HIGH STRENGTH POWDER-METALLURGY COBALT-BASE ALLOYS FOR USE UP TO 650°C

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ABSTRACT

The aim of the present study was to ascertain the possibility of obtaining high strength levels at intermediate temperatures in experimental cobalt-base alloys prepared by powder metallurgy (P/M) techniques. The first part of the work concerned P/M grades containing (in wt. %) 10 to 15%Ni, 20%Cr, 10%Mo and up to 1.8%C, strengthened mainly by solid-solution effects and precipitation of carbides. The second part dealt with P/M grades containing (in wt. %) 16%Cr, 3 to 5%Mo, 5%Ti and less than 0.1%C strengthened by solid-solution effects and precipitation of the ordered f. c. c. γ'-Co_3Ti intermetallic compound.

Prealloyed powders sizing less than 500 μm were prepared by N_2 atomization and, for some of the Ti-containing grades, by the rotating electrode process. After consolidation by hot extrusion of canned powders, the alloys were hot worked by rolling or swaging and subjected to a final aging treatment.

At the present stage of the work, ultimate tensile strengths up to 1850 MN/m^2 at room temperature and 1350 MN/m^2 at 650°C (1200°F) were obtained in the γ'-Co_3Ti strengthened alloys. Relationships between microstructures and mechanical properties are discussed in terms of the powder characteristics, and the extrusion and subsequent hot-working and aging conditions.

Introduction

Current developments in the field of gas turbines for aircraft and industrial applications call for materials with improved strength properties at temperatures up to about 650°C. In particular, such materials are required for turbine discs operating at ever higher temperatures and, generally speaking, must exhibit the following properties :

- high and stable tensile strength;
- high resistance to low cycle fatigue;
- high resistance to crack propagation;
- good creep-rupture strength.

Numerous studies described in recent literature have shown that the application of powder metallurgy (P/M) techniques, viz. hot extrusion and hot isostatic pressing (HIP) of prealloyed powders followed by conventional or isothermal forging, markedly enhances the tensile and fatigue strength of nickel-base superalloys at intermediate temperatures. (1-3)

As compared to nickel-base superalloys, the information available on P/M cobalt-base alloys is scanty. Previous work conducted on conventionally cast and carbide-strengthened alloys such as X-40,Mar-M-509 (4) and Stellite 6 (5) has shown that the carbide network formed during solidification is completely destroyed by hot deformation or processing by P/M techniques and is replaced by a homogeneous dispersion of carbides. These structural changes have a beneficial effect on strength and ductility at temperatures up to about 700°C (4).

Simultaneously, the high-temperature stress-rupture strength is decreased. However, it is possible to improve the stress-rupture properties by heat-treating the hot-worked or P/M materials at a temperature above the solidus temperature as shown for Mar-M-509 (4) and X-40 (6) alloys. It has been reported that this effect is related to the presence of a fairly large amount of "cast structure" at the grain boundaries, as well as to an increased grain size (6).

The aim of the present work was to obtain experimental cobalt-base P/M alloys, characterized by a fine-grained and stable microstructure, a uniform distribution of fine carbides and/or intermetallic compounds, and a stable dislocation substructure. In this respect, previous work showed that hardening of cobalt-base alloys by means of uniform precipitation of a f. c. c. ordered γ'type phase was of particular interest in obtaining high strength levels at intermediate temperatures (7). This work also showed that among the various possible γ'-Co_3X compounds, where X represents elements such as Ti, Ta, Nb, Mo or W, the γ'-Co_3Ti phase was the most stable at elevated temperatures.

Experimental procedure

Materials

Prealloyed powders of carbide-strengthened alloys containing 10 to 15% Ni, 20%Cr, 10%Mo and up to 1.8%C were obtained by nitrogen atomization. Powders of alloys containing 15%Cr, 3 to 5%Mo, 0.005 to 0.1%C and 5%Ti were also prepared by either nitrogen atomization or the rotating electrode process (REP). The purpose of these powders was to study strengthening by precipitation of a γ'-Co_3Ti type phase, and their Ni and Mo contents were reduced in order to overcome γ'destabilization (7).

Table I gives the actual composition of the powders, including the O_2 and, in some cases, the N_2 contents. After nitrogen atomization, the O_2 content is relatively high, in particular for the Ti-containing powders V 6 ; in the carbide-strengthened V 0 to V 5 powders, this content decreases sharply as the carbon content is raised up to about 0.6%.

On the other hand, the REP Ti-containing powders are characterized by a low O_2 content of less than 100 ppm.

Table I

Actual composition (wt. %) of the prealloyed cobalt-base powders.

Grades(*)	Ni	Cr	Mo	Ti	C	O_2 (ppm)	N_2 (ppm)
V 0	14.9	20.1	10.0	-	0.03	703	nd**
V 1	11.0	21.1	10.5	-	0.29	522	"
V 2	14.7	20.1	10.2	-	0.65	226	"
V 3	14.5	20.1	10.4	-	0.95	296	"
V 4	14.7	20.0	10.0	-	1.36	280	"
V 5	14.8	20.0	10.0	-	1.8	273	"
V 6	-	15.7	5.0	5.1	0.05	1806	"
V 13	-	15.3	3.3	4.5	0.103	60	16
V 14	-	16.2	3.0	5.0	0.005	100	32

(*) V 0 to V 6 powders obtained by N_2 atomization
V 13 and V 14 powders obtained by REP
(**) n. d. : not determined

The size of the powders lies below 400-500 μm. Fig. 1 shows that the powders are spherical and exhibit a dendritic structure; in addition, the REP powders contain pores located within the interdendritic areas.

Compaction and hot-working.

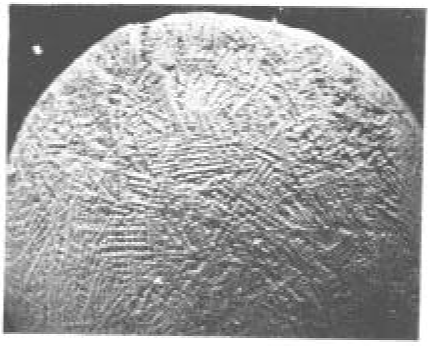
The prealloyed powders were compacted by hot extrusion in mild steel cans 45 mm in diameter and 100 mm long at temperatures ranging from 1050 to 1200°C, with extrusion ratios comprised between about 4.5 and 6.2. The extruded compacts were then hot worked by swaging or rolling. For the carbide-strengthened V 0 to V 5 alloys, the amount of reduction per pass was limited to 20%, the total deformation ratio being about 50%. For the Ti-containing grades, the amount of reduction per pass was dependent on the O_2 and C contents in the powders ; it was of the order of 5 and 15% for the V 6 and V 13 grades, respectively.

Experimental results.

Carbide-strengthened materials.

Fig. 2 illustrates the microstructure of the 0.03%C and 0.65%C extruded P/M alloys V 0 and V 2, after hot working and aging. The low-carbon V 0 grade exhibits a coarse-grained microstructure with $M_{23}C_6$ carbides precipitating on grain boundaries during heat-treatment. Both $M_{23}C_6$ and M_7C_3 carbides were identified in the microstructure of V 1 to V 5 grades, the amount of M_7C_3 carbides increasing with the carbon content. Increasing the carbon content to above 0.3% gives rise to an important grain refinement and the primary carbide distribution is uniform after hot working.

Fig. 3 shows the relationship between the room-temperature and 650°C tensile properties and the carbon content, after rolling at 1100°C and a final 800°C/48h/AC aging treatment to enhance precipitation of carbides. The tensile properties of the low carbon V 0 alloy are to be attributed mainly to solid-solution and work hardenings. With increasing carbon contents, the R. T. ductility is seen to decrease continuously, whereas the R. T. ultimate tensile strength first increases up to 1450 MN/m^2 and then decreases slightly, for carbon contents above 0.65%, due to the formation of increasing amounts of coarse carbides at grain boundaries.



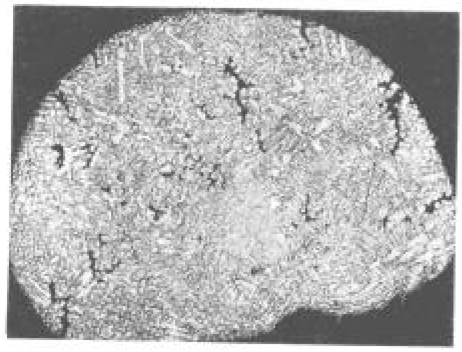
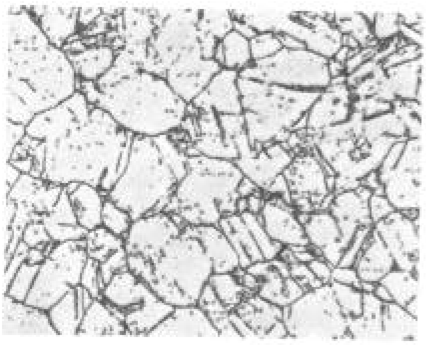
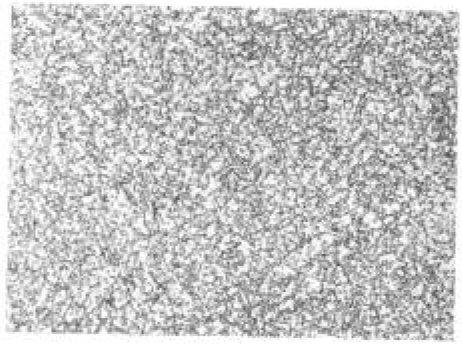


Fig. 1. V 13 (Co-15Cr-3Mo-5Ti-0.1C) REP powders (x 200)



V 0 alloy



V 2 alloy

Fig. 2. Extrusion at 1200°C (R.A. : 4.6), rolling at 1100°C and aging at 800°C (48h, A.C.)(x 500)

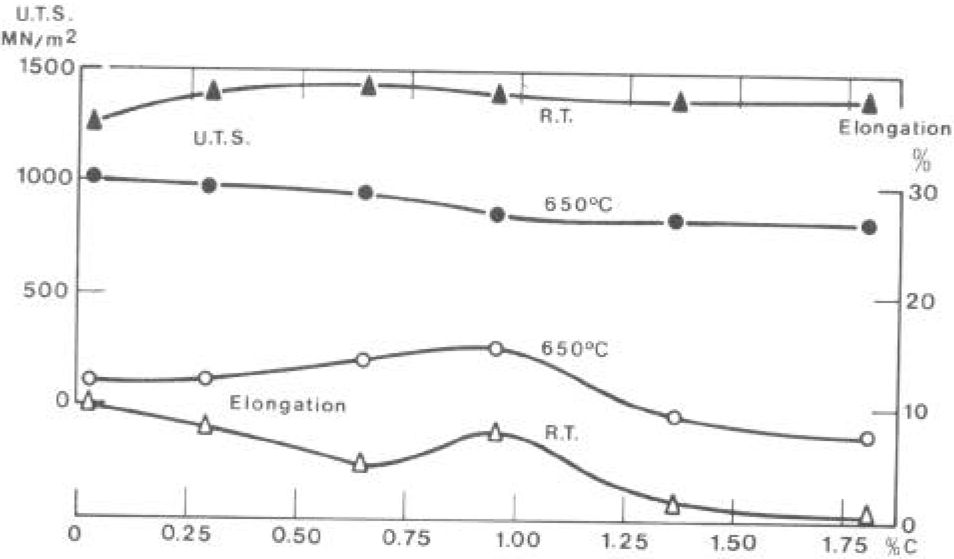


Fig. 3. Tensile properties of Co-20Cr-10/15Ni-10Mo-C alloys

On the other hand, the 650°C tensile strength decreases continuously from about 1000 to 800 MN/m^2 with increasing carbon contents. This variation is probably related to the removal of solid solution strengtheners throug formation of $M_{23}C_6$ and M_7C_3 carbides.

Fig. 4 illustrates the effect of carbon content on the 650°C stress-rupture life after rolling at 1100°C and applying final 800°C/48h/AC aging treatment, with or without an intermediate 1200°C/1h solution treatment. The applied stress, 363 MN/m^2, is that leading to a rupture life of 100 hours in the as-cast X-40 alloy. As compared to the X-40 alloy, the low-carbon V 0 P/M alloy exhibits an improved stress-rupture life after both types of heat-treatment.

After rolling and direct aging, the stress-rupture life decreases down to the level of the as-cast X-40 alloy as the carbon content is increased up to about 1%. On the other hand, after solutioning and aging, the stress-rupture life increases with the carbon content to a maximum of 15 times the life of as-cast X-40 for the 1.8%C grade V 5. This relationship probably results from the fact that the carbides are solutioned during the 1200°C heat treatment so that the amount of grain-boundary carbides present after aging increases. As shown in Fig. 5 for the 1.8%C alloy V 5, the intermediate solution treatment gives rise after aging, to a "duplex" microstructure in which coarse carbides are present in both the grain boundaries and the matrix.

γ'-strengthened materials

Fig. 6 illustrates the longitudinal microstructure of the V 6 and V 13 P/M alloys in the as-extruded condition. Both materials are characterized by internally recrystallized and elongated prior particles with numerous fine precipitates on the prior particle boundaries (PPB).

Electron and ion microprobe analyses performed on longitudinal sections of the as-extruded V 6 alloy showed that the prior particle boundaries are enriched mainly in titanium, oxygen and carbon (Fig. 7). The corresponding PPB precipitates are probably Ti-rich oxides, in relation with the high oxygen content of the N_2 atomized powders (Table I), and MC carbides formed when heating the canned powders prior to compaction.

Electron microprobe examinations were also made on the low-oxygen REP powders (Table I) of the 5%Ti-0.1%C grade V 13. As shown in Fig. 8, the dendritic microstructure of the as-received powders is related to Ti segregation, in the interdendritic regions. The dendritic structure tends to disappear after holding the powders under argon for 1 hour at 1100 to 1200°C. There is a corresponding decrease of internal Ti segregation but a Ti-rich envelope forms at the same time on the particles. The occurrence of this envelope around heat-treated V 13 powders seems to be related to the carbon content, as confirmed by similar experiments made on powders of two IN-100 grades containing 0.18 and 0.007%C and less than 100 ppm O_2 : after a 1150°C/1h treatment under argon, the Ti-rich envelope is observed only around the high-carbon IN-100 powders and it has been identified by X-ray diffraction analysis as a carbo-nitride phase.

On the other hand, transmission electron microscope observations on the Ti-containing compacts reveal a uniform precipitation of small and coherent particles of a f.c.c. ordered γ'-Co_3Ti type phase within the grains. The γ' phase does not remain stable during exposure at 800°C, but gives rise to the discontinuous precipitation of a hexagonal ordered η-Co_3Ti compound starting from the grain boundaries. This reaction has previously been studied in cast or wrought experimental cobalt-base alloys strengthened by the γ'-phase (7).

In order to overcome the problems associated with the PPB precipitation of oxides and MC particles, and with the $\gamma' \rightarrow \eta$ phase transformation during heat treatment, further tests were made on REP powders of the grade V 14,

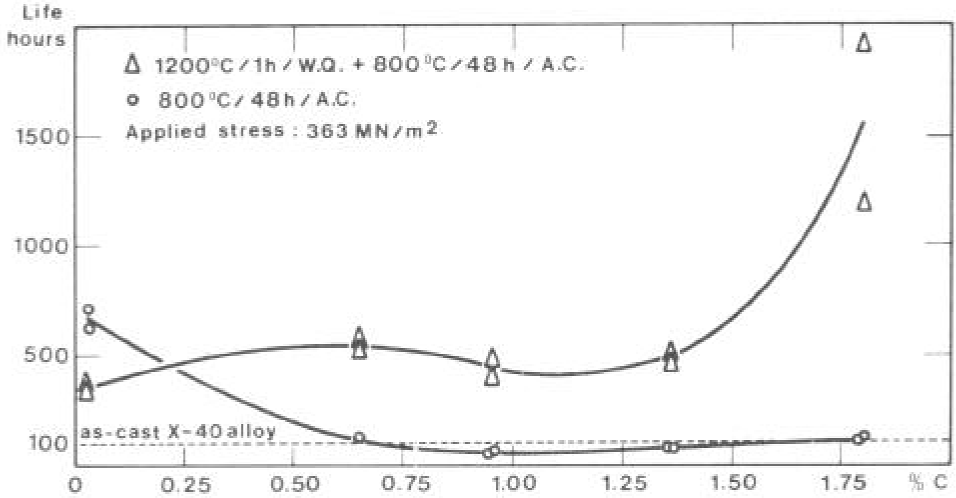
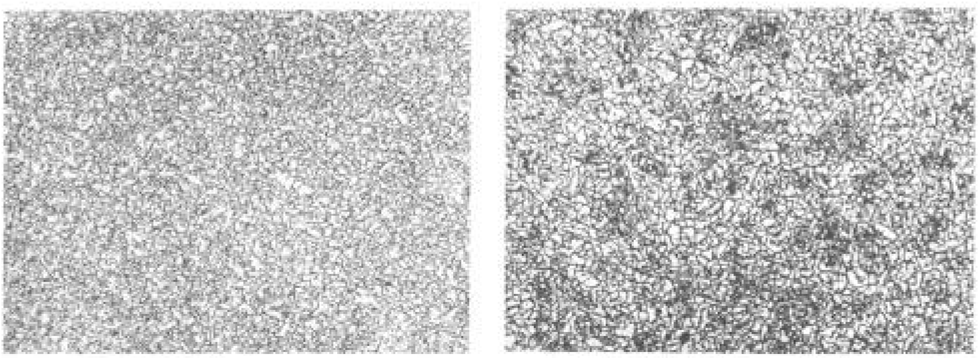
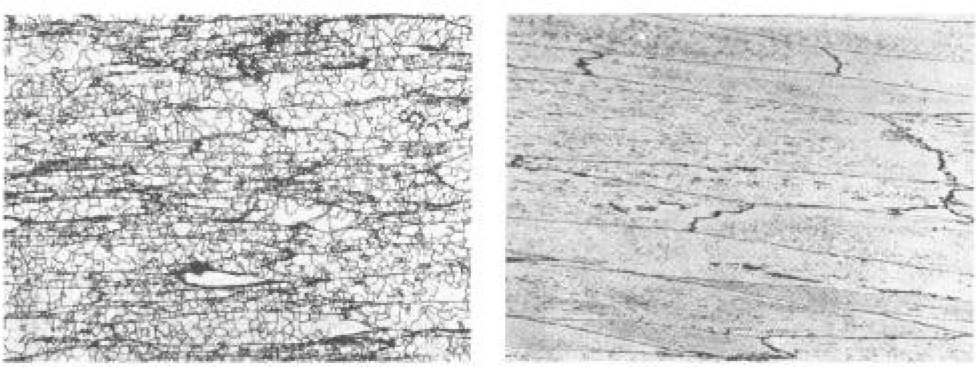


Fig. 4. 650°C stress-rupture life of Co-20Cr-10/15Ni-10Mo-C alloys.



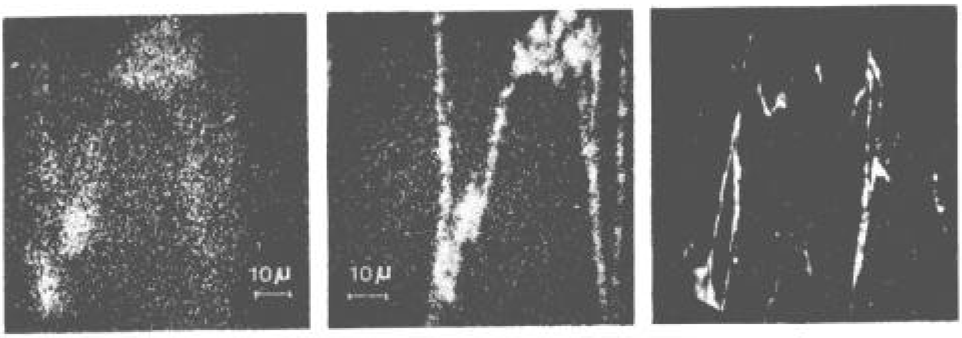
800°C/48h/A.C. 1200°C/1h/W.Q. + 800°C/48h/AC

Fig. 5. 1.8%C-containing V 5 alloy after rolling at 1100°C (x 500)



V 6 (5Mo-0.05C) alloy (x 100) V 13 (3Mo-0.1C) alloy (x 100)

Fig. 6. Longitudinal microstructure of as-extruded alloy.



Oxygen Titanium $24\ C_2^-$

Electron-microprobe Ion microprobe

Fig. 7. Distribution of elements in PPB's particles (V 6 alloy)

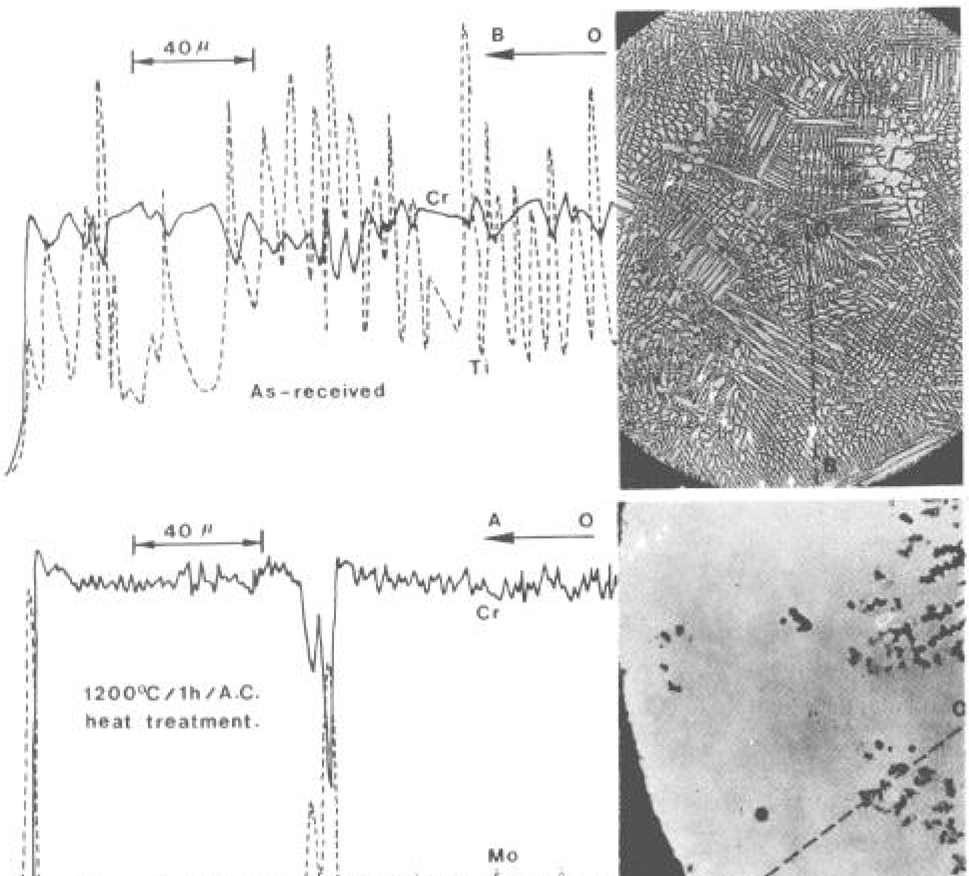


Fig. 8. Electron-microprobe analysis of the V 13 REP powders.

the C and Mo contents of which were reduced respectively to 0.005 and 3% (Table I). As shown in Fig. 9 for the as-extruded material, the prior particles are finely recrystallized and their boundaries seem to be relatively clean as compared to the as-extruded V 6 and V 13 alloys (Fig. 6) although few Ti-rich PPB particles have been identified by electron microanalysis. In this respect, it has been shown for the V 14 alloy that the O_2 and N_2 contents increase to 280 and 150 ppm respectively after extrusion, as compared with the 100 ppm O_2 and 30 ppm N_2 determined on the as-received powders. This enrichment is probably due to the fact that heating before extrusion was carried out in air without prior degasing of the canned powders.

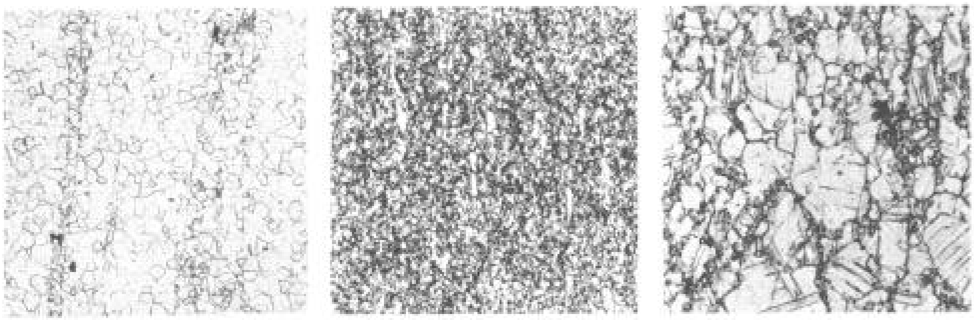
Hot-rolling tests performed on the as-extruded V 14 alloy have shown that the prior particle boundaries tend to disappear and that recrystallization of new grains starts to occur during hot working at temperatures of at least 1000°C. As a matter of fact, a fine recrystallized microstructure is obtained after rolling at 1000°C with a reduction in area of about 80% and Fig. 9 shows that after rolling at 1100°C, the grain size increases, under the experimental conditions considered, with the total amount of deformation. Recrystallization during hot-working at temperatures above 1000°C may be related to a structural modification occurring at 1000-1015°C for the V 14 alloy as evidenced by thermal analysis during cooling. Furthermore, hardness measurements and transmission electron microscopy observations after a 4-hour exposure at increasing temperatures have shown that the γ' solvus temperature for the wrought Co-15%Cr-3%Mo-5%Ti-0.1%C alloy is about 1000-1050°C.

The variations in hardness as a function of rolling conditions and aging time at 700°C are given in Fig. 10 for the V 14 P/M alloy. As was the case for previously studied γ'-strengthened cobalt-base alloys (7), the hardness first increases for short aging periods due to the uniform and coherent precipitation of γ' particles. Overaging occurs so much more rapidly as the amount of deformation increases, in relation with the γ' destabilization giving rise to the discontinuous precipitation of the η phase starting from the grain boundaries. On another hand, it has been also shown that the hardness peak is achieved after aging at 750°C for 8 or 4 hours for the V 14 alloy rolled at 1100°C for 30% (fine-grained) or 70% (coarse-grained) total reduction in area.

Fig. 11 summarizes most of the tensile properties determined so far on the γ'-strengthened P/M grades. As compared to the V 13 alloy, the relatively low strength and ductility of the V 6 alloy at R. T. and 650°C probably stem from the formation of significant amounts of PPB oxides. The V 13 alloy exhibits a good compromise between tensile strength and ductility, better than those achieved with the carbide-strengthened grades (Fig. 3), although the ultimate tensile strength decreases from about 1700 to 1200 MN/m^2 as the test temperature is raised from R. T. to 650°C.

As regards the V 14 alloy in the as-rolled condition, the highest tensile strength levels are found in the fine-grained materials, with ultimate tensile strengths of about 1850 and 1350 MN/m^2 at R. T. and 650°C, respectively. On the other hand, the coarse-grained materials exhibit better tensile ductilities.

The influence of a 100-hour exposure at 700°C on the tensile properties of the rolled material seems to depend of the grain size and the extent of recrystallization. Aging the fine-grained material reduces the tensile strength at R. T. and 650°C to about 1400 and 1300 MN/m^2 respectively, as well as the R. T. ductility. According to the hardness evolution shown in Fig. 10, these variations at R. T. can tentatively be attributed to grain-boundary embrittlement through transformation of γ' to η, probably enhanced by the work hardening of the microstructure. On the contrary, aging the coarse-grained material improves both tensile strength and ductility, at least at 650°C.



As-extruded (x 100) Total R.A. : 30% (x 200) Total R.A. : 70% (x 200)

Fig.9. V 14 alloy extruded and rolled at 1100°C

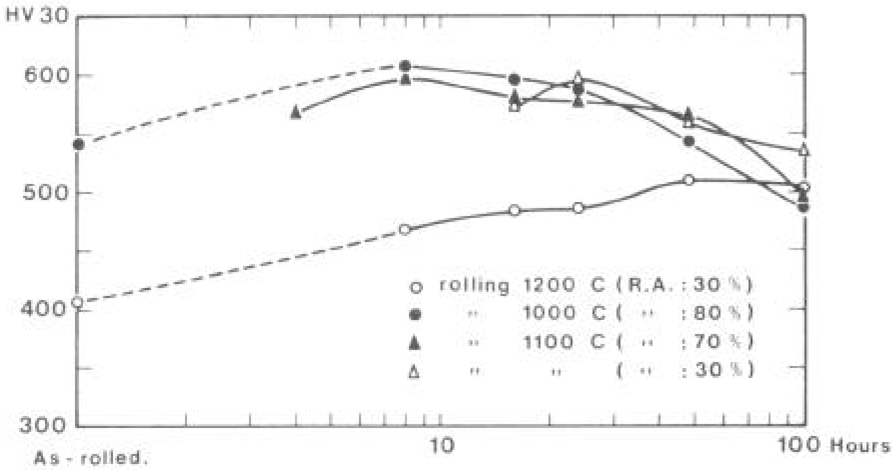


Fig.10. V 14 alloy hot-rolled and aged at 700°C

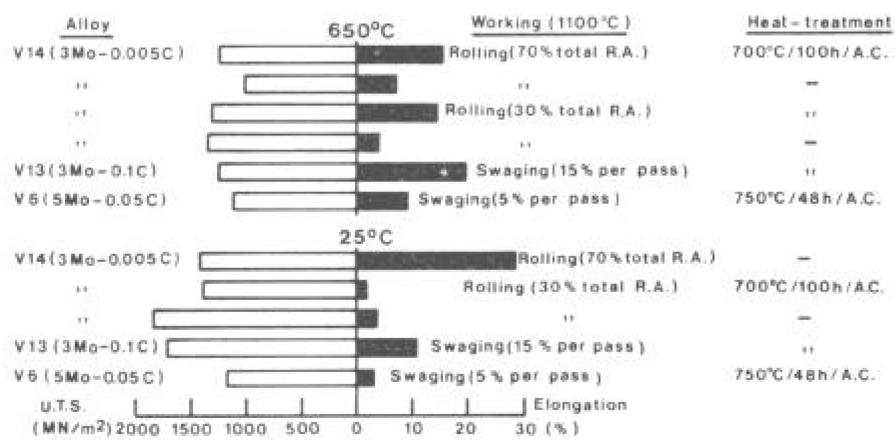


Fig.11. Temperature dependence of tensile properties of Co-15Cr-5Ti-Mo-C P/M alloys.

Further tensile tests after hot-rolling and optimum aging treatment as well as microstructural examinations are in progress in order to clarify the effect of the aging treatment on the tensile properties of the rolled V 14 P/M alloy.

Conclusions.

At the present stage of the work, the following conclusions can be drawn :

- carbide strengthening of Co-10 to 15%Ni-20%Cr-10%Mo P/M alloys gives rise to a moderate tensile strength. The most stable properties are obtained with the low-carbon 0.03%C grade, which exhibits an ultimate tensile strength of about 1300 at R. T. and 1000 MN/m^2 at 650°C.
- combined γ' and carbide strengthening in Ti-containing P/M alloys gives rise to problems related to the precipitation of Ti-rich carbides at prior particle boundaries (PPB) even with carbon additions as low as 0.05 to 0.1%.
- strengthening of Co-Cr-Mo-Ti [illegible] alloys by means of a uniform precipitation of a γ'-Co_3Ti type phase calls for the use of prealloyed powders with very low oxygen and carbon contents, in order to overcome the PPB problem. Furthermore, the contents of solid-solution hardeners must be limited to less than 3-5% in order to restrict the extent of the γ'-η transformation and the resultant grain-boundary embrittlement.
- the tensile properties of the γ'-strengthened P/M alloys can be controlled by acting on the hot-working conditions, which can give either a fine- or coarse-grained recrystallized microstructure, and [illegible] the final aging conditions.
  Ultimate tensile strengths of about 1850 at R. T. and 1350 MN/m^2 at 650°C have been achieved in the fine-grained Co-16%Cr-3%Mo-5%Ti P/M alloy with the corresponding ductilities limited to 4%. The ductility is markedly higher for the coarse-grained material ; however, the corresponding strength is limited to 1400 at R. T. and 1000 MN/m^2 at 650°C but can be improved through a final aging treatment.
- Further improvements in the tensile properties should be possible by adapting the aging treatment to the prior hot-rolling conditions and by increasing γ'-strengthening. In this respect, work is in progress on a Co-16%Cr-3%Mo-7%Ti-0.005%C P/M alloy prepared by hot extrusion and controlled hot working.

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