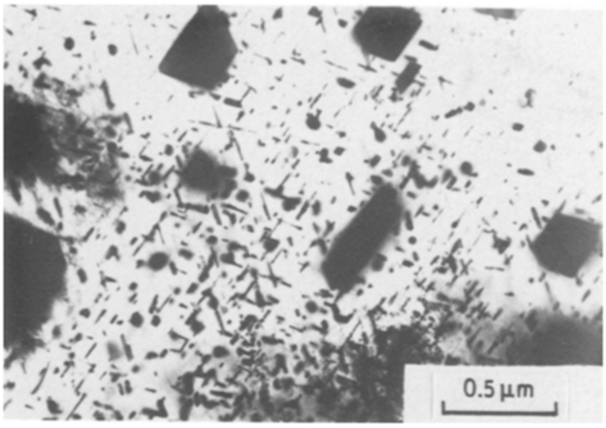


Figure 10 Electron micrograph of Alloy No. 3, after solution heat-treatment at 1260° C for 4 h in air and ageing at 900° C for 25 h in air and ageing 975° C for 200 h.

was connected with an increase of chromium concentration in the matrix. Zirconium, by carbon assimilation into carbonitrides, causes reduction and consequent disappearance (Alloy No. 6) of primary $M_{23}C_6$ type carbides of high chromium content. This action of zirconium has an influence on the strengthening of the matrix and the refinement of dendritic grains.

Matrix modifications in Alloys 1 and 5, resulting from solution heat-treatment at 1270° C for 5 h with air cooling and ageing at 975° C for 25, 75, 160, 260, 390 and 450 h were tested by microhardness measurements (Fig. 14), using a Vickers pyramid and 50 g load.

Both the alloys, No. 1 and No. 5, after solution heat-treatment, have a similar microhardness equal to about 260 μHV_{50}. Alloying ageing results in increased matrix microhardness, and this is evidence of the strengthening action of secondary carbides $Cr_{23}C_6$. Alloy No. 5, after ageing at 975° C for about 75 h, achieved maximum matrix microhardness when it was kept at the same level for all the time of annealing, i.e. about 450 h. On the other hand Alloy No. 1 achieved maximum matrix microhardness after annealing at 975° C for about 260 h, but longer times of annealing at this temperature resulted in a moderate decrease of matrix microhardness. Matrix microhardness stability during a long time of annealing, in respect to Alloy No. 5, results from the influence of zirconium; minute quantities of zirconium dissolved in the alloy matrix inhibit the diffusion process and prohibit coarsening of secondary carbides $Cr_{23}C_6$. In the case of Alloy No. 1, which contained no zirconium, a decrease of matrix microhardness during annealing at 975° C for above 260 h results from a breaking of coherence with the matrix and a coarsening of secondary carbides $Cr_{23}C_6$.

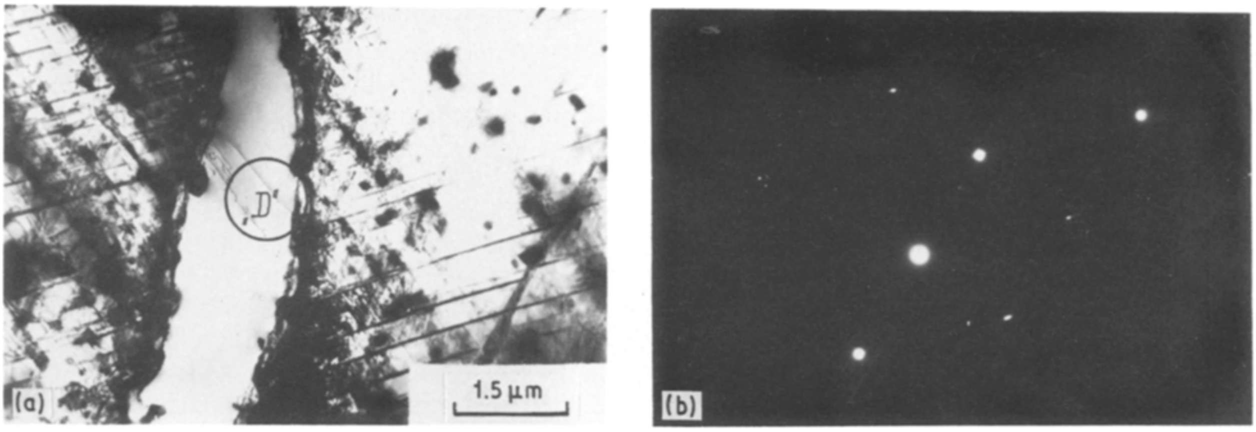
3.2.2. Creep strength

The creep strength of Alloys 1 to 6 was determined using specimens of 4 mm diameter and threaded grips, tested at high temperature with a tension creep-testing machine (Louis Schopper der S.A.G., Awtowelo, GDR). Two specimens were tested for each alloy in the as-cast condition and for each type of heat

TABLE III Creep strength of alloys

Alloy No.	Test temperature (° C)	Stress (kg mm^{-2})	Stress (10^3 p.s.i.)	Heat treatment	Rupture life (h)	Elongation (%)
1	975	10.0	14.4	As-cast	32	27
					46	25
2					50	22
					38	25
3					52	12
					68	16
4					62	12
					75	17
5					168	18
					202	15
6					50	8
					31	12
1	975	10.0	14.4	Solution heat-treatment at 1260° C for 4 h in air, and ageing at 900° C for 25 h in air	65	10
					72	8
2					76	20
					83	26
3					70	12
					76	18
4					90	22
					83	19
5					248	12
					217*	16*
6					76	14
					89	10
1	975	10.0	14.4	"As-cast" condition, ageing at 850° C for 720 h in air	37	8
					56	7
5					139	7
					152	10

*Specimen was tested for 175 h at a loading of 10.0 kg mm^{-2} (14.4 × 10^3 p.s.i.) and for an additional 42 h at a loading increased up to 15.0 kg mm^{-2} (21.2 × 10^{-3} p.s.i.).



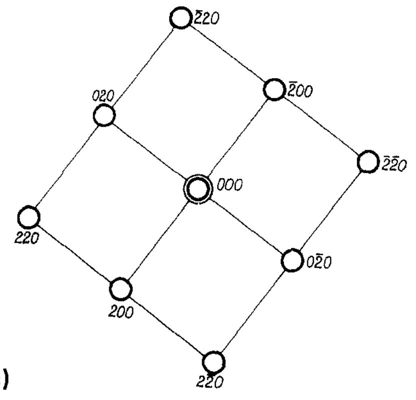
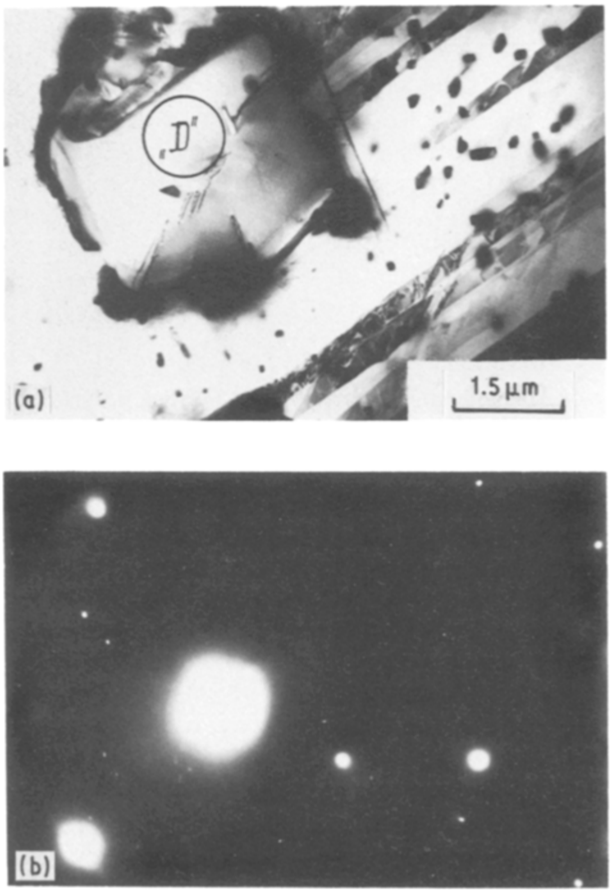


Figure 11 Microstructure of Alloy No. 5, after solution heat-treatment at 1260° C for 4 h in air and ageing at 900° C for 25 h in air and ageing at 975° C for 400 h. (a) Electron micrograph; (b) diffraction pattern of primary carbides TaC′ from area D in (a); (c) indexed diffraction pattern, TaC′ {0 0 1}.

treatment. Creep was carried out at the temperature of 975° C and a load of $10\,\mathrm{kg\,mm^{-2}}$ (14.4 p.s.i.); rupture life and elongation after rupture were measured. All the results obtained are listed in Table III.

Creep strength testing showed that No. 5 Alloy has the longest rupture life, both in the as-cast condition and after solution heat-treatment (1260° C for 4 h in air) and ageing (900° C for 25 h in air). This heat treatment causes a visible increase in creep strength for all the alloys tested in comparison with the as-cast condition. About 20% shorter rupture life in the case of Alloy No. 5 after ageing at 850° C for 720 h, as compared with the as-cast condition, provides evidence of high stability (no tendency to coarsening) of secondary carbides $Cr_{23}C_6$, which provide strengthening for the matrix. In the case of Alloy No. 1 (without zirconium), in spite of the high tendency to coarsening of secondary carbides, the rupture life has not changed, as compared with the as-cast condition, but it is much shorter (by about 100 h) than in the case of Alloy No. 5.

Fractography of creep – tested specimens, with the Novascan 30 Type SEM (Carl Zeiss, FRG), showed that in the alloy matrices there are ductile fractures with secondary carbides $Cr_{23}C_6$ in "recesses", and crack initiate at the boundaries of primary phases and the matrix γ (Fig. 15).



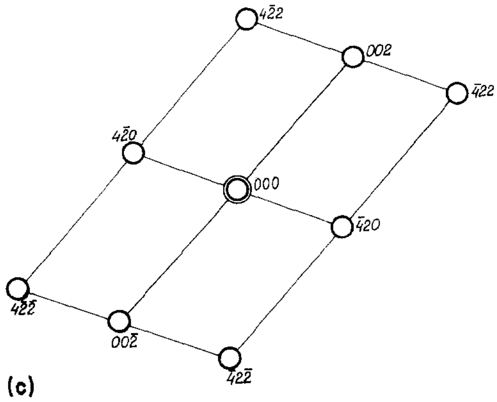


Figure 12 Microstructure of Alloy No. 5, after solution heat-treatment at 1260° C for 4 h in air and ageing at 900° C for 25 h in air and ageing 975° C for 400 h. (a) Electron micrograph; (b) diffraction pattern of carbonitrides Zr(C′, N) from area D in (a); (c) indexed diffraction pattern, Zr(C, N) {1 2 0}.

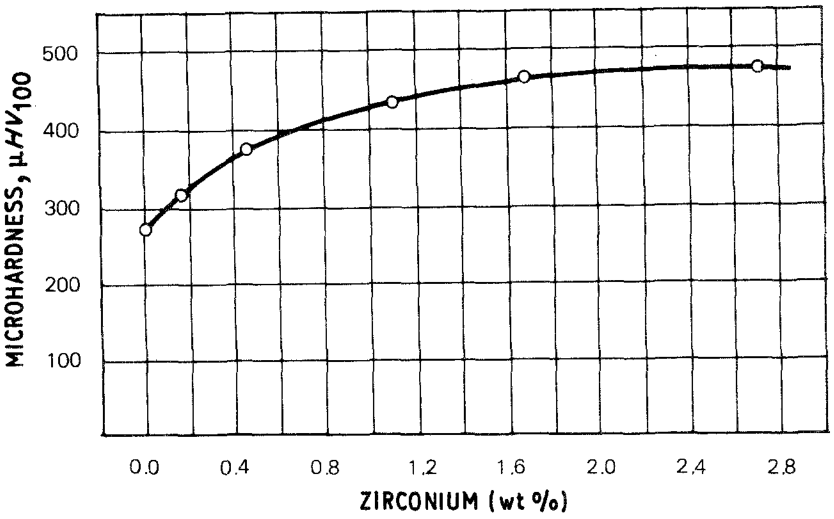


Figure 13 Effect of zirconium on alloy matrix microhardness in the as-cast condition.

4. Conclusions

The study presented in this paper provides further particulars concerning the influence of zirconium on cobalt-base casting alloys of MAR-M509 type, that are in the air.

It has been found that zirconium additives modify the alloy by the formation of carbonitrides Zr(N, C) of high zirconium content. Carbonitrides, having high melting points (about 3420° C), crystallize from the liquid at first, and form nuclei of crystallization, and reduce the size of dendritic grains of cobalt austenite γ.

It was found that γ grain size reduction in Alloy No. 5, as compared with Alloy No. 1, was about 140%.

In Alloy No. 1 (not containing any zirconium), besides the matrix, there are two phases: carbides $(Cr, Co)_{23}C_6$ and carbides (Ta, W)C. Alloy No. 2, in spite of the fact that it contains about 0.17% Zr, has no separate phases of high zirconium content. However, we can notice an effect of modification by the size reduction of γ grains and primary carbides. In Alloys 3, 4 and 5 an increase of zirconium content results in the appearance of the third-phase carbonitrides (Zr, Ti) (C, N) in their matrices. As the zirconium content increases, there is also a gradual increase in the carbonitride percentage in the alloy structure, but $(Cr, Co)_{23}C_6$ carbide percentages decrease. Finally, in Alloy No. 6 (of highest zirconium content) there is no evidence of $(Cr, Co)_{23}C_6$ carbides in the phase constitution of the alloy, but only (Ta, W)C carbides and large polygonal (Zr, Ti) (C, N) carbonitrides.

Among six alloys tested, Alloy No. 5 has the highest creep strength at 975° C and loading $10\,\mathrm{kg\,mm^{-2}}$ (14.4×10^3 p.s.i.), in the as-cast condition and after solution heat-treatment (1260° C for 4 h in air) and ageing (900° C for 25 h in air). This fact results from the suitable phase constitution and stable secondary carbides of $Cr_{23}C_6$. In this alloy there are only about 0.8% of $M_{23}C_6$ type primary carbides but about 2.5% of MC type carbides and about 0.6% of M(C, N) type carbonitrides. During solution heat-treatment these phases are finer than in other alloys. Carbides of $M_{23}C_6$ type partially dissolve in the alloy matrix and enrich the matrix with chromium and carbon. It is necessary to precipitate, during ageing, secondary dispersion carbides of $Cr_{23}C_6$, that strengthen the matrix. However zirconium, minute quantities of which are dissolved in the alloy matrices (below 0.001% by weight) inhibits diffusion processes (surface – active element) and prohibits the tendency to coarsening of secondary carbides $Cr_{23}C_6$.

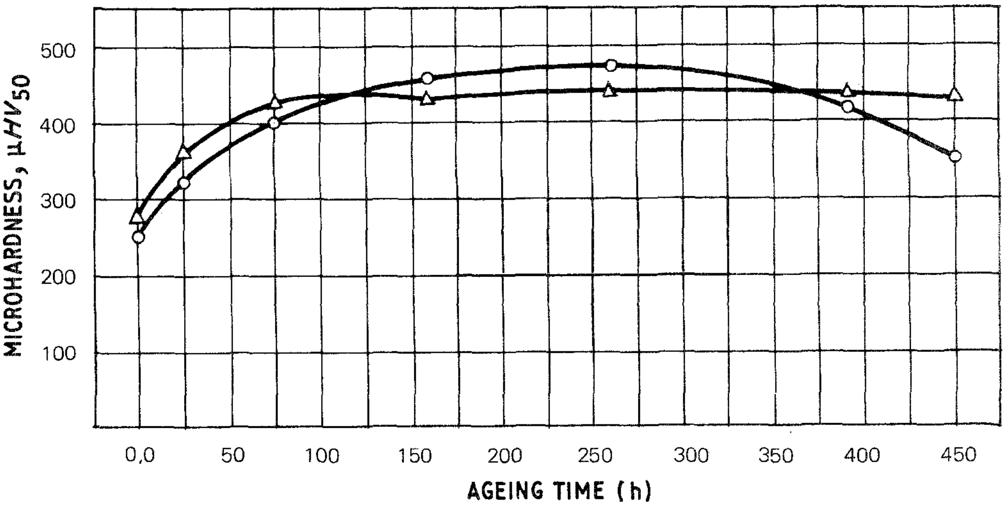


Figure 14 Effect of ageing time at 975° C on matrix microhardness for (○) Alloy No. 1 and (△) Alloy No. 5, after solution heat-treatment at 1270° C for 5 h and air cooling.

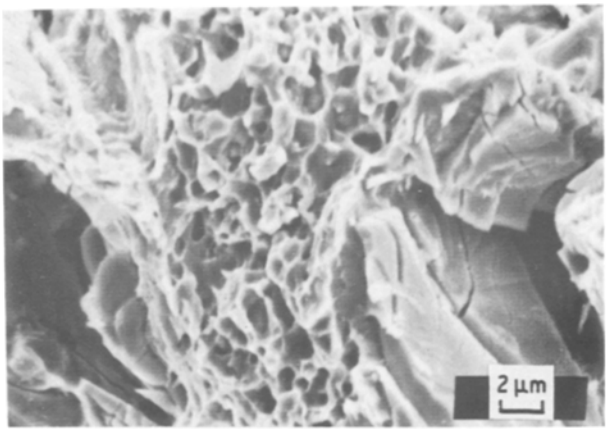


Figure 15 Fracture of Alloy No. 5, as-cast and annealed at 850° C for 720 h, after creep test at 975° C and loading at 10 kg mm^{-2} (14.4 × 10^3 p.s.i.).

Cracking of the alloys during high – temperature creep is initiated at carbide–matrix boundaries. So the finer the primary phases and the more stable the secondary carbides $Cr_{23}C_6$ the longer the rupture life.

It should be noted, however, that matrix strengthening with zirconium plays a primary part in comparison with the heat-treatment effect, and consequently, in the case where Alloy No. 5 is used for parts that are not very highly loaded and work at lower temperatures (up to about 850° C), expensive heat-treatment may be unprofitable.

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