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(54) **LOWER COST HIGH STRENGTH SINGLE CRYSTAL SUPERALLOYS WITH REDUCED RE AND RU CONTENT**

(57) An embodiment of a nickel based alloy consists essentially of from 1.0 to 3.0 wt% chromium, up to 2.5 wt% molybdenum, from 11 to 16 wt% tungsten, from 4.0 to 8.0 tantalum, from 5.7 to 6.5 wt% aluminum, from 11

to 15 wt% cobalt, from 2.0 to 4.0 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium, up to 3.0 wt% ruthenium, and the balance nickel.

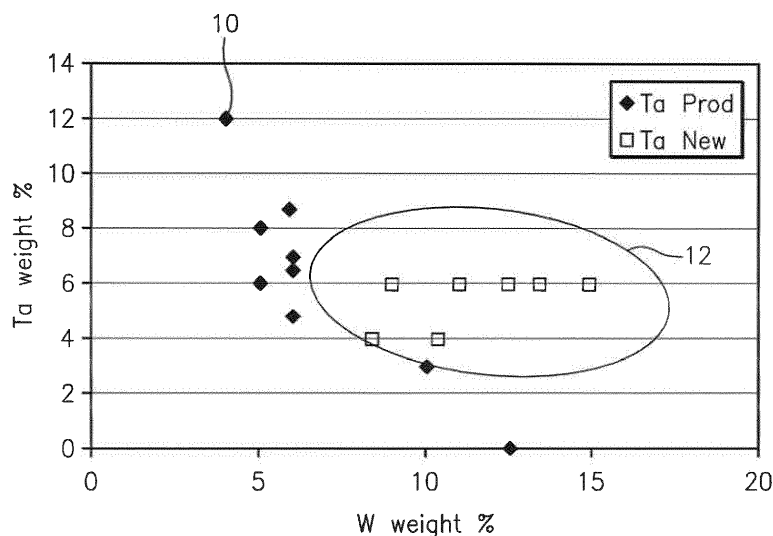


FIG. 1

Description

[0001] Lower cost high strength single crystal superalloys with reduced rhenium and ruthenium content are described.

[0002] All second and higher generation nickel-base directionally solidified and single crystal superalloy compositions contain additions of rhenium of at least 3 wt%. Fourth generation and higher single crystal alloys contain some percentage of the element ruthenium. With the significant escalation of spot prices of these elements, there is an economic need for alternate alloy compositions with comparable levels of performance, but with reduced concentration of these expensive elements.

[0003] Nickel-base superalloy single crystals are primarily used for high temperature turbine components, such as blades and vanes, where temperature capability is typically assessed by its high temperature creep resistance. Simplistically, it is well understood that to improve creep resistance, additions of refractory elements with high melting point is desirable. Such elements include almost all Group IVA to VIIIA transition metals, especially Ti, Nb, Ta, Mo, W, Re, and Ru with melting points in excess of 4082°F (2250°C). Among these elements, Ti, Nb, and Ta are known to almost exclusively replace Al in the ordered precipitate phase γ' (Ni₃Al), whereas Re and Ru are known to exclusively partition to the nickel base solid solution γ -matrix. W on the other hand is known to partition evenly between the γ -matrix and γ' phase.

[0004] There are of course limits to the extent to which these elements can be accommodated in the alloy. It is common knowledge that optimum mechanical properties are obtained when the volume fraction of the γ' phase is around 60 to 70%. Thus, individually or combined (Al + Nb + Ta + W/2) in atom % cannot exceed about 18%. Moreover, Al concentrations cannot be reduced below 10 atom% to preserve oxidation resistance. Similarly excessive addition of refractory elements in the γ -matrix is limited by the undesirable phases these elements can form after a long time exposure. The formation of so-called topologically closed packed (TCP) phases are undesirable as they reduce the creep resistance of the alloy. The concentration at which such phases will form can be approximately predicted by calculating, what is called an electron vacancy number or Nv number for the γ -matrix. This calculation is based on a weighed average of Nv assigned to each element. It is an industry wide practice to use such calculations, but it is known that it is not completely accurate and there are exceptions to the rule.

[0005] There is a need for a lower cost high strength nickel based superalloy.

[0006] Thus according to a first aspect, the present invention can be seen to provide a first embodiment of a lower cost high strength nickel based alloy that broadly comprises from 3.0 to 5.2 wt% chromium, from 1.5 to 3.0 wt% molybdenum, from 6.0 to 12.5 wt% tungsten, from 5.0 to 11 wt% tantalum, from 5.5 to 6.5 wt% aluminum, from 11 to 14 wt% cobalt, from 0.001 to 1.75 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium, up to 3.0 wt% ruthenium, and the balance nickel.

[0007] From a second aspect, the present invention can be seen to provide another embodiment of a lower cost high strength nickel based alloy broadly comprises from 1.0 to 3.0 wt% chromium, up to 2.5 wt% molybdenum, from 11 to 16 wt% tungsten, from 4.0 to 8.0 tantalum, from 5.7 to 6.5 wt% aluminum, from 11 to 15 wt% cobalt, from 2.0 to 4.0 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium, up to 3.0 wt% ruthenium, and the balance nickel.

[0008] Certain preferred embodiments of the lower cost high strength nickel based superalloys of the present invention will now be described in greater detail and by way of example only and with reference to the accompanying drawings, in which:

FIG. 1 is a plot of tantalum weight % vs. tungsten weight %; and

FIG. 2 is a bubble chart of Ta weight% vs. tungsten weight% with the bubble size proportional to (Re + Ru) weight %.

[0009] The combinations of compositions with the elements Ti, Nb, Ta, Mo, W, Re, and Ru along with primary elements Ni, Co, Cr, and Al, is so large that it is cost prohibitive to explore the entire alloy space. Traditionally, alloys are evolved based on prior experience and once the target performance benefit is realized, there is little motivation to visit the unexplored alloy compositional space. There is no simple quantitative way to map out a space bounded by a dozen elements and pinpoint the gaps. In a limited sense, a bubble plot of Ta weight % vs. W weight %, as shown in Figure 1, graphically represents maps out a desirable space. In this plot, the size of the bubble or plotting point for each alloy is proportional to the total concentration of (Re + Ru) in the alloys of interest.

[0010] Prior to the development of the first generation single crystal alloy PWA 1480, the best known equiaxed and columnar grain alloys were based on Mar M200, which contain 12.5 weight% of W. Also the alloy contained 2.0 weight % Ti. Development of PWA 1480 was marked by the addition of 12 weight% Ta. Subsequent development of second generation single crystal alloys such as PWA 1484 all had a marked absence of Ti. An improved second generation DS alloy, PWA 1426, was developed with Re additions similar to PWA 1484. The fourth generation of single crystal alloys such as PWA 1497 have an increase in Re concentration concurrent with Ru additions. As can be seen in Fig. 1, these alloys do not overlap in the Ta, W, (Re + Ru) space. In these higher strength alloys, the concentration of Ta never decreased below 4 wt% and W never increased beyond 6.0 wt%.

[0011] The successful development of second generation single crystal alloys has been attributed to Re additions and

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it is generally believed that Re makes the lattice misfit between the γ' precipitate and the γ -matrix become more negative. Re is also thought to reduce the coarsening rate of the γ' phase, contributing to improving creep strength.

[0012] Useful alloys are listed in Table I and are also depicted in FIGS. 1 and 2. Fig. 1 clearly depicts that in Ta weight % vs. W weight % plots, current production alloys are outside the alloy space. The Ta in production alloys is showed by the diamond points 10 on FIG. 1 and the space with the Ta in the alloys set forth herein are shown by the squares in the space 12. The same information is plotted in FIG. 2 as a bubble chart, where the size of plotting points is proportional to the concentration of (Re + Ru). In FIG. 2, bubble 20 is alloy PWA 1422, bubble 22 is alloy PWA 1480, bubble 24 is alloy PWA 1497, bubble 26 is alloy PWA 1484, bubble 28 is alloy 2a in Table I, bubble 30 is alloy 2b in Table I, bubble 32 is alloy 1a in Table I, bubble 34 is alloy 1b in Table I, bubble 36 is alloy 3a in Table I, bubble 38 is alloy 3b in Table I, bubble 40 is alloy 3c in Table I, bubble 42 is alloy PWA 1426, bubble 44 is alloy PWA 1426a, and bubble 46 is alloy PWA 1426b.

TABLE I

Alloy	Cr	Mo	W	Ta	Al	Co	Ro	Ru	Hf	P	Density	Creep Life	Nv3B	Stability	COMMENTS
Single Crystal															
1a	4	2	11	6	6	12.5	0	0		48.5	0.322	PWA 1484	2.07	S	Creep = 1484 No Re/Ru
1b	5	2	9	6	6	12.5	0	3		48.5	0.318	PWA 1484	2.07	S	Creep = 1484 No Re (3Ru)
1c	4	2	9	6	6	12.5	1.5	0		48.5	0.32	PWA 1484	2.04	S	
2a	2	1.75	11.5	6	6	12.5	3	3		58	0.331	PWA 1497	2.02	S	Creep = 1497 with 3Re. 3Ru
2b	2	1	12.5	6	6	12.5	3	0		55.75	0.331	1497-15F	2.02	S	Creep -1497 with 3Re. 0Ru
3a	2	1.75	15.5	6	6	12.5	0	3		58	0.334	PWA 1497	2.09	S	Creep = 1497 with 0Re. 3Ru
3b	2	2	13.5	6	6	12.5	1.5	0		55.25	0.331	1497-20F	2.08	S	creep < 1497 with 15Re.0Ru
3c	2	2	15	6	6	12.5	0	0		54.5	0.331	1497-25F	2.08	S	creep <1497 with 0Re. 0Ru
PWA 1484	5	1.9	5.9	8.7	5.65	10	3	0		48	0.323		2.08		
PWA 1497	2	1.8	6	8.25	5.65	16.5	6	3		58	0.331				
DS															
PWA 1426	6.4	1.7	6.4	4	5.9	12.5	3	0	1.5	44.9	0.316	Base	2.07	S	
PWA 1426a	6.4	1.7	8.4	4	5.9	12.5	1.5	0	1.5	44.9	0.318	Base	2.11	S	creep = 1426 1.5Re
PWA 1426b	6.4	1.7	10.4	4	5.9	12.5	0	0	1.5	44.9	0.322	Base	2.24	Mg	creep = 1426 0Re

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[0013] Listed in Table I are baseline compositions of the second and fourth generation single crystal alloys PWA 1484 and PWA 1497, respectively, and the second generation columnar grain (DS) alloy PWA 1426. It can be seen from FIG. 2 that using the useful alloys described herein, one can achieve the same level of creep resistance as PWA 1426, for reducing Re-containing alloys (PWA 1426a and PWA 1426b), by increasing the W content of these alloys.

[0014] One embodiment of a useful alloy contains from 3.0 to 5.2 wt% chromium, from 1.5 to 3.0 wt% molybdenum, from 6.0 to 12.5 wt% tungsten, from 5.0 to 11 wt% tantalum, from 5.5 to 6.5 wt% aluminum, from 11 to 14 wt% cobalt, from 0.001 to 1.75 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium, and the balance nickel.

[0015] Table II is a comparison of alloys having compositions within the aforesaid range with Rene N5. The data shows the alloys described herein to have higher density, an equivalent or better life, better yield strength, and equivalent or better ultimate tensile strength than Rene N5.

TABLE II

	Casting Chemistry Weight%								Act lbs/cu In Density	1850F/38ksi				1200F Tensile		
	Cr	Mo	W	Ta	Al	Co	Re	Hf		Life	1%	EI	YS	UTS	EI	
Alloy 1	3.97	2.07	10.82	6.07	6.15	12.81	0	0.32	0.320	40.2	16	38.1	124.5	140.2	22	
										31.7	10	23.4	124.8	139.1	23.1	
										37.5	16	25.6	126.2	139.3	24.2	
								AVE		36.5	14	29	125.2	139.5	23.1	
Alloy 2	3.99	2.03	8.81	6.01	5.78	12.23	1.54	0.34	0.320	61.7	24	28.4	135.8	143.5	21.8	
										63.1	24	39.3	130.1	137.9	19	
										68.6	26	36.9	130.7	139.1	21.8	
								AVE		64.5	24.7	34.9	132.2	140.2	20.9	
Alloy 3	5.09	2.09	10.97	5.62	6.15	12.9	0	0.36	0.319	48.7	16	41.3	120.6	139	17.8	
										45.5	14	38.3	127.3	145.4	17.2	
										40.6	13	37	127.6	147.2	21.1	
								AVE		44.9	14.3	38.9	125.2	143.9	18.7	
Alloy 4	5.01	2.08	9.41	7.04	5.9	12.45	0	0.35	0.320	41.2	14	36	130.2	145	21.9	
										41.1	14	37.2	134	150	21.3	
										42.8	14	41.7	133.3	146.3	20.9	
								AVE		41.7	14	38.3	132.5	147.1	21.4	
Alloy 5	3.93	2.06	8.87	9.03	5.89	12.38	0	0.34	0.323	39.6	10	40.1	132.2	144.7	13.5	
										38.6	9	35.9	137.7	149.6	25.6	
										43.4	13	37.4	134.9	146.9	22	
								AVE		40.5	10.7	37.8	134.9	147.1	20.4	
Alloy 6	5.04	2.1	11.82	5.65	5.58	12.46	0	0.34	0.323	40.1	17	29.9	138.1	152.7	18.9	
										40.1	14	26.1	140.8	154.1	23.2	
										39.6	15	24	139.5	154.9	23.2	
								AVE		39.9	15.3	26.7	139.5	153.4	21.8	

(continued)

	Casting Chemistry Weight%							Act lbs/cu In Density	1850F/38ksi			1200F Tensile		
	Cr	Mo	W	Ta	Al	Co	Re	Hf	Life	1%	EI	YS	UTS	EI
Alloy 7	4.51	2.06	7.06	10.07	5.8	12.84	1.43	0.33	0.3235	26	42.3	148	179.6	9.3
									65.2	25	39.4	148.2	179.2	12.6
									59.9	20	36	149.6	181	7.8
									63.9	23.7	39.2	148.6	179.9	9.9
Alloy 8	5.08	2.05	8.81	7.32	6.14	12.85	0	0.34	0.317	11	41.7	129.8	148.3	148.3
									37.2	12	40	129.4	148	16.8
									39.4	14	41.8	128.2	145.4	18.4
									37.5	12.3	41.2	129.1	147.2	17
Rene N5 Nom	7	1.5	5	6.5	6.2	7.5	3	0.15	0.312			122	145	

[0016] A second embodiment of a useful alloy contains from 4.0 to 5.0 wt% chromium, from 1.7 to 2.3 wt% molybdenum, from 7.0 to 12.5 wt% tungsten, from 5.5 to 10 wt% tantalum, from 5.6 to 6.25 wt% aluminum, from 11.5 to 13.5 wt% cobalt, from 0.001 to 1.75 wt% rhenium, from 0.2 to 0.4 wt% hafnium, from 0.001 to 0.01 wt% yttrium, and the balance nickel.

[0017] A third embodiment of a useful alloy contains from 1.0 to 3.0 wt% chromium, up to 2.5 wt% molybdenum, from 11 to 16 wt% tungsten, from 4.0 to 8.0 tantalum, from 5.7 to 6.5 wt% aluminum, from 11 to 15 wt% cobalt, from 2.0 to 4.0 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium and the balance nickel.

[0018] A fourth embodiment of a useful alloy contains from 1.5 to 2.5 wt% chromium, from 0.5 to 1.5 wt% molybdenum, from 11.5 to 13.5 wt% tungsten, from 5.0 to 7.0 tantalum, from 5.8 to 6.25 wt% aluminum, from 11.5 to 13.5 wt% cobalt, from 2.5 to 3.5 wt% rhenium, from 0.2 to 0.4 wt% hafnium, from 0.001 to 0.01 wt% yttrium, and the balance nickel.

[0019] The above alloys may contain up to 3.0 wt% ruthenium. The total rhenium and ruthenium content of each of the alloys may be no greater than 6.0 wt%.

[0020] Oxidation resistance can be maintained by the addition of at least 15 - 30 ppm yttrium or other equivalent active elements such as Ca, Mg, and other rare earth elements. Previously, yttrium and other rare earth additions have not been added to alloys containing elevated levels of W, i.e. greater than 6.0 weight%.

[0021] The alloys described herein can fulfill the low cost requirements. Since Re and Ru raw material prices have risen in the last few years, reducing their concentration in new alloys by 50% or more (compared to existing second generation and higher alloys) will have a significant effect on master heat cost.

[0022] It should be apparent that there has been provided in accordance with the present disclosure lower cost high strength single crystal superalloys with reduced rhenium and ruthenium content. While the superalloys have been described in the context of specific embodiments thereof, other unforeseeable alternatives, variations and modifications make become apparent to those skilled in the art having read the foregoing description. Accordingly, it is intended to embrace those alternatives, modifications, and variations as fall within the broad scope of the appended claims.

[0023] The following clauses set out features of the invention which may not presently be claimed but which may form the basis for future amendment and/or a divisional application

1. A nickel based alloy consisting essentially of from 3.0 to 5.2 wt% chromium, from 1.5 to 3.0 wt% molybdenum, from 6.0 to 12.5 wt% tungsten, from 5.0 to 11 wt% tantalum, from 5.5 to 6.5 wt% aluminum, from 11 to 14 wt% cobalt, up to 1.75 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium, up to 3.0 wt% ruthenium, and the balance nickel.

2. The nickel based alloy of clause 1, wherein said chromium is present in an amount from 4.0 to 5.0 wt%.

3. The nickel based alloy of clause 1 or 2, wherein said molybdenum is present in an amount from 1.7 to 2.3 wt%.

4. The nickel based alloy of clause 1, 2 or 3, wherein said tungsten is present in an amount from 7.0 to 12 wt%.

5. The nickel based alloy of any preceding clause, wherein said tantalum is present in an amount from 5.5 to 10 wt%.

6. The nickel based alloy of any preceding clause, wherein said aluminum is present in an amount from 5.6 to 6.25 wt%.

7. The nickel based alloy of any preceding clause, wherein said cobalt is present in an amount from 11.5 to 13.5 wt%.

8. The nickel based alloy of any preceding clause, wherein said rhenium is present in an amount from 0.001 to 1.75 wt%, said hafnium is present in an amount from 0.2 to 0.4 wt%, and said yttrium is present in an amount from 0.001 to 0.01 wt%.

9. The nickel based alloy of any preceding clause, wherein the total ruthenium and rhenium content is no greater than 6.0 wt%.

Claims

1. A nickel based alloy consisting essentially of from 1.0 to 3.0 wt% chromium, up to 2.5 wt% molybdenum, from 11 to 16 wt% tungsten, from 4.0 to 8.0 tantalum, from 5.7 to 6.5 wt% aluminum, from 11 to 15 wt% cobalt, from 2.0 to 4.0 wt% rhenium, from 0.2 to 0.6 wt% hafnium, up to 0.05 wt% yttrium, up to 3.0 wt% ruthenium, and the balance nickel.

2. The nickel based alloy of claim 1, wherein said chromium is present in an amount from 1.5 to 2.5 wt%, said molyb-

denum is present in an amount from 0.5 to 1.5 wt%.

3. The nickel based alloy of claim 1 or 2, wherein said tungsten is present in an amount from 11.5 to 13.5 wt%.

5 4. The nickel based alloy of claim 1, 2 or 3, wherein said tantalum is present in an amount from 5.0 to 7.0 wt%, said aluminum is present in an amount from 5.8 to 6.25 wt%, and said cobalt is present in an amount from 11.5 to 13.5 wt%.

10 5. The nickel based alloy of any of claims 1 to 4, wherein said rhenium is present in amount from 2.5 to 3.5 wt%, said hafnium is present in an amount from 0.2 to 0.4 wt%, and said yttrium is present in an amount of from 0.001 to 0.01 wt%.

6. The nickel based alloy of any of claims 1 to 5, wherein the total ruthenium and rhenium content is no greater than 6.0 wt%.

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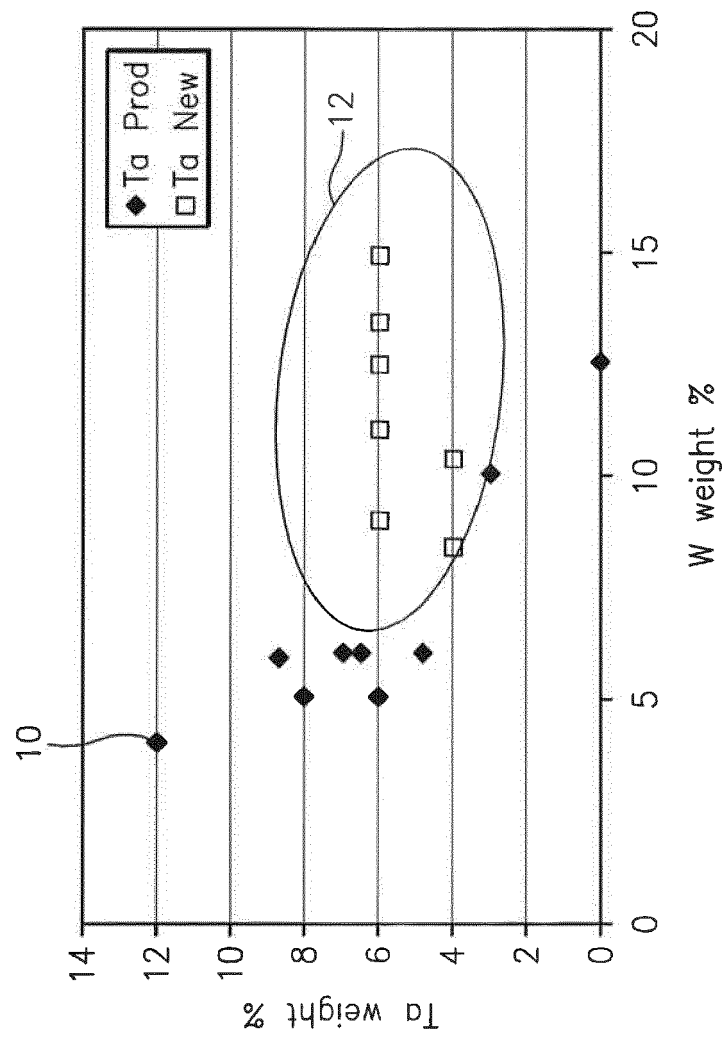


FIG. 1

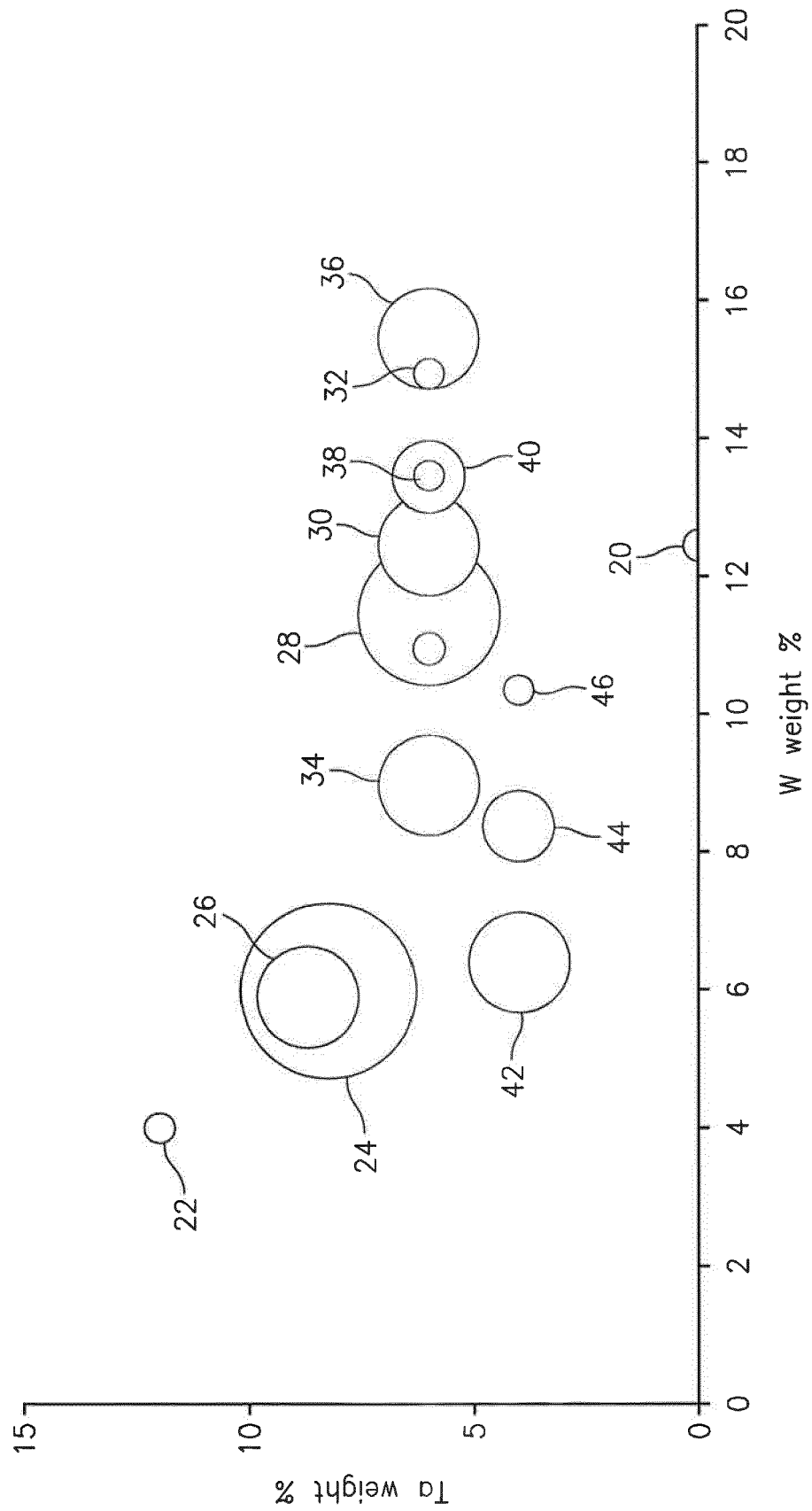


FIG. 2



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Application Number
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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