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Allen et al.

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[54] **ELIMINATION OF CARBIDE SEGREGATION TO PRIOR PARTICLE BOUNDARIES**

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[51] **Int. Cl.** **C22c 19/00**

[58] **Field of Search** ..... 75/0.5 R, 0.5 BB, 0.5 BC, 75/0.5 AA, 0.5 AC, 0.5 C, 170, 171

[56] **References Cited**

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[57] **ABSTRACT**

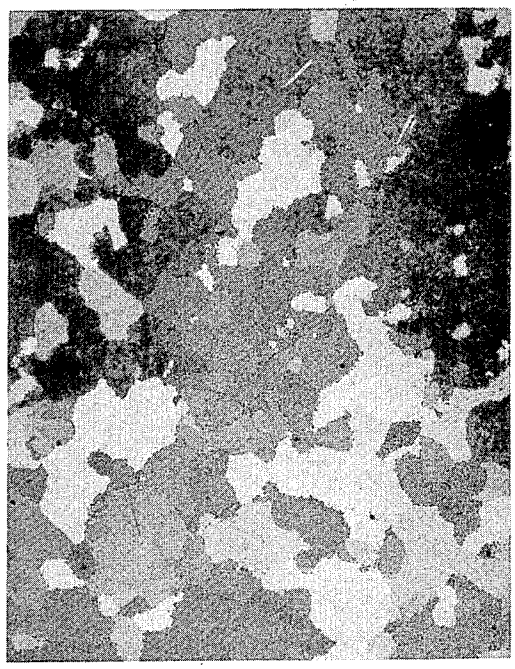
Carbide segregation to the prior boundaries of particles used in powder metallurgy to generate an article is eliminated through the use of a nickel-base alloy powder which coordinates carbon with the amount of Mo and W which can form detrimental amounts of undesirable carbides and with Cb, Ta, Hf and Zr which are strong formers of a desirable MC-type carbide.

5 Claims, 2 Drawing Figures

Fig 1



Fig 2



ELIMINATION OF CARBIDE SEGREGATION TO PRIOR PARTICLE BOUNDARIES

The invention herein described was made in the course of or under a contract, or a subcontract thereunder, with the United States Department of the Air Force.

BACKGROUND OF THE INVENTION

This invention relates to powder metallurgy and, more particularly, to the elimination of carbide segregation to prior particle boundaries in nickel-base alloys.

The microstructure of consolidated articles produced from atomized powder may exhibit preferential positioning of carbides in a definite spatial array. The morphology of this array suggests that the carbide particles are located in the consolidated solid on interfaces which were external surfaces of the powder prior to compaction.

Carbide segregation to prior particle boundaries generally is undesirable because it reduces workability and mechanical properties. For example, in extrusions such segregations are aligned in the extrusion direction resulting in serious impairment of transverse properties. Thus, whereas longitudinal properties of a powder metallurgical compact, for example of a nickel-base superalloy, may be excellent, transverse strength properties, particularly ductility have been found to be very low. For example, in one commonly used nickel-base superalloy, the transverse ductility at 1400°F as measured by percent elongation was only 1% while longitudinal elongation was 16%, although both the ultimate tensile and the yield strengths were substantially the same in both directions. Examination of fractured transverse specimens has shown that failure had occurred through the carbide stringers. Thus the loss in transverse ductility seems to be the direct result of the low strength fracture path afforded by the carbides segregated at prior particle boundaries. It has been found that, in many cases, carbides had formed on the surface of the powder prior to or during consolidation. Also, it has been observed that such segregated carbides are not broken up or solutioned during the working or the subsequent high temperature exposure during article manufacture.

SUMMARY OF THE INVENTION

It is a principal object of the present invention to provide an alloy powder composition the interrelationship of the elements of which inhibit formation of undesirable carbides which lead to carbide segregation to prior particle boundaries during manufacture of an article by powder metallurgy techniques.

Another object is to provide an improved article having a structure including essentially carbides of the MC-type, predominantly in the size range of about 0.2 to about 1 micron, and further characterized by the absence of $M_{23}C_6$ carbide and the absence of carbide segregation to prior particle boundaries.

These and other objects and advantages will be more clearly understood from the following detailed description, the examples and the drawing, all of which are intended to be typical of rather than limiting in any way on the scope of the present invention.

Briefly, the present invention provides a nickel-base alloy powder of appropriate size for use in powder metallurgical techniques and comprising 0.03 to less than 0.3 weight % C, no more than about 3.6 atomic % of the m_6C carbide formers Mo and W, and at least about 0.3 at. % of the strong MC carbide formers Cb, Ta, Hf and metallurgical The alloy powder is further characterized by the substantial absence of $M_{23}C_6$ carbide. In one form, the powder consists essentially of, by M3–8% Al, 2–8% Ti, 4–30% Cr; 0.03 to less than 0.3% C, at least one of the elements Mo and W with Mo, when selected, being up to 6% and W, when selected, being up to 12% (provided no more than 3.6 at. % of the two are present), up to 10% Ta, up to 10% Cb, up to 8% Hf, up to 5% V, up to 1% Zr, up to 1% B, up to 30% Co, with the balance essentially Ni and incidental impurities.

One form of the article provided by the present invention includes the alloy powder composition and is characterized by the absence of carbide segregation to prior particle boundaries, the substantial absence of $M_{23}C_6$ carbide and the carbide which is present being predominantly MC-type carbide in the 0.2–1 micron size range.

BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** is a photomicrograph at **100** magnification of an alloy displaying carbide segregation to prior particle boundaries; and

FIG. **2** is a photomicrograph at **100** magnification of an alloy displaying no carbide segregation to prior particle boundaries.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The design of advanced power producing apparatus such as jet engines has defined for metallurgists the need for strong higher temperature operating alloys. However, as the alloys have been developed, it has been recognized that there is an increasing difficulty in manufacturing the alloy both from the standpoint of making sound ingots as well as working the alloy into engine articles using conventional practice such as forging. As a result, increasing emphasis has been placed on the powder metallurgy approach to article manufacture.

In order to manufacture a part by powder metallurgy techniques, it is necessary to prepare first an alloy which is placed in powder form prior to its being consolidated, such as by compaction including extrusion and hot isostatic pressing into a desired shape. It has been recognized as a result of such powder metallurgical efforts that certain known and widely used nickel-base superalloys, particularly of the type used in making castings, have a tendency as a result of powder metallurgy consolidation to segregate carbides along the boundaries which had been the prior surfaces of the powder particles. Such carbide segregation generally is detrimental to workability and mechanical properties, particularly those relating to ductility in the direction transverse to the direction of working. In addition, during the evaluation of the present invention, it has been recognized that such carbide segregation to prior particle boundaries is associated with the alloy's tendency to form even very small amounts of $M_{23}C_6$ carbides. It has been found that by confining the carbide structure in an alloy essentially to the more stable MC-type carbide, in the presence of a limited amount of elements which form M_6C carbide, there can be defined a nickel-base alloy powder which, as a result of powder metal-

lurgical consolidation into a shape, does not result in the segregation of carbides along prior particle boundaries.

This invention recognizes that control of and coordination between the amounts of the groups of elements which tend to form, respectively, the desirable and the undesirable types of carbides can provide an improved article made with a powder by a method which avoids segregation of carbides along the boundaries of particles used in the powder metallurgical technique. In accordance with the invention, carbon is included in the range of 0.03 to less than 0.3 wt. %. At the same time, the elements Mo or W, which tend to form the undesirable M_6C, are limited individually or in their sum to no more than about 3.6 at. %. Further, the alloy includes at least about 0.3 at. % of elements selected from Cb, Ta, Hf and Zr, which are the strong formers of the desirable and stable MC-type carbide. The powder metallurgy consolidated article which results from use of this controlled type of nickel-base alloy powder is characterized by a structure which has substantially no $M_{23}C_6$ carbide, the balance of the carbide being essentially MC in the size range of about 0.2 to about 1 micron, with no carbide segregation to prior particle boundaries, and any small amounts of M_6C carbide being insufficient to result in such carbide segregation. In one form of the invention, the only other phase in the Ni matrix in addition to borides and carbides is gamma prime because the composition is controlled to eliminate tendency to form such phases as eta, mu, sigma, laves, etc.

During the evaluation of the present invention, a large number of alloys were prepared in powder form and consolidated into shapes for further evaluation. The following Table I gives the composition of some of these alloys.

TABLE I

Alloy	COMPOSITION (weight percent) BALANCE NICKEL AND INCIDENTAL IMPURITIES												
	Co	Cr	Mo	W	Al	Ti	Ta	Cb	Zr	Hf	B	C	V
1	14.3	9.4	0	6.0	4.2	3.2	0	3.9	.05	0	.02	.19	0
2	8.4	11.7	0	6.1	4.3	3.3	0	2.8	.05	0	.02	.05	0
3	7.8	8.9	1.1	1.6	4.7	3.5	0	2.3	.05	2.0	.02	.15	0
4	15.1	10.7	2.9	5.9	3.8	3.9	0	1.7	.05	2.0	.02	.15	0
5	14.8	10.1	0	9.0	5.2	3.0	0	0	.05	0	.02	.05	0
6	16.0	12.0	3.0	0	5.5	2.5	0	1.5	.05	0	.02	.05	0
7	10.0	9.3	2.0	7.0	4.3	4.0	3.8	0	.05	0	.015	.17	0
8	8.0	12.0	6.0	3.0	4.5	3.5	0	1.5	.05	2.0	.02	.15	0
9	16.0	11.5	5.0	0	5.5	3.5	0	0	.05	0	.02	.15	0
10	13.8	9.6	8.9	0	4.7	3.7	0	0	.05	2.1	.02	.15	0
11	14.5	10.0	6.2	5.8	3.4	4.4	3.6	0.8	.05	0	.02	.15	0
12	14.8	10.2	4.8	5.8	4.3	4.4	0	0.6	.05	0	.02	.15	0
13	12.8	7.9	2.3	5.7	4.6	5.1	0	2.2	.05	0	.015	.15	0
14	10.2	4.7	1.8	5.4	5.3	6.0	0	2.7	.05	0	.015	.15	0
15	12.1	12.3	2.4	7.6	3.7	4.1	2.6	0.9	.05	0	.015	.17	0
16	9.2	7.8	1.8	7.0	3.6	4.6	4.4	0	.05	0	.015	.17	0
17	8.6	7.1	1.7	6.7	4.8	4.7	4.5	0	.05	0	.015	.17	0
18	6.7	4.0	1.3	6.2	5.6	5.6	5.5	0	.05	0	.015	.17	0
19	12.5	7.3	4.6	0	4.3	6.2	0	0	.06	0	.014	.18	1.4
20	11.0	5.7	2.2	0	5.3	5.8	3.2	0.6	.06	0	.014	.18	1.3
21	12.4	7.5	2.3	5.6	4.7	5.3	0	2.3	.05	0	.02	.30	0
23	13.0	8.4	2.6	5.3	4.0	4.1	0	2.0	.05	4.6	.02	.15	0
25	15.5	16.7	3.3	0	6.5	2.7	0	0.7	.06	0	.02	.18	0.3
28	7.8	6.8	4.9	0.8	7.1	2.6	0	0	.06	1.0	.02	.18	0
A	11.0	19.0	9.8	0	1.5	3.2	0	0	0	0	.01	.12	0
B	18.5	15.0	5.0	0	4.2	3.2	0	0	.06	0	.03	.10	0
C	15.2	10.0	3.0	0	5.6	4.6	0	0	.07	0	.01	.17	1.0
D	9.5	14.1	4.0	3.9	3.0	5.0	0	0	.03	0	.02	.18	0
E	8.0	14.0	3.5	3.5	3.5	2.5	0	3.5	.05	0	.01	.07	0

The alloy compositions in Table I were vacuum induction melted and cast prior to being converted to powder by inert gas atomization. The powder was then sized for use in making test specimens by screening to −60 +325 mesh size. The powder was placed in deformable containers, in this case metal containers of stainless steel, which were evacuated to about 10–15 microns pressure prior to their being sealed. The billets were then extruded to square bars in the temperature range of about 1850°–2250°F. Below that temperature range excessive forces are required to extrude or to obtain full density. Above about 2250°F, the nickel-base superalloy melting point is approached too closely.

After extrusion, a variety of evaluations were conducted on the alloys including heat treatment, mechanical property testing, metallographic studies and calculations of the volume percent of carbides and atomic percent of critical elements included in the alloy composition. The following Table II presents certain of these data.

TABLE II

	Alloy	Carbides (Vol. %) M_6C	Carbides (Vol. %) $M_{23}C_6$	Carbides (Vol. %) MC	b Ta Hf Zr (at %)	Mo W (at %)
I	1	0	0	1.8	2.4	1.9
	2	0	0	0.5	1.7	1.9
	3	0	0	1.4	2.0	1.1
	6	0	0	0.5	0.9	1.7
	7	0	0	1.7	1.2	3.4
	13	0	0	1.4	1.4	3.2
	14	0	0	1.5	1.7	2.8
	16	0	0	0.8	1.5	3.4
	17	0	0	0.8	1.5	3.1
	18	0	0	0.8	1.8	2.8
	20	0	0	0.8	1.4	1.3
	23	0	0	1.5	2.8	3.3
	25	0	0	1.6	0.4	1.8
	28	0	0	1.6	0.4	3.0
	E	0	0	1.4	2.2	3.3
II	5	0	0.6	0.2	0	2.8
	9	0	1.7	0.7	0	2.9
	19	0	2.0	0.4	0	2.6

TABLE II-Continued

	Alloy	Carbides (Vol. %) M_6C	$M_{23}C_6$	MC	b Ta Hf Zr (at %)	Mo W (at %)
	21	0	0	2.8	1.4	3.1
	A	2.8	0.4	0.2	0	5.9
	B	0	1.1	0.4	0	2.9
	C	0	1.9	0.8	0	1.7
	D	0.1	2.1	0.8	0	3.6
III	4	0.2	0	1.4	1.8	3.6
	10	2.1	0	1.4	0.7	5.3
	12	1.4	0	1.0	0.4	4.7
	15	0.5	0	1.5	1.4	3.9

The data of Table II has been divided into three groupings of alloys depending on their tendency for carbide segregation to prior particle boundaries. Group I lists alloys the structure of which includes neither $M_{23}C_6$ nor M_6C carbides but only MC carbide. Of these alloys in Group I, none showed carbide segregration to prior particle boundaries. Alloy E is a commercially available nickel-base superalloy used for manufacture of wrought products but not, prior to the present invention, for use in powder metallurgical compaction. It should be noted that the elements Mo and W, which tend to result in the formation of M_6C carbide, are maintained within the range of the present invention of a maximum of 3.6 at. %. In addition, the strong MC formers of Cb, Ta, Hf and Zr are included within the range of the present invention of at least about 0.3 at. %.

By way of contrast, the alloys of Group II all were found to have carbide segregation in prior particle boundaries. All of such Group II alloys, except for Alloy 21, which will be discussed later, included $M_{23}C_6$ carbide within their structure. Except for Alloy 21, the absence of the above-listed strong MC carbide formers should be noted. Alloys A, B, C and D all are commercially available nickel-base superalloys. Alloy 21 is included in Group II of Table II as an alloy having a tendency toward carbide segregation to prior particle boundaries because of its 0.3 wt. % carbon content. It has been found during the evaluation of the present invention that alloys including such amounts of C after hot isostatic pressing displayed carbide segregation to prior particle boundaries. Therefore, the present invention is defined as including an alloy having less than 0.3 wt. % C. The lower limit for C has been defined as about 0.03 wt. % because alloys including less than that amount have insufficient C to form carbides which would create such segregation problems.

Any presence of the $M_{23}C_6$-type carbide is detrimental to the present invention. It has been found that the complete absence of M_6C-type carbide is not quite as critical. Depending on the composition of the alloy, small amounts of M_6C-type carbide can be tolerated. Typical examples of alloys which can or cannot tolerate M_6C-type carbide in respect to the tendency to carbide segregation in prior particle boundaries are shown in Group III of Table II. Evaluation has shown that Alloy 4 does not show such carbide segregation in prior particle boundaries whereas Alloys 10, 12 and 15 do result in such detrimental carbide segregation. Therefore, the present invention defines the alloy as including a total content of no more than 3.6 at. % of the sum of Mo and W to limit the formation of M_6C-type carbide and thus further limit the tendency of the alloy to carbide segregation in prior particle boundaries.

In Table II, the volume percent of carbides were calculated with the following assumptions: if the sum of Mo and W are greater than or equal to 3.5 at. %, the excess above that amount forms M_6C; if the sum of Cb, Ta, Hf and Zr are greater than or equal to 0.3 at. %, the carbon forms MC; and if the sum of Cb, Ta, Hf and Zr is less than 0.3 at. %, half of C forms $M_{23}C_6$ and half forms MC. Representing the specifically preferred form of the present invention as shown in Tables I and II are Alloy forms 4, 7 and 13 within the composition range, by weight, of 3–5% Al, 3.5–5.5% Ti, 7–11% Cr, 0.15–0.2% C, 2–3% Mo, 5–7% W, up to 4% Ta, up to 2.5% Cb, up to 2% Hf, up to 0.1% Zr, 0.01–0.05% B, 10–16% Co, with the balance essentially Ni and incidental impurities.

As was mentioned, the present invention involves an alloy having a controlled and coordinated composition for a number of reasons, an important one of which is the avoidance of carbide segregation to prior particle boundaries. However, other elements in the composition are limited for a variety of reasons:

Al, which is preferably included within the range of 3–7 wt. %, is limited to no more than about 8% because greater than that amount would lead to too much gamma prime or to a eutectic formation.

Ti is preferably included within the range of 2–6 wt. % but should not exceed about 8 wt. % because of the formation of too much gamma prime and the formation of eta phase.

Cr, if included in amounts greater than 30 wt. %, leads to the formation of sigma phase whereas less than about 4 wt. % results in corrosion problems. The preferred range for Cr is 4–17 wt. %.

As has been discussed in detail, the elements Mo and W, which provide an alloy with a tendency toward the formation of the less desirable M_6C carbide, are included in a total of no more than about 3.6 at. %. In addition, for density reasons, individually Mo should not exceed about 6.2 wt. % and W should not exceed about 12 wt. %.

Both Ta and Cb in excessive amounts can lead to eta phase formation. In addition, excessive Cb results in too much gamma prime for fabrication. Therefore, each of Ta and Cb should be limited to no more than about 10 wt. %.

Hf can have a significant effect on the incipient melting point of an alloy. Therefore, no more than about 8 wt. % Hf should be included in the alloy.

The element V is a carbide former and should be limited to no more than about 5 wt. %.

Co, which has been widely described in the literature, generally is included for formability. It should not be included in amounts greater than about 30 wt. %.

Each of the elements Zr and B are included in amounts up to about 1% each. An excess of that amount will tend to lower the incipient melting point of the alloy.

Thus, one form of the alloy involved with the present invention in its broad range consists essentially of, by weight, 3–8% Al, 2–8% Ti, 4–30% Cr, 0.03 to less than 0.3% C, up to 6% Mo, up to 12% W, up to 10% each of Ta and Cb, up to 8% Hf, up to 5% V, up to 1% each of Zr and B, up to 30% Co with the balance nickel and incidental impurities with the further condition that the sum of the elements Mo and W be no more than about 3.6 at. % and that there be included at least about 0.3 at. % elements selected from Cb, Ta, Hf and Zr. A

more preferred range of such alloy is 3–7% Al, 2–6% Ti, 4–17% Cr, 0.05–0.2% C, up to 6% Mo, up to 9% W, up to 6% Ta, up to 4% Cb, up to 5% Hf, up to 3% V, up to 0.1% each of Zr and B, 5–20% Co with the balance essentially nickel and incidental impurities.

As was described before, the method associated with the present invention for making a nickel-base alloy article by powder metallurgy consolidation includes the steps of enclosing the powder in a deformable container, such as a metal, which is then evacuated prior to working into an article shape. It should be understood that as used in this specification, the term "article" is intended to include within its meaning rods, bars, billets, etc., as well as more finished article shapes such as gas turbine wheels, blading members, etc.

Although after consolidation as a result of the present invention prior particle boundaries are not discernible from photomicrographic examination, the article which results can be distinguished from articles manufactured by conventional non-powder metallurgical techniques by the size of the carbides in the microstructure. The article which results from the present invention has carbides which exist predominantly in the size range of about 0.2 to about 1 micron. By way of contrast, conventional practice, such as forging from a cast billet, generally results in the generation of carbides predominantly at least about 5 microns or larger in size.

A comparison of consolidated alloy specimens which display carbide segregation to prior particle boundaries and those which do not are shown in FIGS. **1** and **2**. With reference to the drawing, FIG. **1** is a photomicrograph at 100 magnifications of Alloy D displaying the circular evidence of carbide segregation to prior particle boundaries after having been processed by hot isostatic pressing at 2175°F and 15,000 psi. By way of contrast, FIG. **2** is a photomicrograph at **100** magnifications showing Alloy E displaying no carbide segregation to prior particle boundaries after having been processed under the same conditions. Only the irregularly shaped grains are seen.

Although the present invention has been described in connection with specific examples and embodiments, it will be recognized by those skilled in the art of powder metallurgy the variations and modifications of which the present invention is capable. For example, such variations can be in the selection of elements which, within the scope of the claimed invention, avoid carbide segregation to prior particle boundaries.

What is claimed is:

1. A nickel-base alloy powder, sized for use in making an article by powder metallurgical techniques, consisting essentially of:

0.03 to less than 0.3 wt. % C;

up to 16 wt. % total of elements selected from the group consisting of Al and Ti;

about 4–30 wt. % Cr;

up to about 3.6 at. % of elements selected from the group consisting of Mo and W;

at least one element selected from the group consisting of Cb, Ta, Hf and Zr, the Cb when selected being up to about 10 wt. %, the Ta when selected being up to about 10 wt. %, the Hf when selected being up to about 8 wt. %, and the Zr when selected being up to about 1 wt. %, the sum of selected elements being at least about 0.3 at. %;

up to about 5 wt. % V;

up to about 1 wt. % B;

up to about 30 wt. % Co;

with the balance essentially Ni and incidental impurities;

the alloy being characterized by the substantial absence of $M_{23}C_6$ carbide, the balance of the carbide being predominantly MC-type.

2. The alloy powder of claim **1** in which Al is 3–8 wt. %; Ti is 2–8 wt. %; Mo, when selected, is up to about 6 wt. %; and W, when selected, is up to about 12 wt. %;

the carbides being predominantly in the size range of about 0.2–1 micron.

3. The alloy powder of claim **2** consisting essentially of, by weight, 3–7% Al; 2–6% Ti; 4–17% Cr; 0.05–0.2% C; Mo, when selected, up to 6%; W, when selected, up to 9%; up to 6% Ta; up to 4% Cb; up to 5% Hf; up to 3% V; up to 0.1% Zr; up to 0.1% B; 5–20% Co with the balance essentially Ni and incidental impurities.

4. The alloy powder of claim **3** in which the W, when selected, is up to 7%, the V is up to 1.5%; the Zr is 0.1–0.1%; the B is 0.01–0.1% and the Co is 6–16%.

5. The alloy powder of claim **4** in which Al is 3–5%; Ti is 3.5–5.5%; Cr is 7–11%; C is 0.15–0.2%, Mo is 2–3%; W is 5–7%; Ta is up to 4%; Cb is up to 2.5%; Hf is up to 2%; B is 0.01–0.05% and Co is 10–16%.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,890,816

DATED : June 24, 1975

INVENTOR(S) : Robert E. Allen, Jon L. Bartos, & Peter Aldred

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, claim 4. should read as follows:

--4. The alloy powder of claim 3 in which the W, when selected, is up to 7%, the V is up to 1.5%; the Zr is 0.01-0.1%; the B is 0.01-0.1% and the Co is 6-16%. --

Signed and Sealed this

fourteenth Day of *October 1975*

[SEAL]

Attest:

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Commissioner of Patents and Trademarks