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3,383,206

NICKEL BASE ALLOY AND ARTICLE

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No Drawing. Continuation-in-part of application Ser. No. 333,619, Dec. 26, 1963, now Patent No. 3,304,176, dated Feb. 14, 1967. This application Oct. 11, 1965, Ser. No. 494,966

5 Claims. (Cl. 75-171)

This is a continuation-in-part of application Ser. No. 333,619, filed Dec. 26, 1963, now Patent No. 3,304,176.

This invention relates to nickel base alloys and, more particularly, to a solid solution type nickel base alloy of improved dynamic oxidation resistance.

In copending application Ser. No. 333,619, filed Dec. 26, 1963 and assigned to the assignee of this invention there is described a nickel base alloy of improved oxidation resistance and fabricability resulting from the addition of about 0.05 to less than 0.3 weight percent La to a Ni-Cr-Fe type nickel base alloy solution strengthened with either or both Mo and W.

The alloy of the copending application provides an unexpected improvement in oxidation resistance over similar known alloys. This improvement is now seen to be significant when used in a relatively static application such as in a furnace. However, it has been recognized that such an alloy requires further improvement for use under dynamic oxidation conditions. One example of a use under dynamic conditions is as a combustor material in a gas turbine engine where there is a rapid flow of combustion gases including excess oxygen.

A principal object of the present invention is to provide an alloy of the type described in the above identified copending application but having improved oxidation resistance under dynamic oxidation conditions as well as under static oxidation conditions.

Another object is to provide such an alloy which, under dynamic oxidation conditions, will form an improved surface as a thermal reaction product in an oxidizing atmosphere to resist further oxidation of the alloy and to act as a barrier to internal oxidation.

Still another object is to provide an article including such an alloy and having an oxidation resistant surface.

These and other objects and advantages will be more readily recognized from the following detailed description and examples. These are intended to be exemplary of rather than any limitation on the scope of the invention.

It has been found that the above objects can be accomplished by combining lanthanum with certain spinel formers in the type of alloy described.

Briefly, the present invention provides an improved nickel base alloy of the solution strengthened type from which an improved article can be produced, the alloy consisting essentially of, by weight, 20-23% Cr; 8-10% Mo; 17-20% Fe; up to 0.15% C; up to 2% W; 0.05 to less than 0.3% La; 0.5-6% of the spinel forming elements selected from the group Co and Mn, the Co when selected being in the range of 1-3% and the Mn when selected

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being in the range of 0.5-3% with the balance nickel and incidental impurities.

In a preferred form, the alloy of the present invention includes 0.1-0.2% La along with 1.5-2.5% Co and 0.5-1.5% Mn.

During further evaluation of the alloy of the above identified co-pending application and its comparison with the alloy claimed in U.S. Patent 2,703,277, Spendelow et al., it was recognized that much of the advantage in oxidation resistance which resulted from the addition of the specified amount of lanthanum was lost during oxidation in high velocity combustion products. Consideration of the mechanism through which the lanthanum addition is effective indicated that unlike the known alloy of the above identified United States patent wherein the main reaction or surface products were Cr<sub>2</sub>O<sub>3</sub> and spinel (NiCr<sub>2</sub>O<sub>4</sub>), the reaction or surface products of the lanthanum modified alloy of the copending application consisted only of Cr<sub>2</sub>O<sub>3</sub>. Although this rhombohedral surface scale was very protective under static exposure conditions, the absence of spinel overgrowths above the Cr<sub>2</sub>O<sub>3</sub> layer resulted in chromium volatilization in high velocity environments. This led to chromium depletion and an increased oxidation rate under such conditions.

As a result of understanding this mechanism, it was recognized that the control and definite inclusion of certain levels of strong spinel formers such as Mn and Co could provide an alloy having a combination of improved oxidation resistance under both static and dynamic conditions. However, other spinel formers such as iron already included in the alloy had little, if any, effect on the reaction products.

The spinel formers manganese and cobalt were identified as impurities in the composition of the alloy of the copending application and of the alloy of the Spendelow et al. patent. They were not specifically included nor were their amounts controlled. In the Spendelow et al. patent, cobalt is included as an impurity generally at less than 1% and in no event greater than about 2.5%; manganese is listed as an impurity permissible up to about 1% along with silicon and the like.

It has been recognized that when certain spinel formers such as Mn and Co are specifically controlled within the range of 0.5-6% for the total of such elements, a different kind of alloy surface is formed as an oxidation reaction product during and retained after both static and dynamic oxidation. Such a surface reaction product is different from that formed in either of the known alloys, and is highly stabilized. Its spinel portion is of the form Ni(Cr, Mn, Co)<sub>2</sub>O<sub>4</sub> rather than merely the NiCr<sub>2</sub>O<sub>4</sub> of the known alloys. The following Table I lists the types of surfaces found with each of the prior alloys and of the alloy of the present invention both under static and dynamic conditions. Example A is the alloy listed in U.S. 2,703,277, Example B is one form of the alloy of the copending application and Example 1 is the preferred form of the alloy of the present invention because of its relative ease of reduction. The compositions for these examples are found in Table II.

TABLE I.—SURFACE COMPARISON AFTER 1,000 HRS. AT 2,000 ° F.

Ex.	Static Oxidation		Dynamic Oxidation	
	Outer Surface	Subsurface	Outer Surface	Subsurface
A.....	Cr <sub>2</sub> O <sub>3</sub> plus Spinel A.....	SiO <sub>2</sub> plus Spinel A.....	Spinel A.....	SiO <sub>2</sub> plus Spinel A.....
B.....	(Cr, La) <sub>2</sub> O <sub>3</sub> .....	do.....	do.....	do.....
1.....	(Cr, La) <sub>2</sub> O <sub>3</sub> plus Spinel B.....	.....	(Cr, La) <sub>2</sub> O <sub>3</sub> plus Spinel B.....	.....

Spinel A = NiCr<sub>2</sub>O<sub>4</sub>  
Spinel B = Ni(Cr, Mn, Co)<sub>2</sub>O<sub>4</sub>

During the evaluation of the alloy of the present invention, the alloy of the co-pending application was modified by the inclusion of 2-3% Co with nominal variations of 1, 3 and 5% manganese. The following Table II compares the composition of the alloys melted in this evaluation with the known alloys of this type.

TABLE II  
[Weight Percent-Balance Ni]

Example	Cr	Mo	Fe	C	W	La	Co	Mn	Si
A.....	22.1	9.2	17.7	0.10	0.65	0	1.5	0.5	0.9
B.....	21.5	9.6	18.3	0.10	0.33	0.09	0	0	0.3
1.....	21.8	9.2	18.5	0.09	0.64	0.17	1.9	1.0	0.8
2.....	22.1	8.6	18.6	0.09	0.43	0.05	2.4	2.8	0.8
3.....	21.2	8.5	18.2	0.10	0.39	0.17	3.0	5	0.8

These alloys were melted in a 100 pound vacuum induction furnace. The 1% Mn variation shown as Example 1 in Table II was successfully reduced to sheet and subjected to extensive oxidation evaluation and some mechanical testing.

As was mentioned above, the alloy of the copending application, shown in the tables by Example B has significantly improved oxidation resistance under static conditions over the known alloy, represented by Example A. The following Table III gives a comparison of Examples A and B with each other and with the preferred form of the alloy of the present invention, represented by Example 1, under static oxidation resistance.

TABLE III.—AVERAGE STATIC OXIDATION TESTING

Exposure		Weight Gains (mg./cm. <sup>2</sup> )			Internal Oxidation, depths in mils./side		
Temp. (° F.)	Time (hrs.)	A	B	1	A	B	1
1,800	400	1.8	-----	1.9	1.7	-----	0.5
1,800	1,600	2.3	0.8	2.3	1.5	0	0.8
2,000	100	1.9	-----	1.8	1.4	-----	0.7
2,000	400	12.6	1.1	3.2	2.5	0.2	1.5
2,000	1,000	12.7	-0.4	5.1	2.2	>0.1	1.1

<sup>1</sup> Spalling of surface reaction products occurred on cooling.

<sup>2</sup> Additional 2 mils./side of fine uniformly distributed internal oxide also observed.

While Example B has oxidation resistance under static conditions better than does Example 1, the alloy of the present invention shown as Example 1 in Table III has static oxidation resistance at least equal to that of Example A. Although Example A experienced a lower weight gain at 2000° F. after 400 and 1000 hours static exposure, nevertheless, the reaction product surface of Example A spalled upon cooling. The surface of Examples B and 1 did not. The effectiveness of the reaction product surface to prevent internal oxidation is significantly greater in Alloys B and 1. Thus the alloy of the present invention has good oxidation resistance under static conditions, in general better than that of Example A.

The most significant difference between the alloy of the present invention and the other listed alloys is in dynamic oxidation resistance. Whereas the alloy of Example B is better under static oxidation conditions, it has significantly lower resistance in dynamic oxidation testing. This is shown more particularly in the data of Tables IV and V.

TABLE IV.—DYNAMIC OXIDATION TESTING IN FLAME TUNNEL

Example	[Avg. Wt. loss mg./cm. <sup>2</sup> ]							
	1,800° F., hours				2,000° F., hours			
	100	400	700	1,000	100	200	200	600
A.....	10.1	0.8	1.4	1.9	0	1.3	6.8	11.1
B.....	1.2	3.6	5.2	6.3	2.4	4.8	14.1	22.0
1.....	10.3	0.3	1.0	1.7	+0.2	0.7	4.6	8.2
<sup>1</sup> Weight gain.								
								9.3

The data of Table IV shows that the alloy of the present invention experiences a significantly lower weight loss than does either Examples A or B. More significantly in connection with its application as a useful article such as a combustor in a gas turbine engine, the alloy of Example 1 has greatly improved resistance to internal oxidation compared with Examples A and B. This is

shown by the data of Table V. With regard to potential dimensional change of articles made from the alloy of Example 1 and after dynamic cyclic thermal experience, it is interesting to note that the alloy of Example 1 experienced no loss in width as a result of formation of its improved surface.

TABLE V.—DYNAMIC OXIDATION TESTING IN FLAME TUNNEL

[Average after 1,000 hours]				
Example	Temp., ° F.	Avg. Depth Internal Oxidation (mils./side)		Avg. width loss (mils./side)
		Front	Rear	
A.....	1,800	2.0	1.5	0.3
B.....	1,800	1.4	1.0	1.3
1.....	1,800	0.6	0.4	0
A.....	2,000	7.5	5.0	0.5
B.....	2,000	7.5	3.3	2.2
1.....	2,000	3.0	2.5	0

Thus the alloy of the present invention particularly represented by Example 1 is characterized by a combination of good static oxidation resistance and significantly better dynamic oxidation resistance.

The dynamic oxidation testing was conducted as thermal cyclic evaluations performed on 2.0" x 0.375" specimens.

The surface of all specimens to be used for oxidation testing were prepared by mechanical abrasion up to and including 600 grit paper. Final surface preparation consisted of vapor blasting the surface of the specimen using 1250 grit abrasive.

The specimens were supported in one end of a flame tunnel in a fire-brick with the majority of the specimen exposed to an uninterrupted gas/air flow of about 100 lbs./in.<sup>2</sup>/hr. The tests were performed by cycling from 20 minutes at temperature followed by a 15 second blast of cooling air to reduce the specimen to a temperature of 1000° F. The entire cooling and heating cycle took approximately 30 seconds. Thus virtually the whole test period was spent at temperature. Weight and dimensional changes as shown in the above tables, as well as metallographic examination were used to determine the amount of oxidation. The following tensile properties of the alloy of the present invention particularly as represented by Example 1 were obtained on 60 mil sheet.

TABLE VI.—AVERAGE TENSILE PROPERTIES

Temp. (° F.)	Ultimate Tensile, K s.i.	0.2 percent Yield, K s.i.	0.2 percent Yield, K s.i.	Percent Elong.
Room.....	98.5	40.0	31.2	51.2
1,200.....	65.5	23.0	21.0	53.8
1,600.....	30.6	20.2	17.2	8.3
1,800.....	20.9	19.9	16.7	14.3

As was mentioned above, not all elements which promote the formation of a spinel are effective in forming an improved alloy surface in the presence of lanthanum. For example, the spinel former iron, present in all of the alloys listed does not form an improved spinel overgrowth in the surface. However, certain effective spinel formers such as manganese and cobalt do form such a surface. In addition, it was recognized that too little of such effective spinel formers, for example, less than about

0.5 weight percent manganese and less than about 1.5 weight percent cobalt, is ineffective in forming the desired surface spinel to prevent volatilization of the chromium oxide. Furthermore, an excessive amount of the effective spinel formers such as manganese and cobalt at levels greater than about 3 weight percent each result in an alloy which is "hot short." Thus the alloy is too brittle and

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too difficult to reduce from an ingot. The particular combination of lanthanum along with controlled amounts of such effective spinel forms as manganese and cobalt in the type of alloy to which this invention relates provides an improved alloy having oxidation resistance under dynamic conditions significantly better than those known prior to this invention as well as good mechanical properties and good oxidation resistance under static conditions.

Although the present invention has been described in connection with specific examples such as of the effective spinel formers, it will be recognized by those skilled in the art other modifications and variations of this invention can exist. It is intended by the appended claims to cover such variations and modifications.

What is claimed is:

1. An improved nickel base alloy of the solution strengthened type consisting essentially of, by weight, 20-23% Cr; 8-10% Mo; 17-20% Fe; up to about 0.15% C; up to about 2% W; 0.05 to less than 0.3% La; 0.5-6% of the spinel forming elements selected from the group consisting of Co and Mn, the Co when selected being in the range of 1-3% and the Mn when selected being in the range 0.5-3%; with the balance nickel and incidental impurities.

2. An improved nickel base alloy of the solution strengthened type consisting essentially of, by weight, 20-23% Cr; 8-10% Mo; 17-20% Fe; up to about 0.15% C; up to about 2% W; 0.05 to less than 0.3% La; 1-3% Co; 0.05-3% Mn; up to about 1% Si; with the balance nickel and incidental impurities.

3. An improved nickel base alloy of the solution strengthened type consisting essentially of, by weight, 20-23% Cr; 8-10% Mo; 17-20% Fe; 0.05-0.15% C;

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up to about 2% W; 0.1-0.2% La; 1.5-2.5% Co; 0.5-1.5% Mn; up to about 1% Si; with the balance nickel and incidental impurities.

4. An article including an alloy consisting essentially of, by weight, 20-23% Cr; 8-10% Mo; 17-20% Fe; up to about 0.15% C; up to about 2% W; 0.05 to less than 0.3% La; 0.5-6% of the spinel forming elements selected from the group consisting of Co and Mn, the Co when selected being in the range of 1-3% and the Mn when selected being in the range of 0.5-3%; with the balance nickel and incidental impurities; the alloy having a surface bonded with the alloy and comprising an integral combination of Cr and La oxides and a spinel of the  $\text{Ni}(\text{Cr}, \text{Mn}, \text{Co})_2\text{O}_4$  type.

5. A combustion means for a gas turbine engine, the means including an alloy consisting essentially of, by weight, 20-23% Cr; 8-10% Mo; 17-20% Fe; up to about 0.15% C; up to about 2% W; 0.05 to less than 0.3% La; 1-3% Co; 0.05-3% Mn; up to about 1% Si; with the balance nickel and incidental impurities; the alloy having a surface bonded with the alloy and comprising an integral combination of Cr and La oxides and a spinel of the  $\text{Ni}(\text{Cr}, \text{Mn}, \text{Co})_2\text{O}_4$  type.

#### References Cited

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